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Fathi Zereini · Clare L.S. Wiseman (*Eds.*)

Urban Airborne Particulate Matter

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Volume Editors

Urban Airborne Particulate Matter

Origin, Chemistry, Fate and Health Impacts

Springer

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ISSN 1863-5520

ISBN 978-3-642-12277-4 e-ISBN 978-3-642-12278-1

DOI 10.1007/978-3-642-12278-1

Springer Heidelberg Dordrecht London New York

Library of Congress Control Number: 2010934783

Cover design: deblik, Berlin

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

Preface

Particles have been a recognized ingredient in polluted air for decades if not centuries. Despite the fact that their atmospheric concentrations have decreased substantially in developed countries over the last 50+ years, due to government policies and evolving technologies, particles continue to be a high priority environmental issue. This is because of growing evidence, starting in the early 1990s, of significant health effects at lower ambient concentrations than expected and because of the recognition that our understanding of their net effect in regulating the Earth's climate is insufficient. In particular, the magnitude and direction of their indirect effect on the radiation budget and the extent to which particles will play a role in positive or negative climate feedbacks are not known. Geoengineering responses to climate change may also involve atmospheric particles, but much more information is needed before the risks and benefits of such measures can be properly evaluated. Engineered nanoparticles represent another pressing environmental issue for which our knowledge is incomplete.

There are many directions in need of research to further our understanding in support of wise environmental and public health management pertaining to particles. In this book readers will find unique contributions to our knowledge on atmospheric and indoor particles and related pollutants or exposures. The context for much of what is presented is geared towards pollution issues and health effects as opposed to climate and engineered nanoparticles. However, many of the methods developed and/or applied in the papers in this book are quite relevant to particle research related to these latter two issues. For example, there are several papers that describe and apply advanced particle measurement methods, including chemical analysis techniques, for trace and ultra-trace metals and gas/particle phase organics. While these methods are shedding new light on the chemical characteristics and sources of particles to the benefit of risk assessment and exposure reduction strategies, they can be turned towards studying particle properties related to global aerosols and climate. Other papers in this book present new data on concentrations and important chemical constituents, including levels in the biota, indoor dust and other microenvironments. These are helping to complete the picture for particles, their sources and sinks across the globe, and human and biological exposures. Yet other papers focus on quantifying exposure to combustion nanoparticles or studying the fate of motor vehicle exhaust catalyst materials, both of which provide scientific insights that will benefit efforts to study the potential impacts of engineered nanoparticles. Rounding out this book are a number of subject reviews from health effects and the mechanisms of oxidative stress, to persistent organic pollutants and motor vehicle emissions and to the challenges of setting ambient and emissions standards.

PM2.5 and/or PM10 levels exceed current standards or guidelines in many countries and are they alarmingly high in several megacities, particularly in some developing nations. Solving these public health problems represents a tremendous scientific challenge as well as an economic one. This is especially the case in countries where the 'easier' policies have been implemented so the options that remain are potentially more complex and more costly to undertake. Therefore, in addition to scientific research to quantify, by size, concentrations of total mass, chemical constituents and the main sources contributing to the problem, devising more cost-effective ways to achieve maximum benefits to public health is important. This necessitates, as one of the papers in this book discusses, that research continues working towards identification of the types and/or sources of particles that pose greater risk, including consideration of the combined effects of particles and gaseous co-pollutants. While this seems to be a straightforward endeavour, there is more than one particle type and or pollutant mix that can be considered 'most harmful' given the range of acute and chronic health outcomes linked to particle exposure. Consideration of environmental impacts further expands the list of emission sources and subsequent particle types that might warrant preferential control. I am sure that readers will find that this book provides a diverse, yet complementary range of information helpful in gaining the insight needed to make further headway on the challenges posed by particulate air pollution.

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Preface of the Editors

The idea for this edited volume originated in 2008, after much discourse with colleagues regarding the need for a multidisciplinary book which pulls together the most up-to-date research on the chemistry and environmental fate of airborne particulate matter (PM) and its impact on exposed populations. Over the last decade, a great deal of evidence has been gathered which shows that airborne PM plays a strong role in patterns of morbidity and mortality among urban populations. Airborne PM with an aerodynamic radius of less than 2.5 μm has been especially implicated in eliciting negative human health effects in exposed individuals, particularly in more vulnerable persons such as children, the elderly and those with compromised immune systems and/or pre-existing health problems. While it is clear that fine and ultrafine fractions of airborne PM can impact human health, however, it is not known what chemical constituents found in PM may contribute to patterns in observed morbidity and mortality. Airborne PM contains a vast number of compounds, from metals to organic constituents such as lead and polyaromatic hydrocarbons, which have the potential to negatively impact human health. The composition of airborne PM can vary significantly over time and space, depending on number of factors such as season, prevailing meteorological conditions and the time of day, week, month and year, and may be associated with certain sources such as traffic and industry or even activities in specific world regions. Currently, most countries base their air quality and emissions policies and regulations on the measured mass of ambient PM (i.e. PM_{10} and/or $PM_{2.5}$). As the toxicity of the various constituents of airborne PM are likely to significantly vary, with some of the most toxic ones contributing little to the overall PM mass, this may not be the most effective way to minimize risks among exposed populations. As we begin to shed more light on the role of specific constituents found in airborne PM in cardiopulmonary and other health effects, countries will be in a better position to regulate emission sources and shape policy in a manner that is more protective of human health.

Despite the work yet to be done, we have made progress in recent years in developing analytical methods to measure the chemical constituents of airborne

PM, determining their sources and transport pathways, identifying the processes behind their environmental fate and transformation and the toxicological mechanisms involved in their human health effects. In pulling together the research on this highly interdisciplinary topic area, we have made an attempt to be as comprehensive as possible in both disciplinary and geographical terms, involving highly respected researchers from different fields and different parts of the globe.

This edited volume has a total of eight chapters. The contributions of invited authors have been divided into six chapters which correspond to specific theme areas that relate to the topic of airborne PM and its chemical composition, environmental fate, behaviour and impact on exposed populations, as follows: 1. Airborne Particulate Matter: Sources, Composition and Concentration, 2. Metals and Organic Compounds in Airborne Particulate Matter: Analytical Methods, 3. Airborne Particulate Matter: Environmental Pathways, Behaviour and Fate in Urban Environments, 4. Bioavailability and Toxicology of Airborne Particulate Matter, 5. Airborne Particulate Matter Exposures and Health Risks and 6. Protecting Human Health: Policy Measures and Scientific Uncertainty. Chapters 7 and 8 include the author and subject indices, respectively.

The individual contributions of the authors, which number 30 in total, have been compiled and sorted accordingly. It should be noted that many of the contributions fall under two or more of the major theme areas, given the interdisciplinary nature of much of the research that has been undertaken by the authors. As editors, we attempted to assign the specific papers to certain theme areas as best we could give the foci of the respective topics.

This book has truly been a transnational effort, involving 78 individuals from Algeria, Austria, Australia, Canada, Czech Republic, Denmark, Germany, Greece, Italy, Japan, Korea, Lebanon, Morocco, Singapore, Spain, Sweden, UK and USA. The editors would like to personally thank each author for their contributions and cooperative efforts in helping us compile this book in a very timely and efficient manner.

We would also like to extend our gratitude to the reviewers and the insightful comments they provided regarding the individual contributions. Many thanks go to Dr. R. Schierl from the Institute and Clinic for Occupational and Environmental Medicine, University of Munich, Prof. Dr. S. Hann from the Department of Chemistry, University of Natural Resources and Applied Life Sciences, Vienna, Austria, Prof. Dr. E. Helmers from Applied University FH Trier, Germany, Dr. Jeffrey Brook from Environment Canada and Prof. Dr. Athanasios Valavanidis from Department of Chemistry, University of Athens, Greece.

Special thanks go to Prof. Dr. Harald Bathelt, Department of Political Science and Department of Geography & Program in Planning, University of Toronto, Canada und to our families for their support.

In addition, we would like to express our thanks to Mrs. A. Oelschläger from Springer, who made this publication possible. We would also like to extend our gratitude to Mr. H.-H. Dülfer for his support in the formation of this book.

Frankfurt am Main, Germany Toronto, Canada Prof. Dr. Fathi Zereini
February 2010 Prof. Dr. Clare L. S. Wiseman

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Part I
Airborne Particulate Matter: Sources, Composition and Concentration

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Airborne particulate matter (PM) is a complex mixture of solid and liquid particles of primary and secondary origin, which contain a wide range of inorganic and organic components. PM mass and composition is also highly variable in spatial–temporal terms and is strongly influenced by climatic and meteorological conditions. It can be emitted from both natural and man made sources, including forest fires, dust storms, traffic and industry, and is found both outdoors and indoors. In terms of the latter, PM may be generated within the built environment or may be transported from outside via various mechanisms. Typically, PM is defined according to size or the diameter of the particles which make up a particular fraction, as this is what determines how long they will reside in the air, how far they may be transported and, in terms of health, how they will be deposited in the respiratory system. Air quality policy and emissions regulations are typically based on the mass of size fractions PM_{10} and/or $PM_{2.5}$, for these fractions are the most likely to impact human health as they are small enough to be inhaled and respired. Particles in PM_{10} are inhalable and may reach the upper part of the airways and lung, while smaller $PM_{2.5}$ particles are more able to deeply penetrate the lungs and perhaps reach the alveoli. Ultrafines, which have a cut-off of 0.1 μm, may make up a small proportion of the total mass but may have the greatest health impacts due to their ability to pass from the lung directly into the bloodstream and their larger reactive surface area which may be capable of inducing greater damage.

In addition to size, PM mass and number concentrations, volatility, morphology and chemical composition (e.g. organic, metal, salt content) are critical factors to be considered in the assessment of risk. The evidence regarding the relationship between airborne PM mass exposures (i.e. $PM_{2.5}$) and patterns of cardiopulmonary morbidity and mortality is quite solid. It is not clear, however, what chemical constituents may be particularly responsible for the observed effects.

This part includes six chapters which address various issues and topics which relate to how airborne PM is generated, where it comes from, its chemical composition and concentrations. In the first chapter, Saliba and Massoud summarize research on the levels and origins of airborne PM and related chemical processes and implications for human health in the Eastern Mediterranean region. In the studies discussed, they reveal the complexity of airborne PM and how its concentrations and composition are strongly impacted by source (e.g. local industry, marine, Sahara Desert) and season. Celo and Ewa Dabek-Zlotorzynska discuss the concentration and origins of trace metals measured in collected $PM_{2.5}$ from May 2004 to December 2006 at various monitored sites in Canada as part of the Canadian National Air Pollution Surveillance network in the second chapter. They compare data collected from both rural and urban sites as a function of annual and seasonal trends and source origin and discuss how the major sources of trace metals in $PM_{2.5}$ at urban sites include natural dust resuspension processes, industrial and traffic emissions and fossil fuel refining/burning. $PM_{2.5}$ mass concentrations at rural sites were found to be most strongly impacted by season. In the third chapter, Lammel et al. also discuss the strong influence of seasonality on the concentratraion, source and mass size of polyaromatic hydrocarbons (PAHs) in ambient PM collected at urban and rural sites of central (Czech Republic) and south-eastern Europe (Bosnia and Herzegovina) in 2006–2008. In addition, they also present their results on the phase distributions of parent PAHs and their toxicity. They found that PAH levels were higher in winter compared to the summer, due to higher emissions and slower photochemical degradation and mixing during this time of year. Limbeck and Puls provide a comprehensive review of the literature on particulate emissions from on-road vehicles under real world conditions in the fourth chapter. As they argue, data on traffic emissions, as they occur under real world conditions, are critical in assessments of risk and have been shown to differ from that obtained in the lab using dynamometer-based studies. As part of this, they focus on published data on size segregated emissions factors of particle mass, elemental and organic carbon, as well as crustal components and selected trace metals. In the fifth chapter, Ki-Hyun et al. present data collected on the trace metals Pb, Mn, Cr and Cd over a 16-year period from 1991 to 2006 in 15 major cities in Korea. They discuss the temporal and spatial variability of these elements over time and how concentrations are influenced by varying environmental conditions and source–sink processes. Part I then concludes with a contribution from Marx and McGowan on the long-distance transport of urban and industrial metals and their sources and environmental fate over time (sixth chapter). Their contribution discusses the importance of historical trends in understanding regional and global patterns of metal contamination in spatial–temporal terms and the importance of considering long-range pollution sources and pathways as contributors to local pollution levels. As they point out, this is often overlooked with the result that many urban studies incorrectly ascribe pollution to local sources.

A Comparative Review of PM Levels, Sources, and Their Likely Fates in the Eastern Mediterranean Region

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1 Introduction

Particulate matter (PM) has become a public concern ever since the British Clean Air Act was published in 1956. The publication came after a series of pollution episodes (1930 and 1952) that led to a serious increase in mortality, hospital admissions and insurance claims (Anderson 2009; Chen et al. 2007; Greenbaum 2003; Pope 2004) (Dec. 1930 Meuse valley, Belgium; Oct. 1948 Pennsylvania, USA; Dec. 1952 London, UK). In 1969, the USA's Environmental Protection Agency issued the "Criteria Document", which summarized findings from previous studies on health effects related to exposure to PM, total suspended particles (TSP) and sulfur dioxide (SO_2) (Greenbaum 2003). This led to the establishment of the Clean Air Act in 1970 in the USA, followed by the first National Ambient Air Quality Standards (Chen et al. 2007; Greenbaum 2003). Concurrently, the World Health Organization (WHO) set in its guideline a standard for the levels of suspended particles followed by a global guideline for the levels of ambient particles (Anderson 2009). Hence, the increasing interest among scientists in PM levels and health implications culminated in an increase by almost 5,000-fold in publications between 1980 and 2008 (Scopus 2009).

Particulate matters are classified in different types, depending on their origins. While marine aerosols are formed of sea salt particles, remote continental aerosols are of primary particles (like dust, pollens and plant waxes), as well as secondary oxidation products. Moreover, desert aerosols, which resemble remote continental aerosols in their shape and size, are found over deserts and adjacent regions and strongly depend on the wind velocity. Urban aerosols are then considered a

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_1,

mixture of biogenic (natural sources), primary anthropogenic (vehicle emission, industrial processes, combustion of fuel, domestic heating, power plants, and road dust resuspension) and particulate emissions, and of secondary material (gas-to-particle conversion) (Seinfeld and Pandis 1998).

Aerosol fates are not confined to a particular source or local region, and so a better understanding of their transformation processes should be addressed at a global scale and calls for the understanding of the local sources and the multi-processes the aerosol undertakes once emitted into the atmosphere. The emission of sea salt aerosol and their reactions with local pollutants at coastal regions result in a unique environment that defines urban marine aerosols (Kerminen et al. 1997; Kocak et al. 2004a, b; Niemi et al. 2005; Pathak et al. 2004; Zhuang et al. 1999). On the other hand, particles emitted from deserts can also react with nearby city pollutants like acid precursors (NOx and SO_2) and acids (HNO_3, and H_2SO_4) to produce airborne pollutants highly loaded with crustal and non-crustal elements. Sources of these pollutants can be attributed to vehicle emission, industrial processes, combustion of fuel, domestic heating, power plants, and road dust resuspension.

2 PM in the Eastern Mediterranean Region

2.1 Climate

The Eastern Mediterranean area including Cyprus, Egypt, Palestine, Israel, Jordan, Syria, Lebanon and Turkey (Fig. 1) is characterized by winters with abundant precipitation and summers with nearly no precipitation at all, separated by short transition seasons: spring and autumn. The thermal variations can be large without being excessive (Combier 1945). Rain is especially abundant during 4 or 5 months of winter; however, during hot summers; the air remains humid despite the absence of rain.. These low rainfall rates coupled with weak advections and frequent recirculation episodes of air masses result in frequent regional pollution events that increase the aerosol's residence time in the region and give rise to high PM background levels recorded in summer. This specific setting of the Eastern Mediterranean (including the high radiation intensity) enhances the formation of secondary aerosols and ozone (Kostopoulou and Jones 2007).

In addition, there are other features favoring the occurrence of higher ambient air concentrations of mineral dust in the Mediterranean basin. First, the Mediterranean is frequently affected by African dust outbreaks. Second, because of the low precipitation rates in the Eastern Mediterranean, soils exhibit a poor vegetal coverage in such a way that resuspension of natural and accumulated road traffic dust is enhanced with respect to cities located in more rainy regions (Graham et al.

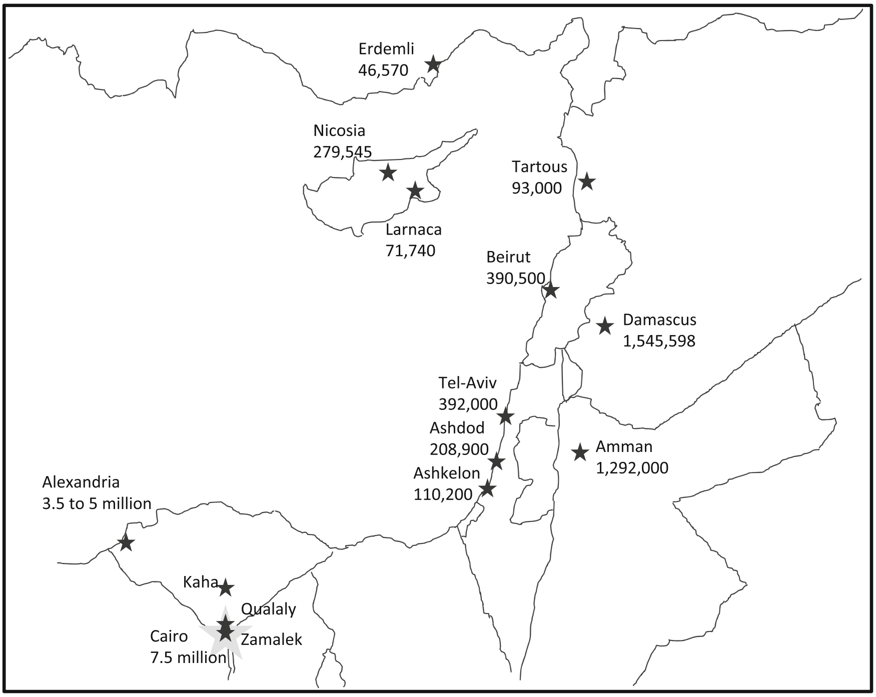

Fig. 1 Map of the Eastern Mediterranean region showing the reported cities lying along the Mediterranean coast. Numbers below the name of each city represent the city's population

2004; Millan et al. 1997, 2002; Rodriguez et al. 2001, 2003). Third, weak prevailing winds from sea breezes are formed due to the high pressure build-up some hours after sunrise during the warm season (summer and late spring). This leads to a change in the wind direction from east to west as well as an increase in the wind speed and the trapping of pollutants which renders PM rich in sea salt (Bleeker et al. 1960).

Several studies in the Eastern Mediterranean region have emphasized the effect of the aforementioned factors in affecting the type and level of pollutants in the region. During the ADIOS-EU funded program, Guieu et al. (2009) established a comparison between fluxes of metals of biogeochemical interest in the Western and Eastern Mediterranean regions. The Fe/Al ratio was found slightly higher in the Eastern region, due to its proximity to the Saharan desert. In non-dusty days, and during the summer, particles over the Eastern Mediterranean are found to be mainly composed of SO_4^{2-} and carbonaceous materials. They originate from the Balkans, Turkey and Central/Eastern Europe (Bryant et al. 2006; Vrekoussis et al. 2005). Additional sources could be attributed to extensive forest fires from southern Europe and desert dust plumes from North Africa (Bonnet and Guieu 2006; Guieu et al. 2005).

2.2 PM Levels

Despite the low recirculation probability of pollutants in the Eastern Mediterranean due to its geographical setting, and the consequences of such geography on the chemical composition and levels of aerosols, the literature review reveals a serious gap in long term air quality monitoring data along the Eastern Mediterranean coast (Levy et al. 2008). With the exception few articles (Elbir et al. 2000; Im et al. 2008; Kleanthous et al. 2008; Kocak et al. 2004a, b; Kubilay et al. 1997; Levy et al. 2009; Middleton et al. 2008; Tasdemir et al. 2005; Yuval and Broday 2006), reports in the region are restricted to short term measurements (Abed et al. 2009; Abu-Allaban et al. 2002, 2006, 2007a, b, 2008; Akkoyunlu and Tayanc 2003; Al-Masri et al. 2006; Al-Momani et al. 2005; Arafa et al. 2002; Asaf et al. 2008; Borai and Soliman 2001; Erel et al. 2002; Falkovich et al. 2001; Freiman et al. 2006; Ganor et al. 1998; Genc et al. 2009; Griffin et al. 2007; Kocak et al. 2007a, b, 2009; Kouyoumdjian and Saliba 2006; Mamane et al. 2008; Matvev et al. 2002; Othman and Al-Masri 2007; Perrino et al. 2009; Saliba et al. 2006, 2007; Schlesinger et al. 2006; Shaka and Saliba 2004; Tecer et al. 2008; Vrekoussis et al. 2005; Waisel et al. 2008a, b; Yatkin and Bayram 2008; Zakey 2008).

As shown in Fig. 2, the reported averages range between 93 and 9.7 μg/m^3 for $PM_{2.5}$ and 202.6 and 36.4 μg/m^3 for PM_{10} with the highest values of PM_{10} and $PM_{2.5}$ being measured in a residential site in Egypt. In fact, PM_{10} levels in Egypt exceeded in residential sites by 63% the maximum level that was measured in other Mediterranean countries. This could be attributed to the high population (7.5 million in Cairo city), its proximity to the Arabian and Saharan deserts and

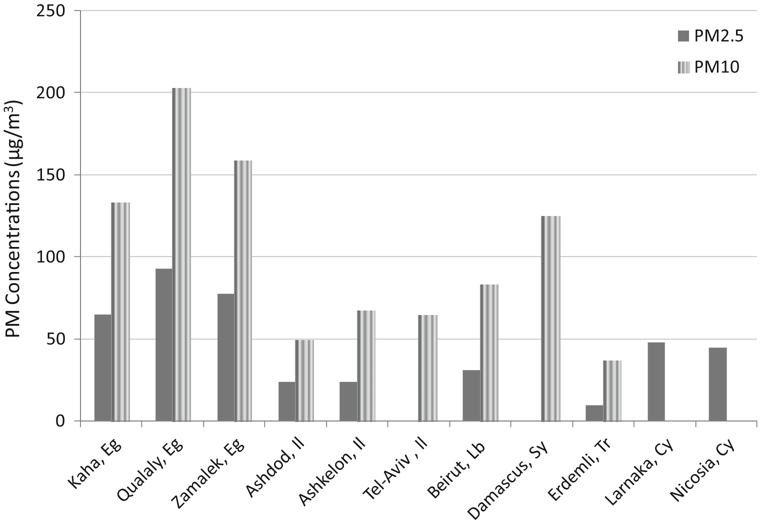

Fig. 2 Average concentrations of PM_{10} and $PM_{2.5}$ in different Eastern Mediterranean cities. Outbreaks due to desert storms and local industrial activities were omitted

the small amount of precipitation in the winter season (around 24 mm yearly average).

According to Abu-Allaban et al. (2007a, b), PM levels measured in the Cairo district (also called the greater Cairo area) in several sites of various characteristics, such as industrial (Shobra; downwind of Pb smelters and El-Massara; Cement plants), traffic (El Qualaly), and residential (Helwan and Zamalek), showed a PM_{10} concentration increase by 157% in industrial sites over the background site taken in Kaha that is situated 16 km north west of Cairo city. High PM_{10} concentrations in El-Massara originated from the cement plant while in Shobra, sources were assigned to Pb smelters. In the greater Cairo, however, the major contributors to PM_{10} included geological material, mobile source emissions, and vegetative burning. $PM_{2.5}$ tended to be dominated by mobile source emissions, vegetative burning, and secondary species (Abu-Allaban et al. 2002; Borai and Soliman 2001; Zakey 2008).

Israel showed lower $PM_{2.5}$ and PM_{10} levels. While Cairo is considered a megacity with 6.8 million population, Ashdod and Ashkelon are much smaller in size (around 47 km^2 each), and for both cities $PM_{2.5}$ levels were around 30% smaller than Cairo, and 19 and 40% for PM_{10}, respectively. In the rural site in Gedara, a $PM_{2.5}$ average of 25 μg/m^3 was measured (Mamane et al. 2008). Steinvil et al. 2008 conducted a short-term exposure to air pollution and inflammation-sensitive biomarkers study in Tel-Aviv, Israel, and reported a mean PM_{10} of 64.5 μg/m^3. Due to the proximity of the cities to the Saharan and Arabian deserts, the contribution of the background was assessed by sampling during different dust episodes (Schlesinger et al. 2006). A dust storm events lasting between few hours to 1–3 days, generated PM_{10} levels from 100–200 to 300–1,500 μg/m^3 and more, respectively. On the other hand, assessment of the effect of traffic reduction volume on PM_{10} levels was studied during the military conflict in Israel in summer 2006 (Yuval et al. 2008). Results showed that PM_{10} concentrations in most stations decreased by 4–18% during the conflict when compared to data from previous dates. The very low $PM_{2.5}/PM_{10}$ ratio (0.26–0.32) for spring supports this observation, in accordance with Vallius et al. (2000) and Gehrig and Buchmann (2003). The effect of the sea breeze on TSP levels was found to be much lower than that of the land breeze (7.8 and 8.6 μg/m^3 vs. 41.3 and 116.9 μg/m^3). This reversed behavior is due to heavy industry over the land in Haifa (Ganor et al. 1998).

In Jordan, high variation of PM_{10} concentrations depended on dust resuspension due to desert storms and abundant limestone quarries. Yearly averages ranging between 39 and 630 μg/m^3 were reported (Abu-Allaban et al. 2007a, b; Alsawair and Solieman 2007). No levels up to our knowledge were reported in Palestine. In Beirut, PM_{10} mean concentrations measured in various sites varied from 44 to 110 μg/m^3 (Moussa et al. 2006; Saliba et al. 2006, 2007; Shaka and Saliba 2004). Populated and inner city sites showed over 70% exceedances of the WHO PM_{10} annual average (20 μg/m^3), whereas coastal sites showed only 30%. Averages of $PM_{2.5}$ concentrations varied between 27.6 and 32.2 μg/m^3. $PM_{2.5}$ concentrations, at any given site, were usually between 36 and 51% of those of PM_{10}.

In the city of Tartous, Syria, TSP levels ranged between 171 and 397 $\mu g/m^3$ with sources attributed to traffic, a cement factory and phosphate and coal loading activities into ships. Moreover, concentrations reached 2,269 $\mu g/m^3$ during the phosphate loading around the Tartous port (Al-Masri et al. 2006; Othman and Al-Masri 2007). In Damascus PM_{10} values varied between 44 and 188 $\mu g/m^3$, levels were affected by wind direction (Meslmani 2004). PM_{10} and $PM_{2.5}$ measured at a rural site in Erdemli, Turkey, were 36.4 and 9.7 $\mu g/m^3$, respectively (Kocak et al. 2007a, b). Daily variations of PM_{10} and $PM_{2.5}$ concentrations were observed with the highest deviation from the mean due to mineral dust transported from North Africa and to sea spray generation. During summer, $PM_{2.5}$ levels exhibited higher concentrations resulting from an enhanced production of secondary aerosols due to high insolation. Similar behavior with high winter background at the traffic site, higher summer PM_{10} background levels and high seasonal influence of Saharan dust were observed at the majority of the 31 studied cities in Cyprus (Kleanthous et al. 2008; Kocak et al. 2004a, b, 2007a, b).

The low $PM_{2.5}/PM_{10}$ ratio ($\sim$0.25) in the Eastern Mediterranean region indicates that the particle size distribution has a large contribution of coarse particles which are either affected by a background level of naturally occurring dust (mineral dust particles from the Saharan Desert and sea salt particles from the Mediterranean Sea itself (Kocak et al. 2007a, b) or that the region is characterized by high levels of primary coarse PM emissions (Kocak et al. 2007a, b). Even though the $PM_{2.5}/PM_{10}$ ratio showed seasonal variations, the values remained lower than 0.5 in most cases (Abu-Allaban et al. 2002, 2007a, b; Asaf et al. 2008; Freiman et al. 2006; Kocak et al. 2007a, b; Moussa et al. 2006; Peled et al. 2005; Saliba et al. 2007; Shaka and Saliba 2004; Zakey 2008), a value that is least two times lower than those of the Western Mediterranean.

2.3 PM Chemical Profiles

In Alexandria, Egypt, the analysis of total Polycyclic Aromatic Hydrocarbons (PAH) concentrations of street dusts and particulate fallout samples revealed values that are similar to reported levels in different cities around the world. The major contributor to PAH levels is traffic, including diesel and gasoline vehicles (Barakat 2002), steel work (Mostafa et al. 2009), petroleum residues and traces of terrestrial organic compounds (Aboul-Kassim and Simoneit 1995). In addition to organic and elemental carbon, crustal components (Si, Ca, Fe, and Al) were found to be significant at various sites in Cairo. The latter exhibited higher levels in industrial and heavy traffic areas due to resuspended road dust. High levels of Pb and Cl measured in industrialized sites like Shobra area, which includes over 450 industrial units, were assigned to Pb smelters and textile factories (Abu-Allaban et al. 2002). The detected high amount of ammonium chloride in Cairo was attributed to traffic and neighboring industries (Abu-Allaban et al. 2007a, b; Borai and Soliman 2001; Zakey 2008).

In Al-Hashimya, crustal elements were also shown to have high concentrations in summer (dry season) while anthropogenic elements increased in winter. Abed et al. (2009) found that dust particles collected during the Khamaseen are predominantly aluminosilicates, quartz and carbonates with minor amounts of phosphate. Factors assigned as PM sources are attributed to natural aluminosilicates that are heavily loaded with Si, Al, Fe, K, Ga, Rb, Cs, Nb, Co, Ni and V, anthropogenic sources composed of Cd, Pb, Cu, Sn, Hg, Zn, Se, Mn, Mo and Ni, phosphorite provinces in Morocco, North Africa and Jordan rich in P and Si, and the abundance of calcite and limestone loading the atmosphere with Ca.

In Haifa, carbonaceous $PM_{2.5}$ aerosols constituted up to 80% of their mass and are mainly due to vehicle-induced emissions. However, a clear correlation between traffic density and levels of PM carbonaceous aerosols could not be established. This was attributed to several factors, like the prevailing synoptic winds that were observed at all sites, the sea and land breezes, the thermotopographic mountain and valley winds, and urban vegetation. Using stable Pb isotopes, an aerosol sampling study in Jerusalem showed that Pb in Israel is emitted and transported from Egypt, Turkey, and Eastern Europe. In their route from remote sources, dust storms were shown to carry with them both inorganic and organic anthropogenic pollutants (Abed et al. 2009; Erel et al. 2002, 2006). During a field experiment in Tel Aviv (2–15 Dec, 2000), the chemical composition of PM was compared to simultaneous measurements made in a semi-remote site in the Negev-Desert. In both sites, high contents of SO_4^{2-} and dust, originating from neighboring regions of the Middle East were observed. The increase of black carbon, organic carbon, V, Cu, Ni, Zn, Br, Pb, NO_3^{-}, and PAHs in the Tel-Aviv area indicated that vehicular emissions/industrial activities were the major contributors to local anthropogenic sources. This suggestion was confirmed by a nighttime increase in these concentrations due to pollutants trapping under the nocturnal inversion layer (Graham et al. 2004). A study on the shores of Haifa during summertime classified the aerosols into four categories: (1) gypsum particles from the sea and industrial sources, (2) continental aluminosilicate and quartz, (3) sea salt mixed with sulfates and (4) abundance of sulfate particles (Ganor et al. 1998). Sulfates originate from land and sea breezes, but their chemical composition differs; calcium sulfate, sodium sulfate and sulfuric acid are predominant in the latter. During land breezes, however, the sulfate and nitrate concentrations are 5–10 times higher than during sea breezes (Ganor et al. 1998; Perrino et al. 2009).

In Beirut, the elemental composition study of coarse and fine particles showed that crustal elements like Si, Ca, K, Ti, Mn and Fe were prevalent in the coarse fraction while in the fine fraction S, Cu, Zn and Pb predominated. All-time high Ca concentration was due to the abundance of limestone rocks, rich in calcite, in Lebanon, and increased Cl levels correlated with marine air masses. In $PM_{2.5}$, sulfur concentrations were more prominent in the summer due to the enhancement of photochemical reactions. Sources of sulfur were attributed to local, sea-water and long-range transport from Eastern Europe, with the latter being the most predominate. Anthropogenic elements like Cu and Zn were generated from worn brakes and tires in high traffic density areas. Spikes of Pb were directly linked to a southerly wind originating from Egypt and/or Israel as determined by the air trajectory HYSPLIT model (Saliba et al. 2007). In an inorganic analysis, NO_3^-, SO_4^{2-}, CO_3^{2-} and Cl^- ions constituted coarse particles, whereas SO_4^{2-} predominated the fine fraction in the form of $(NH_4)_2SO_4$ (Kouyoumdjian and Saliba 2006).

In Syria, the phosphate industry is abundant and so assessment of the impact of such an industry on the Syrian port, its coastal shore and the Mediterranean region is important. The work was based on evaluating naturally occurring radionuclide concentration (^{226}Ra, ^{nat}U, ^{210}Po, ^{210}Pb) by means of low background gamma and alpha spectrometry. High concentrations of ^{210}Po in sediments collected from Tartous shore were reported (Al-Masri et al. 2006; Othman and Al-Masri 2007; Othman et al. 1994). Air filters in Tartous were also analyzed for Zn, Pb, Cu. Organic and oxide lead were attributed to incomplete burning of vehicle fuels, residential heating and mineral acids soluble compounds. Cu and Zn were found to be present in the oxide form with zinc oxide being related to the emission from Tartous cement factory and phosphate loading cargoes (Al-Masri et al. 2006).

PM_{10} and $PM_{2.5}$ collected samples at a rural site in Erdemli, Turkey, showed that PM_{10} exceedance was mainly due to mineral dust and sea salt, whereas exceedence in $PM_{2.5}$ was due to ionic mass and carbonaceous aerosols (Kocak et al. 2007a, b). PM ionic concentrations were found to be season-dependent (Kocak et al. 2004a, b). A temporal and variability study in aerosol trace metal concentrations in the Levantine basin showed an enhanced concentration of Al, Fe and Mn in the transitional seasons attributed to desert sources. Zn increased in the summer, due to local anthropogenic emissions. Cr and Cu concentrations were enhanced northern of the Levantine region due to local emissions (Dogan et al. 2008; Kocak et al. 2004a, b; Kuloglu and Tuncel 2005; Yatkin and Bayram 2008).

2.4 PM Events and Seasonal Evolution

Storms in the Middle East occur in autumn, winter and spring. They mostly originate from the Saharan desert and only a small fraction from the Arabian Desert. It has been estimated that the Saharan dust load transported eastward every year is about 70 million tons, of which 20–30 million tons are deposited in the Eastern Mediterranean (Mamane et al. 1980). Elevated PM levels are therefore measured in the spring with low $PM_{2.5}/PM_{10}$ ratios (i.e. higher natural coarse particles). In the summer, crustal elements concentrations are reduced by half, hence, low variability between PM levels in different days is observed. On the other hand, levels of fine particles increase as a result of increased humidity, photochemically induced secondary PM, and long-range transport of sulfur. The latter constitutes 50% of the fine mass fraction. Chloride depletion was also detected by the Cl/Na ratio of 1.69 due to the reaction of sea salt with nitrogen oxides. Nitrate variation in the aerosols is dependent on mineral dust loading in the air. Interaction of nitrate with mineral dust episodes is suggested to lead to the formation of N_2O_5 which, by hydrolysis, converts into nitric acid in the atmosphere (Freiman et al. 2006; Mamane et al. 2008; Moussa et al. 2006; Saliba et al. 2006; Schlesinger et al. 2006; Wankel et al. 2009). Seasonal variation of PM levels allowed the identification and classification of PM episodes in the Eastern Mediterranean as follows: local urban PM pollution events, regional PM pollution episodes, marine air advection events and African dust outbreaks.

2.5 Source Apportionment

In the Mediterranean region, a semi-arid region, coarse particles significantly contributed to different sizes of PM content (Freiman et al. 2006), due to major crustal emissions from southern Algeria, northern Chad (Falkovich et al. 2001, 2004) and the Saharan and Arabian deserts. Urban particles, however, originated from both anthropogenic and biogenic sources like power plants, refineries, chemical and metal industries, cargo ports, road traffic sea-spray and desert dust (Kocak et al. 2004a, b, 2007a, b; Kouyoumdjian and Saliba 2006; Mamane et al. 2008; Saliba et al. 2007; Waisel et al. 2008a, b).

Anthropogenic sources, like unburned lubricating oil, automobile exhaust, and diesel exhaust from diesel powered vehicles, were identified through the analysis of particle hydrocarbon distributions and the analysis of the PAHs and PAH derivatives of samples collected from different cities in Egypt (Aboul-Kassim and Simoneit 1995; Mostafa et al. 2009). Using the chemical mass balance receptor model in the greater Cairo Area, the major contributors to PM_{10} were found to include mobile source emissions and open burning, in addition to geological material. $PM_{2.5}$ was identified to be dominated by mobile source emissions, open burning and secondary species (Abu-Allaban et al. 2002, 2007a, b; Vrekoussis et al. 2005; Yatkin and Bayram 2008). In addition to the aforementioned sources, Mediterranean regions are recipients of long-range transported air pollutants generated in Europe. Using sulfur dioxide and particulate sulfates as markers, an aircraft measurement study showed that the long-range pollutant transport, depending on the season, accounts for up to 50% by mass of the total sulfur content in particles. Furthermore, approximately 15% of the estimated pollution transported from Europe towards the Mediterranean basin contributes to the yearly flux of sulfur arriving at the Israeli coast (Matvev et al. 2002). On the other hand, using particulate Pb as a tracer, transport of dust and industrial emission from Egypt toward the Levant region was determined (Erel et al. 2002; Griffin et al. 2007; Kouyoumdjian and Saliba 2006; Mamane et al. 2008; Saliba et al. 2006, 2007; Vrekoussis et al. 2005). Dust contribution to PM levels is highly manifested in Jordan, where high levels of desert dust and dust resuspension, due to local emissions and long-range transport, have been reported (Abed et al. 2009; Abu-Allaban et al. 2006; Al-Momani et al. 2005; Chen et al. 2008). In fact it has been estimated that the North African Sahara causes the deposition of about 0.3

million ton of dust during spring every year in Jordan, and particles are found to be chemically homogeneous, rich with upper continental crustal elements.

Investigation of sources of aerosols over the Gulf of Aqaba indicated that, even in an area dominated by mineral dust deposition and surrounded by deserts, about 50% of TSPs are found to be associated with anthropogenic sources (Chen et al. 2008). In a study to characterize organic species adsorbed onto mineral dust particles, Falkovich et al. (2004), showed that most particles consist of aggregates of various minerals and organic material adsorbed on particle surfaces in a heterogeneous manner. Water soluble organic compounds were evidently affected by the change in relative humidity in addition to dust loading. Dust, therefore, becomes an efficient medium for pollutant transport in the troposphere and consequently is an important health concern. Since the adsorption phenomenon occurs in the fine as well as in the coarse mode, its removal from the atmosphere and its residence time is a function of the particle size distribution (Falkovich et al. 2001).

Furthermore, the marine influence in the region was manifested in several locations by a clear chloride deficit due to the reaction of sea salt with acidic anions like sulfates and nitrates (Kocak et al. 2004a, b; Kouyoumdjian and Saliba 2006; Saliba et al. 2007). It has been reported that PM_{10} composition along the Mediterranean coast (i.e. Erdemli, Turkey) contained up to 90% of sea salt and mineral dust, whereas $PM_{2.5}$ mainly contained anthropogenic pollutants emitted locally and/or transported from neighboring locations (Hassanien and Abdel-Latif 2008; Kocak et al. 2007a, b, 2009).

2.6 Health Implications

Although PM exposure affects all age-groups, especially babies (Brunekreef and Holgate 2002; Kryzanowski M and WHO European Centre for Environment and Health B, Germany 2007) and elderly (Aben et al. 2002; Brunekreef and Holgate 2002), there is still no evidence of a threshold below which no adverse effects are anticipated. Studies from different countries, in the region as well as in American, European and Asian cities, associated elevated PM levels with an increased risk of mortality and morbidity, with smaller particles being more crucial to cardiovascular and respiratory problems since they are capable of reaching alveolar regions (El-Zein et al. 2007; Kobrossi et al. 2002; Middleton et al. 2008; Peled et al. 2005; Peled et al. 2004).

3 Conclusions and Recommendations

The current review has produced an extensive database of PM levels, chemical composition, variations as well as their sources and fates in the atmosphere of the Middle Eastern region. The following conclusions may be made:

1. There is a general decrease in PM concentrations and their crustal material load from south to north across the Levantine Basin due to their remoteness from Saharan dust events. Concentrations of Si, Al, Fe and Mn were found to decrease from Egypt to Turkey.
2. The value of $PM_{2.5}/PM_{10}$ was lower than 0.5 in most cases due to the abundance of coarse particles originating from frequent dust storms in the region.
3. Dust storms originating from the Saharan desert occur in autumn, winter and spring lead to the increase in coarse particles. In the summer, levels of fine particles are enhanced as a result of increased humidity, photochemically and induced secondary PM, and long-range transport of sulfur.
4. Pb, originating from lead smelters in Egypt or from Eastern Europe, decreased as it travels with dust particles across the Levantine Basin. Hence, its daily variation is a function of the wind direction and weather conditions.
5. The influence of marine aerosol was manifested in several locations by a clear contribution of sea salt to the mass of PM_{10} in the region and chloride deficit is due to the reaction of sea salt with acidic anions like sulfates and nitrates. Also, nitrate interacts with mineral dust to lead to N_2O_5 high by hydrolysis converts into nitric acid in the atmosphere.
6. Sulfate was identified to originate from both land and sea breezes with its concentrations bing higher during land breezes. Local particulate sulfate was found to increase during summer due to the enhanced SO_2 to sulfate conversion rates because of the involvement of photochemistry. The long-range transported of air pollutants that originated over various parts of Europe varied seasonally with minimum values observed during summer.
7. In dry and hot seasons, road vehicles enhanced dust resuspension, making traffic a major contributor to PM elevated levels in the region.

In brief, the distribution and nature of particles in the Eastern Mediterranean region are influenced by high recirculation potential in the region and strong interactions between land and sea breezes. Future work should focus on examining spatial and seasonal variations in order to assess the contribution of local and distant sources. Furthermore, given the importance of the chemical composition and particle size in cloud formation, aerosol solubility and ocean productivity, it is vital that data on particle mass closure in the semi-arid region be extensively developed. This information will be directly impacted by wet precipitation and climate change.

Acknowledgments The authors would like to thank the Lebanese National Council for Scientific Research for supporting this work.

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Concentration and Source Origin of Trace Metals in $PM_{2.5}$ Collected at Selected Canadian Sites within the Canadian National Air Pollution Surveillance Program

Valbona Celo and Ewa Dabek-Zlotorzynska

1 Introduction

Airborne particulate matter (PM) is a complex mixture of thousands of organic and inorganic species that emerge from a wide range of natural and anthropogenic sources. Numerous epidemiological studies have confirmed that PM and especially the respirable fraction of PM, the $PM_{2.5}$ (for particles <2.5 µm diameter), has adverse effects on human health. Although there is no evidence to pinpoint any single feature or component of PM as the cause for the observed epidemiological effects, it is apparent that metals contribute, at least in part, to the toxic and carcinogenic effects associated with exposure to airborne PM and for this reason have been the object of several epidemiological studies (Goldoni et al. 2006; Kawata et al. 2007; Lippmann et al. 2006). In addition, trace metals are proven to be useful tracers and are extensively used to identify sources of emissions to be targeted by the emission reduction policies (Querol et al. 2001; Lee et al. 2003; Gotschi et al. 2005; Querol et al. 2006; Querol et al. 2007b; Viana et al. 2007; Jeong et al. 2008). Therefore, monitoring of elemental composition of PM has become a crucial part of air quality programs in many countries around the world.

The Canadian National Air Pollution Surveillance (NAPS) network is one of the major air quality monitoring initiatives in the country. It was established in 1969 as a joint program of the federal and provincial governments to monitor and assess the quality of the ambient air in Canada's urban centers. Air quality data are measured at 319 sites, located in 216 communities in all provinces and territories with the aim of providing the information needed to evaluate air pollution control

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_2,

strategies, identify air quality trends and warn of emerging air pollution issues (NAPS 2008).

The objectives of this study were to quantify the trace metals in $PM_{2.5}$ of Eastern and Western Canada, to analyze their annual and seasonal trends and identify their source origin, by evaluating a database of trace metal concentrations obtained over a 2-year period (May 2004–December 2006) from the NAPS network. Over 1000 $PM_{2.5}$ samples collected at seven selected sites were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) after microwave assisted acid digestion. This technique offers low detection limits, wide linear dynamic range, multielement capability, ability to measure isotope ratios and high sample throughput. Principal Components Analysis (PCA) was used to identify sources of trace metals at each sampling site.

2 Materials and Methods

2.1 Sample Collection

The sampling sites were selected to represent different urban and rural settings, and were located from East to West of Canada as shown in Fig. 1 and described in Table 1. NAPS network sampling sites are equipped with R&P Partisol-Plus

Fig. 1 Locations of the seven NAPS sampling sites included in this study

Table 1 The sampling sites geographical location, site classification and major local emission sources

Location	Latitude and longitude	Site classification	Local PM sources		
			Traffic related	Industrial pollution	Other sources
Abbotsford, BC	49°01′ N, 122°20′ W	Urban-residential	Airport traffic	Building materials, mining and quarrying	–
Vancouver, BC	49°12′ N, 122°59′ W	Urban-commercial	Urban traffic	Building materials, oil and gas refining, storage and distribution, sand mills and wood products	–
Simcoe, ON	42°51′ N, 80° 16′ W	Rural-agricultural	Farming related traffic	–	Farming processes
Toronto, ON	43°39′ N, 79°23′ W	Urban-commercial	Urban traffic	Building materials	–
Windsor, ON	42°17′ N, 83°04′ W	Urban-residential	Urban traffic	Primary metal manufacturing, building materials, waste treatment, electricity generation, auto industry	–
Montréal, QC	45°31′ N, 73°33′ W	Urban-commercial	Urban traffic	Building materials, oil and gas refining, storage and distribution, chemical products manufacturing	–
Canterbury, NB	45°57′ N, 67°28′ W	Rural-undeveloped	–	–	Local heating

Model 2025-D sequential dichotomous sampler that simultaneously collects coarse ($PM_{2.5\text{-}10}$) and fine PM ($PM_{2.5}$) particles, with flow rates of 1.7 and 15 L/min, respectively. Samples were collected over 24 h using a one-in-three day schedule, on Teflon filters (PTFE, 47-mm diameter) with a polyethylene support ring (PALL Corporation, NY, USA). Compared to other materials used for sampling of airborne PM, such as quartz, glass, cellulose or polycarbonate, Teflon filters had the lowest blanks for metals and were used throughout this study. The Teflon filters were weighed before and after sample collection using a Mettler Microbalance (MT-5, Mettler-Toledo Inc., Highstown, NJ), under controlled relative humidity (45 ± 5%) and temperature (23 ± 3 °C).

2.2 Sample Digestion and Analysis

A closed vessel microwave assisted reaction system (MARS 5, CEM Corporation, Matthews, NC) was used for acid digestion of samples. All digestions were performed in 7-mL Teflon digestion microvessels (Micro Vessel^{TM}, CEM Corporation, Matthews, NC) accommodated inside the standard 100-mL Teflon liners (HP-500 Plus, CEM Corporation, Matthews, NC). The pressure inside the liners and the internal temperature of the microvessels were monitored in a control vessel assembly, which is equipped with pressure and temperature sensor units. The $PM_{2.5}$ laden Teflon filters were digested at 175 °C with 2 mL of 40% (v/v) HNO_3, following a two-step digestion program (Celo et al. 2005a, b). Reagent blanks, filter blanks and other QA/QC samples were prepared in the same manner.

The ICP-MS measurements were performed using an Agilent Technologies 7500c ICP-MS system (Agilent Technologies, Wilmington, DE, USA), equipped with an octopole collision/reaction system (ORS), a Babington nebulizer, a Peltier cooled (2 °C) quartz Scott-type double pass spray chamber and an Agilent I-AS integrated autosampler. Spectral interferences were minimized or eliminated either by choosing a non-interfered isotope or by using the ORS with H_2 as the reaction gas. The instrument conditions for ICP-MS measurement were summarized by Chen et al. (2008). The precision and accuracy of the ICP-MS measurements were checked by analyzing Certified Reference Materials (CRMs) prepared in the same matrix as the digested samples, spikes and duplicates. The 95% expanded relative uncertainties above quantitation limit (3 times limits of detection) (CAEAL January 2006) ranged from 10 to 25%. Results were accepted when measured concentrations of CRMs and spiked samples were within 10–20% of target values and the relative percent deviation (RPD %) of duplicates was less than the reported uncertainty.

The limits of detection (LOD) were established from at least seven replicate analysis of reagent blanks fortified at a concentration no greater than 5–10 times the instrument detection limit and treated the same way as samples. The standard deviation value was then multiplied by the one-tailed Student's test value for 99%

confidence level. LOD of most of the elements of interest were below 1 ng/m^3. The only exceptions were Zn and Fe with LOD of 4 and 3 ng/m^3, respectively.

2.3 Treatment of Data Less Than Limits of Detection

Chemical data resulting from trace and ultratrace analysis are usually characterized by a certain percentage of observations that are below LOD. These data are generally reported as “less than the detection limit” and data sets with “less-than” observations are termed “censored data” in statistical terminology. Censored data may not present a problem in monitoring studies when most of the concentrations of analytes of interest are well above detection limits. However, for most of environmental studies this is not the case. Analyses of trace metals in PM are one example of data sets with a considerable amount of observations being below the respective LOD.

During the recent years several studies have been focused on the statistical methodologies that should be used for estimation of summary statistics (mean, standard deviation, median and interquartile range) or for performing other statistical analysis of censored data sets (Gilliom and Helsel 1986; Helsel and Gilliom 1986; Helsel 1990; Kuttatharmmakul et al. 2000; Finkelstein and Verma 2001; Jain et al. 2008; Jain and Wang 2008). In many monitoring studies, the censored data are substituted by LOD/2 or LOD/$\sqrt{2}$ (Helsel 1990; Finkelstein and Verma 2001). Also the Maximum Likelihood Estimation (MLE) method has been used in many environmental disciplines, such as air quality studies (Owen and DeRouen 1980) and traces level water quality (Helsel and Gilliom 1986) and was shown to provide an accurate estimate of summary statistics for highly censored data sets (Helsel 1990; Kuttatharmmakul et al. 2000; Finkelstein and Verma 2001). Nevertheless, MLE and other robust statistical methods require computations using statistical software which are not practical or available for routine analysis of monitoring programs. Thus, these are recommended only for compounds which have a significant impact in the risk assessment and for which the data sets are adequate (Smith 1991).

The percentages of censored observations (less than LOD) of data sets included in this study are summarized in Table 2. The number of observations was above 200 at all sites except for Simcoe and Windsor which had 149 and 89 observations, respectively. Although the sample size was quite large, the percentage of censored data for some elements was quite significant. For example, concentration of Be was below LOD in all samples whereas Co, Ag and Tl were more than 50% censored at all sites. Other elements such as Cr, Mo and Se were censored at 40% or more at several sampling sites. For this reason, choosing the best way of treating the data sets for estimation of summary statistics becomes an important issue in this study.

With the goal of choosing a method that provides the best estimations of summary statistics without the need of extensive statistical calculations, we

Table 2 Percentages of censored observations (less than LOD) for each site included in this study (2004–2006)

	LOD (ng/m^3)	Abbotsford N = 217	Vancouver N = 224	Simcoe N = 150	Toronto N = 226	Windsor N = 91	Montréal N = 209	Canterbury N = 261
Be	0.03	100	100	100	100	100	99	100
V	0.1	12	0	6	12	1	6	8
Cr	0.4	67	31	46	37	13	29	93
Mn	0.1	0	0	1	0	1	1	3
Fe	3	1	0	1	1	1	0	9
Co	0.03	94	76	97	89	59	63	94
Ni	0.3	36	5	17	36	8	11	39
Cu	0.3	5	0	1	0	1	0	5
Zn	4	18	5	3	5	1	2	37
As	0.1	3	4	3	2	1	2	27
Se	0.2	64	59	7	15	8	29	73
Sr	0.1	20	3	7	8	1	3	56
Mo	0.06	45	5	40	18	1	13	84
Ag	0.07	93	86	98	95	84	73	94
Cd	0.02	17	13	3	3	1	1	31
Sn	0.1	13	1	21	8	1	13	45
Sb	0.1	16	0	18	6	2	6	55
Ba	0.1	1	0	3	0	1	1	15
Tl	0.03	94	91	88	83	68	75	95
Pb	0.1	1	0	1	1	0	0	11

N is number of samples analyzed at each site

compared the simple substitution of "less than" data with LOD/2 and LOD/$\sqrt{2}$ against the MLE method as described by Finkelstein and Verma (2001). We found out that using substitution with LOD/$\sqrt{2}$, summary statistics for highly censored elements such as Cr, Co, Ag and Tl, were closer to MLE than substitution with LOD/2, whereas for the other elements both substitution methods yielded values that were within ±15% of MLE results. Thus the simple substitution with LOD/$\sqrt{2}$was used as the best approach for the calculations of summary statistics in this study.

Methods of hypothesis testing based on data sets with censored observations have also been discussed in several publications (Helsel 1990 and references therein). The widely used parametric statistical tests are based on the assumption that the observations follow a known distribution which is usually assumed to be of normal shape. Alternatively, the non-parametric or robust tests do not require any assumption of the distributional shape and the results are less depended on the "less than LOD" observations (Helsel and Gilliom 1986; Helsel 1990). As illustrated in Fig. 2, the distributions of $PM_{2.5}$ mass and metal concentrations in our study are lognormal rather than normal. Therefore, using average and standard deviation to estimate summary statistics and parametric tests for testing of hypothesis may result in erroneous conclusions. Consequently, our further discussions and conclusions are based on the median and interquartile range (IQR) values and the non-parametric methods for testing of various hypotheses.

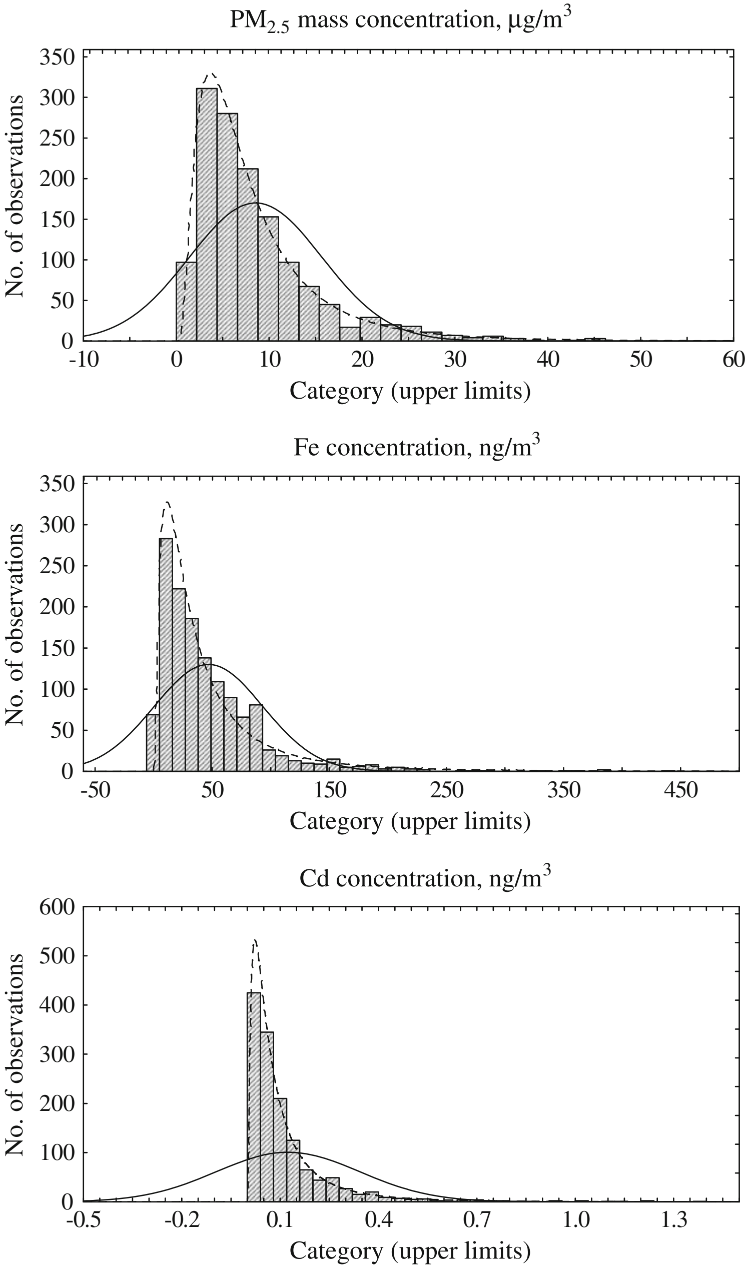

Fig. 2 Distributional plots of $PM_{2.5}$ mass, Fe and Cd concentration; normal distribution fitting and lognormal distribution fitting

STATISTICA ver. 8 software (StatSoft Inc., Tulsa, OK, USA) was used for all statistical analyses.

3 Results and Discussion

3.1 Particle Mass Concentrations

The presence of particulate matter in the atmosphere is a consequence of both natural and anthropogenic sources. Background PM is generally defined as the distribution of PM concentrations that would be observed in the absence of primary and secondary anthropogenic emissions (Health Canada and Environment Canada 1998). The range of expected background concentrations on an annual basis is from 4–11 μg/m^3 for PM_{10}, and 1–5 μg/m^3 for $PM_{2.5}$ for remote sites in North America (Health Canada and Environment Canada 1998). Summary statistics for mass concentrations of $PM_{2.5}$ collected at selected NAPS sites during May 2004–December 2006 sampling period are presented in Table 3. The IQR of mean 24-h $PM_{2.5}$ concentrations at all sites was 5–11 μg/m^3. These levels were substantially above background concentrations indicating that anthropogenic activities make a significant contribution to ambient $PM_{2.5}$ loadings. The sampling site with the highest median concentration of $PM_{2.5}$ was Windsor (9.9 μg/m^3) followed by Simcoe site with a concentration of 8.7 μg/m^3. Canterbury had levels of $PM_{2.5}$ comparable with the background level for remote sites in North America. The medians of average 24-h concentration of $PM_{2.5}$ at all sampling sites were below 15 μg/m^3 that is recommended by the Canadian National Ambient Air Quality Objective (NAAQO) as the level of $PM_{2.5}$ (24 h averages) above which there are demonstrated effects on human health and/or environment (Health Canada and Environment Canada 1998). The $PM_{2.5}$ standard in Canada, referred to as the Canada-Wide Standard (CWS) has been set at 30 μg/m^3 (24-h average), based on 98th percentile ambient measurement annually, averaged over 3 consecutive years (http://www.ccme.ca). The standard is to be achieved by 2010. With

Table 3 Summary statistics of $PM_{2.5}$ mass concentrations (μg/m^3) (2004–2006)

	Abbotsford	Vancouver	Simcoe	Toronto	Windsor	Montreal	Canterbury
Arithmetic mean	7.1	6.7	10.5	9.9	11.8	9.9	4.5
Geometric mean	6.0	6.0	8.0	7.5	10.0	8.1	3.5
Median	6.4	6.2	8.7	7.5	9.9	8.0	3.43
Minimum	0.5	0.8	0.9	0.3	2.6	1.1	0.4
Maximum	20.5	18.9	35.6	36.2	32.4	36.0	29.5
Lower quartile	4.1	4.4	4.9	4.4	6.3	5.2	2.4
Upper quartile	9.4	8.5	13.5	12.8	15.5	12.7	5.2
98th percentile[a]	18.0	15.7	26.1	35.8	34.0	29.9	16.6

[a] Calculated as the average of the 98th percentile of each year from 2004 to 2006

Table 4 Mean levels and range of $PM_{2.5}$ (μg/m^3) reported at different regions of the world

Country	Years	Mean	Range	Source
Oxford, Ohio	2005	15.6	3.3 to 38	Wojas and Almquist (2007)
Spain	NR	NR	20 to 30	Moreno et al. (2006b)
Toronto, Canada	2000–2001	12.7*	NR	Lee et al. (2003)
Korea	2002	29	7.5 to 246	Kim et al. (2005)
Europe	2000–2001	19.1	3.7 to 45	Gotschi et al. (2005)
Taichung, Taiwan	2005	38.1	22 to 46	Fang et al. (2007)
Beirut, Lebanon	2004	38.5	20 to 67	Saliba et al. (2007)
Cartagena, Spain	2004–2005	22	7 to 47	Negral et al. (2008)
Hong Kong	2002–2003	42.3	29 to 71	Hagler et al. (2007)
Singapore	2000	22.2*	12.2 to 48.1	Balasubramanian and Qian (2004)
Guangzhou, China	2004	97.5	52 to 187	Wang et al. (2006)
South Brazil	2001–2002	15	1 to 44	Braga et al. (2005)
Edinburg, UK	1999–2000	7.1*	3.6 to 18.3	Heal et al. (2005)
Hong Kong	2000–2001	79.6	28 to 117	Ho et al. (2003)
Barcelona, Spain	2005–2006	29		Perez et al. (2008)

The asterisk (*) indicates median concentrations
NR non-reported values

the exception of Canterbury, $PM_{2.5}$ levels at Eastern sites were close to or exceeded the CWS whereas Western sites had $PM_{2.5}$ concentrations well below this standard. On the other hand, the $PM_{2.5}$ mass concentrations found at all Canadian sites were generally lower than values reported for other regions of the world (Table 4).

3.2 Trace Metals Concentrations

3.2.1 Spatial Variations

The median concentrations of most of the trace metals ranged from 0.1 to 1 ng/m^3 (Fig. 3). Be, Tl, Co and Ag were detected at the level of the respective LOD (less than 0.1 ng/m^3) at all sites. Ba, Mn, Pb, Cu, Zn and Fe had concentrations that exceeded 1 ng/m^3 at most of the sampling sites. The most abundant metals at each site were Fe and Zn with overall median concentrations of 35 and 9 ng/m^3, respectively. The least polluted site was Canterbury where the average sum of metal concentration was 20 ng/m^3. The metal concentrations increased with the anthropogenic inputs and reached the maximum at Windsor site (average sum of metal concentration was 189 ng/m^3), which is characterized by intensive industrial activities in the vicinity of the city. Metal concentrations at this site were up to 10 times higher than at Canterbury. Similar trace metal concentrations were observed at Toronto, Montreal and Vancouver sampling sites, which agrees with the similar human activities at these highly dense commercial urban areas. The highest level

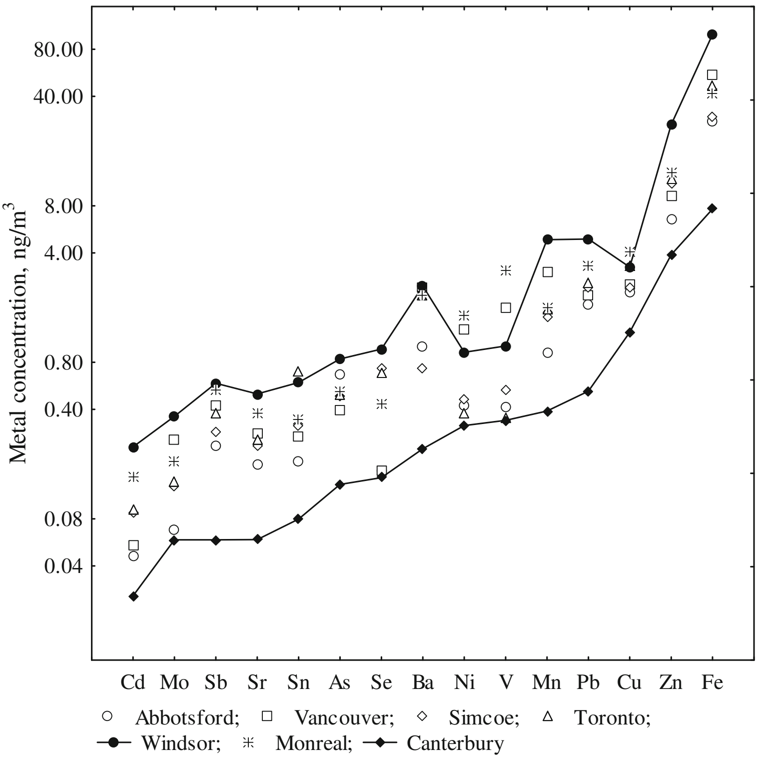

Fig. 3 Median metal concentrations sorted by the concentration values at Canterbury site (2004–2006 data)

of Ni and V, tracers of oil-burning and/or oil-refining industries, were recorded at Vancouver and Montreal, both sites located close to oil refining facilities. Compared to the elemental composition of $PM_{2.5}$ samples collected in urban areas of Europe, Japan, and the USA, the Canadian urban aerosols were equally or less loaded with trace metals (Fig. 4). Although Windsor samples had the highest levels for almost all metals, these were lower than concentrations found in Tokyo and in many European cities. Also, the metal concentrations at all sites were much lower than the guidelines published by WHO (2000).

3.2.2 Seasonal and Annual Variations

The seasonal variations of trace metal composition of atmospheric aerosols are controlled by several meteorological factors such as temperature, humidity and wind velocity and direction. Cold seasons are usually characterized by persistent thermal inversions, high precipitation and low wind velocities which favor the accumulation of anthropogenic exhaust emissions and reduce the presence of road

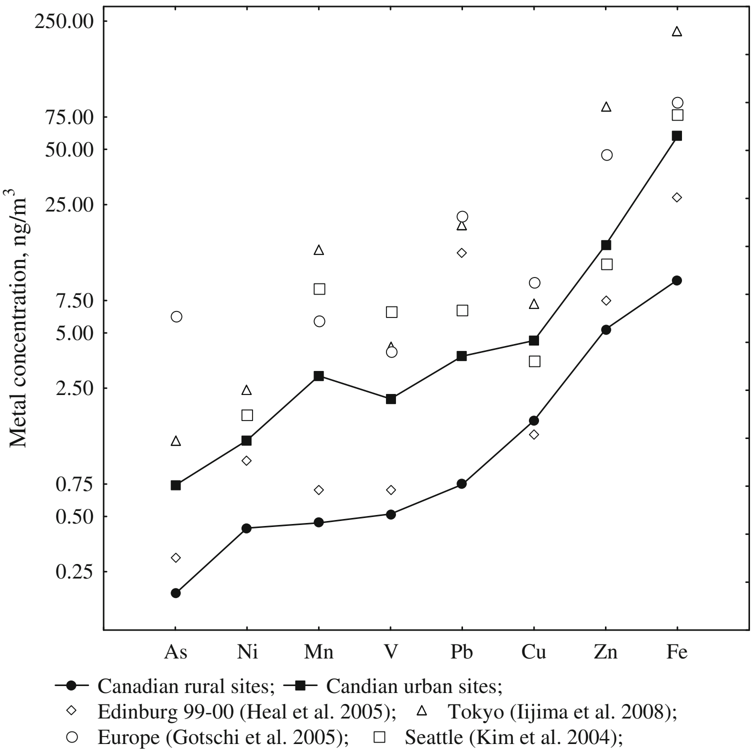

Fig. 4 Median trace metal concentrations at Canadian urban and rural sites, together with values reported for urban sites at different regions in the world

dust in the $PM_{2.5}$ fraction of atmospheric aerosols. Dry climate conditions during the warm seasons favor the formation and lift-up of dust particles, which is often the reason for elevated concentrations of crustal elements in the atmospheric aerosols during that time of the year (Gotschi et al. 2005; Qureshi et al. 2006; Querol et al. 2007b; Teixeira et al. 2009).

In this study, the seasons were defined as cold (October to April) and warm (May to September). With this definition all sites had similar distribution of data between seasons (about 50:50), which avoids any seasonal bias due to coverage period at each site. Also, this classification generally coincided with overall temperature profiles in Canada. Seasonal median concentrations of trace metals are presented in Fig. 5. The concentrations of Fe and Mn were higher during the warm season at all sites, suggesting a link of these elements with crustal component of $PM_{2.5}$. At the Simcoe site the concentrations of all elements were up to 70% higher during the warm seasons (Fig. 5). The highly intensive agricultural activities during this period of the year may enhance the metal concentrations in aerosols by both dust re-suspension and increased human made emissions. Also, the wet washout of metals from the atmosphere is generally less significant during this

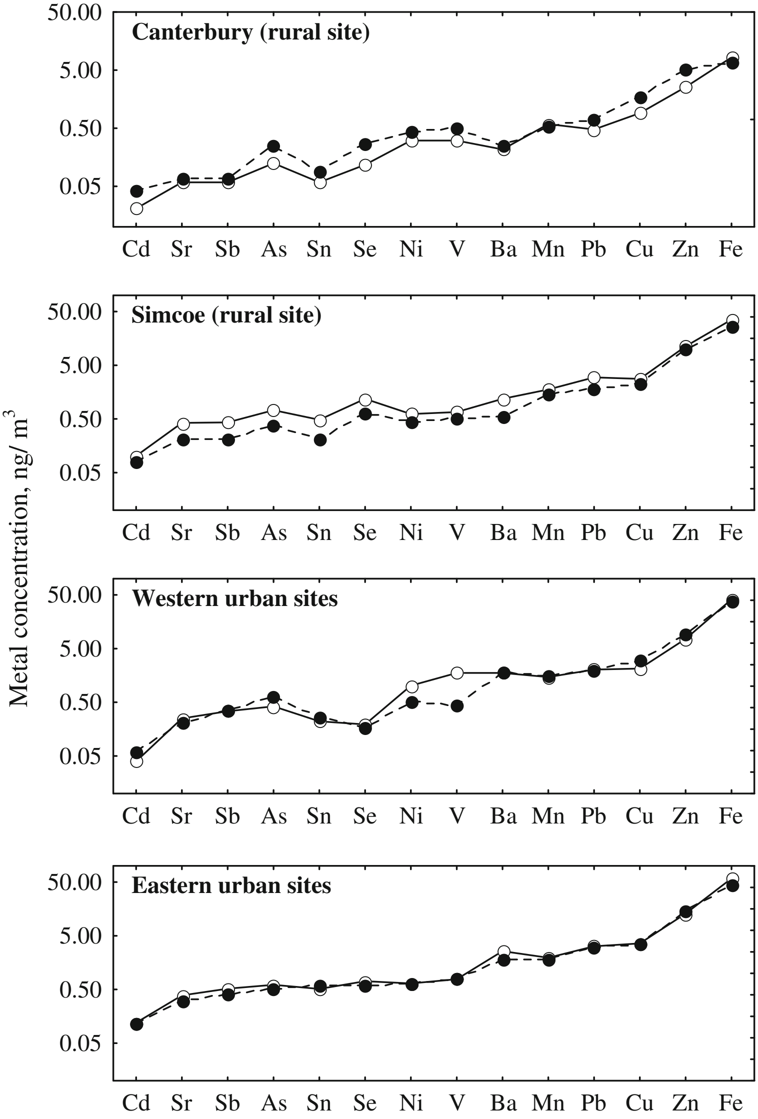

Fig. 5 Median concentrations of trace metals for samples collected during warm (*filled circle*) and cold (*open circle*) seasons of the sampling period

time of the year. The opposite trend was typical at Canterbury site where most of the metals had elevated concentrations during the cold months of the year. Considering that there is no industrial activity in the vicinity of this sampling site, the main pathways of metals in this region are long-range transport and local activities such as house heating, which are generally favored by winter conditions

(Bottenheim et al. 2004). The Abbotsford and Vancouver sampling sites, both located in Western Canada and in the vicinity (20 km or less) of petrochemical facilities, were characterized by a 3- and 6-fold increase in concentrations of Ni and V, respectively, during the warm periods of the year. Similar trends were reported for other regions close to petrochemical and oil fired power plants (Querol et al. 2007a). The seasonal variations of metals at other sites were generally not significant and typically had a slight upward trend in the cold season, especially for elements that are indicators of anthropogenic activities such as As, Se, Cu, Zn and Cd.

The annual variations of trace metal concentrations in urban $PM_{2.5}$ were not statistically significant (Kruskal–Wallis ANOVA, $p > 0.05$), whereas at the rural sites (Canterbury and Simcoe) the sum of metal concentrations dropped significantly (by 19 and 15%, respectively) from 2004 to 2006. Samples from the Toronto site were also collected and analyzed during 2000–2001 sampling campaign from Lee et al. (2003). Compared to the results of this study, the trace metal composition of $PM_{2.5}$ in Toronto has not changed significantly during this period of time.

3.3 Source Apportionment

The principal intention of many monitoring studies related to atmospheric aerosols is the identification and apportionment of pollutants to their sources. This information is crucial for the development and implementation of policies protecting human health and the environment. Receptor modeling, which provides information regarding source characteristics from the measurements of particle chemical composition at a sampling site, is the most commonly used source apportionment technique (Paatero et al. 2005). The most widespread receptor methodologies used in source apportionment studies to date are the Principal Components Analysis (PCA), Positive Matrix Factorization (PMF) and Chemical Mass Balance (CMB). The theoretical basis and applications of these methods have been previously described in many publications (Paatero et al. 2005; Rizzo and Scheff 2007; Viana et al. 2008; Junninen et al. 2009). Viana et al. (2008) summarized the theoretical limitations and advantages of these models and confirmed their agreement in the identification and interpretation of the major PM sources. However, the authors recommended that using a combination of the three models would probably yield a more robust solution. Shi and co-authors (Shi et al. 2009) applied a combination of PCA-CMB and PMF-CMB to identify the major PM sources and their average contributions to particulate pollutants. The authors concluded that the combined models are superior only for some relatively complicated receptors.

In the present study, the source apportionment of the trace metals in $PM_{2.5}$ was carried out using the PCA with normalized varimax rotation of the original variables. The number of factors that were retained in each case was determined by the

Table 5 Factor analysis pattern after normalized varimax rotation for trace metal concentration in $PM_{2.5}$ at all sampling sites (factors loadings >0.7 are highlighted and loadings <0.3 are omitted from this table)

Factor 1		Factor 2		Factor 3		Factor 4		Factor 5	
% variance = 41.2		% variance = 11.2		% variance = 10.9		% variance = 8.7		% variance = 6.8	
Mn	0.876	Se	0.862	V	0.905	Sr	0.923	As	0.923
Fe	0.880	Sn	0.659	Ni	0.906	Ba	0.866	Cu	0.866
Zn	0.803	Cd	0.651	Cu	0.319	Sb	0.375	Sb	0.473
Mo	0.628	Pb	0.465					Cd	0.470
Sb	0.389	Sb	0.330					Zn	0.421
Pb	0.331							Mo	0.358
								Pb	0.375

scree test (Cattell 1996). The metals which were below LOD in more than 50% of the observations, such as Be, Cr, Co and Tl, were not included. The outliers were identified using Grubb's test and were not included in the principal components and correlation analysis.

Applied to the trace metal concentrations in $PM_{2.5}$ at all sites, the PCA revealed 5 factors that accounted for 80% of the variance (Table 5).

Factor 1 accounted for 41% of the variance and had significant loadings on Fe and Mn that are typical mineral elements and consequently, associate this factor with the crustal fraction of $PM_{2.5}$ (Heal et al. 2005; Moreno et al. 2006a; Salvador et al. 2007). Fe and Mn were also loaded at same principal component and were strongly correlated (Spearman Rank Order Correlations more than 0.85) at each sampling site. The presence of these elements in $PM_{2.5}$ is mainly a result of local and regional dust resuspension by wind, convection and other natural processes. The less significant loading of Zn and Mo, at this component suggests some effect of road traffic induced resuspension dust (Heal et al. 2005; Querol et al. 2007b). A similar composition of the crustal component was observed at each sampling site, except for Canterbury where Fe and Mn were grouped together with Ba and Sr, which in low-traffic areas, are also indicators of natural crustal sources (Moreno et al. 2006a, b).

Factor 2 had the highest loading on Se which is considered a tracer of coal combustion processes. The moderate loadings of Sn, Cd, Sb and Pb suggest that this factor may present a mixture of several industrial emissions, including fly ash from high efficiency coal burning industrial facilities (Salvador et al. 2007; Junninen et al. 2009).

Factor 3 had the highest loadings on Ni and V which have been reported as tracers of petrochemical industry and oil combustion (Moreno et al. 2006a; Meza-Figueroa et al. 2007; Salvador et al. 2007; Viana et al. 2007). The same link was identified by PCA at each sampling site with the exception of Simcoe and Toronto where, unlike the other sites, there was no correlation between these elements (Spearman Rank Order Correlations less than 0.5). The Abbotsford, Vancouver, Montreal and Windsor sites have known industrial facilities of oil refining or transportation which explain the strong correlations (Spearman Rank Order Correlations above 0.80) and high concentrations of Ni and V at these sites. At the Canterbury site, these elements were also significantly correlated (Spearman Rank Order Correlations is 0.75), they were loaded at the same factor together with Se and were found at higher concentrations during the cold season, which suggests that domestic fossil fuel burning (oil and/or coal) used for heating during the winter is the main source of these elements in this region.

Factor 4 linked Sr and Ba which were also loaded at the same factor at each sampling site, regardless of the land use and anthropogenic emissions. Sr which is a tracer of crustal source (Moreno et al. 2006b), showed very small variations of concentration between sampling sites (medians ranged from 0.2 to 0.5 ng/m^3) whereas Ba was 3 to 4 times higher at sampling sites located close to high traffic areas. Also, the Ba-Sr factor at each site (except for Canterbury) had moderate loadings on Sb and Cu which are tracers of traffic related sources of emission, due to brake lining and tire wear. Such a chemical composition indicated that this factor represents traffic-related resuspended road dust.

Factor 5 had significant loadings on Cu and As, followed by less significant Pb, Sb, Cd, Zn, which are all identified as tracers of multiple industrial pollution sources (Moreno et al. 2006a; Minguillon et al. 2007; and references therein). When PCA was applied to elemental composition of $PM_{2.5}$ at each sampling site, these elements were grouped together in different combinations and usually accounted for most of the variance. At the Western urban sites, Zn, As Cd and Pb were loaded at the same factor and accounted for 42% of the variance. The concentration of As at Abbotsford site (0.7 ng/m^3) was higher than the overall Canadian median (0.4 ng/m^3). The most likely sources of these elements are the emissions from a building material manufacturing facility and a mine located nearby. Pb, Cu and Mo were also associated with this group which implies some effect of air traffic in the composition of $PM_{2.5}$ in this area. At the Vancouver site Cd, Pb and Zn were grouped together implying that industrial emissions from a nearby metal manufacturing facility may be the major source of these elements in this area. Sn and Sb were also moderately loaded on the same factor (loading factors ca. 0.5) suggesting some effect of traffic related emissions at this component. Cd, Pb, Cu, Mo and As were also loaded at the same principal component at each Eastern urban site and accounted for 40–50% of the total variance. The chemical composition of this factor indicated that the emissions from industrial facilities located close to the sampling sites are the most likely source of these elements in this area.

Based on this analysis, the major sources of trace metals in $PM_{2.5}$ at the urban sites included in this study are, natural dust resuspension processes (indicated by th presence of mineral elements such as Fe and Mn), industrial emissions (Cu, As, Cd, Pb, Mo and Sn), fossil fuel refining and/or burning processes (Ni, V, Se) and traffic related emissions (Ba, Sr Sb, Zn). The mineral component comprises 55–65% of the trace metal concentrations in $PM_{2.5}$ in urban areas and above 70% at rural sites. The contribution of the anthropogenic sources depends on the human

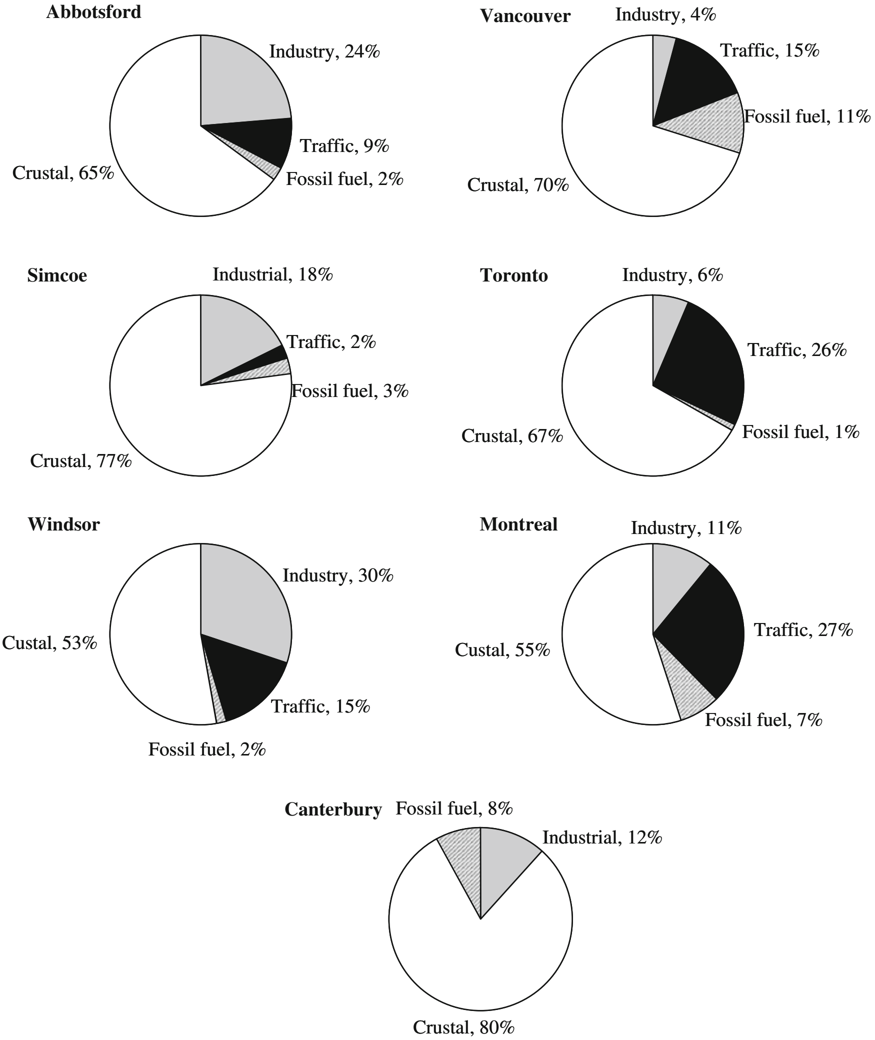

Fig. 6 Contribution of emission sources to the trace metal concentrations

emissions at each sampling site (Fig. 6). The industrial component accounts for 30 and 24% of the total inputs of metals at Windsor and Abbotsford sites, respectively, whereas traffic related sources have a major input at th Vancouver, Toronto and Montreal sampling sites. The principal components of trace metals at the Simcoe and Canterbury sites have a different structure. At the Simcoe site, the "industrial" component is a mixture of transported industrial pollutants and emissions from local farming, whereas at the Canterbury site the "industrial" component signifies the contribution of the long range transport in the region and accounts for 12% of the trace metals concentrations in $PM_{2.5}$. The crustal component which at this site is significantly loaded on Fe, Mn, and Sr is linked to the local dust resuspension. The fossil fuels component indicates the contribution of local domestic emissions.

4 Conclusions

This chapter presents a summary of composition and source origin of trace metals in $PM_{2.5}$ collected at selected urban and rural sites across Canada, within the National Air Pollution Network Surveillance program, during the May 2004 to December 2006 sampling period. The $PM_{2.5}$ mass concentrations found at all Canadian sites ranged from 5 to 11 $\mu g/m^3$ (IQR). The overall median was 7.2 $\mu g/m^3$ and was lower than most of the values reported for other regions of the world. The least contaminated site was Canterbury NB (rural), whereas Windsor ON (urban) was the site with the highest concentration of $PM_{2.5}$.

The trace metals were analyzed by ICP-MS after microwave assisted acid digestion. Our results showed that metal concentrations were significantly higher at sites closer to industrial manufacturing facilities and high traffic areas. Sites located in areas with similar land use had a comparable elemental composition of $PM_{2.5}$. The Windsor site, located close to several industrial facilities, had the highest concentrations of almost all metals. Ni and V concentrations were higher at the Vancouver and Montreal sites which are located close to oil and gas refining, storage and distribution facilities. Compared to the elemental composition of $PM_{2.5}$ samples collected in urban areas in Europe, Japan, and the USA, the Canadian aerosols were equally or less loaded with trace metals. The seasonal trends were more prominent at rural sites which showed elevated concentrations of all elements during warm seasons in Simcoe and during cold seasons in Canterbury. There was no significant annual trend of metal concentrations at urban sites, whereas there was a downward trend at rural sites during the 2004–2006 sampling period.

The source origin of trace metals in $PM_{2.5}$ was analyzed by PCA. The major component at all sites were crustal elements (Fe, Mn) which accounted for up to 70% of trace metals concentration. Industrial component accounted for 30 and 24% of the total inputs of metals at the Windsor and Abbotsford sites, respectively whereas traffic related sources had a major input at the Montreal, Toronto and Vancouver sampling sites, which are located in typical urban areas, close to major traffic routes throughout the cities.

Acknowledgments The authors would like to thank Mr. Tom Dann for his help with the NAPS results database, and Mr. David Mathieu, and all others who contributed to the analysis of the mass and elemental composition of the particle samples. We also gratefully acknowledge the provincial, municipal, and federal regional agencies and site operators for their cooperation.

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Sources and Distributions of Polycyclic Aromatic Hydrocarbons and Toxicity of Polluted Atmosphere Aerosols

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1 Introduction

Polycyclic aromatic hydrocarbons (PAHs; Table 1) are an unavoidable byproduct of any kind of combustion, in particular incomplete combustion processes. Therefore, these substances are ubiquitous in the polluted atmospheric environment in the ng m^{-3} concentration range. The gaseous state is predominant for the lighter molecular weight PAHs, while the substances with more than 4 rings are preferentially associated with the aerosol particles (Finlayson-Pitts and Pitts 2000; EC PAH WG 2001). Gas-particle partitioning is significant for many PAHs (so-called semivolatility, expected for saturation vapour pressures in ambient air in the range $p_{sat} = 10^{-6}$–10^{-2} Pa; Pankow and Bidleman 1991). In terms of water and organics solubility they span a considerable wide range of properties, i.e. 3–4 orders of magnitude, but less than with regard to vapour pressure (9 orders of magnitude; Table 1).

In a wider sense, the substance class also encompasses alkylated, partly oxygenated and other substituted PAHs.

The significance of PAH abundance is caused by the health hazard they pose upon inhalation: Some PAHs show mutagenic activity. Among atmospheric trace

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*, Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_3,

Table 1 Physico-chemical properties saturation vapour pressure, p_{sat}, Henry's law constant, K^H, and octanol–water partitioning coefficient, K_{ow}, and degradability in air as the reaction rate coefficients of the hydroxyl radical with the gaseous and the particulate phase molecules, $k_{g\ OH}$ and $k_{p\ OH}$, respectively, of 17 parent PAHs and 1 alkylated PAH (retene) (298 K; ten Hulscher et al. 1992; Finlayson-Pitts and Pitts 2000; Perraudin et al. 2007)

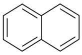
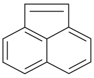
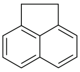
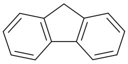
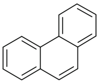
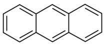
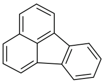
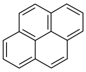
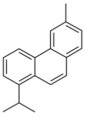
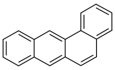
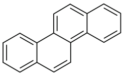
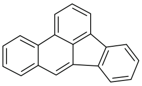
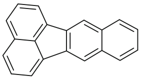
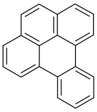
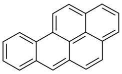
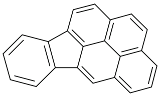
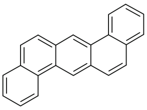
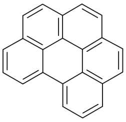
		p_{sat} (Pa)	K^H (M atm^{-1})	log K_{ow}	$k_{g\ OH}$ (10^{-12} cm^3 $molec^{-1}$	$k_{p\ OH}$$^{(a)}$ (10^{-12} cm^3 $molec^{-1}$ s^{-1})
Naphthalene (NAP)		1.0×10^{1}	2.3	3.37	22 (22)	5.0
Acenaphthylene (ACY)		8.9×10^{-1}	8.8	4.07	110 (75)	
Acenaphthene (ACE)		2.9×10^{-1}	5.4	3.92	100 (67)	
Fluorene (FLN)		8.0×10^{-2}	10.4	4.18	16 (9)	3.1
Phenanthrene (PHE)		1.5×10^{-2}	23.6	4.60	13 (13)	
Anthracene (ANT)		8.0×10^{-4}	17.7	4.50	17 (40)	4.4
Fluoranthene (FLT)		1.2×10^{-3}	113	5.22	50 (29)	
Pyrene (PYR)		6.0×10^{-4}	84	5.18	(50)	3.1
Retene (RET)		9.6×10^{-4}	(9.1)	6.35	(42)	
Benzo(a)anthracene (BAA)		2.8×10^{-5}	83	5.61		5.6

Table 1 (Continued)

		p_{sat} (Pa)	K^H (M atm^{-1})	log K_{ow}	$k_{g\,OH}$ (10^{-12} cm^3 $molec^{-1}$	$k_{p\,OH}{}^{(a)}$ (10^{-12} cm^3 $molec^{-1}$ s^{-1})
Chrysene (CHR)		8.4×10^{-5}	191	5.91	(50)	5.0
Benzo(b)fluoranthene (BBF9		6.7×10^{-5}	1522	6.12	(16)	
Benzo(k)fluoranthene (BKF)		1.3×10^{-8}	1712	6.84	(54)	3.5
Benzo(e)pyrene (BEP)		7.4×10^{-7}	3333	6.44	> 4.3 (50)	4.7
Benzo(a)pyrene (BAP)		7.3×10^{-7}	2188	6.50	3.5 (50)	4.1
Indeno(1,2,3-c,d)pyrene (IPY)		1.3×10^{-8}	2874	6.58	(64)	
Dibenz(a,h)anthracene (DBA)		1.3×10^{-8}	7092	6.50	(50)	
Benzo(g,h,i)perylene (BPE)		1.3×10^{-8}	3021	6.63	(87)	5.9

Estimated values (EPIWIN; USEPA 2007) in lack of experimental data are given in brackets^{a} On graphite particles. Second order rate coefficients were calculated similarly to gas-phase reaction rate coefficients, suggesting that reactions occurred between a gaseous OH radical and a surface-bounded PAH molecule (Perraudin et al. 2007) chemical substances, PAHs are considered to pose the highest human health risk (WHO 2003). One parent PAH, benzo(a)pyrene (BAP), is considered as an important substance for toxicity and a criteria pollutant in many countries. Mutagenicity and toxicity in general, is, however, mostly related to reaction products of PAHs in air, in particular nitro-PAHs (Finlayson-Pitts and Pitts 2000). Polluted ambient air contains a complex mixture of bio-effective pollutants, such as aliphatic and partly oxygenated aliphatic hydrocarbons, besides the aforementioned PAHs and substituted PAHs (Claxton et al. 2004; de Kok et al. 2006; Claxton and Woodall 2007).

PAHs have been added to the list of persistent organic pollutants to be regulated under the POPs protocol to the Convention on Long-range Transboundary Air Pollution. Resistance to photochemical degradation, in fact, is not well understood: In the gas-phase the reaction with the hydroxyl radical limits the parent PAHs' atmospheric residence times to hours or days at most ($k_{g\ OH}$ in Table 1; Finlayson-Pitts and Pitts 2000; EC PAH WG 2001). In the particulate phase, however, PAHs may undergo long-range transport and reach pristine areas in high altitudes and latitudes (e.g. Jaffrezo et al. 1994; Fernández et al. 2002; Sehili and Lammel 2007). Obviously, rate coefficients for particle bound PAHs with the hydroxyl radical and ozone determined in the laboratory tend to overestimate atmospheric degradation, most likely as a consequence of matrix effects which so far could not be mimicked in laboratory experiments, i.e. shielding against oxidant attack (e.g. Pöschl et al. 2001).

The distribution and fate of PAHs in the atmosphere has been the subject of numerous studies covering a wide range of spatio-temporal scales and relevant sources (references in Finlayson-Pitts and Pitts 2000; Prevedouros et al. 2005; Tsapakis and Stephanou 2005; Lammel et al. 2009a; Balasubramanian and He 2010). Most studies focused on occurrence of the parent PAHs, while nitro-PAHs gained interest in the chemistry of nitrogen oxides rich atmospheres (Finlayson-Pitts and Pitts 2000) and alkylated and partly oxygenated PAHs had significantly less been addressed so far (e.g. Albinet et al. 2008).

In the following we address levels and sources, mass size and phase distributions of parent PAHs and the toxicity of ambient aerosols at urban and rural sites of central and south-eastern Europe.

2 Methods

2.1 Sites and Sampling Methods

Campaign data from urban and rural sites in the Brno and Banja Luka areas are compared. The Brno area ($\approx$500,000 inhabitants) is located in the southeastern Czech Republic and the Banja Luka area ($\approx$250,000 inhabitants) is located in Bosnia and Hercegovina, 500 km south of the Brno area. To further compare these

Table 2 Characteristics of ambient air sampling data sets presented

	Czech Republic		Bosnia and Hercegovina	Germany
	Brno area	Košetice	Banja Luka area	Zugspitze
Sampling period	4–5 weeks per site in August 2007–February 2008	Every 7th day 2006–2008	3 days in July 2008	Each 2 weeks in June 2007 and February 2008
Number and type of sites	2 urban, 2 rural	1 rural background	2 urban, 1 rural	1 high mountain background
Total number of samples (size resolved samples)	16 (16)	157 (0)	81 (6)	22 (0)

Each sample comprises particulate and gas-phase fractions

results to background sites, long term monitoring data from Košetice (EMEP station, ≈100 km northwest of Brno; Holoubek et al. 2007) and two campaigns data from a high mountain site, Zugspitze, 2670 m a.s.l. (Germany, Alps, ≈450 km westsouthwest of Brno and ≈550 km westnorthwest of Banja Luka; Lammel et al. 2009b) were used (Table 2). One city centre site (road traffic, residential heating, industries, including in Brno power plants) is included from both, the Brno and Banja Luka areas. The rural Brno airport site (little air traffic, agriculture), the urban site Kyjov (glass and screw industries, road traffic) and the rural site Ivaň (agriculture, forest) are located 10, 40 and 30 km, respectively, from the city site. The Banja Luka factory (industrial activities, notably a sawmill, small waste deposits) and hill (Banj hills, forest, advection almost exclusively from the background, i.e. Dinaric Alps) sites are located 3 and 6 km, respectively, from the city site.

All sites were influenced by residential heating emissions, mostly during November–April. Besides coal (coke and lignite) also wood is a significant fuel for residential heating in the Czech Republic. The urban sites were in addition influenced by road traffic and industries. Traffic is also relevant as source for the rural sites with the exception of the Bosnian background site and the high mountain site.

2.2 *Sampling*

PAHs were collected in the gaseous and particulate phases using various high and middle volume samplers equipped with one quartz fibre filter (QFF) and one polyurethane foam (PUF) plug (50 mm diameter, in a glass cartridge, cleaned by extraction in acetone and dichloromethane, 8 h each) in series. Size-resolved samples were collected using high-volume sampling and a 6-stage cascade impactor (Andersen, PM_{10} inlet, cutoffs 7.2, 3.0, 1.5, 0.95, and 0.45 μm of aerodynamic particle diameter and back-up filter, impaction on glass filters).

Sampling artefacts due to losses of sorbed PAH by oxidation with ozone should be minor in our data sets. Significant losses of CHR and BAP, however, up to $\approx$50% based on respective studies (Tsapakis and Stephanou 2003; Schauer et al. 2003), are possible in the Banja Luka area as a consequence of elevated ozone levels.

2.3 Chemical Analysis

All samples were extracted with dichloromethane in an automatic extractor (Büchi B-811). Surrogate recovery standards (D8-naphthalene, D10-phenanthrene, D12-perylene) were spiked on each PUF and QFF prior to extraction. The volume was reduced after extraction under a gentle nitrogen stream at ambient temperature, and fractionation achieved on a silica gel column. Samples were analyzed using a GC–MS (gas chromatograph coupled with a mass spectrometer) HP 5975 with a J&W Scientific fused silica column DB-5MS, 5% Ph for PAHs. Terphenyl was used as an internal standard. Detection and quantification limits were controlled by laboratory and field blanks, are site dependent and were reported elsewhere (Lammel et al. 2009b).

2.4 Toxicological Analyses

Solvent extracts of impactor samples (particulate fraction) and PUF plugs (gaseous fraction) were analysed for genotoxicity, AhR-mediated activity, anti/estrogenic and anti/androgenic activities using in vitro bioassays.

The toxicological endpoints were evaluated using in vitro bioassays. Genotoxicity was assessed using the SOS-chromotest based on the *E. coli* strain K-12 PQ37 that is genetically modified to colorimetrically indicate changes in activity of DNA repairing system SOS (Quillardet and Hofnung 1993). The results are expressed as index of genotoxicity, a reciprocal value of minimal genotoxic concentration. For assessment of the dioxin-like activity of the samples we used the H4IIE-*luc* model, i.e. rat hepatocarcinoma cells stably transfected with a luciferase gene under control of the aryl hydrocarbon receptor (AhR). This is a well-established bioassay for evaluation of AhR-mediated activities of pure substances as well as environmental samples (Hilscherová et al. 2002) and the documented activities are reported as equivalents of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (bioTEQ; Villeneuve et al. 2000). PAH TEQ were calculated from analytical data on 28 indicator PAHs using REP values reported by Machala et al. (2001). Estrogenicity and antiestrogenicity were assessed using an MVLN cell line, human mammary carcinoma cells transfected with luciferase gene whose expression is triggered by the estrogen receptor (Demirpence et al. 1993). Androgenicity and antiandrogenicity were studied using a yeast *Saccharomyces cerevisiae* strain stably transfected with the human androgen receptor along with firefly luciferase under transcriptional control of the ARE (androgen-responsive element). Another strain constitutively expressing luciferase served for the assessment of cytotoxicity (Leskinen et al. 2005). The antiestrogenic and antiandrogenic results are expressed as an index of antiestrogenicity (AE) or antiandrogenicity (AA), respectively. The indexes correspond to the reciprocal value of IC_{25} of the samples in the respective bioassay. The antiestrogenicity and antiandrogenicity values were calculated from the decrease of the activity of a competing level of 17-β-estradiol (11 pM) or testosterone (10 nM), respectively. The bioassay and the cultivation and exposure conditions had been described in more detail previously (Škarek et al. 2007; Novák et al. 2009).

2.5 Meteorological Analysis

Regional and global information about air parcel origin was derived from back-trajectory statistics. For the regional scale the contact to ground of 72 h back-trajectories, started at ground level every 10 min at Košetice were mapped and analysed according to concentration levels of PAHs at the site (Reimer and Scherer 1992). Potential source area distributions were inferred from such maps (Sect. 3.3.1). For tracking air masses back >5 and up to 20 days a Lagrangian particle dispersion model (FLEXPART; Stohl et al. 1998) was used. The fraction of parcels above and below the boundary layer height was budgeted and used to identify samples of free tropospheric as opposed to boundary layer air (Lammel et al. 2009b).

3 Results and Discussion

3.1 Abundance and Sources

3.1.1 Abundance and Substance Patterns

The concentration ranges of PAHs found across the sites studied in 2007–2008 are listed in Table 3 separately for the cold and warm seasons, because of a pronounced seasonality of PAH levels (winter maxima, Fig. 1). A stronger emission source (heating season), a weaker chemical sink (photochemistry) and less efficient mixing (lower mean boundary layer height) contribute to higher abundances in winter. During summer the levels at the background site Košetice are significantly lower than at the urban sites, but similar and even higher levels are observed in winter-time. It had been stressed (Lohmann et al. 2000; Herrmann et al. 2006)

Table 3 Mean total PAH concentrations in air (i.e. sum of gaseous and particulate mass fractions, $c_{i\ g} + c_{i\ p}$, ng m^{-3}) at various types of sites in the Czech Republic (Brno area, Košetice), Bosnia and Hercegovina (Banja Luka area) and at a high mountain site (Zugspitze) during (a) May–October and (b) November–April 2007–2008

	Urban		Rural and background			
	Brno area	Banja Luka area (2 sites, n = 30)	Brno area (Brno airport, n = 4)	Košetice (n = 52)	Banja Luka area (1 site, n = 15)	Zugspitze (n = 8)
(a) May–October						
NAP		2.07–3.69	1.41	0.47		<0.03
ACY		1.41–1.48	0.50	0.050	0.43	<0.002
ACE		1.22–2.78	0.66	0.083	0.12	0.0021
FLN		5.11–5.54	3.71	0.82	1.29	0.010
PHE		12.4–13.9	9.21	2.28	4.97	0.023
ANT		0.56–0.59	0.41	0.057	0.19	0.0004
FLT		3.49–3.69	3.53	0.63	1.57	0.011
PYR		2.40–2.84	2.54	0.39	1.34	0.022
RET		0.47–0.75	0.54	0.17	0.26	0.0022
BAA		0.30–0.45	0.60	0.044	0.13	0.0004
CHR		0.52–0.75	0.92	0.10	0.27	0.0011
BBF		0.64–1.01	1.03	0.10	0.36	0.0005
BKF		0.30–0.52	0.45	0.049	0.19	0.0006
BEP		0.58–0.88	0.69	0.14	0.46	0.0014
BAP		0.44–0.77	0.63	0.055	0.25	0.0003
IPY		0.56–1.14	0.71	0.075	0.40	0.0000
DBA		0.037–0.089	0.053	0.011	0.022	0.0000
BPE		0.55–1.07	0.61	0.087	0.41	0.0001
Sum of 15[a]		32.0–35.9	25.6	4.70	11.93	0.076

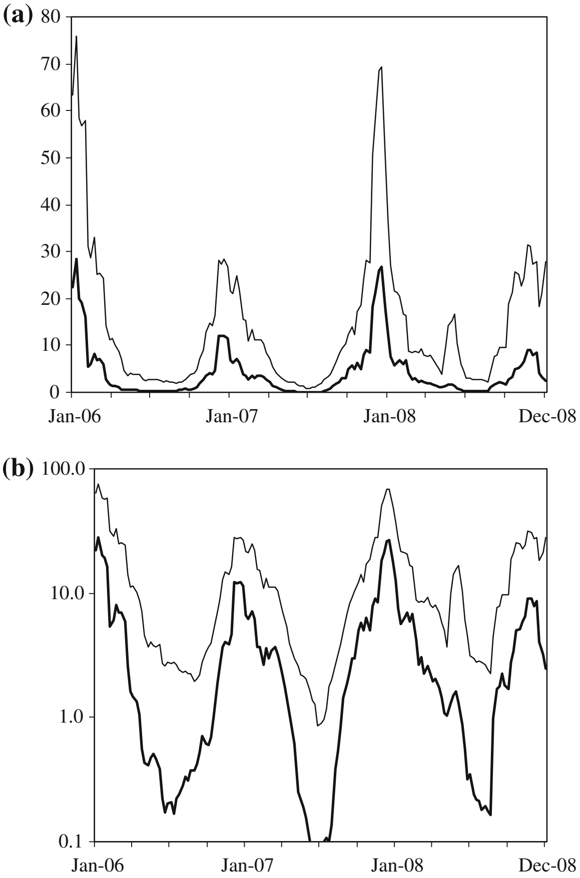
Table 3 (continued)

	Urban		Rural and background			
	Brno area (Brno city, Kyjov, n = 8)	Banja Luka area	Brno area (1 site, n = 5)	Košetice (n = 52)	Banja Luka area	Zugspitze (n = 14)
(b) November–April 2007–2008						
NAP	3.74–4.95		2.59	2.22		
ACY	0.86–2.73		2.12	1.30		<0.04
ACE	0.65–1.10		1.27	0.38		0.15
FLN	5.11–7.61		12.4	3.47		0.23
PHE	15.2–17.5		36.1	6.87		0.41
ANT	1.40–2.14		4.67	0.22		0.013
FLT	6.36–6.87		14.1	2.45		0.14
PYR	5.38–5.89		11.1	1.62		0.55
RET	0.97–1.07		2.23	0.51		0.0084
BAA	1.20–1.43		2.99	0.44		0.0030
CHR	1.63–2.08		3.93	0.74		0.0080
BBF	1.38–1.88		3.07	0.72		0.0053
BKF	0.68–0.88		1.36	0.34		0.0026
BEP	1.01–1.30		1.94	0.50		0.0047
BAP	1.14–1.31		2.46	0.48		0.0019
IPY	1.10–1.35		2.12	0.52		0.0033
DBA	0.068–0.081		0.14	0.038		0.0017
BPE	1.10–1.10		1.71	0.44		0.0043
Sum of 15[a]	45.6–52.0		100.0	20.0		1.05

See Table 2 for data set characteristics

[a] Disregarding NAP, RET, BEP

Fig. 1 2006–2008 time series of total (*thin line*) and particulate phase (*thick line*) PAH concentration in air in Košetice, plotted **a** linearly and **b** logarithmically (sum of 15 PAHs, gliding monthly mean of weekly 24 h-samples, ng m^{-3})



that, influenced by domestic burning sources, PAH can be higher at a rural than at an urban site. Winter-time PAH peak levels are 1–2 orders of magnitude higher at boundary layer sites in central Europe than summer minima (Fig. 1). Winter maxima are certainly influenced by residential heating, but not in a simple way correlated to ambient temperature ($r = -0.5$). Summer maxima are rare. One such example was observed in May–June 2008. When comparing November–April with May–October levels (Table 3a, b) seasonality is reflected by a difference of a factor 4 for the background site Košetice. Levels are found more than one order of magnitude even lower at the high mountain site. A strong seasonality is also found there, although free tropospheric air was sampled in winter time, while mixed boundary layer/free tropospheric air was sampled during the summer campaign (Lammel et al. 2009b).

The levels at the urban sites range 30–50 ng m^{-3} (sum of 15 PAHs) and are remarkably similar in both geographic areas, although sampling was during the hot season in the Banja Luka area, while it was in winter (November–February) in the Brno area. Similar levels at other urban sites in Bosnia and Hercegovina had been observed during the summer of 2004 (Radonić et al. 2009). Summer levels in Bosnia and Hercegovina are somewhat higher than at comparable sites in the Czech Republic. The levels found here compare well to other urban sites in central (Schauer et al. 2003; Herrmann et al. 2006), western (Lohmann et al. 2000; Ravindra et al. 2006) and southern (Tsapakis and Stephanou 2005) Europe and are significantly below those found for Manchester, Rome and Gliwice (Poland) ($\approx$200–250 ng m^{-3} in winter; Lohmann et al. 2000; Possanzini et al. 2004; Grynkiewicz Bylina et al. 2005).

The PAH patterns (Fig. 2) are quite similar within areas (correlation coefficients $r > 0.9$), but partly differ significantly across areas. E.g., the patterns at the Brno area sites do not resemble the patterns at the Banja Luka sites ($r < 0.0$), but the pattern found in Košetice does ($r > 0.9$). Still, the main components (FLT, PYR, BAA, CHR, BBF, BAP and IPY in the particulate phase and FLU, PHE and FLT in the gaseous phase) as well as some less concentrated components show similar mass fractions in the Brno and Banja Luka areas. At the high mountain site PHE and PYR account for >90% of the PAH mass, which certainly indicates relative photochemical stability of these (mostly) gaseous compounds. Also, BEP/(BEP + BAP) > 0.6 indicates aged air, as this ratio $\approx$0.5 close to most sources BAP should be degrading faster than its isomer BEP (Kamens et al. 1988; see also values of $k_{i\ OH}$ in Table 1). This is reflected by BEP/(BEP + BAP) = 0.45–0.53 at the urban sites and rural sites, including the rural background site in winter, but 0.62–0.72 at the rural and high mountain background sites in summer (Table 3).

3.1.2 Local Sources

PAH source patterns are to some extent preserved in air and can be used for source apportionment. In central Europe road traffic and residential heating contribute most to PAH levels in air. The ratio $c_{BAA}/(c_{BAA} + c_{CHR})$ provides a simple measure (so-called diagnostic ratio) to assess the relative contributions of these two major sources: Low values, 0.2–0.3 indicate the predominance of road traffic and high values, $\approx$0.4–0.5, the predominance of residential heating (coal, wood). This is illustrated for a number of sites, which are obviously either heavily traffic influenced (10–200 m to main roads) or residential heating influenced (located in town residential areas or villages; Fig. 3). This measure, $c_{BAA}/(c_{BAA} + c_{CHR})$ is not valid, however, at sites influenced by strong other combustion sources emitting BAA or CHR, such as industrial. RET, a tracer for wood combustion (Ramdahl 1983), can be more significant in the rural than in the urban environment (Table 3).

Apart from primary sources, PAHs may be re-emitted upon atmospheric deposition. Re-suspended dust (or other coarse particulate matter) and air–soil exchange could constitute such secondary sources. Re-suspension would not affect the source distribution as these carriers are short-lived and, hence, short-ranged. Air–soil exchange is occurring (Hippelein and McLachlan 1998; Bozlaker et al. 2008), despite sorption of PAHs to and accumulation in soils. The significance of this process as a local or regional PAH source has not been assessed so far.

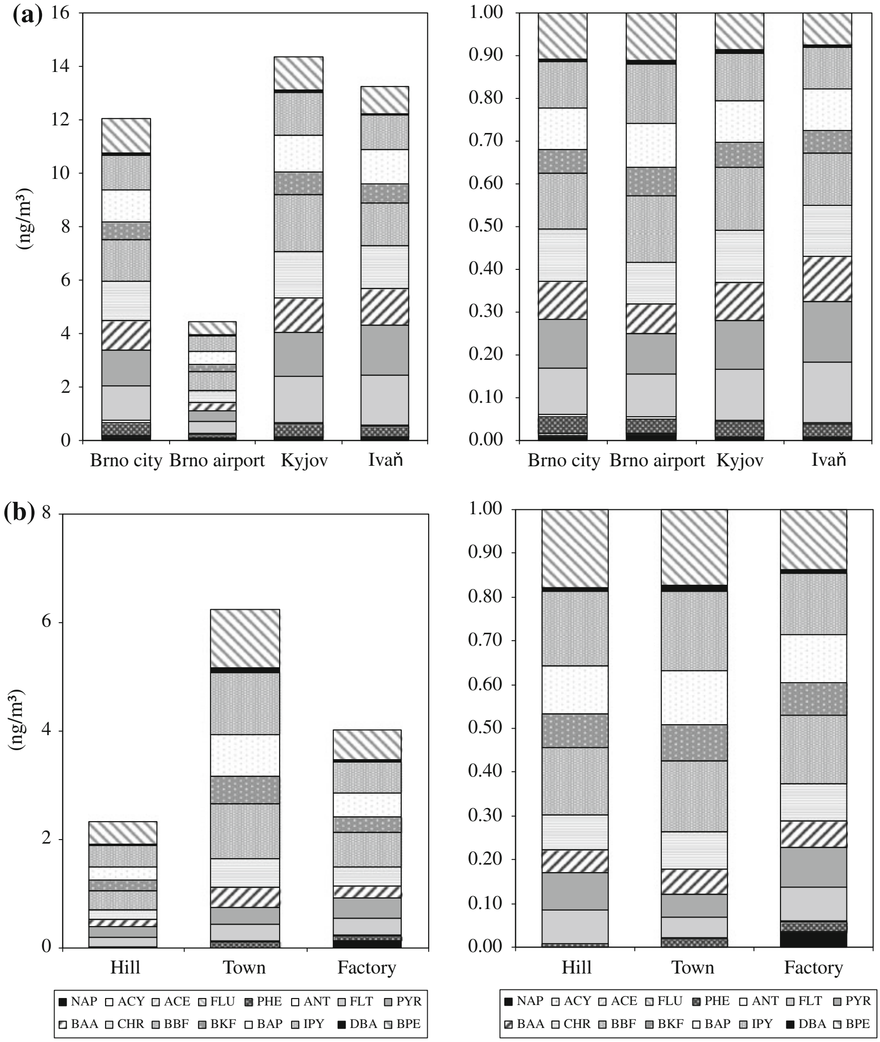


Fig. 2 PAH concentrations and pattern (16 indicator PAHs) **a** in the particulate phase in the Brno area, Czech Republic (4 sites, n = 16, 2007–2008), **b** in the particulate phase in the Banja Luka area, Bosnia and Hercegovina (3 sites, n = 45, 2008)

3.1.3 Regional Sources

The back-trajectory analysis identifies potential source areas in large parts of Europe. As a consequence of the prevailing circulation, the coverage is not uniform. In particular, the channelling of the flow by high mountain ridges (Alps, Carpatian Mtns.) is reflected as areas with low coverage by trajectories.

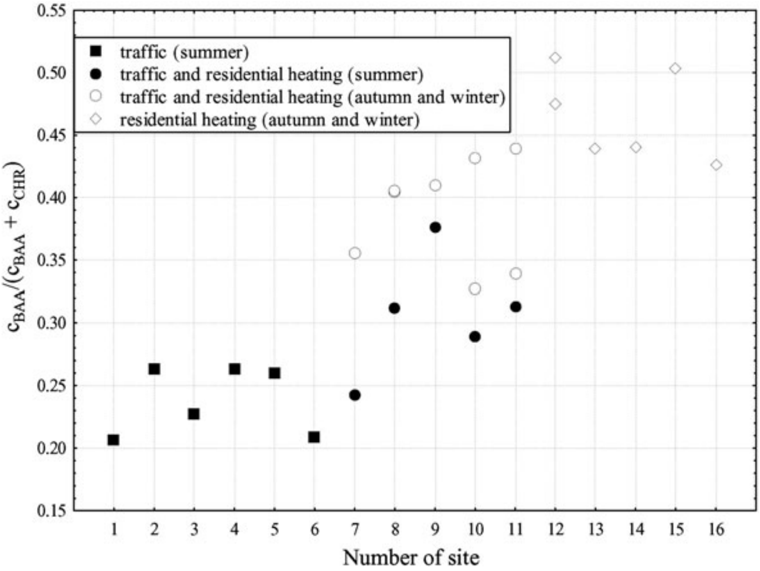


Fig. 3 Values of the diagnostic ratio $c_{BAA}/(c_{BAA} + c_{CHR})$ (c_i refers to total atmospheric concentration, $c_{i\ g} + c_{i\ p}$) at 16 sites with well defined sources (Czech Republic) during various seasons in 2001–2008 influenced by road traffic and residential heating emissions

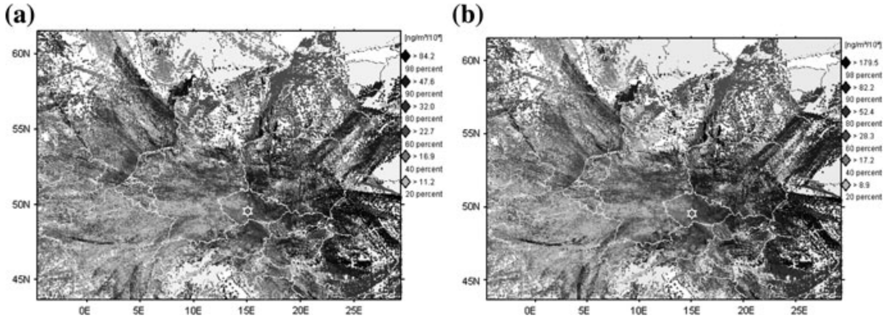


Fig. 4 Potential source area distribution for a central European background monitoring site, Košetice, Czech Republic (marked by star), 1997–2005. *Light* and *dark grey* denote low and elevated levels of FLT (*left*) and BAP (*right*) in air at the monitoring site

The distributions are similar for a number of PAHs studied (shown for FLT and BAP in Fig. 4). Areas of maximum sources apparently are in eastern and south-eastern Europe (Ukraine, Romania, Poland, Belarus), while western European countries emit less and the seas (except Skagerrak) do not contribute. This is in agreement with observations in recent years, which find elevated levels in Poland and Slovakia compared to countries neighbouring to the west and south (Söderström et al. 2005; Grynkiewicz Bylina et al. 2005).

3.2 Gas-Particle Partitioning and Mass Size Distributions

The particulate matter mass mixing ratio, f_m, of PAHs is in the upper ppm range (97–623 for the sum of 15 PAHs, Table 4) and does not significantly differ between urban and rural sites. This compares well with other urban sites in Europe (Schauer et al. 2003; Tsapakis and Stephanou 2005). Low temperatures favour condensation of PAHs on particulate matter (see mass fraction in the particulate phase, θ, Table 4). As a general trend a doubling of θ per $\approx$5 K temperature decrease had been found (Pankow 1991). The gaseous mass fraction is significantly higher in summer (Table 4 and visible in Fig. 1b). While up to half of total PAH content in winter time in Košetice is in the particulate phase, it is only about 10% in the summer time (Fig. 1). A similar trend is even observable in the Mediterranean climate (Tsapakis and Stephanou 2005). Condensation, however, can by far not explain gas-particle partitioning of PAHs. Gas-particle partitioning may to some extent be irreversible, the extent of which is basically unknown. It is in particular the sorption to soot which is important for the process (Dachs and Eisenreich 2000; Lohmann and Lammel 2004). The soot content of particulate matter is usually higher in winter (e.g. Lammel et al. 2003; Herrmann et al. 2006). θ is, furthermore, increasing with distance to source. Therefore, higher values of θ are reported from background sites. For the sum of 15 PAHs θ equals 0.30 at Košetice and even 0.39 on the high mountain site, while $\theta = 0.20 \pm 0.05$ (0.14–0.31) at the urban and rural sites. The reason for this is photochemical degradation in the gas-phase being faster than in the particulate phase. Therefore, the largest differences are found for PAHs with high $k_{ig\ OH}$. E.g., for ANT $\theta = 0.30$ at Košetice and even 0.94 on the high mountain site, while for the isomer PHE $\theta = 0.09$ at Košetice and 0.22 on the high mountain site, but $\theta < 0.05$ at the urban and rural sites for both isomers (Table 4).

In the particulate phase PAHs are found unimodally distributed. Upon emission in combustion processes and close to the sources mass size distributions of PAHs are peaking in the ultrafine and accumulation modes (0.01–0.1 and 0.1–1 μm size ranges, respectively; Plewka 2001; Yang et al. 2006). Accordingly, the dominance of one mode is found at the urban and rural sites, with mass median diameters, D_m, found almost exclusively in the accumulation mode (0.1–1.0 μm of size; Table 4, Fig. 5). The same was found in other studies of urban and rural environments (e.g. Schnelle et al. 1995; Kiss et al. 1996; López Cancio et al. 2004; Chrysikou et al. 2009; Kawanaka et al. 2009). During atmospheric transport re-distribution in the aerosol occurs, at least of the semivolatile PAHs, which undergo gas-particle partitioning. In consequence, the mass size distribution is shifted towards the surface size distribution, which has a maximum in the accumulation mode. This trend is only partly reflected in this study, as the data are influenced by close sources while no size-resolved data from background sites are included. However, the mass median diameters are found >0.1 μm, i.e. they are shifted as compared to the sources, and by average higher for semivolatile PAHs (i.e. ANT, FLT, PYR, RET, BAA, CHR and BBF; $D_m = 0.72$ and 0.61 μm at the urban and rural sites,

Table 4 Mass median diameter, D_m (μm of aerodynamic site), particulate matter mass mixing ratio, f_m (ppm), and mass fraction, $\theta = c_p/(c_g + c_p)$, of PAHs and particulate matter mass, m, at urban and rural sites in the Brno (4 sites, 2007–2008) and Banja Luka (2 sites, 2008) areas, and at the rural (Košetice, 2006–2008) and high mountain (Zugspitze, 2007) background sites

m	Urban						Rural and background						
	Brno area, 2 sites ($n = 8$, $T = 275.5$–277 K)			Banja Luka area (1 site, $n = 6$, $T = 290$–308 K)			Brno area (2 sites, $n = 9$, T = 270–286 K)			Košetice ($n = 157$, $T = 255$–301 K)	Banja Luka area (1 site, $n = 6$, T = 292–309 K)		Zugspitze ($n = 8$, T 272–283 K)[a]
	D_m 1.40–2.10	f_m 10^6	θ	D_m 1.82	f_m 10^6	θ	D_m 0.94	f_m 10^6	θ	θ	f_m 10^6	θ	θ
NAP		2.6–3.2	0.02		<0.03	0.00		2.6–2.4	0.03–0.04	0.05			
ACY		1.11–1.14	0.01–0.03		0.04	0.01		0.32–1.3	0.01–0.02	0.11	<0.03	0.00	
ACE		0.10–0.11	0.00		0.05	0.00		0.04–0.11	0.00	0.03	0.10	0.00	0.00
FLN		1.4–1.5	0.01		0.12	0.00		0.69–1.4	0.00	0.02	0.08	0.00	0.07
PHE		14.8–22.4	0.03		1.10	0.01		7.2–21.7	0.02	0.09	2.9	0.00	0.22
ANT	0.83–1.03	1.9	0.03	0.61	0.09	0.02	0.69–0.73	0.83–2.5	0.02–0.04	0.30	0.27	0.04	0.94
FLT	0.74–0.81	40.1–75.4	0.21–0.25	1.11	2.2	0.08	0.63–0.68	21.5–92.2	0.14–0.22	0.44	5.1	0.12	0.60
PYR	0.68–0.74	41.5–70.8	0.23–0.30	1.00	2.4	0.12	0.60–0.62	19.9–89.2	0.19–0.28	0.57	5.6	0.15	0.54
RET	0.73–0.74	7.2–12.6	0.24–0.27		0.51	0.07	0.60–0.70	3.0–22.9	0.12–0.34		0.74	0.09	0.66
BAA	0.54–0.63	32.7–56.1	0.89–0.91	0.73	3.3	0.84	0.51–0.62	15.2–65.6	0.75–0.94	0.96	4.5	0.84	0.91
CHR	0.57–0.66	45.0–76.0	0.86–0.90	0.80	4.9	0.57	0.52–0.58	20.7–74.9	0.64–0.90	0.92	7.3	0.60	0.99
BBF	0.56–0.65	48.2–92.8	0.97–0.99	0.65	16.4	0.97	0.52–0.55	33.2–71.5	0.97–1.00	0.99	27.9	1.00	0.97
BKF	0.53–0.64	20.7–36.5	0.98	0.66	8.1	0.98	0.53–0.56	14.3–31.3	0.96–1.00	0.98	12.3	0.91	0.99
BEP	0.56–0.67	33.7–56.3	0.98–0.99	0.67	15.2	0.98	0.53–0.57	23.1–46.3	0.98–1.00		23.9	0.95	0.91
BAP	0.54–0.64	35.8–61.1	0.98–0.99	0.61	11.3	1.00	0.49–0.54	21.7–59.6	1.00	0.98	17.4	1.00	0.88
IPY	0.53–0.62	40.2–68.6	0.99	0.54	23.6	1.00	0.48–0.55	29.3–57.1	1.00	0.98	38.7	1.00	
DBA	0.60–0.61	2.1–5.0	0.99	0.54	1.9	0.80	0.49–0.53	1.9–3.4	1.00	1.00	2.7	0.59	
BPE	0.53–0.63	39.5–54.4	0.98–0.99	0.62	20.9	1.00	0.49–0.55	23.8–44.6	1.00	0.95	37.5	1.00	
Sum of 15[b]	0.61–0.70	365–624	0.23–0.31	0.62	97.5	0.14	0.55–0.59	211–616	0.19–0.21	0.30	162	0.17	0.39

[a] Summer campaign

[b] Disregarding NAP, RET, BEP, mass-weighted

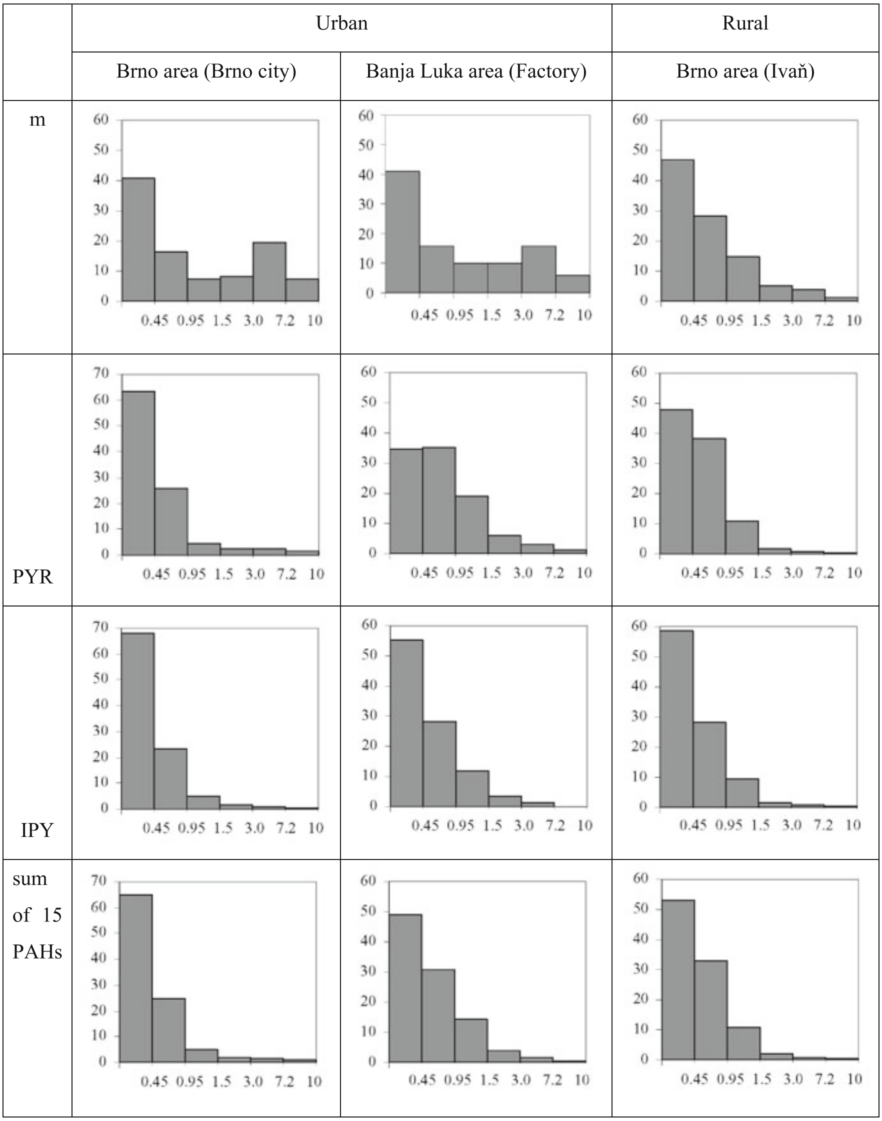


Fig. 5 PAH and particulate matter mass (m) size distributions (%) in the Brno (2 sites, 2007–2008) and Banja Luka (1 site, 2008) areas. Upper cut-off of impactor stage given in μm of aerodynamic particle size

respectively) than for non volatile PAHs (i.e. BKF, BEP, BAP, IPY, DBA and BPE; $D_m = 0.58$ and 0.55 μm at the urban and rural sites, respectively). This can be explained by re-distribution even close to sources and mixing with aged air. For the semivolatiles FLT and PYR remarkably high mass median diameters, $D_m = 1.00$–1.11, are found at the urban site in the Banja Luka area (PYR mass size distribution shown in Fig. 5). In fact, the highest values, up to $D_m = 1.39$ μm,

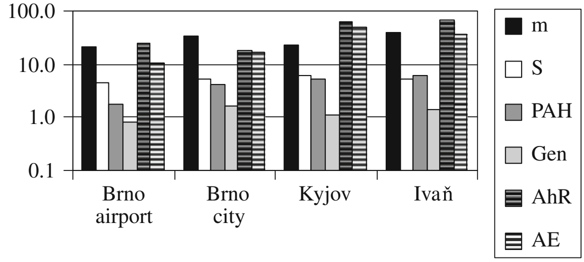


Fig. 6 TSP related toxicities: PAH (sum of 28 substances) calculated dioxin-like toxicity (TEQ fg m^{-3}), genotoxicity (*Gen*, reciprocal minimum genotoxic concentration, (MGC m^3 $ml^{-1})^{-1}$), dioxin-like activity (*AhR*, 10^{-3} bioTEQ fg m^{-3}), antiestrogenicity (*AE*, (IC_{25} m^3 $ml^{-1})^{-1}$), together with particulate matter mass (*m*, μg m^{-3}) and specific surface (*S*, 10^{-2} m^2 g^{-1}) at sites in the Brno area, airport (rural), city (urban), Kyjov (urban), and Ivaň (rural)

were observed during sampling intervals when light brown smoke was emitted occasionally from the nearby (0.35 km) sawmill chimneys. A similar observation had been made at a background site, which was strongly influenced by dust particles (López Cancio et al. 2004). In principle, also different degradability by radical attack could cause a differentiation in D_m, in the sense that faster degrading PAHs would be preferentially depleted from small particles as these have a higher surface-to-volume ratio. Differences in degradability are, however, less significant than differences in partial pressure (Table 1). The difference in mass median diameter is relevant for the atmospheric residence time and, hence, the long-range transport potential as well as for penetration in human airways and, hence, health risk.

The particulate matter mass size distributions were found unimodal at the rural site ($D_m = 0.94$ μm, in the Brno area) with maxima at sub-micrometer size, too, but bimodal at the urban sites ($D_m = 1.40$–2.10 μm, in the Brno and Banja Luka areas; Fig. 5), with a second maximum in the coarse mode. Note, however, that the coarse size resolution (6 size fractions) might hide more modes.

3.3 Toxicology

The distribution of compounds which produce biological effects in the inhalable fraction of atmospheric particulate matter and the gas-phase were addressed at the 4 sites in the Brno area.

Genotoxicity and AhR-mediated (i.e. dioxin-like) activity were found in all size classes at all 4 sites in the Brno area in similar magnitudes, i.e. the total suspended particulate matter (TSP) toxicity at rural sites was not lower than at urban sites (Fig. 6). Note, that also TSP mass and specific surface were not lower at rural sites. Activities were found in general highest in the small size ranges (Fig. 7). This

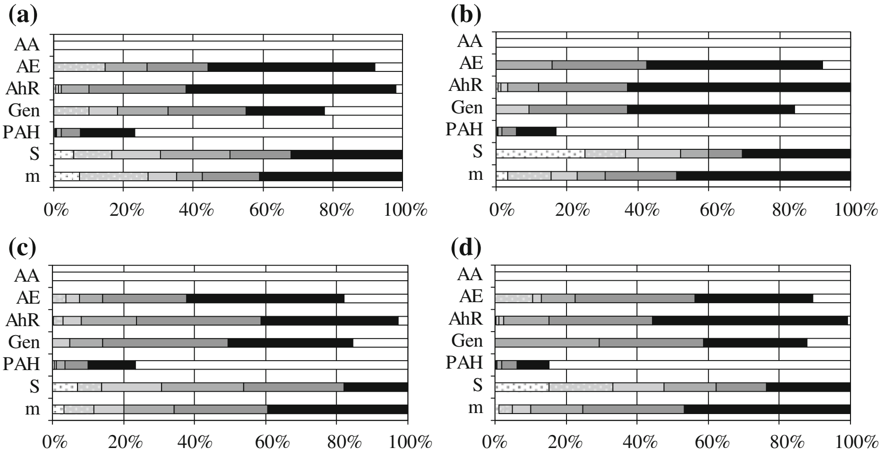


Fig. 7 Normalized activity distributions (%) across 6 particle size fractions (*grey* and *black*, from left to right: 7.2–10.0, 3.0–7.2, 1.5–3.0, 0.95–1.5, 0.45–0.95 and <0.45 μm of aerodynamic size) and of the gaseous phase (*white*) of antiandrogenicity (AA, in the presence of testosterone), antiestrogenicity (AE), dioxin-like activity (AhR), and genotoxicity (Gen), and PAH (sum of 28 substances) calculated dioxin-like toxicity (TEQ) together with particulate matter mass (m) and specific surface (S) size distributions sites in the Brno area, **a** city (urban), **b** airport (urban), **c** Kyjov (urban), and **d** Ivaň (rural). Effects too low to derive IC_{25} values are reflected as zero

result is in agreement with numerous other studies (e.g. Chao et al. 2003; Kawanaka et al. 2009). A higher activity associated with small particles is probably related to the organic fraction, higher in the fine and ultrafine size fractions, and a larger active surface (e.g. Sioutas et al. 2005). This is not visible in our study (see S in Fig. 7), probably because specific area does not necessarily reflect active surface area. A similar distribution across particle size and sites, however, was found for the antiestrogenic activity (Fig. 7). Estrogenic activity was not found in the particulate phase. All toxicities tested were also found in extracts of the gas-phase and PAH TEQ and antiandrogenicity were even mostly associated with gaseous pollutants.

The campaigns at the 4 sites were conducted consecutively, not simultaneously. Therefore, seasonal changes in aerosol composition will have influenced the results. Although the consecutive sampling pattern is not very suitable for a direct comparison of the localities, our study provides a detailed information on distribution of compounds producing multiple biological effects in the inhalable fraction of atmospheric particulate matter and the gas-phase.

Genotoxicity results: The observed results are possibly mediated mainly by direct genotoxins such as nitro-PAHs and oxygenated PAHs whose genotoxicity is not dependent on the activation. Emissions of diesel engines were described to be an important source of these compounds (Rosenkranz 1982; Finlayson-Pitts and Pitts 2000) and this might explain the high genotoxic potential of samples at the Brno city site, which is strongly influenced by road traffic. Nitro-PAHs might have been partly degraded during sample storage and before the biotests, however. PAHs are mostly less genotoxic without the activation and thus their contribution to the effects is probably less significant.

AhR-mediated activity results: Dioxin-like activity is a useful marker of compounds that are able to activate the AhR receptor, which had been shown to be involved in numerous health effects such as impairment of immunity and nervous system or reproduction (Mukerjee 1998). There have been several studies describing AhR-mediated effects of the PM_1 (Wenger et al. 2009) and PM_{10} (Clemons et al. 1998; Ciganek et al. 2004; Brown et al. 2005) aerosol size fractions. The TEQ calculated from the data of 28 PAHs (25 parent PAHs, retene, biphenyl and triphenylene) represents by average 7.5 and 95% of the dioxin-like activity associated with the particulate and gaseous fractions, respectively. Most of the activity could be produced by dioxins and furans, but also by partly oxygenated PAHs, such as polycyclic aromatic ketones and quinones that were also shown to activate AhR and to be produced by combustion pollution sources (Misaki et al. 2007). The results, furthermore, confirm that a significant portion of the AhR-mediated activity was produced by compounds present in the gas-phase at many polluted localities as it have been shown previously (Klein et al. 2006; Novák et al. 2009).

Antiestrogenicity results: Interaction of particulate phase air pollutants with estrogen receptors had been reported previously (Clemons et al. 1998; Klein et al. 2006), while there are only two studies which report estrogenicity (Klein et al. 2006) and antiestrogenicity (Novák et al. 2009) associated with gaseous pollutants so far. Because some PAHs have been shown to be estrogenic it has been proposed that the estrogenic activity of PM extracts might be due to the presence of these compounds (Clemons et al. 1998). Alternatively, another report suggested that the estrogenicity of the particulate phase of air could be caused by bisphenol A, which was relatively abundant in the air on the studied urban locality (Matsumoto et al. 2005). Our results document strong antiestrogenic effects produced by extracts from both the particulate and the gaseous aerosol fractions. It has been described that extracts from motorcycle exhaust particles were antiestrogenic, both in vitro (MCF-7 cell line) and in vivo (immature female rats; Ueng et al. 2004). This study indicated that antiestrogenicity is probably produced by AhR-dependent cytochrome induction. This finding is in agreement with the correlation of bioTEQ and antiestrogenicity observed in our study. The link between dioxin-like activity and antiestrogenicity has been thoroughly described by mechanistic studies reviewed in Safe and Wormke (2003).

Antiandrogenicity results: While there were no obvious androgenic as well as antiandrogenic effects of any of the samples in the absence of androgen, some of them caused statistically significant antiandrogenicity in the presence of testosterone. These effects were associated almost exclusively with the gas-phase in agreement with results from a previous study (Novák et al. 2009), which so far was the only study reporting androgenicity in ambient air. Thus, the antiandrogenicity seems to be caused by volatile substances such as some pesticides that were shown to be antiandrogenic (Kojima et al. 2004). Anti/androgenicity had been found to be associated with combustion of diesel (Okamura et al. 2004; Taneda et al. 2004) and wood (Owens et al. 2006).

4 Conclusions

Similar PAH levels have been observed in various seasons at rural and urban sites in the Czech Republic and Bosnia. This study suggests that elevated levels of PAH are ubiquitous in the populated areas and not necessarily lower in the rural than in the urban environment. This is supported by other recent studies in Europe. High levels of PAH in air in central Europe have been related to advection of air from and across Ukraine, Romania, Poland, and Belarus. The PAH sources and abundances in these countries should be investigated.

Environmental exposure is particularly high and extended to remote areas, when pollutants undergo long-range transport. In the case of PAHs long-range transport, if not limited by degradability, will be limited by phase partitioning in combination with the mass size distribution. In this study the PAH mass median diameters were found almost exclusively in the accumulation mode (0.1–1.0 μm of size), higher for semivolatile PAHs than for non volatile PAHs. The atmospheric lifetime of these particles is longest. Strong sorption (e.g. to soot) may prevent semivolatile PAHs to re-distribute within aerosols, but sorption of PAHs is insufficiently understood and should be in the focus of future studies. Re-emission may be significant for long-range transport, if re-volatilisation from ground surfaces were involved. Air–soil exchange should be addressed in future studies in order to assess its significance as a local or regional PAH source.

Acknowledgments We thank Milan Vana (Czech Hydrometeorological Institute), Zoran Bořović, Igor Kovacić (Hydrometeorological Service of Bosnia and Hercegovina), Jaromir Dostálek (Masaryk University), Bojan Gasić (Swiss Federal Institute of Technology) and Ludwig Ries (German Federal Environment Agency) for on-site support. This project was supported by the Ministry of Environment (SP/1a3/29/07) and the Ministry of Education (MSMT 0021622412) of the Czech Republic and by the European Commission (7th FWP R&D 226534, ArcRisk).

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Particulate Emissions from On-Road Vehicles

Andreas Limbeck and Christoph Puls

1 Introduction

The short term standard defined by the European Union (Directive 2008/50/EC) (European Parliament, Council of the European Union 2008) for particulate matter smaller than 10 μm (PM_{10}) is violated in many European cities (Querol et al. 2004; Van Dingenen et al. 2004), therefore the current air quality status of PM_{10} is under investigation in many countries, in particular to understand the source terms of the particulate matter and to propose a catalogue of measures to avoid further exceeding of the limiting value. For a targeted reduction of PM_{10} levels, detailed knowledge of sources and their respective contribution to the PM levels is required.

Emissions from motor vehicles are among the major contributors to fine particle concentrations in the urban atmosphere (Schauer et al. 1996; Kleeman et al. 2000); they make substantial direct and indirect contributions to ambient PM levels. Direct particulate emission sources from vehicles include their exhaust (Mulawa et al. 1997; Sagebiel et al. 1997), the mechanical wear of tires and brakes (Rogge et al. 1993; Garg et al. 2000), and the ejection of particles from the pavement (Kupiainen et al. 2005) and unpaved road shoulders (Moosmüller et al. 1998) as well as re-suspension processes (Nicholson et al. 1989; Sternbeck et al. 2002). Indirect contributions include the emission of reactive gases, both organic and inorganic, which form secondary particulate matter via atmospheric transformations.

For assessment of the contribution of traffic derived emissions to total pollution levels in an urban atmosphere, detailed information about the emission characteristics of motor vehicles operated under real-world conditions is needed.

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_4,

Emission factors can be used for this purpose; they may be expressed as the amount of species emitted per vehicle km driven or per volume of fuel consumed.

So far, considerable information of the gaseous exhaust pipe emission factors and some of particulate matter is available from the 1990s. More recent studies reported emission factors for PM mass, organic carbon (OC), elemental carbon (EC) and some metals, which improved present knowledge about composition and size distribution of particulate motor vehicle emissions, and more important which allowed the creation of emission profiles—a prerequisite for source apportionment studies with statistic methods such as chemical mass balance models. However, since fuel composition, engines and vehicle technologies evolve (Kleeman et al. 2000) data on the combined mass emission rate and chemical composition of primary particle emissions from motor vehicles need to be updated periodically.

This contribution comprehensively reviews the literature reported for particulate emissions of motor vehicles operated under real-world conditions. This article will mainly focus on the results published for size segregated emissions factors of particle mass, elemental and organic carbon, crustal components and selected trace metals, since information is important for health effects studies and source reconciliation modeling efforts.

2 Sources and Composition of Motor Vehicle Emissions

According to a number of studies are the particles emitted from motor vehicles made up of mineral oxides, soot, numerous organic compounds, a variety of metals and metal compounds and water (Puxbaum et al. 2000). The inorganic ions sulfate, nitrate and ammonium, which were normally major constituents of airborne particulate matter, were also found in particulate vehicle emissions, but only to a minor degree since these compounds were primary formed by gas-to-particle conversion processes of gaseous precursor substances.

Composition and size distribution of the emitted particles depend on the contribution of the individual emission sources related with road traffic—in particular combustion and non-tail-pipe emissions. Tailpipe emissions are vehicle exhaust emissions which are produced during fuel combustion (including additives) and released through the vehicle tailpipe (Rogge et al. 1993; Cadle et al. 1999). The particles derived from tail-pipe emissions are mainly composed of EC and OC, thus average total carbon emission rates are usually very close to the PM mass emission rates. Inorganic anions account for some percent of total tail-pipe emissions, the contribution of the elemental fraction is also in the order of few percent.

Additionally to these combustion derived emissions a motor vehicle also produces so called non-tailpipe emissions, which result from wearing of tires and brakes (Rogge et al. 1993; Garg et al. 2000), abrasion of road pavement (Kupiainen et al. 2005) and from the resuspension of road dust churned up by cars (Nicholson et al. 1989; Sternbeck et al. 2002; Rogge et al. 1993). Though brake and tire wear are

Table 1 Important vehicular emission sources for individual species

Species	Emission source	References
PM	All of the mentioned sources contribute to particulate vehicle-emissions	
OC	Unburned hydrocarbons; tire wear; road dust	Rogge et al. (1993)
EC	Incomplete combustion of diesel fuel	Sagebiel et al. (1997)
NH_4^+	Secondary product of gaseous HNO_3 emissions	Fraser et al. (1998)
NO_3^-	Secondary product of gaseous HNO_3 emissions	Kleeman et al. (2000)
SO_4^{2-}	Sulfur containing fuels	
Cl^-	Salts used as deicing agents;	Lough et al. (2005)
	Sea salt	He et al. (2008)
Na^+	Salts used as deicing agents;	Lough et al. (2005)
	Sea salt	He et al. (2008)
K^+	Resuspension of road dust and fugitive soil	Lough et al. (2005)
Si	Resuspension of road dust and fugitive soil;	Sternbeck et al. (2002)
	Street abrasion; pavement wear	Kupiainen et al. (2005)
Al	Resuspension of road dust and fugitive soil;	Sternbeck et al. (2002)
	Street abrasion; pavement wear	Kupiainen et al. (2005)
Fe	Motor oil; tire wear; brake wear;	Garg et al. (2000)
	Resuspension of road dust and fugitive soil	Sternbeck et al. (2002), Lough et al. (2005)
Ca	Motor oil additives; brake wear;	Cadle et al. (1997)
	Resuspension of road dust and fugitive soil	Lough et al. (2005), Kupiainen et al. (2005)
Mg	Motor oil additives;	Sternbeck et al. (2002)
	Resuspension of road dust and fugitive soil	Lough et al. (2005)
S	Sulfur containing fuels	Sagebiel et al. (1997)
	Motor oil additives	Lough et al. (2005)
Mn	Brake wear; resuspension of road dust and fugitive soil	Allen et al. (2001), Gillies et al. (2001), Sternbeck et al. (2002)
Zn	Brake wear; tire wear; motor oil	Garg et al. (2000), Cadle et al. (2001)
Ba	Brake wear; tire wear	Garg et al. (2000), Sternbeck et al. (2002)
Ti	Brake wear; pavement wear Resuspension of road dust and fugitive soil;	Garg et al. (2000), Sternbeck et al. (2002)
Pb	Brake and tire wear; fuel and motor oil additives resuspension of road dust and fugitive soil	Westerlund et al. (2002), Lough et al. 2005
Cu	Brake wear; tire wear; wheel bearings; fuel and motor oil additives	Cadle et al. (1997), Westerlund et al. (2002)
Sb	Brake wear; tire wear;	Garg et al. 2000
	Motor oil additives	Cal-Prieto et al. 2001
Pd	Catalytic converter	Moldovan et al. (2002)
Pt	Catalytic converter	Moldovan et al. (2002)

only one fraction of total roadway PM emissions, brake wear has been identified as a significant contributor to levels of some trace metals detected in emissions from motor vehicles and in the urban atmosphere (Nicholson et al. 1989; Pakkanen et al. 2003). Elemental analysis indicated that metallic species (in particular titanium, iron, copper, and barium) together with silicon, phosphorus, sulfur, and chlorine accounted for the main part of PM mass (Garg et al. 2000). Only a minor fraction of the airborne PM could be attributed to carbonaceous material (18% on average). Analysis of the particles derived from pavement wear and traction sanding revealed that over 90% of the emitted PM was mineral particles. Mineralogy of the dust and source apportionment showed that they originated from both traction sand and pavement aggregates (Kupiainen et al. 2005). The remaining portion was mostly carbonaceous and originated from tires and road bitumen.

Fugitive dust emissions caused from vehicles travelling on roads are known to be an important source of coarse particles in urban areas (Rogge et al. 1993; Chow et al. 1996; Pakkanen et al. 1996). Particulate emissions from roadways are a complex mixture derived from different sources. The particles originating from the roadway consist of direct emissions from tailpipes (Pierson and Brachaczek 1983) and particles created through tire, brake, and general vehicle wear processes (Rogge et al. 1993). In case of unpaved roads it has to be considered that the rolling wheels of the vehicles impart a force to the surface that pulverizes the roadbed material and ejects particles from the shearing force as well as by the turbulent vehicle wakes. In addition, particles that settle onto the road from both nearby and distant anthropogenic as well as natural sources become part of the mixture and can be subsequently resuspended by vehicles or wind (Moosmüller et al. 1998; Nicholson et al. 1989). The composition of road dust has been reported to be highly variable; depending on the main contributing sources road dust shows significant enrichment in the contents of crustal components, carbonaceous species and several trace metals.

A compilation of the main emission sources for OC, EC, crustal components and selected trace metals is presented in Table 1.

3 Determination of Emission Factors

The composition and quantity of the particles emitted from motor vehicles could be determined by direct and indirect methods. The most widely used methods for evaluating vehicle tailpipe emissions are dynamometer tests, which involve measurements of emissions from selected vehicles using standardized driving cycles under controlled conditions. However, a key concern with these tests is that they do not fully represent real-world driving conditions and emissions. A number of studies reported that particulate emissions from motor vehicles operated under real-world conditions can be significantly different from the results obtained from dynamometer-based studies conducted in the laboratory (Fraser et al. 1999).

These variations may arise from a difference in the way that vehicles are driven between standardized test conditions and real-world situations, but they may also result from differences in the maintenance condition of the single vehicles tested in dynamometer studies and the vehicle fleet as a whole (composition, age and type distributions). Furthermore it has to be considered that non-tailpipe emissions such as those originating from the wear of brake linings, tires and asphalt, and resuspension of road and soil dust are not covered by this test method. Therefore, it is advantageous to collect real-world traffic emission data with indirect methods, which involve the determination of individual pollutant levels in various environmental compartments, and to model the analytical data together with traffic statistics. A common approach for the indirect determination of primary vehicle emissions involves highway tunnel studies which enable the estimation of the average emission of a large number of cars under real-world conditions (Lough et al. 2005).

In order to obtain accurate results for vehicle emissions a simultaneous measurement of pollutant concentrations at the entrance and exit of the tunnel as well as monitoring of traffic density, vehicle speed, wind speed, temperature and pressure is required (Lough et al. 2005; Weingartner et al. 1997; Fraser et al. 1998; Allen et al. 2001; Gillies et al. 2001; Handler et al. 2008). This method is believed to result in representative emission factors for the on-road vehicles and less cost and complexity than the traditional dynamometer method (Jamriska et al. 2004).

The calculation of the emission factor follows the method of Pierson (Pierson et al. 1996). The vehicle emission factor is the mass of specific pollutants produced in a unit kilometer. It can be determined from

$$\mathrm{EF}_{\mathrm{veh}} = \frac{(c_{\mathrm{out}} - c_{\mathrm{in}}) \cdot A \cdot U \cdot t}{N \cdot l}$$

where $\mathrm{EF}_{\mathrm{veh}}$ is the average vehicle emission factor in mg veh^{-1} km^{-1} traveled; c_{out} and c_{in} represent the mass concentration of specific pollutants in mg m^{-3}, at the tunnel exit and entrance; A is the tunnel cross-section area in m^2; U is the wind speed in m s^{-1}; t is the sampling duration in s; N is the total traffic number during the sampling period; and l is the distance in km between the two monitoring stations.

4 Results

The emission rates derived from the tunnel studies conducted so far show that the amount of emitted particulate matter is in the order of tens to hundreds of mg veh^{-1} km^{-1}. The emission factors determined for individual species varied from several mg veh^{-1} km^{-1} for main components to some µg veh^{-1} km^{-1} for trace metals, indicating that particulate emissions from motor vehicles are dominated by carbonaceous species and mineral components. A compilation of most relevant PM_{10} studies is presented in Table 2; corresponding data for the PM fraction smaller than 2.5 µm ($\mathrm{PM}_{2.5}$) is summarized in Table 3.

Table 2 On-road PM_{10} emission rates for selected species in mg vehicle^{-1} km^{-1}

	Kaisermühlen tunnel (2008)	Kilborn tunnel (2005)	Howell tunnel (2005)	Sepulveda tunnel (2001)	Jânio Quadros tunnel (2009)
PM	62 ± 18	120 ± 28	140 ± 33	69 ± 30	197 ± 118
EC	21.3 ± 3.4	11.4 ± 1.8	14.7 ± 5.2	31 ± 4.3	16 ± 5
OC	18.8 ± 3.5	34.1 ± 5.4	44.4 ± 11.0	25 ± 8.5	–
Cl^-	–	–	–	0.7 ± 1.7	–
NO_3^-	–	–	–	2.5 ± 5.3	–
SO_4^{2-}	–	–	–	2.7 ± 5.7	–
NH_4^+	–	–	–	0.8 ± 1.0	–
ΣIons	–	9.7 ± 3.3	15.9 ± 3.6	–	–
Si	6.2 ± 2.4	8.7 ± 1.4	9.1 ± 2.7	2.56 ± 3.40	0.12
Fe	3.4 ± 0.74	13 ± 11	2.9 ± 0.9	12.4 ± 1.2	1.04
Ca	2.1 ± 1.2	10.2 ± 2.3	8.5 ± 2.5	0.80 ± 0.53	–
Al	1.4 ± 0.73	0.97 ± 0.50	2.6 ± 0.8	0.56 ± 1.03	7.76
Mg	0.54 ± 0.27	0.84 ± 0.22	1.9 ± 0.5	0.24 ± 0.94	–
Na	–	0.57 ± 0.33	0.56 ± 0.34	0.79 ± 0.90	–
K	–	0.83 ± 0.15	1.1 ± 0.4	0.26 ± 0.25	–
S	0.28 ± 0.16	1.9 ± 0.6	1.2 ± 0.6	1.0 ± 11.9	0.46
P	–	0.15 ± 0.09	0.11 ± 0.07	0.13 ± 0.37	–
V	0.003 ± 0.002	0.0016 ± 0.0006	0.0017 ± 0.0009	0.03 ± 0.23	–
Mn	0.042 ± 0.013	0.022 ± 0.007	0.033 ± 0.010	0.07 ± 0.02	0.096
Zn	0.160 ± 0.038	0.11 ± 0.03	0.19 ± 0.04	0.32 ± 0.04	0.17
Sr	0.005 ± 0.002	0.0075 ± 0.0025	0.0070 ± 0.0027	0.07 ± 0.01	–
Ba	0.055 ± 0.013	0.14 ± 0.04	0.33 ± 0.10	1.04 ± 0.93	–
Ti	0.047 ± 0.028	0.044 ± 0.022	0.10 ± 0.04	0.06 ± 0.52	0.047
Sn	0.025 ± 0.018	0.008 ± 0.011	0.008 ± 0.010	0.07 ± 0.32	–
Pb	0.017 ± 0.005	0.020 ± 0.007	0.0074 ± 0.0052	0.08 ± 0.04	0.014
Cu	0.156 ± 0.034	0.083 ± 0.017	0.10 ± 0.04	0.53 ± 0.06	0.261
Sb	0.100 ± 0.036	0.016 ± 0.003	0.016 ± 0.003	0.22 ± 0.30	–
Ni	–	0.031 ± 0.074	0.032 ± 0.062	0.01 ± 0.02	0.002
Co	–	0.002 ± 0.010	0.0030 ± 0.0091	0.01 ± 0.36	–
Cr	–	0.011 ± 0.005	0.017 ± 0.009	0.02 ± 0.06	–
Pt[a]	25 ± 9	150 ± 90	200 ± 170	–	–
Pd[a]	9.7 ± 4.0	370 ± 360	30 ± 10	–	–

[a] Pt and Pd: emission rates given in ng veh^{-1} km^{-1}

4.1 Bulk Emission Rates

Table 2 indicates a distinct variation between the PM_{10} mass emission factors of different tunnel studies, lowest averaged emissions rates of 62 ± 18 mg veh^{-1} km^{-1} were reported for the Kaisermühlen tunnel (Handler et al. 2008), highest PM_{10} emissions of 197 ± 118 mg veh^{-1} km^{-1} were determined in the Jânio Quadros tunnel (Sánchez-Ccoyllo et al. 2009). Similar findings were observed for $PM_{2.5}$ mass emission rates, which ranged from 24.1 ± 6.4 mg veh^{-1} km^{-1} in the Kilborn tunnel (Lough et al. 2005) to 110 ± 4 mg veh^{-1} km^{-1} in the Zhujiang

Table 3 On-road $PM_{2.5}$ emission factors for selected species in mg veh^{-1} km^{-1}

	Kaisermühlen tunnel (2008)	Kilborn tunnel (2005)	Howell tunnel (2005)	Sepulveda tunnel (2001)	Söderleds tunnel Sternbeck et al. 2002	Zhujiang tunnel (2008)
PM	26 ± 10	24.1 ± 6.4	39.3 ± 15.3	52 ± 27	67 ± 5	110
EC	17.8 ± 3.2	6.87 ± 1.58	10.8 ± 3.88	25.50 ± 4.98	6.7	49.6
OC	5.4 ± 1.9	6.41 ± 3.29	12.9 ± 6.91	19.27 ± 8.46	11.2	24.3
Cl^{-}	–	–	–	0.67 ± 0.99	–	0.98
NO_3^{-}	–	–	–	3.27 ± 1.17	–	1.37
SO_4^{2-}	–	–	–	1.77 ± 2.06	–	3.87
NH_4^{+}	–	–	–	1.61 ± 1.06	–	0.8
ΣIons	–	3.65 ± 0.81	6.75 ± 1.85		–	–
Si	1.8 ± 0.95	0.45 ± 0.16	0.64 ± 0.16	0.56 ± 0.12	4.48 ± 1.22	–
Fe	0.77 ± 0.38	0.51 ± 0.16	0.55 ± 0.12	2.79 ± 0.29	0.70 ± 0.26	1.12
Ca	0.27 ± 0.26	0.31 ± 0.07	0.43 ± 0.12	0.30 ± 0.07	0.44 ± 0.14	0.64
Al	0.47 ± 0.38	0.12 ± 0.09	0.00 ± 0.00	0.22 ± 0.15	2.99 ± 0.68	–
Mg	0.08 ± 0.07	0.077 ± 0.034	0.044 ± 0.022	0.26 ± 0.29	–	0.22
Na	–	0.98 ± 0.98	0.038 ± 0.038	0.30 ± 1.17	–	0.37
K	–	0.13 ± 0.04	0.065 ± 0.041	0.08 ± 0.07	0.42 ± 0.13	0.14
S	0.03 ± 0.02	1.1 ± 0.4	0.090 ± 0.090	0.32 ± 0.56	0.34 ± 0.07	–
P	–	0.15 ± 0.06	0.037 ± 0.037	0.09 ± 0.15	–	–
V	0.002 ± 0.004	0.0007 ± 0.0002	0.0004 ± 0.0003	0.05 ± 0.21	–	0.0015
Mn	0.006 ± 0.005	0.0058 ± 0.0018	0.0060 ± 0.0038	0.02 ± 0.03	0.017 ± 0.005	0.019
Zn	0.034 ± 0.021	0.023 ± 0.010	0.028 ± 0.017	0.14 ± 0.02	0.024 ± 0.006	0.078
Sr	0.001 ± 0.001	0.0016 ± 0.0005	0.0014 ± 0.0010	0.02 ± 0.02	0.006 ± 0.002	–
Ba	0.015 ± 0.007	0.065 ± 0.013	0.082 ± 0.038	0.36 ± 1.37	–	–
Ti	0.008 ± 0.010	0.010 ± 0.007	0.19 ± 0.18	0.09 ± 0.50	0.09 ± 0.02	0.027
Sn	0.012 ± 0.007	0.0016 ± 0.0075	0.016 ± 0.014	0.10 ± 0.31	–	–
Pb	0.006 ± 0.002	0.0031 ± 0.0005	0.0010 ± 0.0010	0.03 ± 0.06	0.005 ± 0.002	0.014

(continued)

Table 3 (continued)

	Kaisermühlen tunnel (2008)	Kilborn tunnel (2005)	Howell tunnel (2005)	Sepulveda tunnel (2001)	Söderleds tunnel Sternbeck et al. 2002	Zhujiang tunnel (2008)
Cu	0.041 ± 0.017	0.041 ± 0.007	0.012 ± 0.010	0.17 ± 0.02	0.0002 ± 0.005	0.034
Sb	0.012 ± 0.008	0.0081 ± 0.0022	0.0047 ± 0.0020	0.15 ± 0.37	–	–
Ni	–	0.00 ± 0.12	0.009 ± 0.044	0.01 ± 0.02	0.0001 ± 0.0001	0.034
Co	–	0.000 ± 0.015	0.0004 ± 0.0060	0.00 ± 0.10	0.005 ± 0.002	0.0001
Cr	–	0.012 ± 0.007	0.0018 ± 0.0018	0.02 ± 0.05	0.0001 ± 0.0015	0.0054
Pt[a]	8.1 ± 5.4	20 ± 10	10 ± 10	–	–	–
Pd[a]	4.6 ± 2.2	120 ± 100	40 ± 30	–	–	–

[a] Pt and Pd: emission rates given in ng veh^{-1} km^{-1}

Tunnel (He et al. 2008). As can be deduced from the relatively large standard deviations presented in Tables 2 and 3 varied the emission rates in all studies significantly. The rather large range observed for individual emission rates, reflects the continuous changes in the parameters influencing vehicle emissions (fleet composition, traffic density and driving conditions).

However, comparable PM_{10} emission rates were reported for the Kaisermühlen tunnel (Handler et al. 2008) and the Sepulveda Tunnel (Gillies et al. 2001), but significantly higher particle mass emission rates were found in the Howell and Kilborn tunnel (Lough et al. 2005). Emission rates for the size fraction $PM_{2.5}$ where comparable for most sites, only for the Zhujiang tunnel remarkable higher emission rates have been reported (He et al. 2008). The most likely explanation for this observation are differences in the fleet composition (contribution of heavy duty vehicles), but higher emissions rates are also likely due to an older and possibly more poorly maintained vehicle fleet. Additionally differences in the road surface conditions have to be considered, which are known to influence the resuspension of road dust.

Particulate vehicle emissions were dominated in all reported tunnel studies by the carbonaceous fraction consisting of OC and the EC. The averaged emission rates for EC and OC in PM_{10} varied between 11.4 and 44.4 mg veh^{-1} km^{-1}, together they accounted for approximately 40–60% of the total PM_{10} emissions, for the Sepulveda tunnel an enhanced contribution of $\sim$80% is reported (Gillies et al. 2001). Emission rates of OC in $PM_{2.5}$ ranged from 5.4 to 19.3 mg veh^{-1} km^{-1}, while EC emission varied between 6.9 and 49.6 mg veh^{-1} km^{-1}. The contribution of OC to total particle emissions varied in this size fraction from 20 to 40%, for EC the corresponding results ranged between $\sim$30 and 50%. For the Kaisermühlen tunnel a distinctly enhanced contribution is reported (Handler et al. 2008), at this site the EC emissions accounted on average for 63.6 ± 10.5% of $PM_{2.5}$ roadway mass emissions. The increase observed in all studies for the relative contribution of EC in $PM_{2.5}$ emissions results from differences in the major sources of EC and OC, namely combustion processes for EC and abrasion, resuspension and combustion for OC. Street abrasion and resuspension of road dust is known to generate particles prevailing in the PM_{10} fraction, in contrast to combustion processes which yield predominantly particles with aerodynamic diameters in the fine mode. Thus EC emissions were usually enriched in the $PM_{2.5}$ fraction, whereas OC is more dominant in the coarse mode of particulate vehicle emissions. However, when comparing the EC emissions observed in the individual tunnel studies differences in their magnitude and in their contribution to total emissions become apparent. The great variation observed in the emission rates for EC in $PM_{2.5}$ reflects differences in the fleet composition. As heavy duty vehicles are known to emit much more PM and EC than low duty vehicles (Cadle et al. 1999), the higher EC emissions in the Zhujiang Tunnel (49.6 mg veh^{-1} km^{-1}) (He et al. 2008) are consistent with the enhanced contribution of heavy duty vehicles (19.8%) in this study. In the Söderleds tunnel heavy duty vehicles comprised only about 5% of the fleet leading to lowest EC emission rates of only 6.7 mg veh^{-1} km^{-1} (Sternbeck et al. 2002). But even for studies with comparable contributions of heavy duty vehicles distinct differences were observed. E.g. in the Kaisermühlen tunnel approximately 2/3 of vehicular $PM_{2.5}$ emissions are made up by EC (Handler et al. 2008), whereas in the Howell tunnel EC accounted in the size fraction $PM_{2.5}$ for less than 30% of total particle emissions (Lough et al. 2005). Similar results were reported for the Squirrel Hill tunnel (Grieshop et al. 2006). This discrepancy in the relative contribution of size segregated EC emission rates in the Kaisermühlen tunnel and the mentioned US-studies can be explained with the more frequent use of diesel powered engines in Austria (56.1% of total car fleet), causing enhanced EC emissions when compared to fleets with an increased contribution of gasoline powered vehicles.

4.2 Soluble Ions

Emission rates of the inorganic ions sulfate, nitrate, chloride and ammonium were found to be in the order of several mg veh^{-1} km^{-1} (see Tables 2, 3), together they composed around 10% of PM_{10} emissions, and approximately 15% of $PM_{2.5}$ emissions (Lough et al. 2005; Gillies et al. 2001). Ammonium, nitrate and sulfate in the particulate form are generated in the atmosphere from gaseous precursor substances such as SO_2 or NO_x which are formed and emitted during fuel combustion. As diesel exhaust usually contains more sulfates due to the higher sulfur content in diesel fuel (Lowenthal et al. 1994), enhanced emission levels of sulfate were observed in studies with higher heavy duty vehicles contributions. However, accurate measurement of ammonium and nitrate is difficult, since particle-phase ammonium nitrate is known to volatilize at enhanced temperatures, thus the collected amount depends on the temperature during sample collection—which hampers comparison of the results from different tunnel studies. Interpreting the data derived from summer and winter tests in Kilborn and Howell tunnel Lough et al. concluded that chloride varied distinctly with seasons (Lough et al. 2005), averaging $2.5 \pm 0.9\%$ of PM_{10} mass in summer tests, and $34 \pm 7.9\%$ in winter tests, due to application of salt to melt ice on roadways in winter. The resuspension of sea salt has been identified as another potential source for chloride (He et al. 2008).

4.3 Mineral Components and Sulfur

Crustal elements were reported to be the major inorganic constituents of particulate vehicle emissions. In the Kaisermühlen tunnel (Handler et al. 2008) averaged emission rates of the elements Si, Al, Ca, Mg and Fe varied between 0.54 and 6.2 mg veh^{-1} km^{-1} in PM_{10} (Table 2) and 0.08–1.8 mg veh^{-1} km^{-1} in $PM_{2.5}$ (Table 3). The cumulated mass of these five elements accounted for $18.2 \pm 6.3\%$ of PM_{10} emissions, their mean contribution to $PM_{2.5}$ emissions was $14.9 \pm 9.3\%$ respectively. These results are in good agreement with findings of Gillies et al. and

Lough et al. who reported mean contributions in the order of 18–28% for PM_{10} emissions in the Sepulveda, Howell and Kilborn tunnel (Lough et al. 2005; Gillies et al. 2001). Important roadway sources for these elements include combustion of motor oil additives and wearing of pavement, engines, tires, and brakes. Particles liberated from mechanical processes, such as the wear of engines, brakes, and tires, have been found to be important sources of Fe in aerosols (Garg et al. 2000; Cadle et al. 1997). Combustion of motor oil additives is another potentially important source of Ca and Mg (Cadle et al. 1997). However, the major part of inorganic vehicle emissions is predominantly attributed to resuspension of road dust, since these elements are major components of crustal materials and soil.

Emissions of crustal components occur predominantly in the coarse mode since the products of tire and brake wear as well as the resuspended road dust are dominated by particles $>10\ \mu m$ (Garg et al. 2000; Kupiainen et al. 2005; Sternbeck et al. 2002), whereas particulate matter in the vehicle exhaust is dominated by particles smaller than PM_{10} (Baumgard and Johnson 1996; Ristovski et al. 1998). Thus differences in the size distribution of individual crustal components reflect variations in the relative contribution of the different emission sources. For example observed Lough et al. that iron followed by calcium and silicon were the most abundant mineral components in the Howell and Kilborn tunnel (Lough et al. 2005), their presence in PM_{10} has been explained with the resuspension of road dust. The relative shift in composition between motor vehicle emissions and crustal material [PM_{10} emissions averaged 3.9% Si and 0.69% Al by mass, whereas crustal materials typically contain about 28% Si and 8.1% Al (Lutgens and Tarbuck 2000)] was attributed to the contributions of other roadway sources and enrichment of roadway soil with previously deposited PM from motor vehicles. In $PM_{2.5}$ for these elements more than 20 times lower emission rates were observed. Since particle mass concentrations decreased from PM_{10} to $PM_{2.5}$ only by a factor of 4–5, a distinct reduction in the relative contribution of crustal elements to total $PM_{2.5}$ emissions resulted, indicating that Al, Ca, Fe, Mg and Si were predominantly emitted in the coarse mode. In contrast to this reported Handler et al. that in the Kaisermühlen tunnel the emissions of mineral components in PM_{10} were dominated by Si, followed by Ca, Fe, Al and Mg (Handler et al. 2008), whereas for fine particle emissions ($PM_{2.5}$) a changed order in their relative abundance (Si, Fe, Al, Ca and Mg) was observed, indicating that the investigated elements were emitted from different sources. The increased occurrence of Ca and Mg in the coarse fraction has been attributed to resuspension of road dust and soil as the most important source for these elements, whereas the fine fraction ($PM_{2.5}$) normally is controlled by emissions from additives in motor oils (Cadle et al. 1997). A different behavior was observed for Al and Si, which showed a clear shift to enhanced fine particle emissions. For these two elements the fine fraction accounted for approximately 30% of PM_{10} emissions, in case of Ca and Mg the mean contribution of the $PM_{2.5}$ fraction to PM_{10} emissions was less than 14%. The relatively constant emission ratio observed for Si and Al in all size fractions indicates that the emission of these two elements depends on the same sources, in particular pavement wear which consists mainly of aluminosilicates

(Kupiainen et al. 2005). Iron emissions originate from the resuspension of road dust as well as from the abrasion of road construction material; additionally particles liberated from processes such as engine and brake wear have to be considered (Garg et al. 2000). These supplementary iron sources are responsible for the different size distribution of iron emissions compared to the results for Ca, Mg and Si, Al emissions.

Emission rates for sulfur varied between hundreds of μg veh^{-1} km^{-1} in $PM_{2.5}$ and some mg veh^{-1} km^{-1} in the size fraction PM_{10}. For the Kaisermühlen tunnel averaged sulfur emission rates of 0.28 ± 0.16 mg km^{-1} vehicle^{-1} and 0.03 ± 0.02 mg km^{-1} vehicle^{-1} were reported for the size fraction PM_{10} and $PM_{2.5}$ (Handler et al. 2008), slightly increased results were found in the Sepulveda tunnel (Gillies et al. 2001), highest emission rates were observed in the Kilborn tunnel (PM_{10} 1.9 ± 0.6 mg km^{-1} vehicle^{-1}, $PM_{2.5}$ 1.1 ± 0.4 mg km^{-1} vehicle^{-1}) (Lough et al. 2005). Important sources for sulfur emissions are fuel, motor oil, and additives such as zinc dithiophosphate (Cadle et al. 1997). Although different sulfur fuel contents and percentages of diesel powered vehicles can be assumed for the car fleets in the investigated tunnels, the observed differences were relatively small (see Tables 2, 3) excluding the results of Lough et al. who reported distinctly higher emissions (Lough et al. 2005). However, due to the introduction of sulfur free fuel a remarkable reduction of particulate sulfur emissions can be expected for the future, although it has to be considered that the primary gaseous emissions, which are the most relevant sulfur emissions, were not investigated in the mentioned studies.

4.4 Trace Metals

Trace metal emissions were found to vary between some few and several hundred μg veh^{-1} km^{-1} with decreasing values for reduced size fractions. In all tunnel studies the most abundant elements were Zn, Ba, Cu followed by toxic elements such as Sb, Pb, As, Cd and Cr—an outcome which further emphasizes the importance to health studies of understanding total roadway emissions of metals (Sternbeck et al. 2002; Lough et al. 2005; Valiulis et al. 2002). Average emission factors for metals in the investigated size fractions are presented in Tables 2 and 3. Although the sum of all determined trace elements did not exceed 1% of PM_{10} mass, they may be important for health effects and can provide some indications of the sources of particulate matter emissions. Potential sources for the emitted metals are combustion products from fuel and oil, wear products from tires, brake linings, bearings, coach and road construction materials, and resuspension of soil and road dust. To gain information about the main sources Handler et al. calculated correlations between the trace metals investigated in the Kaisermühlen tunnel (Handler et al. 2008). In PM_{10} a very good correlation ($r^2 > 0.9$) between Sr, Ti and Mn was found. Since for these metals different sources were reported in literature, Ti is used in the paint for road markings, Sr is at least in Europe found in fuel additives to optimize catalyst performance, and Mn was found in brake wear (Garg et al. 2000), it was supposed that the observed metal emissions originate predominantly from the resuspension of road dust. The high correlation ($r^2 > 0.9$) of these elements to the emission rates of Ca, Mg, Fe, Si and Al confirms this assumption. In $PM_{2.5}$ Sr, Ti and Mn showed still a good correlation to Ca and Mg, whereas compared to Fe, Si and Al only poor correlations were found, indicating that $PM_{2.5}$ emissions of Ti, Sr and Mn were determined by Ca and Mg sources. Furthermore a good correlation between the emission factors of Cu and Ba was found in PM_{10} ($r^2 > 0.8$), which indicates that Ba and Cu emissions depend on the same sources, in particular brake linings (Garg et al. 2000). Compared to the emissions of mineral components only to Fe a good correlation was observed, which was expected since brake wear is an important source for iron emissions. Antimony, which has been suggested as a tracer for brake wear (Dietl et al. 1997), was correlated to a lesser extent with Cu, Ba and Fe (0.6 in TSP and 0.3 in PM_{10}), which could be explained by the use of certain organic Sb compounds in greases, motor oils and fuels (Cal-Prieto et al. 2001). These additional Sb sources were responsible for the high correlation ($r^2 > 0.9$) to Ca and Mg which are also used as additives in motor oils (Cadle et al. 1997). The remaining trace metals Pb, V and Zn showed neither a good correlation to other trace metals nor to the investigated mineral components, which appears to be a result of the diversity of possible sources. Zn is known as a constituent of tires (Sörme et al. 2001) and motor oil additives (Huang et al. 1994), Pb is emitted from sources such as break wear, road dust as well as fuel and motor oil combustion (Garg et al. 2000; Lowenthal et al. 1994; Young et al. 2002). Similar findings were reported from the studies performed in the Zhujiang tunnel, the Howell and Kilborn tunnel, and the Söderleds tunnel (Sternbeck et al. 2002; Lough et al. 2005; He et al. 2008).

4.5 Platinum Group Elements

Platinum group elements (PGE) can be naturally found only at very low concentration in the earth crust, a situation which changed with the introduction of PGE based catalytic converters in the automobile industry. Platinum (Pt), rhodium (Rh), and palladium (Pd) are used in the catalyst as active compounds to facilitate the oxidation of hydrocarbons and other incompletely oxidized components with nitrogen oxides, which leads to a reduction of 90% for the amount of hydrocarbons and nitrogen oxides in the exhaust gas. Even for diesel engines oxidation catalysts were developed and integrated in new manufactured cars. While improvement in air quality is an important benefit of catalytic converters, the use of these devices has led to widespread release of PGE in the environment (Barbante et al. 2001; Schäfer et al. 1999). During the release of the exhaust gases from the engine, the surface of the washcoat of the catalyst is chemically and physically stressed by fast changing oxidative/reductive conditions, high temperature and mechanical abrasion, thus, causing the emission of PGE containing particulate matter into the environment (Artelt et al. 1999; Moldovan et al. 1999).

Concerns have arisen that the emitted PGE may have deleterious effects on the health of human beings and other living organisms. For risk assessment detailed knowledge about the entry of PGE into the environment is required. However, literature data about vehicle derived PGE emissions is very sparse. Limbeck et al. presented size segregated emission factors for Pd and Pt (Limbeck et al. 2007), their investigations in the Kaisermühlen tunnel revealed that these noble metals were dispersed into the environment with emission rates in the order of some ng veh^{-1} km^{-1}, indicating that the emitted PGE levels are three orders of magnitude lower than observed for common trace metals like Cu, Pb or Sn. Lough et al. reported from a tunnel study performed in Milwaukee (Wisconsin, US) a mean emission rate of 100 ± 49 ng veh^{-1} km^{-1} for Pt in PM_{10} (Lough et al. 2005), and additionally Pd was measured with an average PM_{10} emission rate of 150 ± 130 ng veh^{-1} km^{-1}. This disparity between the findings of the mentioned US study (Lough et al. 2005) and those determined in the Kaisermühlen tunnel (Limbeck et al. 2007) could be explained with differences in the fleet composition since in Europe the contribution of diesel powered vehicles to the total car fleet is distinctly higher, furthermore variations in the maintenance condition of the vehicles, the fraction of catalyst equipped vehicles, the age and type of the used catalytic converters, etc. have to be considered. The amount of PGE released into the environment by abrasion of the catalyst has been evaluated in some dynamometer studies. A good agreement was found when comparing the achieved emission rates with the findings of these dynamometer-based studies (Artelt et al. 1999; Moldovan et al. 1999).

5 Conclusions and Summary

Real-world emission rates of in-use motor vehicles (road traffic) can be quantified by measurements in road tunnels. The results reported for particle mass emissions in PM_{10} varied from several mg veh^{-1} km^{-1} to some hundred mg veh^{-1} km^{-1}, with reduced amounts for the fine particle fraction $PM_{2.5}$. The particles released mainly consist of EC, OC, soluble ions (NH_4^+, SO_4^{2-}, NO_3^-) and mineral components (Si, Fe, Ca, Al, Mg). Trace metal emissions (Ba, Co, Cr, Cu, Mn, Ni, Pb, Sb, Sn, Sr, Ti, V, Zn) contribute usually for less than 1% of total emissions in all size fractions. Observed particulate vehicle emissions could be attributed to several tailpipe and non-tailpipe sources. The main part of carbon emissions may be contributed to tail-pipe exhaust fraction, whereas the non-carbon emissions are most likely non-exhaust derived components. PM_{10} emissions are usually dominated by resuspended matter as well as by brake wear, whereas fine particles ($PM_{2.5}$) are mainly derived from combustion processes.

However, when comparing the results obtained from tunnel studies performed at varying sited around the world (Tables 2, 3), it is obvious that both emission factors and relative distributions of the elements showed large variations—frequently by more than one order of magnitude. Since the effect of traffic intensity has been already accounted for the calculation of EFs, additional parameters must be considered to explain the observed results—in particular changes in fleet composition and driving conditions. Although light duty vehicle (LDV) comprise the vast majority of the vehicle fleets, total fleet emissions were dominated by heavy duty vehicles (HDV) contributions since they are stronger emitters of fine particles and soot. Thus even small changes in the fraction of HDV can significantly affect the total PM emissions of the vehicle fleet, through tailpipe emissions as well as through increased resuspension of soil and road dust. From dynamometer studies as well as from real word measurements it is known that motor vehicles emissions are also influenced by the driving conditions. Several studies reported reduced vehicle emission rates for free cruising conditions, whereas for stop-and-go traffic enhanced emissions were observed, which result from additional braking and accelerating maneuvers—causing increased brake and tire wear emissions as well as resuspension of road dust. Furthermore differences in the roadway conditions, fleet age, vehicle maintenance conditions, etc. have to be considered.

Thus for risk assessment in health effect studies or for aerosol source apportionment modeling local emission source profiles and emission factors are mandatory.

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The Atmospheric Concentrations of Pb, Mn, Cr, and Cd on the Korean Peninsula Between 1991 and 2006

Kim Ki-Hyun, Nguyen Hang Thi and Ma Chang-Jin

1 Introduction

Potential risks and the adverse impact of metallic pollutants in the air have been evaluated in many different respects (e.g., Ariane et al. 2001). In re-cognition of the fact that the atmosphere can serve as a major medium to transfer most particle bound metals across different environmental reservoirs, enormous efforts have been directed towards a routine monitoring of diverse airborne metal species. Information derived from such efforts helps us determine the direction of emission control strategies, either in the form of various technical applications or through air quality regulations and related policies. In fact, more extreme measures to cope with trace metal pollution were found to involve various bans on the use of certain raw materials or products (e.g., EPSMA 2003).

In an effort to explore the status of metal pollution under diverse environmental conditions, we have been involved in a number of projects to assess the spatial and temporal distribution of the major metallic components on the Korean peninsula such as Pb (Kim 2007a), Cd (Kim 2007b), Cr (Nguyen and Kim 2008), and Mn (Myeong et al. in press). In light of the potential impacts of these hazardous metal species, their concentration data have been monitored routinely at monthly intervals in parallel at 13 major cities with different source characteristics. As these measurements have been conducted over an extended period from 1991 to 2006, a comprehensive evaluation of each metal data set was made to allow in-depth descriptions of their distribution patterns.

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_5,

The results of our initial efforts, focusing on the environmental behavior of each individual metal species, helped us confirm that regulatory efforts to control metal concentration levels have been fruitful in many aspects, although it was confined to a few metal species. Considering that the factors and processes associated with the emissions of various metal species can be interrelated, we attempted to extend our initial efforts by examining the larger picture of different metal species and their associations. As the present study aims to allow a parallel comparison of all four target metals of Pb, Mn, Cr, and Cd, it can offer valuable insights into pollution by different metals and their cycles under diverse environmental conditions.

2 Materials and Methods

A number of heavy metal monitoring stations have been established and maintained by the Korean Ministry of Environment (KMOE). To monitor the extent of airborne metal pollution in major cities (with large populations (e.g., above a half million) or strong industrial activities), the concentrations of some important trace metals have been measured routinely in 13 city areas (Fig. 1) as part of a larger network of up to 59 monitoring stations during the full study period (Table 1). In this work, the concentration data of four metal species (Pb, Mn, Cr, and Cd) were analyzed to assess the status of metal pollution in major cities of Korea for an extended period (1991–2006). At each individual station, the collection and analysis of particle samples were made by following the basic procedures for the standard KMOE air quality measurement method. According to this method, the concentrations of each metal are determined from TSP samples collected by high-volume samplers with the aid of atomic absorption spectrometry. The quality assurance of these original metal concentration data is managed by the procedures of KMOE and stored in its data management network system. Details of analytical approaches used for the determination of airborne metal concentrations and the handling of such data sets have been described in our recent publications dealing with each individual target metal (Kim 2007a, b; Nguyen and Kim 2008; Myeong et al. in press) or as a group (Kim et al. 2004).

To assess the environmental behavior of four metal species measured from each monitoring station throughout the 16-year study period, the analysis was first made to examine the annual data sets of each metal derived from each city. In addition, to facilitate the simple evaluation of temporal variations, the analysis has also been made after evenly dividing the whole study period into period I (1991–1998) and period II (1999–2006). The concentrations of each metal species were determined routinely at monthly intervals at each station. However, the way in which these data were stored and treated in the KMOE database was not standardized until 1998, making it difficult to assess the data from this early period (period I). As a consequence, all metal concentration data were stored as an annual average for each of all 13 cities until 1997. From 1998, all metal data from individual stations

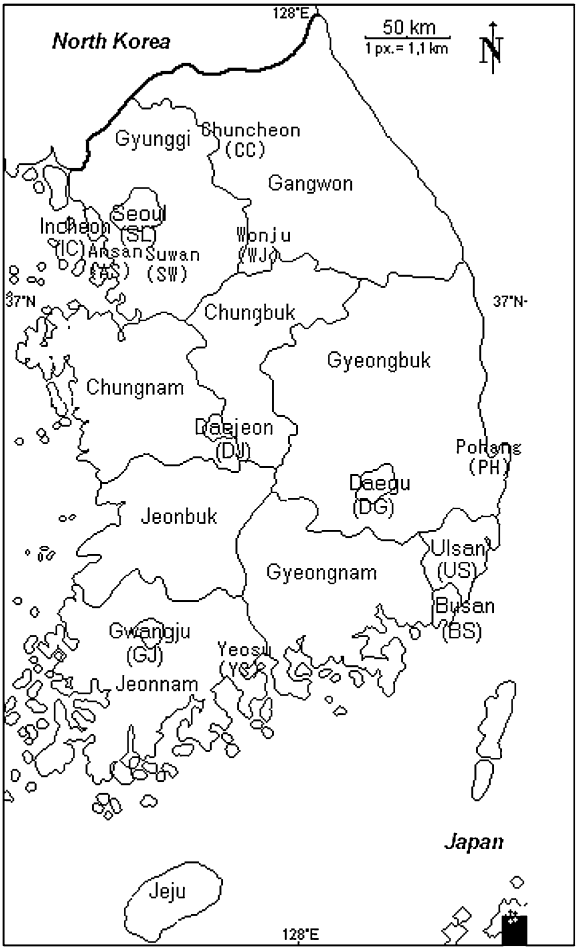

Fig. 1 A map locating all 13 cities for routine monitoring of metal pollution levels in Korea

were stored at monthly intervals to allow the data analysis for wider temporal and spatial scales. The temporal grouping criterion used in this study has hence been modified slightly from those introduced previously for our analysis of Pb and Cd of which the temporal coverage was limited to 2004 (Kim 2007a, b).

It should be noted that both the number and geographical location of individual monitoring stations in certain cities, as seen in Table 1, have continuously changed throughout the study period. For instance, the total number of all monitoring stations in these Korean cities increased from 35 in 1998 to 41 for all 13 cities at the end of 2006. New monitoring stations have been added continuously, while some of the older ones ceased operations. The city of Seoul seems to have suffered the most, due to the frequent upgrading of its management system for various reasons. General information covering the management of the basic air quality and heavy

Table 1 The use of acronym codes and associated information for 13 cities and their individual stations

Order	City (code)	Station code[a]	Station name	Land use[b]	Measurement period	
					Start	End
1	Seoul (SL)	SL1	Gwan Ak Mt.	R	98.1	01.12
2		SL2[c]	Gu Ro	I	01.9	06.12
3		SL3	Mullae	I	98.1	02.5
4		SL4[c]	Bang Yi	G	01.9	06.12
5		SL5[c]	Bang Hak	R	01.5	06.12
6		SL6	Bul Gwang	R	98.1	01.4
7		SL7[c]	Sung Soo	C	02.6	06.12
8		SL8	City Hall	C	98.1	01.4
9		SL9[c]	Yang Jae	R	02.6	06.12
10		SL10	Jam Sil	R	98.1	02.5
11		SL11[c]	Hwa Gok	R	01.5	06.12
12		SL12	Nam Ga Jwa	R	01.9	02.4
13		SL13	Han Nam	R	01.9	02.3
14	Busan (BS)	BS1[c]	Gam Jeon	I	98.1	06.12
15		BS2[c]	Duk Chun	R	98.1	06.12
16		BS3	Bum Chun	C	98.1	03.12
17		BS4[c]	On Chun	G	98.1	06.12
18		BS5[c]	Jun Po	G	04.1	06.12
19		BS6[c]	Yeon San	R	06.1	06.12
20	Daegu (DG)	DG1[c]	Dae Myung	R	98.1	06.12
21		DG2	Sam Duck	C	98.1	99.5
22		DG3[c]	Soo Chang	C	99.6	06.12
23		DG4[c]	Yi Hyun	I	98.1	06.12
24		DG5[c]	Ji San	R	98.1	06.12
25	Incheon (IC)	IC1[c]	Nohn Hyun	I	02.1	06.12
26		IC2[c]	Boo Pyung	C	98.1	06.12
27		IC3[c]	Soong Euo	R	98.1	06.12
28	Gwangju (GJ)	GJ1[c]	Nong Sung	C	98.1	06.12
29		GJ2[c]	Doo Am	R	98.1	06.12
30		GJ3[c]	Seo	G	98.1	06.12
31		GJ4[c]	El Gok	I	98.1	06.12
32	Daejeon (DJ)	DJ1[c]	Goo Sung	G	98.1	06.12
33		DJ2	Dae Hung	C	98.1	03.12
34		DJ3	Yu Chun	R	98.1	04.9
35		DJ4[c]	Eup Nae	I	98.1	06.12
36		DJ5	Moon Pyung	I	03.1	03.2
37		DJ6[c]	Moon Chang	C	04.1	06.12
38		DJ7[c]	Jung Rim	R	04.10	06.12
39	Ulsan (US)	US1[c]	Duk Shin	G	03.1	06.12
40		US2[c]	Sin Jung	C	03.1	06.12
41		US3[c]	Ya Eum	R	98.1	06.12
42		US4[c]	Yeo Chun	I	98.1	06.12

Table 1 (continued)

Order	City (code)	Station code[a]	Station name	Land use[b]	Measurement period	
					Start	End
43	Suwon (SW)	SW[c]	Shin Poong	C	98.1	06.12
44	Ansan (AS)	AS[c]	Won Shi	I	98.1	06.12
45	Wonju (WJ)	WJ1	Myung Ryoon	R	98.1	02.12
46		WJ2[c]	Woo San	I	98.1	06.12
47		WJ3[c]	Hak Sung	C	98.1	02.12
48		WJ4	Haeng Goo	G	98.1	02.11
49	Chuncheon (CC)	CC1[c]	Shin Book	G	03.1	06.12
50		CC2	Yo Sun	C	03.1	03.12
51		CC3	Hyo Ja	C	03.1	03.12
52		CC4	Hoo Pyung	R	03.1	06.1
53		CC5[c]	Ok Chun	C	04.1	06.12
54		CC6[c]	Eun Ha Soo	R	04.1	06.12
55	Yeosu (YS)	YS1[c]	Sam Il	I	98.1	06.12
56		YS2[c]	Ssang Bong	R	98.1	06.12
57	Pohang (PH)	PH1[c]	Jang Hung	I	98.1	06.12
58		PH2[c]	Jook Do	C	98.1	06.12
59		PH3[c]	Tae Song	G	05.3	06.12

[a] All stations are named by two letter acronyms with the numbers

[b] Acronyms of I, C, R, and G are assigned for land use types of industrial, commercial, residential, and grassland, respectively

[c] Stations which are still functioning and are presently continuing to make measurements

metal monitoring stations has been described elsewhere (Kim and Kim 2003; Kim et al. 2003; Nguyen and Kim 2006). Although there were a few newly operating stations in the 13 target cities between 2005 and 2006, the data from these stations were not used in order to make a parallel comparison for all four metals species.

3 Results and Discussion

3.1 *Spatial Pattern of Metal Pollution in All Study Areas*

In this study, the general status of metal pollution was analyzed for each of all four metals based on the annual mean concentration data derived from 13 individual cities (Table 2). In Table 3, a statistical summary of the concentration data is presented to allow inter-annual variations of each metal across 13 cities. To facilitate comparison of metal pollution levels across different cities, the metal concentrations for each city are compared by their mean values for the entire study period (Fig. 2). The results indicate that cities with similar levels of pollution, especially highly industrialized ones, can still be distinguished fairly effectively by

Table 2 The annual mean concentrations (ng m^{-3}) of four metal species from 13 individual cities in Korea from 1991 to 2006

Year	Target city of investigation												
	AS	IC	US	PH	SL	BS	WJ	SW	DJ	DG	GJ	CC	YS
(a) Pb													
1991	–	427	104	85	341	247	221	–	157	138	118	–	54
1992	–	395	91	76	286	141	156	–	143	108	87	–	57
1993	–	259	87	62	209	176	170	–	257	48	54	–	34
1994	–	246	83	57	191	144	225	–	276	44	47	–	32
1995	1,466	243	46	29	184	71	89	199	367	14	49	–	42
1996	656	216	66	24	150	102	81	190	141	32	44	–	29
1997	508	170	69	31	109	83	53	169	181	30	33	–	15
1998	418	126	70	45	94	110	30	125	89	36	11	–	3
1999	227	126	66	47	98	103	49	79	99	37	11	–	7
2000	409	120	67	39	88	100	40	85	81	27	44	–	31
2001	247	132	58	74	76	73	42	69	62	53	40	–	31
2002	170	106	74	83	81	75	47	69	48	70	33	–	35
2003	217	121	57	77	58	51	–	60	46	58	31	60	17
2004	150	141	69	61	79	53	–	55	73	69	42	73	31
2005	121	89	55	47	44	46	–	47	70	45	30	51	44
2006	159	83	42	48	42	59	72	48	58	66	49	54	44
(b) Mn													
1991	–	93.6	82.6	199	90.2	87.7	44.5	–	27.1	55.9	37.7	–	44.1
1992	–	120	65.8	392	98.0	65.0	64.4	–	28.1	45.1	53.2	–	38.3
1993	–	85.3	41.5	216	76.0	54.4	49.2	–	74.9	22.8	37.2	–	29.6
1994	–	114	57.0	153	80.6	75.8	35.8	–	63.9	31.9	58.2	–	29.3
1995	122	105	38.9	150	66.1	55.0	35.8	59.9	79.8	10.2	83.6	–	38.4
1996	138	109	48.6	139	60.7	61.4	50.0	83.7	57.7	19.0	79.1	–	58.0
1997	123	89.0	45.4	136	49.9	53.1	51.2	74.6	45.4	15.6	61.5	–	29.2
1998	68.3	73.9	46.3	274	38.6	51.6	66.3	48.8	25.8	20.0	54.3	–	14.7
1999	59.7	85.9	49.3	345	42.5	59.3	108	29.5	27.5	14.0	64.2	–	18.1
2000	94.9	81.0	47.7	160	49.6	67.2	93.4	46.5	34.8	16.4	59.0	–	37.3
2001	89.9	99.9	51.1	361	78.4	67.6	115	56.5	27.3	46.3	50.2	–	34.8
2002	45.3	115	56.8	357	62.3	67.4	255	37.5	30.7	67.5	40.3	–	40.7
2003	48.6	92.3	32.2	497	39.4	39.8	–	27.5	27.2	40.1	34.8	39.4	10.5
2004	73.8	120	55.3	276	61.4	48.1	–	36.3	38.2	56.1	46.6	55.2	40.2
2005	66.8	85.4	45.7	185.4	41.4	51.3	–	42.4	29.9	40.1	72.3	44.9	54.5
2006	84.5	103	60.5	215.7	49.3	72.6	615	55.4	47.1	73.9	52.8	61.1	42.9
(c) Cr													
1991	–	11.8	7.40	22.6	20.7	18.2	6.78	–	0.17	3.58	17.2	–	13.7
1992	–	20.3	6.50	23.8	23.2	9.83	3.28	–	2.40	18.7	25.2	–	17.4
1993	–	11.5	4.30	8.25	17.1	4.50	10.8	–	3.03	5.35	12.7	–	10.1
1994	–	18.7	8.30	11.3	17.4	13.0	5.98	–	4.93	4.35	5.33	–	7.80
1995	27.6	21.1	8.25	6.30	18.9	9.03	13.6	–	3.47	2.18	3.00	–	4.85
1996	30.1	14.8	12.2	9.20	12.1	11.5	7.05	–	3.78	5.94	1.60	–	1.30
1997	23.5	12.3	18.6	6.50	7.46	20.5	7.63	–	3.83	5.38	1.20	–	0.50

Table 2 (continued)

Year	Target city of investigation											
	AS	IC	US	PH	SL	BS	WJ	SW	DJ	DG	GJ	CC	YS
1998	14.0	11.5	13.9	8.21	7.64	11.9	6.36	6.50	2.90	5.00	0.71	–	2.69
1999	17.2	16.3	13.3	12.4	10.9	12.9	12.2	10.1	4.75	3.24	3.10	–	2.46
2000	25.3	8.56	8.43	8.38	12.1	10.8	12.5	1.78	7.41	2.20	4.23	–	6.27
2001	26.6	10.7	10.7	21.0	17.3	11.7	20.0	4.17	3.37	8.58	7.36	–	14.3
2002	10.6	13.0	11.3	21.9	25.7	9.72	20.8	6.68	2.37	16.6	13.4	–	22.8
2003	10.2	14.1	3.72	27.4	7.65	13.7	–	4.39	2.83	4.63	6.90	3.00	38.8
2004	24.1	22.5	4.37	20.1	11.5	25.9	–	2.66	3.43	6.28	1.27	4.27	13.4
2005	20.4	15.4	3.53	18.1	20.1	13.9	–	6.87	2.70	4.56	7.79	3.48	4.44
2006	23.9	10.2	2.24	19.4	11.4	13.2	112	5.33	3.72	6.17	3.60	4.41	2.17
(d) Cd													
1991	–	8.15	10.75	0.90	5.65	4.35	1.85	–		2.53	3.67	–	2.05
1992	–	19.70	9.45	1.00	9.08	2.05	2.90	–	0.63	2.08	2.07	–	1.20
1993	–	6.00	12.75	1.35	3.45	3.00	1.65	–	1.37	1.35	1.03	–	1.00
1994	–	6.60	11.25	0.85	3.50	2.85	3.00	–	1.73	2.13	1.15	–	1.25
1995	21.70	6.10	7.25	0.30	4.00	2.30	2.20	4.20	2.97	0.50	1.30	–	1.05
1996	12.70	6.25	16.75	0.50	3.10	2.23	1.98	4.50	2.00	3.18	1.40	–	1.10
1997	9.50	6.85	23.75	0.55	2.98	2.35	0.70	3.40	2.60	2.08	0.85	–	0.75
1998	5.82	4.29	15.22	1.00	1.73	2.31	2.29	2.08	1.29	3.12	0.61	–	0.50
1999	3.88	4.79	16.90	1.23	1.76	3.34	1.90	1.78	1.89	2.89	0.70	–	0.39
2000	6.24	4.71	16.74	0.41	2.21	2.98	2.94	1.73	1.89	1.47	1.47	–	1.74
2001	4.47	6.43	11.54	1.60	2.99	2.45	2.42	1.76	1.42	2.42	1.49	–	1.40
2002	4.70	7.09	6.35	1.98	3.48	2.50	2.40	1.76	0.77	2.84	1.62	–	1.21
2003	5.09	9.94	4.44	2.12	2.54	1.99	3.46	1.83	1.05	2.29	1.64	1.96	0.78
2004	5.02	8.33	5.89	1.54	1.70	1.72	3.55	2.08	1.21	2.76	1.21	2.31	1.07
2005	3.40	3.79	3.35	1.26	1.19	1.94	–	1.58	0.98	2.20	1.72	1.54	1.38
2006	5.96	5.63	2.21	1.18	1.19	2.63	2.39	1.13	1.05	2.42	1.45	1.67	1.17

their relative distribution patterns. If the pollution level is examined using Pb data (ng m^{-3}), the city of AS records the highest value of 396 which is followed by IC (187), DJ (134), and SL (133). In contrast, the lower-bound concentrations of Pb are found in the order of YS (32), GJ (45), DG (55), and PH (55). As such, the status of Pb pollution among 13 cities is fairly consistent between the expectation and the actual observation. Compared to Pb, the peak concentration data for Mn, Cr, and Cd are more variable.

The exceptional patterns are best explained by the data sets of Mn and Cr, as shown from the cities of PH and WJ. This is because those two cities represent the highest concentration levels of Mn or Cr, while also representing the lowest concentration levels for the two other metals. The patterns of Mn and Cr varied rather dynamically, as the strongest pollutions are consistently found either from PH or WJ. More specifically, the highest concentrations of Mn are observed in the order of PH, WJ, IC, and AS, while those of Cr are in the order of WJ, PH, AS, and SL. However, the spatial pattern of Cd is altered moderately from all the other metals, as it records the maximum value at US followed by AS, IC, and SL.

Table 3 Comparison of the annual mean values of Pb, Mn, Cr, and Cd (ng m^{-3}) for 13 major cities in Korea throughout the entire study period of 1991–2006

Year	Pb						Mn					
	Mean	Med.	SD	Min.	Max.	CV	Mean	Med.	SD	Min.	Max.	CV
1991	189	148	120	54.0	427	63	55.3	44.5	24.5	27.1	90.2	44
1992	154	124	106	56.9	395	69	56.0	53.2	22.9	28.1	98.0	41
1993	135	128	89	34.2	259	65	49.2	49.2	20.9	22.8	76.0	43
1994	134	113	94	31.8	276	70	53.6	58.2	21.3	29.3	80.6	40
1995	233	79.6	403	13.8	1466	173	53.6	57.5	24.5	10.2	83.6	46
1996	144	91.4	173	24.4	656	120	58.7	59.4	19.7	19.0	83.7	33
1997	121	75.9	135	15.4	508	112	47.6	50.6	18.3	15.6	74.6	38
1998	96.2	79.4	110	2.74	418	114	40.0	43.7	18.3	14.7	66.3	46
1999	79.0	72.4	60	6.88	227	75	45.4	36.0	31.1	14.0	108	68
2000	94.3	73.9	104	26.9	409	110	50.5	48.0	23.3	16.4	93.4	46
2001	79.7	65.6	59	31.0	247	74	59.6	53.4	27.9	27.3	115	47
2002	74.2	71.9	37	33.1	170	50	75.2	51.5	74.1	30.7	255	99
2003	71.1	57.6	52	17.4	217	74	32.3	37.1	10.3	10.5	40.1	32
2004	74.6	68.8	36	30.5	150	48	47.7	47.3	9.2	36.3	61.4	19
2005	57.5	46.9	25	30.0	121	44	47.1	43.7	12.6	29.9	72.3	27
2006	63.4	54.4	31	42.0	159	49	119	55.4	186	42.9	615	157
Mean	113	84	102	28	381	82	55.7	49.3	34.1	23.4	126	52
SD	50	29	91	15	325	35	19.3	7.0	43.2	9.5	139	33
Min	57	47	25	3	121	44	32.3	36.0	9.2	10.2	40.1	19
Max	233	148	403	57	1466	173	119	59.4	186	42.9	615	157
	Cr						Cd					
1991	12.2	12.8	7.6	0.2	22.6	62	4.43	3.67	3.25	0.90	10.8	73
1992	15.1	18.1	8.8	2.4	25.2	58	5.02	2.07	6.08	0.63	19.7	121
1993	8.8	9.2	4.5	3.0	17.1	51	3.30	1.51	3.67	1.00	12.8	111
1994	9.7	8.1	5.2	4.4	18.7	54	3.43	2.49	3.21	0.85	11.3	94
1995	10.7	8.3	8.5	2.2	27.6	79	4.49	2.63	5.84	0.30	21.7	130
1996	10.0	9.2	8.1	1.3	30.1	81	4.64	2.66	5.03	0.50	16.8	109
1997	9.8	7.5	7.9	0.5	23.5	81	4.70	2.48	6.58	0.55	23.8	140
1998	7.6	7.1	4.4	0.7	14.0	58	3.36	2.19	4.04	0.50	15.2	120
1999	9.9	11.6	5.2	2.5	17.2	53	3.45	1.90	4.43	0.39	16.9	128
2000	9.0	8.4	6.2	1.8	25.3	69	3.71	2.05	4.40	0.41	16.7	118
2001	13.0	11.2	7.1	3.4	26.6	55	3.37	2.42	2.97	1.40	11.5	88
2002	14.6	13.2	7.1	2.4	25.7	49	3.06	2.45	2.01	0.77	7.09	66
2003	11.4	7.3	11.1	2.8	38.8	97	3.01	2.12	2.42	0.78	9.94	80
2004	11.6	8.9	9.3	1.3	25.9	79	2.95	2.08	2.20	1.07	8.33	75
2005	10.1	7.3	7.0	2.7	20.4	69	2.03	1.65	0.96	0.98	3.79	47
2006	16.8	6.2	29.5	2.2	112	176	2.31	1.67	1.64	1.05	5.96	71
Mean	11.3	9.6	8.6	2.1	29.4	73	3.58	2.25	3.67	0.76	13.3	98
SD	2.5	3.1	5.9	1.1	22.9	31	0.86	0.52	1.65	0.30	5.74	28
Min	7.6	6.2	4.4	0.2	14.0	49	2.03	1.51	0.96	0.30	3.79	47
Max	16.8	18.1	29.5	4.4	112	176	5.02	3.67	6.58	1.40	23.8	140

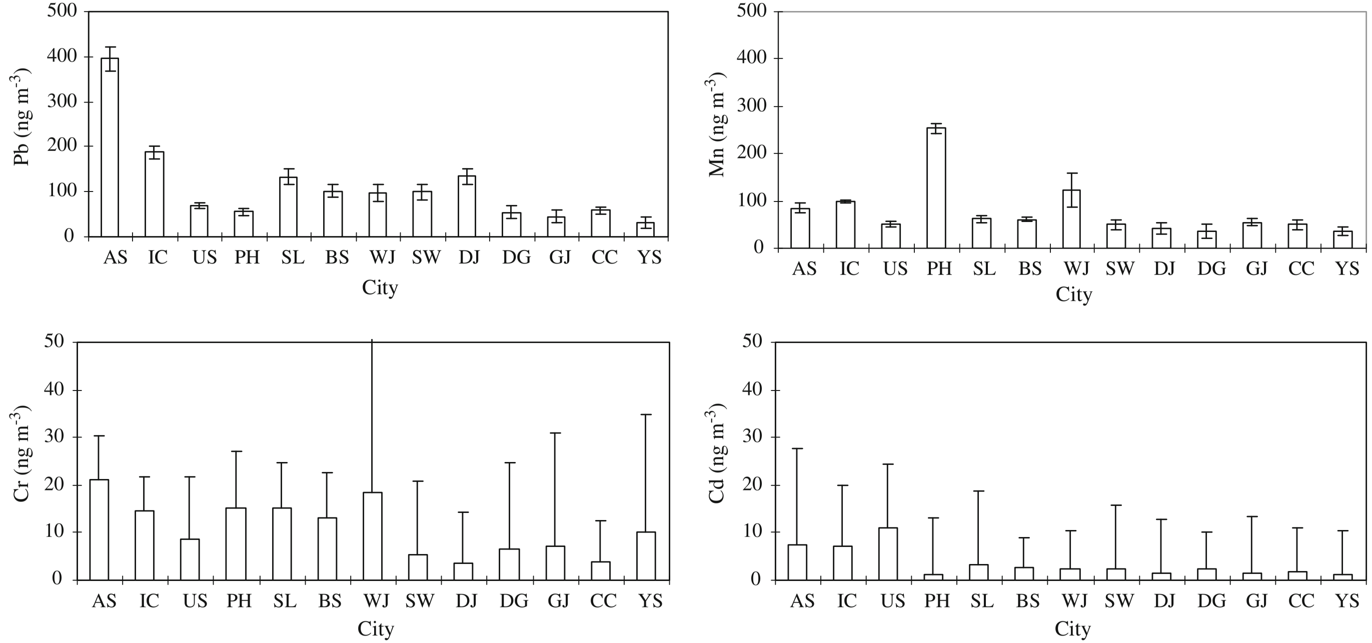

Fig. 2 Comparison of the mean concentration data of four metals across 13 individual cities across the entire study period (1991–2006)

It is well recognized that fine particles tend to be produced mainly through man-made activities and that anthropogenically derived components are preferentially enriched in the fine fraction (Cohen et al. 2005). Considering that all target metals in this study are commonly of anthropogenic origin, their distribution can maintain a moderately strong homogeneity even within a relatively broad spatial scale with a relatively long atmospheric residence time (Sun et al. 2006). Hence, it is reasonable to infer that these unique properties of the target metals help distinguish their distribution and behavior from other metals that are derived mainly from natural sources (e.g., Fe, Al, Si, etc.). As such, we may attribute the existence of strong spatial gradients in the concentration levels of the former species to one of such simple criteria as the strength of man-made activities.

As one simple means to describe the spatial distribution of different metals, the concentration levels of each metal were compared by selecting cities with the four highest and the four lowest concentration levels. According to this criterion, the patterns of metal pollution generally appear to be comparable across the cities. Out of 13 cities, AS is consistently found to be the city with the highest concentrations for all four metals. Likewise, the cities of IC and SL are also found consistently in this upper boundary group for three metals. In contrast, the cities of DG, YS, and DJ are found most frequently (i.e., three times) to have the lowest metal concentrations. A number of cities that appear most frequently in the upper boundary are characteristic of notably strong man-made activities. For instance, both the cities of AS and IC have considerably large industrial facilities within the city boundaries. Although no detailed emission inventories of these metals are available for each city, the emissions of those metals are suspected to come from various industrial activities such as fossil fuel combustion, smelting, and metallurgical processes (Kim et al. 2006). In addition, the enhanced concentration levels of most metals in SL, the capital of Korea may also reflect the effect of highly diversified man-made activities, although the city is not under the direct influence of major industrial activities such as AS or IC.

According to our research, the geographical distribution of metal species is fairly consistent among cities of similar characteristics. In the case of Pb, its concentrations in most polluted areas are still below the guidance level of KMOE (i.e., 1,500 ng m^{-3} averaged over a 3-month period). The existence of spatial gradients in Pb concentration levels is fairly distinctive across different city types. As such, various industrial sources may be an important source of Pb in highly polluted urban areas and their surrounding environments.

To learn more about the spatial distribution of metals, a closer inspection was made by comparing the Mn data among 13 cities. The highest Mn concentrations, observed from the cities of PH and WJ, were seen to be affected mainly by the anomalously high data set from a single station located within each city boundary (e.g., differences of 5–9 times between the stations in those cities). Similarly, high Cr concentrations are also observed for the same cities (like WJ or PH). Comparison of annual Cr data between these cities indicates that Cr levels in WJ recorded an exceptionally high mean value of 112 ng m^{-3} in the year 2006 (Table 2) which is approximately an order of magnitude higher than its mean value for the entire period. In fact, the concentrations of Cr in WJ have been increasing at an exponential rate in recent years. Likewise, PH is well known for its gigantic steel producing facility. It is interesting to note that PH shows the highest Mn concentration levels, while it belongs to an area with the four lowest concentrations of Pb or Cd. The predominance of man-made activities as the sources of these metal emissions has also been reported by a number of studies elsewhere. For example, Lee et al. (2007) reported the mean Cr values in TSP samples from Guangzhou (a major industrial center in South China) and Hong Kong (a highly urbanized metropolitan area) to be 18.9 and 13.9 ng m^{-3}, respectively. Similar levels of Cr were also found in Beijing, China with 19 ng m^{-3} (Okuda et al. 2004). However, other studies on the Asian continent reported much lower Cr values such as 6.09 ng m^{-3} in cities like Tokyo, Japan for 1974–1996 (Var et al. 2000) or 6.70 ng m^{-3} in Kolkata, India in 2003–2004 (Karar and Gupta 2006). As such, highly polluted patterns are observed primarily in certain cities (e.g., AS, IC, and SL). However, the pattern observed from the cities of PH and WJ are unique enough to be accounted for by their own pollution characteristics. If the concentrations for each metal were compared through a stepwise normalization procedure, the unique patterns of PH and WJ among all model cities become more evident (Fig. 3). For this comparison, the mean concentration of each metal at a given city was normalized by its grand mean values covering the whole cities.

As seen from the analysis of the Mn and Cr data sets, the distribution of Cd also exhibits an interesting spatial pattern. The occurrence of a maximum Cd concentration at US also appears to be extraordinary in that no other metals in this city exhibit any prominent pattern at all. However, if one considers that US city is well-known for many industrial activities, including a large automobile production facility, the high Cd levels observed may not necessarily be unusual. To further examine the distribution of Cd in diverse locations, the results of our Cd data were compared against a number of previous studies. For instance, a comprehensive

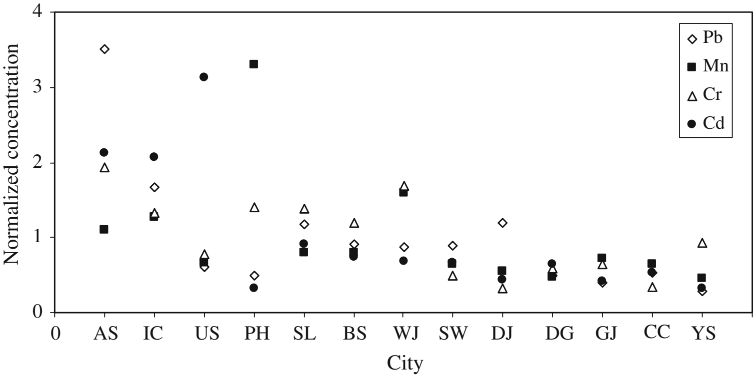

Fig. 3 Comparison of four metal concentrations among 13 cities after normalization

study conducted on European air (European Commission 2001) indicates that the concentrations of Cd, if assessed according to land use characteristics (such as rural, urban background, and industrial sites), exhibit a broad range of values (0.1–0.4, 0.2–2.5, and 2–20 ng m^{-3}, respectively). Hence, all of our Cd data for the three cities, expected to be greatly impacted by industrial sources (US, IC, and AS), are comparable to those seen as the highest class (i.e., industrial sites) of EU countries. It is noteworthy that the Cd values found in most of the urban areas in Korea (except the three industrial ones) fall in a similar range with urban background concentrations observed in Europe and are comparable to the strict guidance values set by several German states (i.e. 1.7 ng m^{-3}) (Beschluss der 1991).

3.2 Temporal Variation Patterns of Airborne Metals in the Study Area

In order to assess the temporal factors controlling the metal pollution levels, the mean metal concentrations for the 13 cities were evaluated over 16 years between 1991 and 2006 (Table 3). The general feature of the metal concentration changes is first described by comparing the data after grouping them into first and second half periods (Table 4). According to this simple comparison, the concentration levels across the two periods differ greatly for certain metals like Pb and Cd. If the statistical significance of differences between the two periods is tested by Student's t test, the observed differences were fairly significant for such matching pairs. For instance, 11 out of 12 cities showed a notable reduction in the Pb concentration across the two periods (no comparison for CC due to the lack of the data at the latter period); it is found that seven cases of them were statistically significant. The data for Mn and Cd also demonstrated a declining trend between the two periods for 9 cities, while four and three cases for these two metals were shown to be statistically significant, respectively. In contrast, the Cr concentrations declined in five cases, but none of them were statistically significant at all. In Fig. 4b, linear regression analysis was conducted to derive a simple trend of metal concentration changes for each metal across the study years. As is shown in Fig. 4b, both Pb and Cd exhibit constantly declining patterns in their concentration levels with strong statistical significance. However, in the case of Mn and Cr, the patterns tend to exhibit slight increases but lack statistical significance. As such, the analysis of inter-annual patterns based on regression analysis yields results that are highly comparable to those between the two grouped periods of I and II.

In order to properly evaluate the temporal trends between metals, their annual data sets were examined with reference to a number of previous studies. As seen in Fig. 4, a long-term distribution of Pb derived by combining all data sets exhibited a notable reduction of its concentration through the years.

Nonetheless, the patterns of Pb, if compared between individual cities, tend to be distinguished greatly, especially between cities of different Pb pollution levels. In the case of cities with higher Pb levels, a pattern of general decline can be

Table 4 Comparison of metal concentrations (ng m^{-3}) between period I and II and the statistical significance in their concentration differences

Data	Name of city selected for comparative analysis													
Category	AS	IC	US	PH	SL	BS	WJ	SW	DJ	DG	GJ	CC	YS	All
(a) Pb concentration														
All	396	187	69	55	133	102	98	100	134	55	45	60	32	113
SD	376	104	16	20	87	53	70	56	94	31	26	9	15	96
P(I)	876	279	78	52	210	138	142	186	217	59	62		38	195
SD	516	95	19	24	79	61	69	16	85	46	30		15	228
P(II)	235	116	62	58	73	74	47	71	70	51	32	60	27	75
SD	109	20	10	16	21	24	14	24	18	16	14	9	15	53
P	3.E−03	2.E−04	5.E−02	6.E−01	2.E−04	1.E−02	7.E−03	2.E−05	2.E−04	6.E−01	2.E−02		2.E−01	
P(I)/P(II)	3.73	2.41	1.25	0.90	2.86	1.85	3.05	2.63	3.13	1.15	1.92		1.40	2.2
(b) Mn concentration														
All	84.63	98.21	51.54	253.46	61.53	61.08	121.84	49.88	41.60	35.92	55.31	50.15	35.04	77
SD	30.27	14.50	11.79	108.59	18.70	11.98	159.39	17.20	18.13	20.23	14.58	9.81	13.00	59
P(I)	127.90	102.21	54.26	197.86	74.50	64.63	47.27	72.73	53.84	28.64	58.64		38.13	77
SD	9.12	13.14	15.56	90.85	16.85	12.90	9.92	12.01	21.14	16.64	18.16		10.50	47
P(II)	70.21	95.10	49.44	296.71	51.44	58.31	208.84	42.26	32.07	41.59	52.72	50.15	32.64	83
SD	17.42	15.48	8.21	105.41	13.44	11.17	209.72	10.46	6.93	21.85	11.59	9.81	14.81	79
P	3.E−04	3.E−01	4.E−01	7.E−02	9.E−03	3.E−01	6.E−02	2.E−03	1.E−02	2.E−01	4.E−01		4.E−01	
P(I)/P(II)	1.82	1.07	1.10	0.67	1.45	1.11	0.23	1.72	1.68	0.69	1.11		1.17	1.2
(c) Cr concentration														
All	21.12	14.53	8.56	15.29	15.07	13.14	18.41	5.39	3.44	6.42	7.16	3.79	10.18	11.0
SD	6.67	4.18	4.52	7.13	5.74	4.97	28.73	2.51	1.51	4.68	6.83	0.67	10.02	5.7
P(I)	27.07	15.75	9.36	12.56	16.70	12.36	7.87		3.09	6.50	9.47		7.94	11.7
SD	3.33	4.17	4.70	7.46	5.32	5.48	3.36		1.50	5.54	9.20		6.27	6.5
P(II)	19.13	13.58	7.94	17.42	13.81	13.74	30.72	5.39	3.72	6.36	5.37	3.79	11.92	11.8
SD	6.38	4.17	4.55	6.48	6.03	4.78	40.38	2.51	1.55	4.25	3.95	0.67	12.29	7.7

Table 4 (continued)

Data	Name of city selected for comparative analysis												
Category	AS	IC	US	PH	SL	BS	WJ	SW	DJ	DG	GJ	CC	YS	All
P	7.E−02	3.E−01	6.E−01	2.E−01	3.E−01	6.E−01	2.E−01		4.E−01	1.E+00	2.E−01		5.E−01	
P(I)/P(II)	1.41	1.16	1.18	0.72	1.21	0.90	0.26		0.83	1.02	1.76		0.67	1.0
(d) Cd concentration														
All	7.37	7.17	10.91	1.11	3.16	2.56	2.37	2.32	1.52	2.26	1.46	1.87	1.13	3.5
SD	5.21	3.70	5.93	0.53	1.96	0.64	0.74	1.09	0.66	0.70	0.70	0.34	0.42	3.0
P(I)	14.63	8.52	13.14	0.78	4.54	2.73	2.04	4.03	1.88	1.98	1.64		1.20	4.8
SD	6.33	4.98	5.53	0.35	2.19	0.79	0.78	0.57	0.84	0.85	0.97		0.41	4.7
P(II)	4.95	6.11	9.18	1.37	2.09	2.43	2.67	1.75	1.28	2.49	1.32	1.87	1.07	3.0
SD	0.96	2.04	5.94	0.52	0.79	0.51	0.59	0.28	0.39	0.49	0.41	0.34	0.44	2.4
P	6.E−04	2.E−01	2.E−01	2.E−02	7.E−03	4.E−01	1.E−01	2.E−06	8.E−02	2.E−01	4.E−01		6.E−01	
P(I)/P(II)	2.96	1.39	1.43	0.57	2.17	1.12	0.76	2.31	1.47	0.79	1.24		1.12	1.4

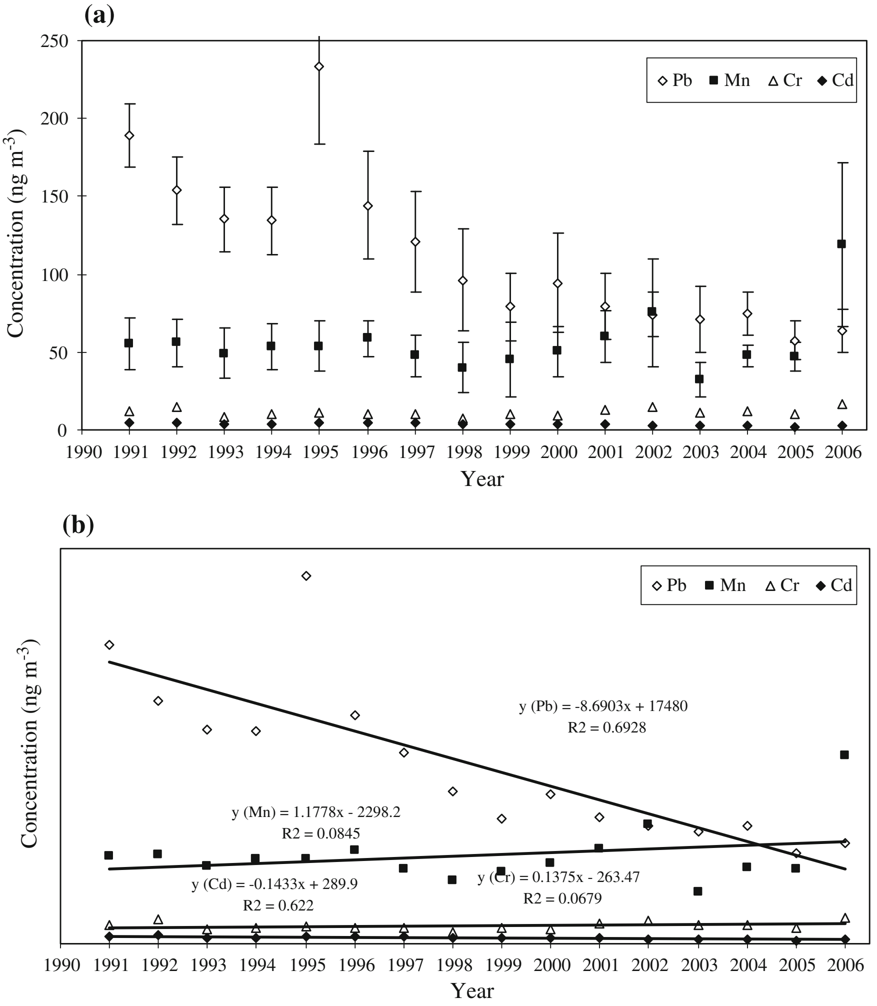

Fig. 4 Long-term changes in concentrations of Pb, Mn, Cr, and Cd using their annual mean values for all 13 cities in Korea; **a** normal plot with error bar, **b** linear regression analysis

observed. It is most striking to find that the Pb concentrations in the city of AS reached as high as 1,500 ng m^{-3} in the mid-1990s but dropped quite dramatically to ~200 ng m^{-3} in recent years. The observed pattern is however not uncommon in many countries where Pb pollution controls were implemented. In the case of CA, USA, Pb concentrations have decreased from ~3,000 to 10 ng m^{-3} over the past decades (Miller et al. 1972; Chow et al. 1996). On the other hand, in the cities with fairly clean environments (YS, GJ, and DG), Pb concentrations decreased in a rather slow phase in the early years but began to fluctuate in more recent years. Such complicated temporal patterns are quite apparent from most cities with low mean Pb values including the city of WJ and others (e.g. with the mean values of around 50 ng m^{-3}).

It is acknowledged that the nationwide reduction in Pb levels in most areas of Korea during the late 1980s and the early 1990s was mainly due to the changes in the consumption pattern of leaded gasoline. However, as the effect of its phase out gradually decreased through the years, a mild increase in Pb concentration levels is often observed for many cities that used to experience moderate Pb pollution in past years. This observation thus suggests that anthropogenic sources of metals in urban areas are diverse and highly variable (e.g., unregulated Pb fabrication, burning of refuse, and the use of paints; Nriagu et al. 1996), while the predominance of certain sources (such as leaded gasoline) has steadily decreased through time. Wang et al. (2003) reported that the Pb isotope ratio (such as $^{206}Pb/^{207}Pb$) in Tianjin, China increased steadily, while its concentration decreased gradually since its phase out. Similar patterns of Pb behavior have also been recognized in other cities in China (Zheng et al. 2004).

To examine the long-term trend of Mn data, annual concentrations for this metal were compared between cities (Table 3). According to this analysis, the cities of PH and WJ began to exhibit extremely high Mn concentrations in recent years. In the case of PH, the highest annual concentration of Mn (497 ng m^{-3}) was recorded in 2003. The results from this city generally exhibit a trend that is consistent enough for a single direction. Although we suspect that abnormally high Mn levels at PH are indicative of the influence of a large steel industry in PH city, those observed in WJ are not fully explainable at this point. However, local officers in WJ city (at WJ2 station) claimed that such an unusual pattern is due to unidentified local point sources in the surrounding area which began operation in very recent years. This evaluation thus confirms that the Mn pollution of both cities (WJ and PH) share similar trends, at least in terms of the predominance of a single station within the city boundary.

To evaluate the inter-annual trends of the Cr distribution for all cities, its data sets collected from all 13 cities were compared at annual intervals (Table 3). The annual Cr values from large urban areas were generally below 40 ng m^{-3} with the exception of WJ (112 ng m^{-3}) in 2006. Hence, contrary to moderate fluctuations observed in the annual Cr distributions for most cities, the strongest annual variations were recorded at WJ. Although not so strong as the result for WJ, large variations are also recognized from other cities with strong industrial activities (e.g., PH and AS) and/or from the big urban areas (e.g., SL and BS). In the case of AS, the annual trends showed a significant decrease since 1996. The trends then shifted to a moderate gain from 1998 to 2000. Following that time period, a decreasing trend resumed to reach a minimum in 2003. Similar to Mn, an unidentified source has clearly contributed to the high Cr concentrations observed at one of the stations in WJ (i.e. WJ2). As seen from PH, the annual Cr levels were constantly maintained near 10 ng m^{-3} during most of the 1990s (e.g., 1993 through 2000). However, its levels increased dramatically after that. In contrast, in the cases of the largest cities in Korea (e.g., SL and BS), the annual trends of Cr seem to be either stable or decreasing in recent years. In fact, such mixed temporal patterns of Cr were seen from most cities with low Cr levels (e.g., around 10 ng m^{-3}).

The overall results of our comparison generally indicate that Cr levels declined during the earlier part of the study period, especially until the late 1990s. The decreases in the annual mean values of Cr and other metals during the 1990s are clearly a consequence of the implementation of strict air quality regulations. In a report of the fuel consumption patterns and the resulting pollutant emission (Kang 2004), the emissions of PM in Korea have decreased by 44.6% for the period between 1991 and 2000 (from 431,300 tons in 1990 to 239,100 tons in 2000). Relatively large variations in the annual trends of Cr values were also observed in a previous study of Pirrone et al. (1995); they demonstrated that the consumption of fossil fuel significantly affected Cr pollution levels in Detroit from 1982 to 1992. Hence, it may be possible to infer that the nature of man-made source processes of Cr is not simple enough to describe.

There have been many attempts to provide an overview of anthropogenic emissions of Cd to the various environmental reservoirs and changes in their emission trend. The long-term trends of Cd derived from many cities in Korea show that diverse temporal patterns can exist, while its concentrations have generally decreased through the years. As recorded in the snow and ice samples of the polar regions, global Cd levels peaked in the 1960s and then decreased constantly until the present (i.e., over the past 40 years) (e.g., Boutron et al. 1994; Candelone et al. 1995). Similar to our observations, long-term variation patterns for Cd made in many EMEP stations over Europe (such as the Czech republic, Norway, and the UK) also indicate that their Cd patterns exhibit diverse temporal patterns; that is, Cd concentrations monitored at many EMEP stations have tended to experience either a rapid or slow decline for a certain period, while at the same time they did not encounter any specific increase or decrease in other periods (European Commission 2001).

3.3 Factors Affecting Metal Concentration Levels in Korea

As the concentrations of four metals in the present study were measured on the same temporal basis for the 13 major cities, one can assess the possible relationships between the different metals over time and between different cities. To examine the factors affecting the metal distributions across different study areas, statistical correlations were determined using the annual data sets for all four metals. Correlations were estimated to assess the relationships for metal concentrations between cities, as well as between different metals in each city. To meaningfully interpret these results, the strengths of the correlation between different data pairs were compared by dividing them into three categories of correlation strengths based on the magnitude of probability of no statistical significance (P): (1) class I (the weakest correlation strength range): $P \geq 10^{-2}$;

(2) class II: $10^{-5} \leq \mathrm{P} < 10^{-2}$; and (3) class III (the strongest correlation range): $\mathrm{P} < 10^{-5}$.

The results of the correlation analysis are summarized in Table 5. According to this analysis, the stronger correlations (e.g., class II and III) tend to occur more abundantly in Pb than other metals (Mn, Cr, and Cd). In the case of Pb, 4 (5%) out of 77 matching cases belong to the strongest correlation group (class III). At the same time, there are no matching pairs with class III for the other metals such as Mn, Cr, and Cd. If the abundance of class type II is compared among the metals, Pb with 25 cases (32%) is still distinguished from others such as 9 (12%) for Mn, 3 (4%) for Cr, and 6 (8%) for Cd. It was noted that the most significantly correlated pairs of Pb occurred between cities with high Pb concentrations such as in the big cities (e.g., SL and BS) and in the industrial areas (e.g., AS and IC). As seen in Fig. 5a, the strongest correlation was observed between SL and IC ($r = 0.988$, $P = 2.31\mathrm{E}{-13}$, and $N = 16$), followed by the AS and DJ pair ($r = 0.959$, $P = 3.74\mathrm{E}{-07}$, and $N = 12$). Moreover, the relationship between the two biggest cities of SL and BS, although they are fairly distant geographically, showed a significant correlation ($r = 0.873$, $P = 7.14\mathrm{E}{-06}$, and $N = 16$). These results clearly indicate that Pb may belong to one of the metal groups with the strongest homogeneity on a spatial scale.

Fewer conclusions can be drawn based on the results of the correlation analysis of different metals in any given city (Table 5b).

For example, the lowest class I was seen to cover 5 out of all 6 matching cases in IC, US, WJ, SW, and DG. However, the matching pair with class I type occurred only once at SL, while all pairs at PH were dominated by class II. The frequency of the strongest correlated cases (class III) are only very scarcely

Table 5 Summary of the correlation analyses between different cities for each metal and between different metals for each city

Class	Metals			
	Pb	Mn	Cr	Cd
(a) Comparison of the correlation analysis between cities/provinces for each metal in terms of absolute frequency of matching pairs				
I	48	68	74	71
II	25	9	3	6
III	4	0	0	0

Class	Cities/provinces												
	AS	IC	US	PH	SL	BS	WJ	SW	DJ	DG	GJ	CC	YS
(b) Results of the correlation analysis between metals derived for each city													
I	3	5	5	0	1	4	5	5	4	5	3	4	4
II	2	1	1	6	5	2	0	0	2	1	3	2	2
III	1	0	0	0	0	0	1	1	0	0	0	0	0

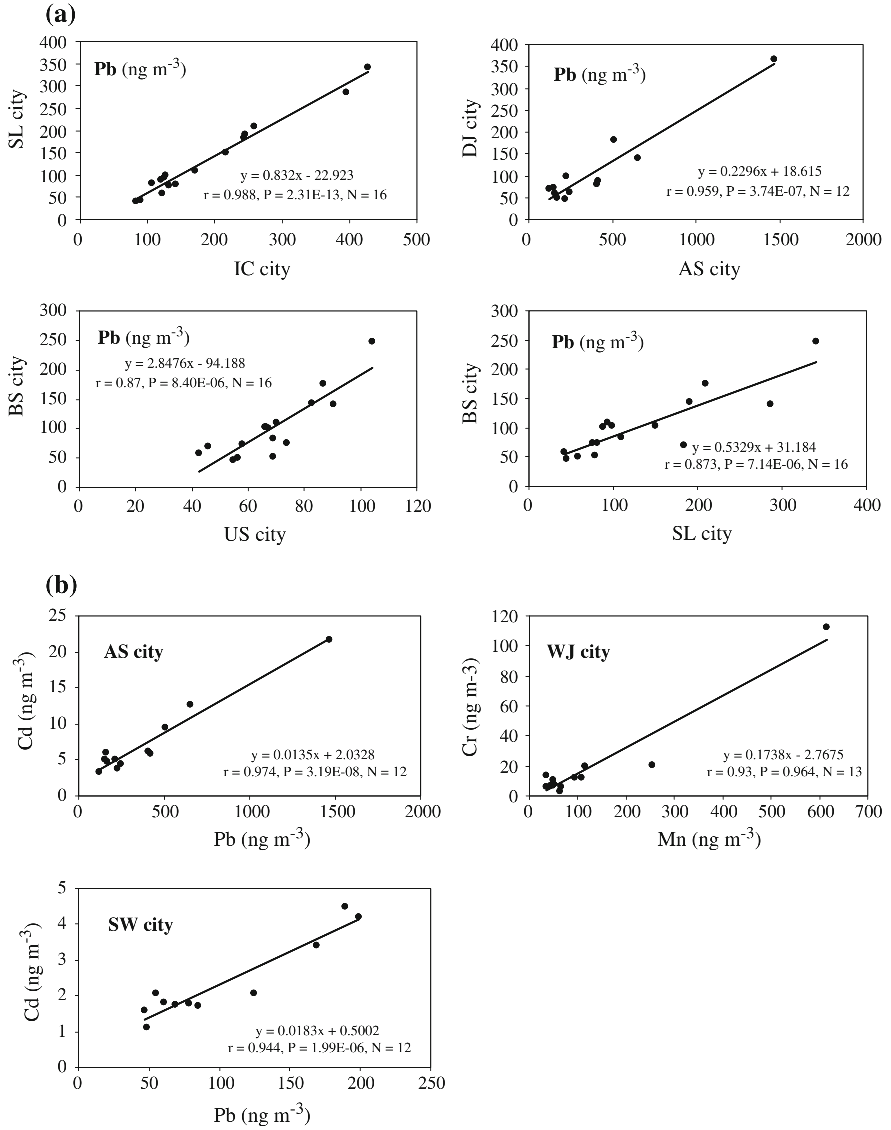

Fig. 5 Some examples of strongly correlated pairs by the two grouping criteria; **a** between cities for each metal, **b** between metals for each city

observed between Pb and Cd in the two cities of AS ($r = 0.974$, $P = 3.19\text{E}{-}08$, $N = 10$) and SW ($r = 0.944$, $P = 1.99\text{E}{-}06$, $N = 12$). Likewise, a strong correlation between Mn and Cr is observed in WJ ($r = 0.930$, $P = 0.964$, $N = 13$) (Fig. 5b). As such, the cases of the strong correlation are observed most commonly between cities of similar pollution status.

4 Conclusions

In this study, the concentration data of Pb, Mn, Cr, and Cd collected in 13 cities over a 16-year period (1991–2006) were analyzed to characterize the environmental behavior of airborne metals under diverse field settings. As a simple means to examine the long-term variability of metal distributions, all data were analyzed after being grouped into the first half (period I: 1991–1998) and the second half term (period II: 1999–2004). These data were also analyzed across the entire study period to account for their long-term trend. Finally, the spatial variability of different metals was also assessed by comparison of their mean values among different cities.

Examination of spatial distribution patterns generally indicates that the Pb and Cd concentration levels have been gradually declining among cities of all types. However, this indicates that a reduction in their concentrations in relatively clean city environments has been insignificant. Rather, a moderate increase has been commonly observed in recent years. The uniqueness of the Mn and Cr distribution patterns observed for such cities as WJ and PH, are clearly a reflection of the industrial origin of these metals. Likewise, the annual mean Cd concentrations peaked in US (20 ng m^{-3}), while its mean values in the other industrialized cities (e.g., AS and IC) were much lower than those of US. On the other hand, our Cd results for other urban areas (1–2 ng m^{-3}) are comparable to those seen in the urban background areas of Europe. Comparison of the spatial distribution of Pb, Mn, Cr, and Cd data between different cities in Korea suggests that there are noticeable differences in their concentration levels in relation to the level of industrialization and to the specific source activities in the area. It is well known that the materials containing certain metals are recyclable to a large extent and that the costs involved in such processes should be in the economically acceptable range.

The temporal patterns of our metal data were assessed both by two largely divided periods and at inter-annual intervals. The results of both analyses consistently indicate that such metals as Pb and Cd have been decreasing consistently throughout the study years. Hence, future studies need to be directed toward the development of effective control methods to further tighten the individual anthropogenic sources so that the present level of metal pollution can be reduced steadily. Evaluation of metal data in terms of two major criteria (their spatial and temporal basis) indicates that all cities are distinguished from each other by the pollution levels of each metal and their unique behavior. However, such patterns can be further complicated depending on the levels of interaction between metal species and the surrounding environmental conditions.

Acknowledgments This work was supported by the Korea Research Foundation (KRF-2006-341-C00026).

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Long-Distance Transport of Urban and Industrial Metals and Their Incorporation into the Environment: Sources, Transport Pathways and Historical Trends

Samuel K. Marx and Hamish A. McGowan

1 Introduction

Atmospheric pollutants are seldom confined to the urban and industrial centers from where they are predominately emitted but are often transported thousands of kilometers impacting regions far from their source. As a result, atmospheric pollutants have been documented to affect all areas including Antarctica, where there are no significant local sources of anthropogenic air pollutants. There are a range of pollution species which have been found to be transported over long distances such as across the Pacific Ocean. These include toxic metals, semi-volatile organic compounds, nitrate compounds, carbon monoxide and polycyclic aromatic hydrocarbons (e.g. Arimoto et al. 1996; Hageman et al. 2006; Jaffe et al. 1999; Parrish et al. 1992; Prospero 1999). In this paper we examine the long-range atmospheric transportation of toxic metals, commonly referred to as heavy metals, and their impacts.

Toxic metals that are known to be transported long distances in the atmosphere include, but are not limited to lead (Pb), mercury (Hg), cadmium, (Cd), zinc (Zn), copper (Cu), nickel (Ni), tin (Sn), arsenic (As) and molybdenum (Mo). These are amongst the most pervasive pollutants in the atmosphere and Earth's surface environments; they are typically released into the atmosphere from industrial processes; are widely distributed and; have been accumulating since humans first started smelting metals in significant quantities during the Bronze Age c. 5000 years ago. Their occurrence in the atmosphere presents a significant health hazard for humans as well the wider environment, often even at low concentrations. In addition, many toxic metals may bioaccumulate, impacting upon human populations in some instances. Here we examine the sources of metal pollutants to

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F. Zereini, C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_6,

the atmosphere, review the means by which toxic metals are identified in the environment, identify the main pollution plume transport pathways and discuss the trends in atmospheric metal pollutants through time and some of the impacts of these metals.

2 Sources of Metals to the Atmosphere

Globally the main sources of toxic metals to the atmosphere are from mining and metal production industries and fossil fuel combustion, in particular coal and oil combustion for energy production. Other processes that may emit toxic metals to the atmosphere include refuse incineration, the manufacture and application of fertilizers, cement production and wood combustion (Nriagu and Pacyna 1988). Pacyna and Pacyna (2001) presented estimates of global emissions to air from such activities using data for 1995 (Table 1). These show the combustion of fossil fuels for energy is the largest source of metal pollution, with metal production also significant. Vehicular traffic was responsible for significant emissions of Pb, however, it should be noted that since the publication of these data, there has been a decline in this source following the phasing out of Pb use in gasoline in most countries.

A comparison of the 1995 inventory with that of an earlier estimate based on data collected in 1983 (Nriagu and Pacyna 1988) would appear to indicate that metal emissions are decreasing (Table 1). This has been attributed to both regulation driven by concerns of the likely health impacts of metals, as well as the implementation of cleaner production methods (Pacyna and Pacyna 2001). This trend should be viewed with some caution, however, because while this may be the case in regions such as Europe and North America, emissions estimates from other regions, such as Asia, are less reliable. In addition, global production of metals along with the combustion of fossil fuels has largely continued to increase through the 1990s and 2000s. For example, global Cu production increased between 1995 and 2007 (Fig. 1) and implies a concomitant increase in Cu pollution during this period. While the implementation of cleaner production practices has undoubtedly had an influence on global emissions, particularly in first world nations (Pacyna and Pacyna 2001), evidence suggests that atmospheric metal pollution is increasing is some regions.

Anthropogenic metals are released to the atmosphere in gas or particle phases, typically as a waste product of high temperature industrial processes, although evaporation from raw or processed materials and entrainment by wind are also possible (Fig. 2). The behavior of metals in the atmosphere is not well understood and depends on their phase and oxidation state. They are often scavenged by existing aerosols such as mineral dust, with which they are transported (Marx et al. 2008; Osterberg et al. 2008). There are a number of possible mechanisms by which the uptake of metals by particles may occur, including absorption/sorption and speciation processes, nucleation of gas phase metal species produced during combustion, coagulation and precipitation controlled processes and binding by

Table 1 The main sources of metal emissions to the atmosphere in 1995 (tonnes/year) (data from Pacyna and Pacyna 2001)

Metal pollutant	Metal emission source							
	Fossil fuel combustion	Vehicle emissions	Non-ferrous metal production	Iron and steel production	Cement production	Waste disposal	Total emissions (1995)	Emissions (1983)[a]
As	809		3,457	353	268	124	5,011	18,820
Cd	691		2,171	64	17	40	2,983	7,570
Cr	10,145			2,825	1,355	425	14,730	30,480
Cu	7,081		18,071	142		621	25,915	35,370
Hg	1,475		164	29	133	109	2,235	3,560
In			45				45	25
Mn	9,417		59	1,060		511	11,047	38,270
Mo	2,642						2,642	3,270
Ni	86,110		8,878	36	134	129	95,287	55,650
Pb	11,690	88,739	14,815	2,926	268	821	119,259	332,350
Sb	730		552	7		272	1,561	3,510
Se	4,101		466	7	3	24	4,601	3,510
Sn	3,517		319		115		3,951	3,790
Tl	1,824						1,824	5,140
V	240,084		77	71		23	240,255	86,000
Zn	9,417		40,872	2,118	2,670	1,933	57,010	131,880
Total	389,463	88,739	89,946	822	4,113	1,319	588,356	740,375

[a] Data from Nriagu and Pacyna (1988)

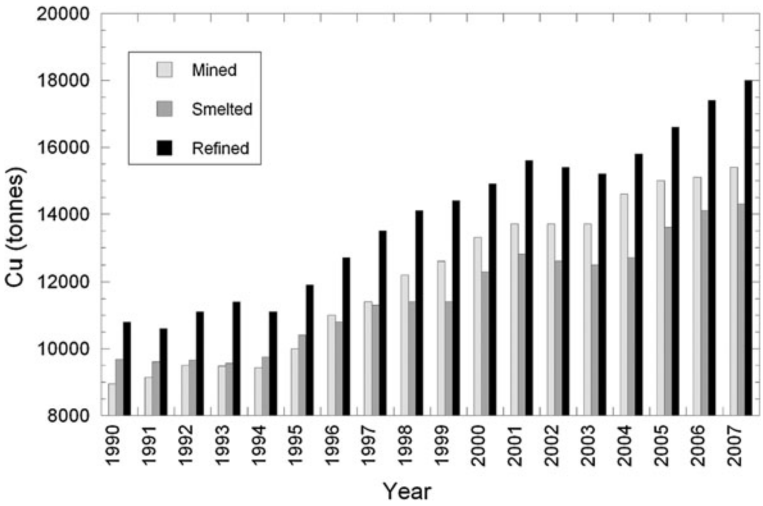

Fig. 1 Global copper (Cu) mining and production (tonnes) is seen to be increasing throughout the 1990s and 2000s implying a concomitant increase in pollution (*Source*: USGS available at http://minerals.usgs.gov/minerals/pubs/commodity/copper)

Fig. 2 A pollution plume being emitted from the Inco Super Stack in Sudbury, ON, Canada, where one of the world's largest Ni mines is located (photo S.K. Marx)

organic substances (Erel et al. 2006; Förstner 1990; Fujiwara et al. 2006; Kabata-Pendias 2001; Spokes and Jickells 2002). These processes are also dependent upon the characteristics of the aerosols themselves. For example, the transport and deposition of metal pollutants which are highly particle reactive, such as Pb, are strongly associated with transportation of aerosols such as mineral dust, while other metals such as Cu may be transported either in association with dust or independently (Marx et al. 2008).

Atmospheric pollution may also originate from a number of secondary processes such as the release of Pb from gasoline combustion in motor vehicles due to Pb being used extensively as an additive in gasoline from the 1920s (Nriagu 1990). The application of fertilisers and pesticides to agricultural lands is also known to be a source of metals to the atmosphere (Marx et al. 2010; Nriagu and Pacyna 1988). It is likely that pollutants of this origin are either released to the atmosphere as aerosols during fertilizer/pesticide application, or they are entrained in association with soil and transported through the atmosphere along with dust.

Recycled atmospheric metal pollution has also been documented. This occurs as soils contaminated by metals are entrained by the wind. For example in Jerusalem, Israel, Pb isotopes (which can be used to trace the sources of pollution Pb) in dust samples were found to exhibit both a historic Pb isotope pollution signature, indicative of the Pb (pre-1992) previously used in gasoline in the region, as well as a current (post-1992) Pb isotope signature reflecting the Pb used in contemporary gasoline in the region. The historic Pb isotope signature was believed to result from the entrainment of soil-dust previously contaminated with gasoline Pb by the wind, while the contemporary pollution gasoline signature resulted from the mixing of the contaminated dust with contemporary pollution aerosol in the atmosphere (Erel et al. 2006).

3 Identification and Accumulation of Atmospheric Metals in the Environment

The presence of metal pollutants in the atmosphere is typically identified during active sampling campaigns using atmospheric samplers such as high volume air samplers, or passive deposition traps. In order to characterise metals as pollutants, as distinguished from natural metals released into the atmosphere, such as natural dust, the enrichment factor (*Ef*) of pollutant metals over natural aerosols is usually calculated. This can be achieved by calculating the ratio of the metal pollutant relative to that of a non-pollutant element, such as Al, in comparison to the expected ratio if the sample was pollution free, i.e., $Ef = (metal/Al_{sample})/(metal/Al_{UCC})$, where Ef is the enrichment factor, $metal/Al_{sample}$ is the ratio of the pollutant metal (e.g. Pb) to Al in the collected sample and $metal/Al_{UCC}$ is the ratio of the metal to Al in a pollution free sample, normally an estimate of the average composition of upper continental crust (UCC) (e.g. Kamber et al. 2005; McLennan 2001). While this is the most widely used approach, it suffers from the difficulty that the Ef calculation assumes the $metal/Al_{UCC}$ ratio accurately describes the pollution free dust chemistry in the region from where the sample was collected. An alternative approach is to calculate the pollutant metal enrichment factor relative to the source sediments from which the dust aerosol was sourced, i.e., $Ef = (metal_{sample}/metal_{source})$ (see Marx et al. 2008). This approach, however, requires accurate knowledge of the dust source areas and/or the ability to provenance dust in the collected sample to its source region. It also assumes that the dust source sediments are pollution free, a condition which is not always true (e.g. Erel et al. 2006).

Identifying long-range metal pollution can be difficult as its deposition typically results in low metal concentrations deposited over a very wide spatial area. Separating long-range pollution from local pollution can be more complex as local pollution sources may mix with, or overwhelm long-range pollution. For this reason, sampling often occurs in remote locations where the influence of local pollution is minimal and can be largely discounted. For example, long-range pollution transport out of Europe is most easily recognised in remote settings such as the Scandinavian Arctic (Brännvall et al. 1999; Reimann et al. 1997), while similarly Australian metal pollution in New Zealand has only been identified in remote locations along the Country's west coast (Arimoto et al. 1990; Halstead et al. 2000; Marx et al. 2008).

Identifying pollutant metals of atmospheric origin in the environment following deposition is more difficult as post-depositional processes can result in further transport, potentially either concentrating or diluting their abundance. This is of critical importance as the impact of metals depends on the degree to which they are incorporated into the environment (Kabata-Pendias 2001). Again studies are typically, although not exclusively, undertaken in remote settings. Some of the most complete records have been developed in alpine environments from geologic archives which are dominated by atmospheric input, such as within lakes, ice and peat bogs (e.g. Brännvall et al. 1999; Hong et al. 1996; Shotyk 2002). Metal enrichment in these environments is typically determined from the ratio of a suspected pollutant metal to that of a refectory element which is not perturbed in the earth's surface or atmosphere, such Sc or Al (Shotyk et al. 2002).

Another approach to identifying pollution metals is to use isotope ratios. These can be used to both detect pollutant metals as distinctive from natural metal aerosol and can often also be used to accurately pinpoint the sources of the pollutants. The radioactive decay products ^{206}Pb, ^{207}Pb and ^{208}Pb and the stable ^{204}Pb isotopes have been used most widely in this capacity. This is possible because the ratios of the isotopes (e.g., ^{207}Pb/^{206}Pb) reflect the age and geology of their source rocks. Thus the isotope composition of pollutant Pb reflects the ore body from which the Pb was extracted. This was first demonstrated by Chow and Patterson (1961) who observed that Pb concentrations entering the modern ocean were higher than they had been in the geologic past and had isotope signatures from known ore bodies which supplied industrial Pb. Consequently, Pb isotopes have been used to track the origin of pollutants in a number of studies. At Enewetak atoll in the mid north Pacific, Pb isotopes were used to show that atmospheric Pb pollution reaching the atoll was sourced from Asia during the wet season and North America during the dry season (Settle and Patterson 1982). This was achieved by showing that the ^{206}Pb/^{207}Pb ratios of aerosols collected during the wet season were less radiogenic and matched the Australian Pb ores used in the gasoline sold in Japan, whereas the ^{206}Pb/^{207}Pb ratios measured in aerosols collected during the dry season were more radiogenic and indicative of the ores used in North American gasoline.

In an example from Australia, the Pb isotope ratios ($^{207}Pb/^{206}Pb$, $^{208}Pb/^{206}Pb$) of atmospheric pollution deposited in alpine peat bogs were found to plot along a mixing curve between the less radiogenic industrial Pb from the Broken Hill Mines, which were at one time one of the world's major Pb sources (and are located approximately 800 km upwind of the studied peat bogs), and the more radiogenic Pb composition of flyash from coal combustion in Australia (Fig. 3). Lead sourced from Broken Hill was also the main source of Pb used in Australian leaded-gasoline (available in Australia from the 1930s and phased out through the early 2000s), consequently, the isotope composition of leaded-gasoline plots close to that of Broken Hill ore. While the Pb isotope composition of the pollutants is closer to that of Broken Hill ore, implying Broken Hill derived Pb is the main source of this pollution, the pollutants plot along a mixing curve with the Pb isotope composition of coal derived fly ash, indicating coal also contributes significantly to this pollution (Marx et al. 2010).

In addition to sampling using deposition traps, environmental archives have been used extensively to study long-range pollution. These have the advantage that they can be used to construct pollution histories, when radiometrically dated, for regions from where no active monitoring has been undertaken. They also allow an assessment of the degree to which metal pollution is being incorporated into the environment. Records of long-range pollution have been constructed from geologic archives, such as from within soils, ice, lake sediments and peat bogs, where the chronological history of pollution deposition has been preserved. These archives should ideally contain a true atmospheric deposition record, meaning the pollutants deposited in them should not have been subject to concentration or dilution processes. Geologic archives have been used to study historical metal

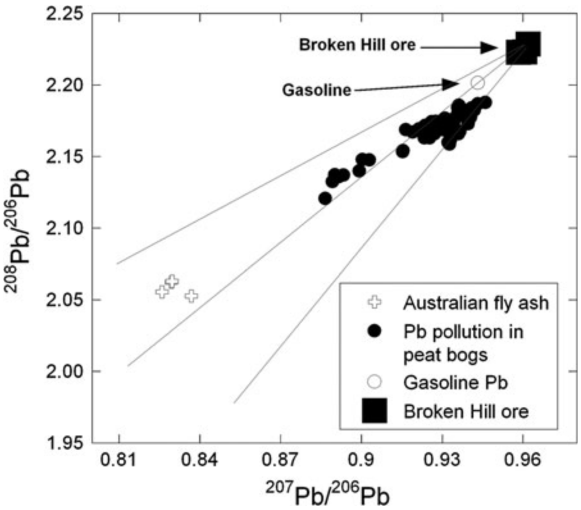

Fig. 3 Pb isotope ratios ($^{207}Pb/^{206}Pb$ versus $^{208}Pb/^{206}Pb$) for polluted sediments deposited in peat bogs in the Australian Alps plotted alongside potential pollution sources, including Pb from the Broken Hill mines (Pb isotope data from Reynolds 1971 and Townsend and Snape 2002), gasoline sold in southern Australia (data from Gulson et al. 1995a, b) and flyash from coal combustion (data from Chiaradia et al. 1997 and Diaz-Somoano et al. 2009)

pollution dating back to the Bronze Age and Roman period, well before the impacts of metal pollution were realised. The results of these studies are discussed later in the paper.

As well as geologic settings, biological repositories have been used to examine atmospheric pollution. Mosses have often been used for this purpose. This is possible because ectohydric mosses receive water and nutrients, along with metal pollutants, directly from the atmosphere (via precipitation), with little uptake of nutrients occurring from the substrate on which they live (Rühling and Tyler 2004). Thus the sampling of moss through time to examine metal deposition patterns has been used in a number of studies (e.g. Harmens et al. 2007). Similarly, ectohydric lichens, with comparable behaviour to mosses, have been used to monitor metal pollutants (Bergamaschi et al. 2002). For both mosses and lichens, rates of metal concentration, uptake and retention have to be considered, while results show most promise when calibrated with rainfall (Szczepaniak and Biziuk 2003). Mosses and lichens have both been used to study the temporal trends in metal deposition and provide a cheaper alternative to direct monitoring using deposition traps. Trees have also been used to investigate metals in the environment. In one such study the origin of pollution being incorporated into trees was determined by analysing the Pb isotope composition of tree rings. In that study, the majority of Pb being incorporated into the trees (pines and spruce trees) was found to be derived from atmospheric pollution, being taken up by the tree either directly from the atmosphere, or from the soil (Bindlera et al. 2004).

4 Transport Pathways of Metal Pollutants

Atmospheric metal pollutants have been identified in almost every setting in which studies have been undertaken. This has included even very remote locations such as Enetewak atoll in the north central Pacific (Settle and Patterson 1982), Samoa in the south Pacific (Arimoto et al. 1987), the Artic (McConnell and Edwards 2008) and Antarctica (Wolff et al. 1999). The fact that metal pollution is found within the atmosphere so far from population and industrial centres shows the degree to which heavy metals are perturbed, as well as their ability to be transported widely through the atmosphere. The transport of metals to regions such as these occurs along major airmass trajectories downwind of significant source areas. These are located predominantly in the Northern Hemisphere where the majority of World's population and industry are located. The main sources of metal pollutants are therefore large urban and industrial conglomerations, including the rapidly growing eastern and south eastern region of China, the northern eastern and Great Lakes region of the USA and Western and Eastern Europe (Fig. 4).

Figure 5 illustrates the documented pollution transport trajectories. The majority of these pathways occur in the mid-latitude and Polar regions of both hemisphere's where stronger winds prevail. By contrast, little long-range pollution has been reported within the tropics. The most well documented long-range

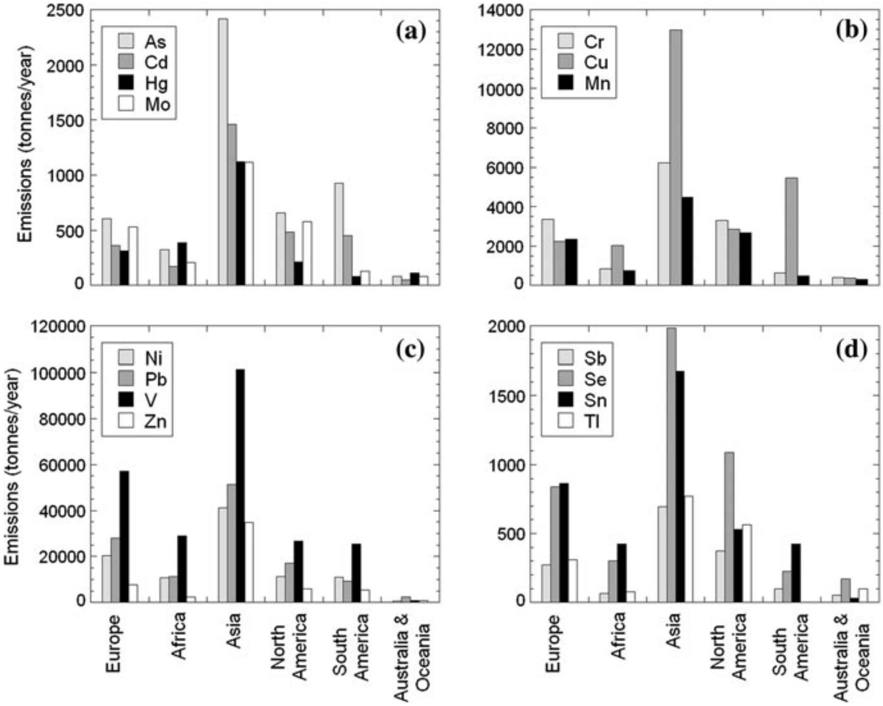

Fig. 4 Global metal emissions to the atmosphere by region (tonnes/year) for arsenic (As), cadmium (Cd), mercury (Hg) and molybdenum (Mo) (**a**); chromium (Cr), copper (Cu) and manganese Mn (**b**); nickel (Ni), lead (Pb), vanadium (V) and zinc (Zn) (**c**) and; antimony (Sb), selenium (Se), tin (Sn) and thallium (Tl) (**d**) (data from Pacyna and Pacyna 2001)

pathways occur out of Europe, resulting in metals being transported from southern Europe to northern and central Europe, and from these regions to the Arctic Circle, as demonstrated by studies undertaken in Scandinavia, the Russian Arctic and Greenland (Barbante et al. 2003; Brännvall et al. 1999; McConnell and Edwards 2008). Pollution transport along this trajectory has a long history going back to the Bronze Age. Similarly, metal pollution from Europe can be transported to the Middle East when a steep pressure gradient develops between the Persian trough and African sub-tropical ridge causing strong westerly winds between Europe and the Middle East (Erel et al. 2007).

Metal pollution transported out of eastern Asia has gained increased attention due to the high concentrations of metals being emitted from this region. Airmass trajectories from Asia result in pollutants being transported across Korea and Japan and into the Arctic Circle above North America (Okuda et al. 2006; Osterberg et al. 2008). They may also be transported to the south-east over Taiwan (Lin et al. 2005) and into the remote central Pacific (Settle and Patterson 1982). Pollution from Asia has also been found to influence the western United States (Jaffe et al. 2003, 2005) and monsoon rainfall over northern Australia (Rotstayn et al. 2007).

The other major pollution transport trajectory occurs out of North America. Pollution generated in the United States is transported north-east in the mid-latitude westerlies to the Canadian Arctic and Greenland (Outridge et al. 2005). In addition, metal pollution from North American may be transported west out of the continent into the Pacific Ocean during the boreal winter (Settle and Patterson 1982). Other Northern Hemisphere long-range pollution pathways result in the transport of metals from northern Africa to USA and the Caribbean, which commonly occurs during the outbreak of large Saharan dust plumes (Arimoto et al. 1992; Prospero 1999). The region impacted by this pollution has been shown to change seasonally with the migration of the Inter Tropical Convergence Zone (ITCZ) (e.g. Prospero 1999; Prospero et al. 1981).

Pollution plume trajectories in the Southern Hemisphere have received less attention in comparison with the Northern Hemisphere. There are few studies of long-range metal transport from Africa or South America despite the fact that these continents are known to be significant emitters of metals to the atmosphere (Fig. 4). A number of studies have been undertaken examining metal pollution accumulation in Antarctica, which being the most remote landmass from urban

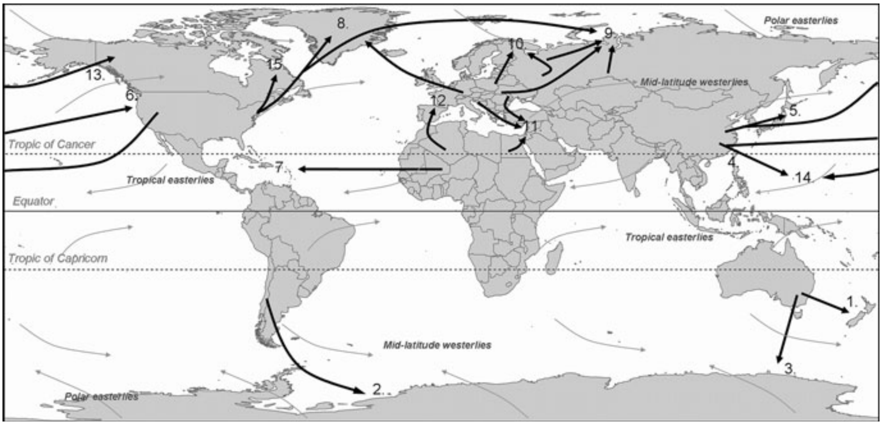

Fig. 5 The major documented pollution plume pathways over which the long-range transport of pollution occurs (as indicated by the *black arrows*). The main windfields are also indicated on the figure by the *grey arrows*. The *numbers* on the figure refer to representative studies documenting pollution transport over these pathways. *1* Australia to New Zealand (Marx et al. 2008); *2* South America to Antarctica (Wolff et al. 1999); *3* Australia to Antarctica (Vallelonga et al. 2002); *4* Asia to Taiwan (Lin 2001); *5* Asia to Japan and Korea (Kim et al. 2009; Okuda et al. 2006); *6* Asia to North America (Jaffe et al. 2003; Osterberg et al. 2008); *7* northern Africa to central America (Arimoto et al. 1992); *8* Europe and North America to Greenland (Hong et al. 1996; McConnell and Edwards 2008); *9* North America, Europe and Russia to the Russian Arctic (Shevchenko et al. 2003); *10* western and eastern Europe to Scandinavia (Brännvall et al. 1999); *11* Europe and North Africa to the Middle East (Erel et al. 2007); *12* North Africa to Spain (Bacardit and Camarero 2009); *13* Asia to the North American Arctic (Osterberg et al. 2008); *14* Asia and North America to the central north Pacific (Settle and Patterson 1982); *15* North America to the remote Canadian Arctic (Outridge et al. 2002)

and industrial centres, should contain the cleanest atmosphere. However, studies in west Antarctica have identified pollutants attributed to metal production and mining operations in Chile (Wolff et al. 1999), while in east Antarctic, Pb isotopes have been used to confirm pollution from Australia is transported to the continent (Vallelonga et al. 2002) (Fig. 5). Similarly the transport of Australian metal pollution to New Zealand has also been recognised (Arimoto et al. 1990; Halstead et al. 2000; Marx et al. 2005, 2008). This occurs as mid-latitude westerly winds transport pollution emitted from eastern Australia, where the majority of Australia's industry and population are located, across the Tasman Sea to New Zealand.

5 Trends in Metal Pollution

The perturbation of metals in the atmosphere has occurred almost since the beginnings of human metal use with significant metal pollution generally accepted to have begun during the Bronze Age with the smelting of Cu and Sn. Consequently, records of atmospheric metal deposition from chronologically intact geologic archives, such as peat bogs, serve as sensitive records of the history of metal production. In addition, they show the degree to which metals have been perturbed within the environment and allow an assessment of the impacts of theses pollutants.

Although some metal use may have begun as early as the ninth century (Tylecote 1976), significant metal perturbation in the atmosphere has been documented from approximately 3000 years ago (~1000 BC) in Europe (Brännvall et al. 1999). For example, cores from peat bogs in the Swiss Alps show the accumulation of anthropogenic Pb after 3000 BP (Shotyk et al. 2001). This early Pb pollution is believed to have been sourced from the Iberian Peninsula, which accounted for the majority of the metal production at this time (Nriagu 1983), from where it was transported through the atmosphere and deposited in the Swiss Alps. In Spain, anthropogenic mercury (Hg) accumulation is recorded in peats from c. 2500 BP (500 BC) (Martinez-Cortizas et al. 1999).

Records of metal accumulation in Europe clearly document the major phases of metal usage. Studies undertaken on both peat bogs near Manchester, England and lake sediments in Sweden contain anthropogenic Pb pollution dating from 900 and 2000 BC, respectively, with initial Pb accumulation occurring during Bronze Age and Iron Age smelting (Fig. 6) (Brännvall et al. 1999; Le Roux et al. 2004). Pollution deposited in Sweden at this time was attributed to long-range transport of Pb from France and England, while in England it was assumed to originate from both long-range transport and local metal production. Peaks in Pb pollution occurred during the Roman period at 0 BC followed by a decline in Pb enrichment during the Dark Ages (~500 AD) when metal use decreased in Europe. Subsequent increases in Pb pollution occurred through the Middle Ages within both geologic archives, although they record a minor decline in pollution after 1200 AD attributed to an economic decline, the Black Death and the Hundred Years' War. Lead

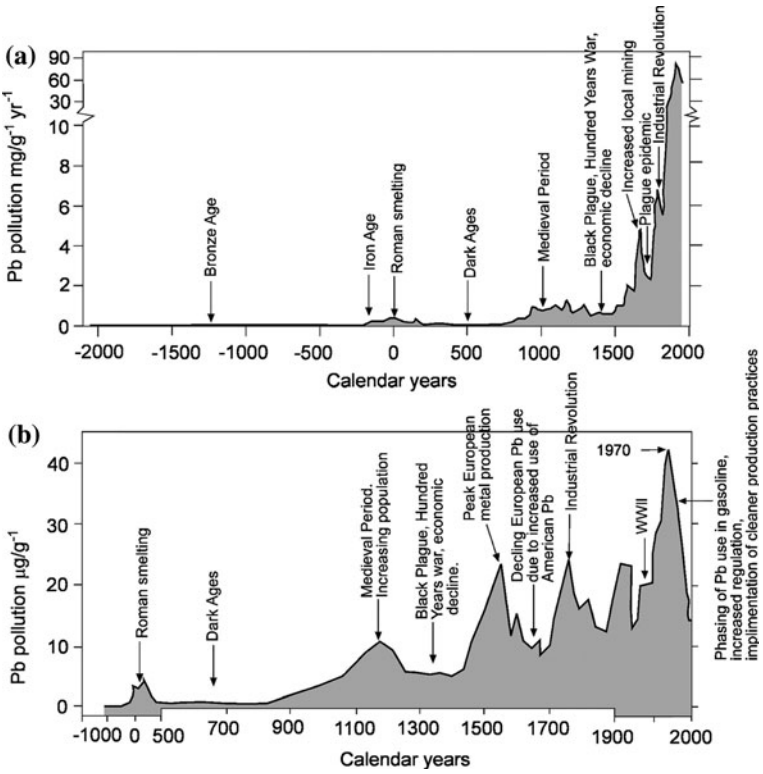

Fig. 6 Lead pollution (Pb) recorded in two European cores. In **a** the Pb pollution accumulation in a peat bog near Manchester, England is shown (after Le Roux et al. 2004), while in **b** Pb pollution accumulation in Koltjärn Lake, central Sweden is shown (after Brännvall et al. 1999)

pollution increased from the 1500s, with more dramatic increases occurring through the 1700s, leading into the industrial revolution in Europe (Le Roux et al. 2004) (Fig. 6a).

The most dramatic increases in metal pollution occurred in Europe during the industrial revolution (Fig. 6b). For example, the concentration of anthropogenic Pb in the atmosphere (as indicated by its deposition in Swiss peat bogs) increased by 20 times (Shotyk et al. 2001). Two pollution peaks occurred in these bogs post 1700 AD; the first in the late 1800s and early 1900s, associated with the period known as the second Industrial revolution, while the second followed World War II (WWII) and culminated in the 1970s associated with the peak of Pb use in gasoline (Shotyk et al. 1998). These results are confirmed by Swedish lake cores which show a largely identical history (Brännvall et al. 1999) (Fig. 6). Metal pollution in Europe declined after this time with reduced enrichment factors recorded for metals such as Cd and Pb within Greenland ice (McConnell and Edwards 2008). The reduction in metal pollution in Greenland coincides with a decline in both European and North American industrial activity. The development of cleaner production as a response to concerns about metal pollution, has also contributed to a decline in metal pollution from these sources (Harmens et al. 2007; McConnell and Edwards 2008; Osterberg et al. 2008; Pacyna and Pacyna 2001).

Declining atmospheric metal pollution has not, however, been ubiquitous across the globe. The decline in atmospheric metal pollution in Europe and North America contrasts with increasing metal pollution being emitted from the growing economies of Asia; notably China and India. For example, in Fig. 7a global coal consumption for OECD and non-OECD countries between 1973 and 2007 is shown. Coal is a significant source of atmospheric metal pollutants and use of coal in the developing, non-OCED, countries has undergone a significant increase

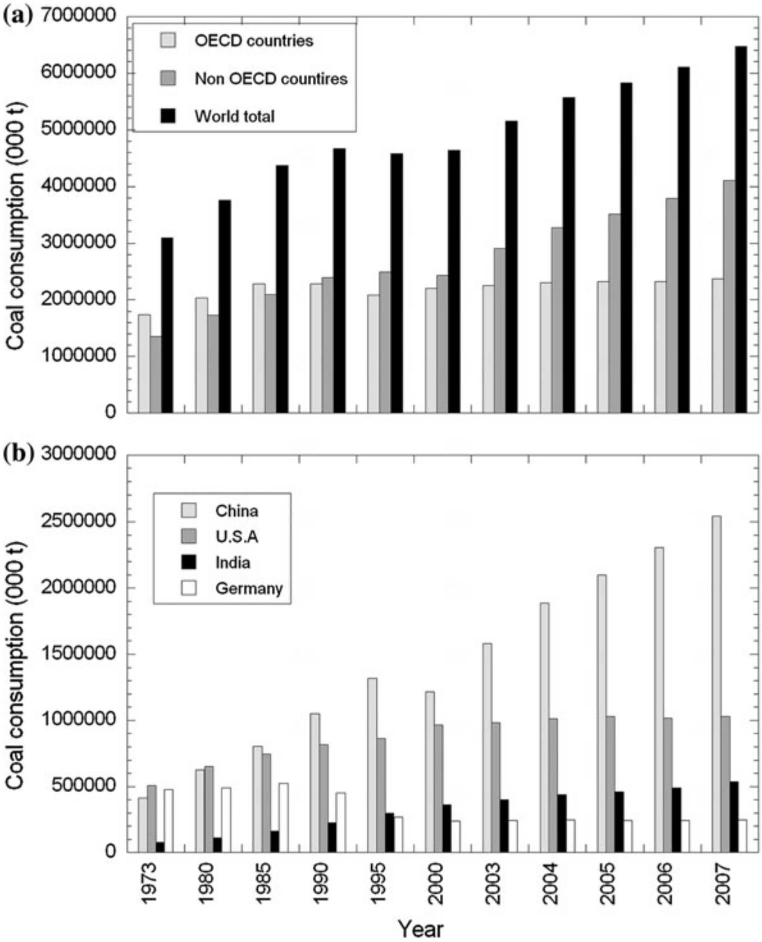

Fig. 7 In **a** the coal consumption of OECD and non-OECD countries in shown. Similarly in **b** coal consumption for shown for selected countries is shown (Anon 2008)

during this period by 3 times. By contrast coal consumption in OECD countries increased by 1.3 times during this period. This is demonstrated further in Fig. 7b, where the coal consumption of selected countries is shown with consumption in India and China increasing by 7 and 6 times, respectively, whereas it has doubled in the USA and halved in Germany.

Atmospheric metal pollution in Asia has a long history, equal to that of Europe. Lake cores from China show accumulation of the metals Cu, Pb, Ni and Zn began after 3000 BC with the beginning of the Chinese Bronze Age (Lee et al. 2008). Further notable increases in metal enrichment occurred after 1500 BC with more significant increases from 206 BC to 220 AD during the Han dynasty when Cu and Pb were smelted extensively. Following the Han dynasty, Cu, Ni and Zn pollution actually decreased slightly as ceramics and iron metals replaced the use of bronze (Lee et al. 2008). After the 1300s metal pollution again increased, which was attributed to increased war and weapons manufacturing. Significant increases occurred from late 1800s and early 1900s associated with the introduction of European technology such as the building of railroads and the establishment of a modern army. Additional increases in metal enrichment occurred up to the end of the WWII, again attributed to increased warfare (Lee et al. 2008).

The most notable increase in metal enrichment has occurred post WWII associated with increased industrialization throughout much of Asia. In contrast to records from Greenland, which reflect the European metal pollution history and show decreasing Pb pollution post 1970 AD, ice cores from north western Canada show an increase in Pb pollution post-1970 which airmass trajectory studies and isotope fingerprinting indicate is transported from Asia (Osterberg, et al. 2008). The increase in pollution in this region coincides with China becoming the world's largest user of coal (Fig. 7) and producer of non-ferrous metals since the 1980s (Osterberg et al. 2008). In addition, lower pollution standards in comparison to Europe and North America also contribute to continued high rates of metal emissions to the atmosphere from Asia (Osterberg et al. 2008; Pacyna and Pacyna 2001).

Despite atmospheric metal pollution being ubiquitous through most of the Northern Hemisphere, there is no evidence of Northern Hemisphere derived metal pollution being transported across the ITCZ to the Southern Hemisphere. Consequently, the history of metal pollution in the Southern Hemisphere began later, with the first records of metal pollution beginning in 1545 AD associated with the Spanish mining of Ag (Miller et al. 2002). Despite the well known history of mining in South America (Nriagu 1994), there are currently few records of metal deposition that span the history of mining and smelting on the continent. Results from Bolivian ice cores show pronounced metal enrichment occurring from the 1800s for Cu, Zn, Ag, Cd and Pb, with possible enrichment occurring as early as 790 AD (Hong et al. 2004). Similar to the Northern Hemisphere, peak Pb emissions were found to occur in the late 1970s and early 1980s, attributed to the global peak of Pb use in gasoline, with a decline following this date. By contrast, the concentrations of Cu, Zn and Cd have continued to increase in the atmosphere, which is attributed to increased metal production and mining in South America

(Espi et al. 1997). Similar increases in Cu and Zn in Western Antarctic ice have also been attributed to South American metal production and mining (Wolff et al. 1999).

As a consequence of its more recent industrial history, many regions of the Southern Hemisphere have much shorter atmospheric pollution histories. For example, Australia's history of atmospheric metal pollution began following European settlement and the advent of mining on the continent approximately 160 years ago (in the 1850s). Despite its relatively recent industrial history, Australia quickly grew to become a significant source of many industrial metals. A pollution history constructed from peat cores in the Australian Alps show rates of metal enrichment are closely tied with Australia's metal mining and production records (Marx et al. 2010). These show that metal enrichment is actually increasing in the Australian environment, coincident with increasing rates of metal production.

6 Impacts of Atmospheric Metal Pollution

The impact of industrial metals on human and ecological health has been recognized for some time. Conditions, such as miners' sickness known to afflict miners and metal workers were recognized as early as the 1500s (Crone 2004). There is also evidence to suggest that the widespread use and smelting of Pb during the Roman period led to significant Pb poisoning effects amongst the population (Nriagu 1983). The potential impacts of Pb pollution came to public attention during the 1960s and 1970s when concerns about the amount of Pb pollution being incorporated into the environment and its potential effects on humans grew. The pervasiveness of Pb in the environment at the height of industrial Pb use, which peaked in the late 1970s, resulted in Pb being incorporated in humans both through direct ingestion from the atmosphere, but also via the use of paints, water service pipes and soldered cans used in the food industry among others. Lead from atmospheric deposition was also found to be accumulating in foods, as demonstrated by Clair Patterson whose early investigations brought the pervasiveness of industrial Pb to public attention (Patterson 1965). These concerns ultimately led to phasing out the use of Pb as an additive in gasoline across most countries.

Despite the fact the toxic effects of metals have long been recognized, the levels at which they are toxic and the effects of metal poisoning are not well understood. For example, the recognized clinical threshold of Pb toxicity in humans has been shown to be decreasing as studies have demonstrated that exposure to Pb at any level is harmful, especially for children (Schwartz 1994; Smith and Flegal 1992). Similarly, the levels at which Hg becomes toxic are subject to considerable debate (WHO 2007). This is significant because there are no regions of the global where atmospheric pollution has not been identified, even in otherwise very clean air environments like Antarctica or the west coast of New Zealand's South Island. As a result of this global perturbation of metals, Pb levels in the blood of modern humans have been estimated to be between 100 and 1,000 times that of pre-industrial humans (Owen and Flegal 1998). In humans Pb exposure occurs mainly through ingestion of contaminated particles, e.g. dust, and is known to have a number of neurological effects, as does Hg, which is believed to be mainly taken up via food (WHO 2007). In addition to Pb and Hg, the long-range transport of Cd is also of particular concern (WHO 2007). Exposure to Cd can deleteriously affect liver and kidney functioning in mammals. Like Hg, Cd is largely taken up via food (WHO 2007).

While the impacts of metal pollutants are known to be highest closest to emission sites (AMAP 1997), long-range transport of metals plays an important role in their distribution, and is the key mechanism controlling the occurrence of industrial metals in many regions. For example, in Europe, which is highly industrialized, 50% of the Cd deposited in the environment is estimated to originate from long-range transport for 16 out of 45 European countries, while in 27 countries 30% of Cd is estimated to originate from long-range deposition. Similarly 33% of the Hg deposited in Europe is estimated to be transported from outside Europe (WHO 2007). Consequently, regions downwind of major plume trajectories (see Fig. 5) are likely to experience the most impacts from long-range metal pollution.

There are few studies examining the effects of long-range pollution in cities and urban areas. This is despite the fact that long-range metals undoubtedly have an impact in many urban settings. Moreover it seems likely that with the exception of a few studies (e.g. Erel et al. 2007), long-range pollution measured in urban environments is largely incorrectly ascribed to local pollution sources. In the major Korean cities of Soul and Busan, the concentrations of most metal pollutants were found to be decreasing (although Cr and Ni concentrations were increasing) (Kim et al. 2009). This contrasts with the findings of pollution monitoring studies elsewhere along the eastern Asian pollution plume pathway from more remote settings where metal pollution was found to be increasing (e.g. Osterberg et al. 2008). The reduction in metal pollution in Korean cities presumably results from a decline in local metal emissions which mask the impact of long-range metals. This shows the difficulties associated with monitoring long-range pollution in urban settings. However increasing levels of Ni and Cr in Korean cities, may reflect the increasing combustion of coal in China, which is the main source of these metals (Nriagu and Pacyna 1988) (Table 1; Fig. 7).

It seems probable, given the increasing strength of the Asian pollution plume, that long-range pollution may have an increasing impact in some urban regions. For example, on the west coast of Japan, Pb-isotope studies have demonstrated that while Japanese sourced Pb pollution was decreasing due to industrial closures, regulation, cleaner production and the phasing out of Pb in gasoline, the contribution of Chinese and Russian derived Pb pollution was increasing (Bellis et al. 2005). Similarly, long-range transport of largely Asian sourced Hg, derived mainly from coal combustion, is a major source of this metal in Japan, while Asian derived Hg accounts for on average 16% of Hg deposited in North America (Jaffe and Strode 2008). As a result of the difficulties associated with determining the provenance of metal pollution in urban environments, the majority of studies of the effects of long-range pollution have been undertaken in remote settings, the Arctic in particular (e.g. AMAP 1997).

Metal pollution not only affects humans but also impacts on the entire ecological system. In the Arctic, reindeer and caribou have been documented to be accumulating Cd which has been linked to kidney dysfunction (AMAP 1997), while filter feeders, such as mussels, have also been shown to accumulate toxic metals such as Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn (Mubiana et al. 2005). Mercury has been found to be bio-concentrating at critical levels in the marine environment, with higher concentrations documented in predatory fish and in marine mammals such as ringed seals (AMAP 1997). This has resulted in subsequent bioaccumulation in human populations who consume large amounts of fish, such as the populations of the Faroe Islands in the Northern Atlantic, Maderia off the west coast of North Africa and the Inuit people of northern Canada (Grandjean et al. 1992; Renzoni et al. 1998; Wheatley et al. 1979).

While atmospheric metal pollution is decreasing in many regions, such in Europe and North America, increasing concentrations being transported out of Asia and even from regions such as Australia, where although metal emissions are considerably lower (Fig. 4) they are still of concern. Also of significance is the toxic legacy of metals which have accumulated in the environment from past industrial activities (see Fig. 6). These have been deposited in soils and water bodies from where they can potentially easily be remobilized. This can occur, for example, via wind entrainment of contaminated soil (e.g. Erel et al. 2006). In addition, the melting of glaciers in Switzerland have been found to be releasing historic organic pollutants into waterways (Bogdal et al. 2009). This pollution was deposited and stored in the ice during peak deposition of these pollutants during the 1960s and 1970s. Recent melting of glaciers has been found to be re-releasing these pollutants into the environment. Metal pollutants have also been documented to be concentrated by water runoff, accumulating in depositional environments such as lakes and estuaries (e.g. Conrad and Chisholm-Brause 2004; Spencer et al. 2003). From these environments deposited metals may be taken up by biological organisms, such as fish and filter feeders (Henry et al. 2004; Kirby et al. 2001; Mubiana et al. 2005) from where they are known to bioaccumulate through the ecosystem (WHO 2007).

7 Summary

Toxic metals remain among the most pervasive pollutants within the atmosphere and surface environments of the Earth. This is because they are easily mobilized and transported. Their transport occurs primarily out of major industrial and urban conglomerations along prevailing airmass trajectories. Metals have been documented to be transported thousands of kilometers through the atmosphere, impacting even the remotest regions of the Earth. These metals are released in the atmosphere as a waste product from industrial processes, with metal production and fossil fuel combustion being the principal sources of emissions. Other sources include cement production, fertilizer use and refuse and wood incineration. Gasoline combustion was previously a major source of atmospheric Pb pollution, although this source has significantly declined as Pb has been removed as an additive in gasoline as a result of health concerns.

The persistence of metals in the environment has allowed histories of atmospheric metal pollution to be constructed. These show significant metal accumulation began during the Bronze Age. Palaeo-pollution records have been shown to serve as a record of human development, tracing the major phases of human industrial development from the Bronze Age until the present. In Europe and North America concerns over the effects of metals in the environment has resulted in a decline in metal accumulation downwind of these regions, following peak metal contamination, which occurred from the Industrial Revolution through to the late 1970s. Declining metal pollution has not been ubiquitous across the globe, with increasing metal pollution transport out of Asia. A paucity of data from other regions such as Africa and South America make assessments of the emissions of metals to the atmosphere form these countries difficult.

There are few studies of the impacts of long-range pollution in urban areas. This is because local pollution typically masks long-range pollution. Consequently, it is likely that in many urban pollution studies long-range pollution is incorrectly ascribed to a local origin. Despite this, long-range transport continues to be a significant source of pollutants contributing up to 30–50% of Cd and Hg pollution to many countries in Europe.

Metal pollution remains a major health concern. In the case of some metals studies, indicate that toxic effects in humans may occur at any level of exposure, with children particularly susceptible. This evidence suggests that reducing metal emissions should remain a high priority. Moreover, as a result of 4000 years of metal perturbation in the atmosphere by human activities and its subsequent deposition, significant quantities of metals have been incorporated into the Earth's surficial environments. This historic metal pollution contained within geologic archives can subsequently be remobilized by geomorphic processes again affecting the wider environment. Metal pollution has been shown to be bio-accumulating in some marine environments, with the accumulation of metals in fish and marine mammals shown to affect human populations.

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Part II
Metals and Organic Compounds in Airborne Particulate Matter: Analytical Methods

Clare L. S. Wiseman and Fathi Zereini

There have been a number of advances made in analytical methods and technologies in recent years that have greatly contributed to our ability to characterize the chemical composition of airborne particulate matter (PM). With these advances, our knowledge regarding the various chemical compounds found in PM, including their concentrations and sources, and their potential to impact human health has significantly improved. This chapter brings together a number of important contributions on the topic of analytical methods. Various technological developments and methodologies to prepare samples, measure the concentrations of metals and organic compounds, determine metal speciation and issues related to quality assurance/quality control are presented and discussed.

In the first chapter of this part, Balasubramanian and He discuss the use of accelerated solvent extraction (ASE) for the trace analysis of persistent organic pollutants such as polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbons (PAHs) in aerosols. They demonstrate the effectiveness of ASE, in combination with GC–MS, which can be applied to both gaseous and particle phase samples, over more traditional procedures, which require long extraction times and are labor intensive. Garcia-Jares et al. describe analytical developments for the determination of emerging pollutants such as organophosphate esters and brominated flame retardants in suspended and settled indoor dust in the second chapter, a medium which has received a great deal of attention in recent years as an important exposure route for various contaminants. This comprehensive section addresses many related issues such as procedures for sampling and enrichment, and methods for analyte isolation, measurement and validation. In the third chapter, Maclean et al. discuss the application of synchrotron radiation-based X-ray absorption and scattering techniques for characterizing the speciation of metals in house dust, which is a complex mix of various compounds. After providing a comprehensive overview of these methods for metal speciation, they then discuss the application of synchrotron radiation-based X-ray absorption and scattering to determine the speciation of Pb and its total and bioaccessible fraction to a house dust sample. Puls et al. discuss the challenges involved in the measurement of palladium (Pd) in the fourth chapter, a metal which has been observed in increasingly greater concentrations in the environment over time, due to its use as a catalyst in automotive catalytic converters. They provide a comprehensive overview of the various methods available for the preparation and measurement of this noble metal in airborne PM samples. In the fifth chapter, Rauch et al. discuss a procedure for the direct quantification of metal concentrations on PM_{10} filters using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). Using airborne PM_{10} samples collected in Boston, they demonstrate the value of this technique and how it allows for the quick and easy determination of metal concentrations, without the labor intensive sample preparatory procedures common to more traditional methods. Jung et al. present the application of an innovative single particle quantification technique, low-Z particle electron probe X-ray microanalysis in the sixth chapter, to examine the particle composition of aerosol samples collected in a subway station in Seoul, Korea. Using this method, they found that the largest proportion of particles contained Fe, most likely originating from within the tunnel such as through rail-wheel-brake interfaces. To conclude in Part II, Alsenz et al. present a method which they developed for the reliable determination of Pd in environmental media. As Puls et al. pointed out in the fourth chapter, an accurate method to measure this metal is needed, as it poses particular analytical challenges. Alsenz et al. describe a method which combines the use of a sample preparation procedure using reductive co-precipitation and He collision gas with isotope dilution-ICP-MS to measure Pd concentrations in airborne PM_{10} collected at three sites in Germany. As demonstrated, this appears to be a promising method which could help overcome many of the past difficulties associated with measuring Pd in environmental media.

Trace Analysis of Persistent Organic Pollutants in the Air Using Accelerated Solvent Extraction

Rajasekhar Balasubramanian and Jun He

1 Introduction

During the last decade, the occurrence of persistent organic pollutants (POPs) has drawn great attention because of their high rates of production and consumption, their considerable environmental persistence, toxic potential, high levels of bioaccumulation and harmful biological effects including their mutagenic and carcinogenic properties (Fernández and Grimalt 2003). Important groups of POPs include: polycyclic aromatic hydrocarbons (PAHs) and halogenated hydrocarbons such as organchlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) (Ritter et al. 1995). Because of their hydrophobicity and resistance to degradation, they are widely distributed in the various components of the environment (Potrykus et al. 2003). The atmosphere has been regarded as the major pathway for the global distribution of POPs (Koziol and Pudykiewicz 2001). Consequently, the characterization of POPs in air has been subjected to intensive study world-wide in order to assess their environmental fate and human exposure (Liu et al. 2005).

Extraction aims to recover as much as possible of the pollutants from the sampling material. So it is a very fundamental aspect in the analytical process (Yusà et al. 2009). The extraction of POPs in air can be achieved through several established methods (Hawthorne et al. 1989; Chee et al. 1997; Lenicek et al. 2000; Yeo et al. 2003; Christensen et al. 2005). USEPA method 3542 (Soxhlet extraction) has been used to extract semi-volatile organic pollutants from air samples such as filters, XAD-2® resin or polyurethane foam (PUF). Sonication is also one of the extraction methods mostly used to prepare air samples for determination of POPs. All of these traditional procedures have some weaknesses of large volumes

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_7,

of solvents used, long extraction time needed and intensive labor required because of little or no automation. In order to achieve faster extraction and reduction of solvent volume, some modern extraction techniques such as supercritical fluid extraction (SFE) and microwave-assisted extraction (MAE) have been developed for extraction of POPs from various environmental samples (Yang et al. 2003; Cortazar et al. 2005; Sun and Li 2005). A recent advance in trace environmental analysis is the use of the accelerated solvent extraction (ASE) method, which represents an exceptionally effective extraction technique compared to alternative methods mentioned above such as SE and UAE (Fisher et al. 1997; Shen and Shao 2005; Sporring et al. 2005; García et al. 2008). This extraction process takes advantage of the increased analyte solubility at temperatures well above the boiling points of common solvents. In addition, the kinetic processes involved for analytes to desorb from the matrix are accelerated, and automated extractions can be carried out. However, despite its significant advantages compared to traditional extraction methods, the effectiveness of ASE has not been sufficiently demonstrated yet for the extraction of POPs from ambient air samples.

In this work, the feasibility of using ASE to extract different groups of POPs collected onto quartz filters and PUF plugs was studied. Different parameters affecting the extraction efficiency such as combination of extraction solvents, extraction temperature, and static extraction time were investigated and optimized. The performance of this optimized method, in terms of recovery on PUF and filter samples, was evaluated and compared with that of SE and MAE. Following optimization, a quality assured ASE method was developed and used for the extraction of POPs in ambient air samples collected in Singapore. The concentrations of POPs in air samples were quantified using GC–MS to demonstrate the practical applications of the ASE method.

2 Experimental Section

2.1 Sampling

Particulate and gaseous air samples were collected using a hi-volume sampler (Model TE-1000PUF, Tisch Environmental, Inc., USA) at the atmospheric research station in National University of Singapore for 24 h duration in July 2006. Total suspended particles were collected by a quartz filter of 4″ diameter loaded onto the filter holder followed by an adsorbent cartridge filled with three pieces of one-inch PUF plugs in series (each plug of 65 mm diameter and 25 mm length). These filters were heated at 450°C for 24 h and conditioned in a desiccator for 24 h prior to use. PUF plugs were pre-cleaned with hexane followed by acetone in 33 mL stainless steel vessels of a Dionex ASE 200 at 1500 psi and 120°C for 10 min; and the same pre-cleaning procedure was conducted six cycles till the targeted POPs on PUF were in the range of blank values of fresh solvents as above.

The hi-volume PUF sampler can collect air at a rate of ca. 250 L/min. The filter and PUF samples were stored at −20°C prior to extraction.

2.2 Materials

All solvents used for this study were of pesticide grade: *n*-hexane (HEX), acetone (ACE), dicloromethane (DCM) and methanol (METH) (Tedia, USA). The standard mixture USEPA 610 includes 16 priority PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B(a)A), chrysene (Chr), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), indeno[1,2,3-cd] pyrene (Ind), dibenz[a,h]anthracene (DB(ah)A) and benzo[ghi]perylene (B(ghi)P)), in methanol: methylene chloride mixture (1:1). The standard mixture of OCPs included in Kit 608-S and PCBs (C-QME-01) were purchased from Supelco (USA) and AccuStandard (New Haven, USA), respectively. Anthracene-d_{10}, fluoranthene-d_{10} benzo[e]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA) and $^{13}C_{12}$-PCBs congeners CB 77, 101, 141, 178 were used as surrogates; phenanthrene-d_{10}, pyrene-d_{10}, benzo[a]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA), $^{13}C_6$-tetrachlorobenzene and $^{13}C_{12}$-PCBs congeners CB 8 and 206 (Cambridge Isotope Laboratories, MA, USA) were used as internal standards. Anhydrous sodium sulfate, silica gel and florisil of GR analysis grade (Merck, Germany) were heated at 600°C for 24 h to remove any organic contamination. SRM 1649a (urban dust) was purchased from the National Institute of Standards and Technology (NIST) (Gaithersburg, MD, USA).

2.3 Sample Preparation

The standard samples were prepared by spiking 20 μL of USEPA 610 PAH mixture (2–20 mg/L), 20 μL of OCPs standard stock solution (500 μg/L), 20 μL of PCBs standard stock solution (400 μg/L) and surrogates for recovery evaluation on pre-baked quartz filters and pre-cleaned PUF plugs respectively, wrapped by pre-cleaned aluminum foils, and then followed by ~4 h drying in a clean hood prior to extraction. Prior to extraction, the same surrogates as above for recovery evaluation were spiked onto the collected real-world air samples.

2.4 Extraction Methods

The ASE method was optimized in this study as discussed below. For SE and MAE, the extraction parameters were selected based on previous successful investigations published in the literature (Sporring et al. 2005; Karthikeyan et al. 2006).

2.4.1 Accelerated Solvent Extraction (ASE)

All extractions were conducted using quartz filters and PUF plugs spiked with standards in 33 mL stainless-steel cells by Dionex (ASE 200). Extractions were performed with 40 mL of solvent(s) at 100 atm pressure by one static cycle. The vessels were rinsed with 10 mL of the same solvent, and the extracted analytes were purged from the sample cells using pressurized nitrogen at 100 atm. Varying the pressure in this range does not affect the results (Li et al. 1998; Saim et al. 1998).

In this study, the effects of the following parameters on the ASE efficiency were investigated and optimized: the combination of extraction solvents, extraction temperature, and static extraction time. To optimize the extraction solvents, three solvents (DCM, HEX, and METH) and two solvent mixtures (1:1 mixture of HEX and METH, 3:1 mixture of HEX and ACE) were compared for their efficiencies in extracting POPs (PAHs, OCPs and PCBs) from the standard-spiked samples. The static ASE extraction was conducted at 100°C for 10 min. All extractions were conducted in triplicate. After the selection of the most appropriate solvent to achieve maximum extraction efficiency, extraction temperature and duration were evaluated by conducting extractions of the prepared samples at 60, 80, 100, 120°C for 10 min initially and 5, 10, 20, 30, 45, and 60 min at the optimum temperature, respectively. Based on the outcome of the preliminary experiments described above, the real air samples in PUFs and quartz filters were extracted separately under the optimum conditions by two static cycles in order to measure the target compounds in both gas- and particle phases. All extracts were concentrated to approximately 5 mL using a rotary evaporator at room temperature and then further to 50 μL using a gentle purified nitrogen gas stream.

After extraction, ASE extracts were splitted into two portions: one portion was cleaned by chromatographic column of silica gel for PAHs; the other portion was cleaned by chromatographic column of florisil for organochlorine compounds. The extract was concentrated to approximately 3 mL at room temperature and further to 20–50 μL by using a gentle nitrogen purge, into which internal standards were added before it being sealed and then stored at −20°C prior to GC–MS analysis.

2.4.2 Soxhlet Extraction (SE)

The standard-spiked samples were placed in Soxhlet extraction thimble (Scheider & Schuell GmbH, Dassel, Germany), and extracted with 200 mL *n*-hexane/acetone (1:1, v/v) for both PUF and filter samples for 8 h in a Soxhlet extractor (4–5 cycles/h), respectively. The clean-up procedures that follow after extraction were the same as used for ASE (see previous section).

2.4.3 Microwave-Assisted Extraction (MAE)

A closed vessel microwave digestion system (MLS-1200 mega, Mileston s.r.l, Italy) was used for the extraction of the standard-spiked PUF and filter samples separately. The procedure used requires 40 mL mixture of acetone:*n*-hexane (1:1) for extraction of OCs at 150 W of microwave energy for 20 min extraction time. The solvents have to be changed manually after each extraction if one more extraction cycle is necessary. The clean-up procedures that follow after extraction were the same as used for ASE.

2.5 GC–MS Analysis

The analysis of extracted samples was performed using a QP2010 GC–MS equipped with a Shimadzu AOC-5000 auto injector and a DB-5 fused silica capillary column (30 m length and 0.25 mm I.D; film thickness 0.25 μm) with purified helium as carrier gas. 4 μL of the sample was injected into the GC–MS in splitless mode with a sampling time of 1.5 min using high-pressure injection mode (pressure 2.47 atm maintained for 2.0 min, initial column flow 3.17 mL/min), as recommended in the GC–MS manual [Shimad-zu, GC–MS application Data Sheet No. 3 (Environment)]. PAH, OCP and PCB standards were measured and air samples were analyzed separately in selective ion monitoring mode (SIM) with a detector voltage 700 V. The most abundant ions were selected for quantification, and then one to four reference ions were used for confirmation of each analyte in SIM mode. GC temperature programs with selected ions were presented in Table 1.

2.6 Quality Control

The analytical quality of the data obtained was determined using limit of detection (LOD), recovery, linearity, checking sampling artifacts and calibration with internal standards. During each set of extractions, the field blanks (filter and PUF plugs) were included and the mean blank value was subtracted from the measured levels. Little or no PCBs congeners were detected while trace amounts of OCPs were detected in the blanks. Limits of detection (LOD) were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks. LODs for POPs ranged from 0.05 ± 0.08 to 2.17 ± 0.95 pg/m^3.

The reliability of the entire analytical procedure for each sample was evaluated by using surrogate standards. The procedural recoveries of surrogates ranged from 86.7 ± 6.8% (anthracene-d_{10}) to 107.2 ± 6.9% (^{13}C12-PCB141). The linearity of calibration standards was calculated by regression analysis with values ranging from 0.99 to 1.00 (r^2) for POPs Breakthrough was evaluated under field conditions by connecting three-one-inch plugs in series and analyzing them separately. For 24 h samples, measured POPs at the third plug were in the range of blanks values. Three-one-inch plugs in series used in hi-volume PUF sampler therefore could trap gas-phase target compounds effectively. Control calibration standards spiked with internal standards were measured regularly to check instrument performance during analysis.

Table 1 GC temperature programs and MS monitoring ions for analysis of POPs

	Compounds	Monitoring ions	GC temperature program
PAHs	Naphthalene (Naph)	128[a]	70°C for 2 min 15°C/min to 200°C for 4 min 5°C/min to 300°C for 5 min
	Acenaphthene (Ace)	152[a]	
	Acenaphtylene (Acy)	154[a]	
	Fluorene (Flu)	166[a]	
	Phenanthrene (Phe)	178[a]	
	Anthracene (Ant)	178[a]	
	Fluoranthene (Flt)	202[a]	
	Pyrene (Pyr)	202[a]	
	Benzo[a]anthracene (B(a)A)	228[a]	
	Chrysene (Chr)	228[a]	
	Benzo[b]fluoranthene (B(b)F)	252[a]	
	Benzo[k]fluoranthene (B(k)F)	252[a]	
	Benzo[a]pyrene (B(a)P)	252[a]	
	Indeno[1,2,3-cd]pyrene (Ind)	276[a]	
	Benzo[ghi]perylene (B(ghi)P)	276[a]	
	Dibenzo[a,h]anthracene (DB(ah)A)	278[a]	
OCPs	α-HCH, β-HCH, γ-HCH, δ-HCH	219[a], 183, 181, 217	4°C/min from 125 to 300°C
	p,*p*′-DDE	246[a], 248	
	p,*p*′-DDD, *p*,*p*′-DDT	235[a], 237	
PCBs	PCB 17 + 18, 28 + 31, 33	256[a], 258	160°C for 10 min 3°C/min to 250°C 8°C/min to 300°C
	PCB 44, 49, 52, 70 + 95, 74	292[a], 290	
	PCB 87, 99, 101, 110, 110, 118	326[a], 328	
	PCB 128, 149, 151, 132 + 153, 156, 169	360[a], 362	
	183, 138 + 158		
	PCB 170, 171, 177,180,187,191	394[a], 396	
	PCB 194, 195, 199, 205	430[a], 428	
	PCB 208	464[a], 394	
	PCB 209	498[a], 428	

3 Optimization of Accelerated Solvent Extraction (ASE)

3.1 Extraction Solvent

Results obtained from the extractions using HEX/METH (1:1), DCM, HEX, HEX/ACE (3:1), and METH are illustrated in Fig. 1. All of the extractions were performed at 100°C for 10 min by using one static cycle. The standard deviation values show the reproducibility of the extraction method used. Among the solvent or solvent mixtures studied, the best yield was obtained using a mixture of 3:1 *n*-hexane and acetone in the range of 81–92% for all POPs while those of n-hexane/methanol (1:1), dichloromethane, *n*-hexane yielded recoveries of 52–83, 62–81 and 53–88%, respectively. When the methanol alone was used, the recovery

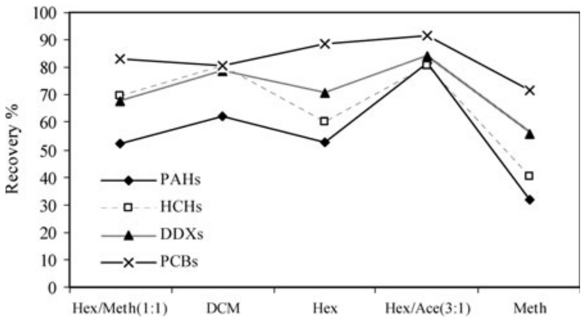


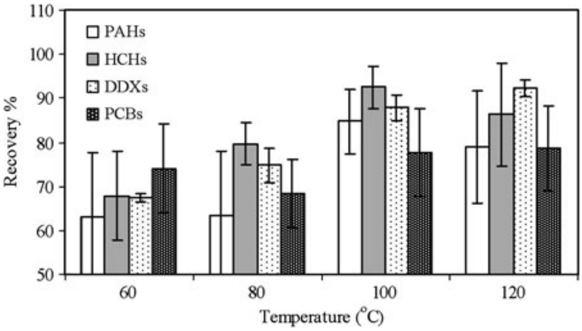
Fig. 1 Effect of solvent on ASE of POPs (PAHs, OCPs and PCBs). OCPs including HCHs, DDXs

was even worse, with a range as low as 32% to a relatively high value of 72%. It has been reported that a combination of different solvent mixtures tends to improve the solvation of the analytes of interest and thus improve overall efficiency of extraction (Karthikeyan et al. 2006; Hawthorne et al. 2000). In addition, the overall low standard deviations obtained for a 3:1 mixture of HEX and ACE solvents are indicative of good reproducibility of experimental data. Based on the results obtained, the mixture of HEX/ACE (3:1) was therefore chosen as the extraction solvent in all subsequent studies

3.2 Extraction Temperature

Temperature is one of the most important parameters that affect ASE efficiency. Elevated temperature could increase desorption kinetics of target compounds, and also lower viscosity of solvent. Consequently the analytes could diffuse into the solvent matrix more easily (Hubert et al. 2000). ASE methods generally use temperatures between 60 and 180°C. According to previous reports, the extraction of POPs depends on both the level of total pollution and the degree of complexity of the matrix (Karthikeyan et al. 2006; Hawthorne et al. 2000; Hubert et al. 2000). The compositions of the filters and PUF plugs are much different from other matrices such as soil, plants and fishes, etc. It was therefore necessary to determine the response of temperature to extraction efficiency. Figure 2 shows the extraction efficiency carried out in the temperature range between 60 and 120°C in 20°C steps using 3:1 HEX/ACE as solvent for 10 min by one static cycle. The highest extraction yields were achieved at 100°C for two groups of pollutants (PAHs and HCHs). For all other compounds, the highest yields were attained at 120°C. The lower extraction efficiency observed at all other temperatures for different groups of compounds can be attributed to the adhesion or fusion of organic matrix containing pollutant fractions (Tao et al. 2002). Within the range of temperatures evaluated, the optimum appears to be somewhere between 100 and 120°C. PUF is known to decompose around 180°C, and it was found that a high extraction temperature led to a relatively high weight loss of PUF of above 7% (Wurl and

Fig. 2 Extraction temperature effect on the recoveries of POPs using a 3:1 HEX/ACE as solvent



Obbard 2005). After decreasing the extraction temperature to around 100°C, the weight loss could be minimized to 2% which is comparable to that encountered upon soaking PUF in hexane (Braun et al. 1986; Wurl and Obbard 2005). Based on the results obtained, the temperature was fixed at 100°C as the optimum for ASE extraction of POPs.

3.3 Static Extraction Time

Extraction time is the time needed for POPs to desorb and dissolve most efficiently from the sample matrix into extraction solvents. In order to determine the optimum extraction time for satisfactory recovery, ASE was performed at 100°C in 40 mL of solvent mixture for 5, 10, 20, 30, 45 and 60 min, respectively. Table 2 shows that the recovery reached a maximum between 20 and 30 min. For the time in excess of 30 min, it can be seen that the extraction yield decreased with increasing extraction time, which could be caused by a thermal degradation or the fusion of organic material within the matrix because of the temperatures reaching inside the vessels (Tao et al. 2002; PiiTeiro-Iglesias et al. 2004). It was therefore decided to use 25 min as static extraction time in all subsequent studies. In summary, the optimum ASE extraction conditions were achieved using a 3:1 HEX/ACE combination at 100°C for 25 min.

4 Method Recovery Evaluation, Comparison and Validation

Previously, both filters and PUF plugs spiked with standards were extracted and analyzed together. In order to determine whether the above ASE optimized conditions were suitable for filter as well as PUF samples, the ASE extractions were applied by two static cycles to standard-spiked filter/PUF samples, respectively, as described above. All recoveries of POPs by ASE are shown in Table 3.

Table 2 Extraction efficiencies (recovery %) depending on extraction time

Recovery (SD) (%)	Extraction time (min)					
	5	10	20	30	45	60
Compounds						
PAHs	70.1 (27.0)	82.3 (51.3)	97.7 (21.6)	107.0 (13.3)	86.7 (18.9)	75.0 (11.9)
HCHs	74.5 (5.8)	74.3 (1.9)	90.6 (13.1)	84.5 (12.6)	75.3 (14.5)	59.8 (6.1)
DDXs	82.6 (6.1)	82.0 (8.2)	96.8 (5.0)	92.6 (8.0)	89.4 (5.8)	93.9 (12.1)
PCBs	85.2 (4.8)	88.2 (13.4)	97.8 (18.1)	98.8 (16.6)	91.9 (14.8)	90.4 (17.2)

With a single extraction step, it can be seen that the recoveries of PAHs, OCPs and PCBs from filters were in the range of 69.2–93.9, 71.1–96.9 and 67.6–108.5%, respectively. The recoveries of those from PUF plugs were in the range of 67.8–92.2, 73.0–90.6 and 62.1–106.0%, respectively. When performing an additional extraction of 25 min with the same solvent mixture, most of the recoveries of POPs increased substantially by up to 20% for both PUF and filter media. These types of observations regarding improvement in recovery with additional extraction cycles have been reported for other environmental matrices as well (Sporring et al. 2005; Björklund et al. 1999). Most of the recoveries resulting from two extraction cycles were in the range of Association of Analytical Communities (AOAC) interval (80–115%) (AOAC 2002).

Reproducibility has been tested on the results after two extraction steps under univariate variance-component analysis at 5% significance level by using SPSS 13.0 for Windows (SPSS Inc. Chicago, IL, USA). All *P* values are greater than 0.05, indicating that no significant difference between both repetitive samples (inter-sample) and different sampling media (filter and PUF, inter-media) was observed by applying the optimized extraction for two static cycles. Consequently, two extraction cycles were selected for both PUF and filter samples in this study.

For the comparison of the performance of ASE with commonly used extraction methods such as SE and MAE, standard-spiked PUF and filter samples were processed separately. An overall comparison between the recoveries is shown in Fig. 3, in which the individual bars represent the average values obtained from triplicate measurements for each target compound. All extraction techniques used the HEX/ACE solvent composition and the optimized extraction time and temperature (for SE and MAE, the optimum conditions are from the literature). The recoveries of SE even after 8 h extraction were significantly lower than those of MAE (20 min) and ASE (40 min; 2 cycles × 20 min/cycle) for both PUF and filter samples, respectively. Although MAE and ASE-1 cycle achieved similar efficiencies, ASE-2 cycles gave the best recovery for all target compounds. Furthermore, good reproducibility was also obtained for ASE, which is most likely due to the automation of the whole extraction procedure.

NIST certified reference material SRM 1649a (urban dust-organics) was applied to evaluate ASE method for the determination of selected PAHs, OCPs and PCBs under the optimized extraction conditions. The concentrations, expressed as mass fractions, for 22 PAHs, 35 PCBs (some in combination) and 8 OCPs have been

Table 3 The recovery (average of duplicates) of POPs by separate analysis of filter/PUF samples spiked with standards

Compounds	ASE-recovery % (mean ± SD)			
	First cycle		First + second cycle	
	Filter	PUF	Filter	PUF
Naph	77.6 ± 13.5	67.8 ± 10.8	90.4 ± 8.6	88.7 ± 6.1
Ace	69.2 ± 10.6	74.1 ± 10.6	93.4 ± 12.8	90.1 ± 9.4
Acy	89.4 ± 5.5	92.2 ± 2.9	95.5 ± 6.3	102.8 ± 9.5
Flu	93.9 ± 4.2	91.0 ± 0.5	97.3 ± 6.5	93.2 ± 2.3
Phe	92.7 ± 4.2	89.3 ± 2.6	95.4 ± 3.8	93.8 ± 5.3
Ant	88.3 ± 3.5	84.5 ± 0.1	95.3 ± 5.3	93.7 ± 5.2
Flt	92.3 ± 5.2	86.7 ± 4.7	98.4 ± 7.1	97.6 ± 5.6
Pyr	86.0 ± 2.6	83.2 ± 0.7	93.7 ± 5.6	96.3 ± 7.1
B(a)A	86.9 ± 4.7	87.2 ± 0.5	98.8 ± 6.8	94.6 ± 5.2
Chr	87.4 ± 3.6	85.5 ± 0.3	94.7 ± 6.3	93.4 ± 4.3
B(b)F	86.8 ± 5.7	82.7 ± 2.6	98.6 ± 5.6	92.5 ± 4.4
B(k)F	85.0 ± 3.7	84.1 ± 2.2	94.9 ± 8.2	95.6 ± 5.3
B(a)P	83.5 ± 2.8	84.0 ± 1.8	95.6 ± 6.5	91.3 ± 4.2
Ind	86.0 ± 5.4	82.3 ± 2.4	95.3 ± 6.7	91.2 ± 4.6
DB(ah)A	90.3 ± 2.8	87.4 ± 3.0	96.1 ± 7.3	94.6 ± 5.0
B(ghi)P	90.2 ± 3.6	81.5 ± 8.3	98.4 ± 6.9	95.5 ± 8.4
α-HCH	90.2 ± 7.6	90.6 ± 14.7	92.2 ± 4.1	96.6 ± 6.8
β-HCH	89.7 ± 7.8	78.5 ± 18.9	101.3 ± 9.7	94.1 ± 4.5
γ-HCH	81.7 ± 7.6	93.1 ± 2.5	93.5 ± 5.9	104.3 ± 8.9
δ-HCH	86.7 ± 19.2	73.0 ± 8.5	98.1 ± 9.6	89.0 ± 5.5
p,p'-DDE	71.1 ± 4.1	85.4 ± 10.6	93.1 ± 7.3	97.7 ± 8.1
p,p'-DDD	96.9 ± 12.5	82.1 ± 13.8	97.4 ± 12.3	98.3 ± 11.5
p,p'-DDT	84.3 ± 8.1	77.9 ± 18.2	93.4 ± 6.8	92.7 ± 13.7
PCB 17 + 18	83.0 ± 9.3	75.2 ± 3.8	96.2 ± 7.4	88.5 ± 5.4
PCB 28 + 31	72.5 ± 11.7	65.0 ± 4.9	87.3 ± 9.2	91.3 ± 7.6
PCB 33	74.4 ± 9.8	67.0 ± 8.1	93.6 ± 12.1	89.3 ± 5.9
PCB 44	89.7 ± 14.4	78.8 ± 11.5	95.6 ± 8.3	93.6 ± 5.5
PCB 49	85.8 ± 9.6	79.7 ± 12.3	91.7 ± 6.5	89.3 ± 9.4
PCB 52	80.5 ± 24.5	62.1 ± 16.0	95.2 ± 12.5	95.3 ± 14.3
PCB 70 + 95	75.8 ± 19.9	63.6 ± 3.1	94.7 ± 10.7	85.2 ± 4.8
PCB 74	78.2 ± 12.6	70.5 ± 1.9	90.8 ± 8.9	91.5 ± 6.9
PCB 87	87.6 ± 12.6	73.9 ± 4.3	96.3 ± 8.6	92.7 ± 8.1
PCB 99	75.7 ± 17.7	68.8 ± 12.3	94.6 ± 12.3	86.6 ± 9.3
PCB 101	86.2 ± 11.8	83.0 ± 15.6	98.9 ± 9.7	96.2 ± 11.3
PCB 110	80.9 ± 10.8	73.7 ± 8.1	95.2 ± 6.5	91.6 ± 6.9
PCB 118	85.3 ± 13.7	77.0 ± 10.6	93.4 ± 7.8	90.8 ± 11.3
PCB 128	77.6 ± 13.5	67.8 ± 10.8	90.4 ± 8.6	88.7 ± 8.1
PCB 149	67.6 ± 10.6	64.1 ± 10.6	93.4 ± 12.8	90.1 ± 9.4
PCB 151	89.4 ± 5.5	92.2 ± 2.9	95.5 ± 6.3	102.8 ± 9.5
PCB 132 + 153	93.9 ± 4.2	91.0 ± 0.5	97.3 ± 6.5	93.2 ± 2.3
PCB 138 + 158	92.7 ± 4.2	89.3 ± 2.6	95.4 ± 3.8	93.8 ± 5.3

Table 3 (continued)

Compounds	ASE-recovery % (mean ± SD)			
	First cycle		First + second cycle	
	Filter	PUF	Filter	PUF
PCB 156	88.3 ± 3.5	84.5 ± 0.1	95.3 ± 5.3	93.7 ± 5.2
PCB 169	92.3 ± 5.2	86.7 ± 4.7	98.4 ± 7.1	97.6 ± 5.6
PCB 170	86.0 ± 2.6	83.2 ± 0.7	93.7 ± 5.6	96.3 ± 7.1
PCB 171	86.9 ± 4.7	87.2 ± 0.5	98.8 ± 6.8	94.6 ± 5.2
PCB 177	87.4 ± 3.6	85.5 ± 0.3	94.7 ± 6.3	93.4 ± 4.3
PCB 180	86.8 ± 5.7	82.7 ± 2.6	98.6 ± 5.6	87.5 ± 4.4
PCB 183	85.0 ± 3.7	84.1 ± 2.2	94.9 ± 8.2	95.6 ± 5.3
PCB 187	83.5 ± 2.8	84.0 ± 1.8	95.6 ± 6.5	91.3 ± 4.2
PCB 191	86.0 ± 5.4	82.3 ± 2.4	95.3 ± 6.7	91.2 ± 4.6
PCB 194	90.3 ± 2.8	87.4 ± 3.0	96.1 ± 7.3	94.6 ± 5.0
PCB 195	90.2 ± 3.6	81.5 ± 8.3	98.4 ± 6.9	89.5 ± 6.4
PCB 199	95.0 ± 8.2	91.1 ± 8.7	96.2 ± 7.8	94.5 ± 7.8
PCB 205	108.5 ± 1.5	106.0 ± 0.8	110.2 ± 8.6	107.0 ± 1.2
PC 208	86.0 ± 2.9	84.6 ± 2.6	94.5 ± 6.7	96.8 ± 6.5
PCB 209	68.0 ± 2.6	66.0 ± 2.3	91.6 ± 8.4	85.9 ± 5.2

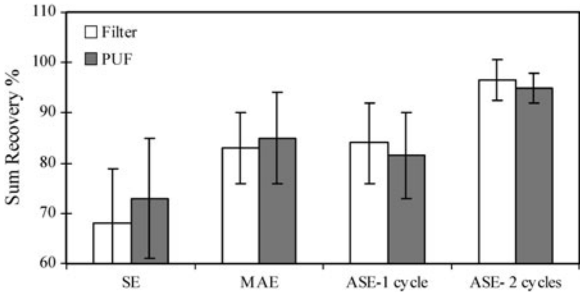


Fig. 3 Average recovery of target compounds for different extraction techniques

certified in SRM 1649a, of which 12 PAHs, 20 PCBs and 3 OCPs covered by our standards and separated well by the above GC–MS analysis methods were chosen for validation in this study. An accurately weighed 200 mg of SRM 1649a in duplicate was extracted by the optimized ASE method, cleaned up according to the procedure as stated above and analyzed by GC–MS. As can be seen from Table 4, the recoveries were in the range of 82–126% for PAHs, 73–136% for OCPs and 73–121% for PCBs, respectively. For the group of PAHs, only the recoveries of Phe (119%) and Ant (126%) were out of the range of Association of Analytical Communities (AOAC) recommended interval (80–115%). In the group of OCPs, the concentration of heptachlor provided by NIST is not the certified value but reference concentration, which was in good correlation with the measured value. The measured concentration of *p*,*p*′-DDE was relatively higher than the NIST-certified value, even though the samples had been cleaned up through the chromatographic column packed with florisil. This problem might be due to some potential interference from co-eluting compounds. To the best of our knowledge, this is the first study to use SRM 1649a to validate the extraction efficiency of PCBs from air samples using ASE, the measured values of PCB congeners chosen are in good agreement with NIST-certified values. Generally, the concentrations determined in this study correlate well with the NIST-certified and reference concentrations for most of the target compounds in SRM 1649a, which demonstrated that the ASE method is suitable for extraction of POPs in air samples at trace levels.

5 Application of Optimized ASE

In this section, concentrations of POPs measured in the urban atmosphere of Singapore are presented and discussed. All of the filters and PUF plugs were extracted and analyzed separately according to the optimized ASE-GC/MS method described above.

Average total (particle and gas) PAHs concentrations ranged between 13.62 and 52.26 ng/m^3 with an overall mean concentration of 33.54 ng/m^3 (see Table 5). The concentration of gaseous PAHs varied from 11.90 to 45.74 ng/m^3 with the mean concentration being 28.82 ng/m^3 (i.e. 87.5% of the total concentration). The PAH concentration in particles was considerably lower and ranged from 1.93 to 7.53 ng/m^3 with an mean value of 4.72 ng/m^3. The most abundant PAHs in all samples were Pyr (7.28 ng/m^3), Phe (7.18 ng/m^3), and Flt (5.56 ng/m^3). In general, the concentration of heavier PAHs with five or more aromatic rings (B(b)F, B(k)F, B(a)P, Ind, DB(ah)A, and B(ghi)P) was low ranging from 0.07 to 1.24 ng/m^3. Average concentrations of the five most abundant PAHs and B(a)P observed in Singapore are compared to those reported in other urban regions. The sum (gas + particle) of mean concentrations of Pyr, Phe, Flt, Flu, Ant, and B(a)P in Singapore were 25.81 ng/m^3 which are higher than those measured in the suburbs of Athens (14.20 ng/m^3) (Mandalakis et al. 2002), while considerably higher levels of these six PAH members were determined in Guangzhou (76.07 ng/m^3) (Bi et al. 2003), Hong Kong (71.79 ng/m^3) (Lee et al. 2001), and Chicago (171.90 ng/m^3) (Simcik et al. 1998).

The concentration levels of ΣHCHs in particulate and gaseous phases were in the range of 2.45–6.97 and 150.89–320.17 pg/m^3, respectively. Those of ΣDDXs in particulate and gaseous phases were 0.46 ± 0.50 and 7.22 ± 3.59 pg/m^3, respectively. It can be seen that, in general, the gaseous phase OCPs were dominant over those in the particulate phase. Mean total concentrations of HCHs were: α-HCH $= 104.17 \pm 17.50$ pg/m^3; β-HCH $= 22.50 \pm 18.87$ pg/m^3; γ-HCH $= 85.66 \pm 34.87$ pg/m^3; δ-HCH $= 27.55 \pm 17.26$ pg/m^3. Both α-HCH and γ-HCH dominated in the present study. The concentrations of HCHs were comparable to those observed over Java sea (75 pg/m^3), Celebes Sea (120 pg/m^3), but much lower than those in South China Sea (1300 pg/m^3) measured one decade ago (Iwata et al. 1993) and the recently reported occurrence (364 pg/m^3) over Qingdao, China (Lammel et al. 2007). At the same time, the concentrations of HCHs measured in Singapore are relatively higher than those recently reported for remote sites in the

Table 4 Analysis of NIST SRM 1649a for PAHs, OCPs and PCBs

Compounds	Measured value[a,b] mean ± SD	Certified value[b] mean ± SD	% Recovery mean ± SD
Phe	4.95 ± 0.64	4.14 ± 0.37	119 ± 15
Ant	0.68 ± 0.12	0.43 ± 0.08	126 ± 28
Flt	5.20 ± 0.42	6.45 ± 0.18	81 ± 7
Pyr	4.59 ± 0.30	5.29 ± 0.25	87 ± 6
B(a)A	2.22 ± 0.16	2.21 ± 0.07	100 ± 7
Chr	2.92 ± 0.25	3.05 ± 0.060	96 ± 8
B(b)F	6.30 ± 0.75	6.45 ± 0.64	98 ± 12
B(k)F	1.80 ± 0.11	1.91 ± 0.031	94 ± 6
B(a)P	2.18 ± 0.19	2.51 ± 0.09	87 ± 8
Ind	3.29 ± 0.38	3.18 ± 0.72	104 ± 12
DB(a,h)A	0.27 ± 0.10	0.288 ± 0.023	94 ± 35
B(ghi)P	3.60 ± 0.62	4.01 ± 0.91	90 ± 15
p,p′-DDE	54.89 ± 4.72	40.4 ± 1.7	136 ± 12
p,p′-DDD	32.39 ± 5.63	34.01 ± 0.48	95 ± 17
p,p′-DDT	155.34 ± 30.29	212 ± 15	73 ± 14
PCB 44	11.29 ± 1.47	15.4 ± 1.6	73 ± 10
PCB 49	9.01 ± 0.82	12.2 ± 1.5	74 ± 7
PCB 52	22.05 ± 2.10	24.65 ± 0.97	89 ± 9
PCB 87	8.18 ± 0.29	10.65 ± 0.62	77 ± 3
PCB 99	8.55 ± 1.20	9.58 ± 0.69	89 ± 13
PCB 101	40.91 ± 3.45	52.9 ± 1.0	77 ± 6
PCB 105	8.90 ± 0.63	8.63 ± 0.80	103 ± 7
PCB 110	23.74 ± 2.47	26.6 ± 1.6	89 ± 9
PCB 118	19.52 ± 2.89	25.7 ± 1.5	76 ± 11
PCB 128	7.68 ± 0.97	6.35 ± 0.69	121 ± 15
PCB 149	74.60 ± 6.54	75.7 ± 1.3	98 ± 9
PCB 151	42 ± 1.81	34.3 ± 3.9	122 ± 5
PCB 156	19.35 ± 1.38	16.25 ± 0.77	119 ± 8
PCB 170	26.27 ± 3.28	30.8 ± 2.2	85 ± 11
PCB 180	58.90 ± 4.13	78.70 ± 8.2	75 ± 5
PCB 183	18.02 ± 1.70	20.34 ± 0.95	88 ± 8
PCB 187	36.10 ± 1.72	40.1 ± 2.5	90 ± 4
PCB 194	26.46 ± 1.53	28.9 ± 3.6	92 ± 5
PCB 195	9.13 ± 0.21	9.63 ± 0.37	95 ± 2
PCB 209	8.66 ± 1.26	8.04 ± 0.77	108 ± 16

[a] Average of duplicate

[b] The units of measured and certified value for PAHs are mg/kg and for OCPs and PCBs are μg/kg

Indian Ocean (18.4 pg/m^3) (Wurl et al. 2006). It is thus confirmed that no significant decline of HCHs has occurred in this area over the past two decades.

During the sampling period, *p,p′*-DDT, *p,p′*-DDE, and *p,p′*-DDD were detected with total concentrations of 0.57 ± 0.44, 1.94 ± 1.83, and 5.17 ± 2.43 pg/m^3, respectively. These concentrations were almost comparable to the recent data obtained in the Indian Ocean (2.5–33.2, mean 10.4 pg/m^3) (Wurl et al. 2006), and the coast of Singapore (3.6 ± 0.3–11.3 ± 1.3 pg/m^3) (Wurl and Obbard 2005),

Table 5 Particle and gas phase concentrations of POPs in the air of Singapore (unit: ng/m^3 for PAHs, pg/m^3 for OCPs and PCBs)

Compound	Particle mean ± SD	Gas mean ± SD	Total mean ± SD
Naph	0.66 ± 0.31	0.79 ± 0.64	1.45 ± 0.95
Ace	0.04 ± 0.01	0.14 ± 0.06	0.18 ± 0.07
Acy	0.06 ± 0.05	0.25 ± 0.13	0.31 ± 0.18
Flu	0.05 ± 0.04	3.71 ± 0.43	3.76 ± 0.47
Phe	0.25 ± 0.16	6.93 ± 3.58	7.18 ± 3.74
Ant	0.06 ± 0.03	1.97 ± 0.22	2.03 ± 0.25
Flt	0.45 ± 0.27	5.11 ± 3.83	5.56 ± 4.10
Pyr	0.37 ± 0.22	6.91 ± 6.22	7.28 ± 6.44
B(a)A	0.17 ± 0.07	0.30 ± 0.09	0.47 ± 0.16
Chr	0.26 ± 0.22	0.62 ± 0.45	0.88 ± 0.67
B(b)F	0.62 ± 0.40	0.62 ± 0.42	1.24 ± 0.82
B(k)F	0.12 ± 0.07	0.11 ± 0.07	0.23 ± 0.14
B(a)P	0.31 ± 0.18	0.21 ± 0.13	0.52 ± 0.31
Ind	0.67 ± 0.39	0.76 ± 0.45	1.43 ± 0.44
DB(ah)A	0.06 ± 0.09	0.01 ± 0.003	0.07 ± 0.09
B(ghi)P	0.57 ± 0.29	0.38 ± 0.20	0.95 ± 0.49
ΣPAH	4.72 ± 2.80	28.82 ± 16.92	33.54 ± 19.32
α-HCH	1.38 ± 0.86	102.81 ± 16.64	104.17 ± 17.50
β-HCH	0.35 ± 0.54	22.50 ± 18.33	22.85 ± 18.87
γ-HCH	1.36 ± 1.84	84.3 ± 33.03	85.66 ± 34.87
δ-HCH	1.62 ± 0.62	25.93 ± 16.64	27.55 ± 17.26
ΣHCH	4.71 ± 2.26	235.53 ± 84.64	244.95 ± 88.50
4,4′-DDE	0.06 ± 0.08	0.51 ± 0.36	0.57 ± 0.44
4,4′-DDD	0.24 ± 0.30	1.70 ± 1.53	1.94 ± 1.83
4,4′-DDT	0.16 ± 0.14	5.01 ± 2.29	5.17 ± 2.43
ΣDDX	0.46 ± 0.52	7.22 ± 3.59	7.68 ± 4.11
PCB 17 + 18	0.23 ± 0.08	6.81 ± 2.65	7.04 ± 2.73
PCB 28 + 31	0.56 ± 0.39	4.94 ± 2.73	5.5 ± 3.12
PCB 44	0.31 ± 0.19	1.92 ± 0.98	2.23 ± 1.17
PCB 52 + 49	0.20 ± 0.32	2.50 ± 1.42	2.70 ± 1.74
PCB 74 + 70	0.15 ± 0.23	2.10 ± 0.83	2.25 ± 1.06
PCB 87	0.36 ± 0.61	1.50 ± 1.47	1.86 ± 2.08
PCB 101 + 99	0.18 ± 0.13	1.25 ± 0.63	1.43 ± 0.76
PCB 110	0.18 ± 0.14	0.83 ± 0.26	1.01 ± 0.40
PCB 118	0.21 ± 0.20	1.19 ± 0.52	1.4 ± 0.72
PCB 128	0.43 ± 0.41	0.82 ± 0.23	1.25 ± 0.64
PCB 132 + 153	0.22 ± 0.32	0.33 ± 0.41	0.55 ± 0.73
PCB 138 + 158	0.60 ± 0.49	0.82 ± 0.95	1.42 ± 1.44
PCB 149	0.13 ± 0.14	0.31 ± 0.24	0.44 ± 0.38
PCB 151	0.17 ± 0.10	0.28 ± 0.44	0.45 ± 0.54
PCB 156	0.40 ± 0.15	0.82 ± 0.67	1.22 ± 0.82
PCB 169	0.28 ± 0.09	0.46 ± 0.14	0.74 ± 0.23
ΣPCB	4.61 ± 3.99	26.88 ± 14.58	31.49 ± 18.56

but were lower than those recently measured in other surrounding areas in Asia, such as Hong Kong (180–970, mean 620 pg/m^3), Pearl River Delta of South China (280–3,700, mean 1,300 pg/m^3), Japan (mean ~38 pg/m^3) (Jaward et al. 2005; Wang et al. 2007), Qingdao of China (mean 128 pg/m^3) and Gosan of Korea (mean 529.5 pg/m^3) (Lammel et al. 2007). The ratio of *p,p′*-DDT to *p,p′*-DDE is generally used as an indicator of aging of DDXs. This ratio calculated from mean concentrations in this study was 9.1, which is much greater than those reported in other areas of the world (0.94 in Tapachula, 1.3 in Chetumal, Mexico, 1.2 in Belmopan, Belize, and generally ~1 in US and Canada) (Shen and Shao 2005; Park et al. 2001; Harner et al. 2004). Consequently, the local composition of DDX indicates a major input of fresh DDT from outside sources.

The mean concentrations of 23 PCB congeners measured during the sampling period were 28.0 ± 15.1 pg/m^3 in the gas phase and 6.1 ± 4.6 pg/m^3 in the particle phase, respectively. About 80% (mean) of total PCBs (particle + gas) was distributed in the gas phase, which is in good agreement with the trend reported in previous studies (Bidleman 1988; Duinker and Bruchertall 1989; Yeo et al. 2003), while the total concentration of PCBs (34.1 ± 19.7 pg/m^3) was lower than those reported in other urban areas such as Seoul (Korea), Athens (Greece), Houston (USA), Birmingham (UK) (Mandalakis et al. 2002; Park et al. 2001; Harrad and Mao 2004; Yeo et al. 2004).

In summary, the prevalence and toxicity of POPs present in the environment justifies the need to establish their content in the atmosphere. An ASE method has been developed for the determination of POPs in both atmospheric particulate and gaseous phases. The best extraction solvent used in this study for the ASE is the mixture of HEX/ACE (3:1). The effective extractions should be performed at 100°C for 25 min. The entire analytical procedure developed in this study proves to be reliable as evident from the analysis of specific surrogate standards with the good recoveries. As compared to SE and MAE, it shows advantages in terms of high efficiency and reproducibility. The optimized method was validated using NIST certified SRM 1649a, of which the results showed good agreement with certified values. The application of the new extraction method was demonstrated by analyzing a set of air samples and the results obtained were compared to the values reported from surrounding areas. Based on our results, the proposed ASE technique appears to be a promising alternative to commonly used extraction techniques, especially when applied to the investigation of a number of air samples due to its complete software-controlled automation.

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Analytical Developments for Emerging Pollutants in Indoor Suspended Particulate Matter and Dust

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1 Introduction

Indoor air quality is a vital factor for the health of occupants in buildings. Indoor air pollution is a growing scientific concern because air can lead to a concentration of many harmful pollutants. Changes in the way of life have altered the kind and concentrations of chemicals that occupants of indoor environments are exposed to in their homes, workplaces and schools. Furthermore, as some chemicals are being banned by international regulations, an increasing number of alternative compounds are being introduced in commercial applications, which may result in a greater contribution of these new formulations to human exposure than they do currently. For example, as the lower brominated (penta- and octa-BDEs) diphenyl ether (BDEs) products are being banned, increasing employment of higher brominated deca-BDE products becomes evident, resulting in a higher contribution of these chemicals to infant exposure (Toms et al. 2009).

The interest in understanding the mechanisms that control indoor air pollution is related to the effects of indoor exposure on human health. People in developed countries spend up to 90% of their time indoors. In addition, modern electrical appliances such as TVs, personal computers, electronic gaming units, or Internet suggest that people, especially children, spend more time in their homes today than

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*, Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_8,

they did years ago (Weschler 2009). Some reports have estimated indoor exposures for children and adults, finding that children are at greater risk from pollutants that accumulate indoors. An example is the study performed by Gevao et al. (2006) who found human non-dietary exposures on polybrominated diphenyl ethers (PBDEs) via dust ingestion of 14.8 and 1.5 ng day^{-1} for children and adults, respectively.

The air in a room may contain particulate matter, which includes dust, flakes of skin, and gases, as well as fumes from the external environment and smoking, electrical particles such as ions, and water vapour (Clements-Croome 2008). Pollution usually arises from infiltrations into the building from outside, people, equipment, dust within the airflow systems, which can be discharged into the space if the systems are not maintained properly, and emissions of volatile organic compounds from building and furnishing materials (Clements-Croome 2008). Aerosols are suspensions of liquids or solids that can stay airborne for long periods. Indoor air recirculation systems may spread pollutants associated with professional activities developed indoors, increasing the risk of exposure to unknown chemicals. This is the case for example of dental offices in which current control of indoor air quality is focused on anaesthetic gases and microorganisms associated with pathologic infections due to the potential risks for staff and patients. However, little is known about other pollutants even if certain procedures can emit particles and contaminants that can migrate throughout the entire building (Godwin et al. 2003).

Particles can be defined as any small bits of material or droplets either organic or non-organic, viable or non-viable, that can become airborne, while particle air pollution refers to a mixture of solid and liquid particles suspended in the air, varying in size, composition and origin (Ormstad 2003). Atmospheric particulate matter is made of a mixture of solid and aqueous species that enter the atmosphere by anthropogenic and natural pathways and possess a range of morphological, physical and chemical patterns in different areas. Particulate matter contains inorganic ions, metallic compounds, elemental carbon, and organic compounds. The organic fraction is especially complex and contains hundreds of compounds. Based on health considerations, PM_{10} and $PM_{2.5}$ (fraction of particulate matter with aerodynamic diameter range smaller than 10 and 2.5 μm, respectively), are usually selected as indicators of air pollution rather than total suspended particulate (TSP) matter, since those particles are small enough to enter the thoracic region (Wilson et al. 2002).

While the number of particles is important as they are related to health effects, so too is the size, shape, material properties and chemical composition. Chemicals absorbed or adsorbed into the particles may also have different toxicological effects. In addition to carbon particles and polycyclic aromatic hydrocarbons (PAHs), indoor air can accumulate environmental tobacco smoke as well as chemicals such as biocides, formaldehyde, and volatile organic compounds (VOCs) classified by the International Agency for Research on Cancer (IARC) as carcinogenic (benzene, 1,3-butadiene) (IARC 1995). Since children are the most affected by chronic household exposure, they may be at higher risk of cancer. It was demonstrated a relative increase in leukaemia and lymphoma caused by indoor VOCs as well as by the indoor use of insecticides (Weaver et al. 1998; Menegaux et al. 2006). Thus, it is important to determine both the particle concentration and size distribution as well as determine the chemical constituents of particles.

According to the United States Environmental Protection Agency (US EPA) (US EPA 1997), house dust is a complex mixture of biologically derived material, particulate matter deposited from the indoor aerosol, and soil particles brought in by foot traffic. Many contaminants are adsorbed by particulate matter suspended in indoor air, which later settles out as house dust. Furthermore, these compounds have the potential to persist and accumulate in indoor dust, as they are not subjected to the same degradation processes that occur outdoors (Maertens et al. 2004). In addition, the prevalence of pesticides and industrial chemicals, which have been banned many years ago, suggests limited indoor degradation and on-going environmental accumulation (Tan et al. 2007).

Hence, indoor dust has been recognized as an important exposure pathway for organic pollutants, acting as a sink for semi- and non-volatile hazardous substances like phthalates, PAHs, pesticides, biocides, or flame-retardants. Inhalation, dermal adsorption and unnoticed ingestion of indoor dust have been recognized as important transport routes for organic contaminants, especially in the case of crawling children exhibiting hand-to-mouth behaviour (Butte and Heinzow 1994; Lewis et al. 1994).

To estimate the total exposure to a given chemical in an indoor environment, its distribution between the gas phase, airborne particles and settled dust compartments must be investigated. If partitioning/sorption is the dominant mechanism of association, then there should be a predictable relationship between the particle concentration of a given organic compound and its dust concentration. The contribution of each of these compartments to indoor phthalate exposure has been estimated by Weschler et al. (2008).

The ubiquitous distribution of many pollutants highlights the fact that we are continuously exposed to low doses of chemicals in the indoor environment. For example, indoor dust collected in office buildings has been found to contain microorganisms, microfungi, endotoxins, allergens, inorganic and metal particles, fibers, including textile and paper fibres, organic compounds, human and animal skin fragments, glass wool, and wood (Molhave et al. 2000). Equilibrium concentrations on dust particles generally far exceed those in the gaseous portion of indoor air.

Therefore, dust and its associated fine particulate matter tend to become a sink for semivolatile organic compounds (SVOCs) (Butte and Heinzow 1994). Calculations suggest that many SVOCs have long indoor persistence, even after their primary sources have been removed. If the only removal mechanism is ventilation, moderately sorbing compounds (with octanol–air partition coefficients (K_{oa}) $> 10^{10}$) may persist indoors for hundreds to thousands of hours, while strongly sorbing compounds ($K_{oa} > 10^{12}$) may persist for years (Weschler and Nazaroff 2008).

Exposure to pollutants in the indoor environment has been associated with numerous adverse health effects, including allergenic and immune effects, asthma and other respiratory effects, cardiovascular and nervous system effects, skin irritation and mucous membranes, cancer and reproductive effects (Maertens et al. 2004). In a very recent study, the impact of environmental exposures through dietary intake, contact, or inhalation of indoor dust on male reproductive health was conducted, providing compelling evidence of altered hormone levels in relation to PBDE exposure, and concluding that house dust is an important source of human PBDE exposure (Meeker et al. 2009). Special attention should be paid when dust is settled on a hot surface, because harmful adsorbed organic compounds may be easily released, increasing the risk of exposure. Ren et al. (2006) demonstrated that PAHs may be emitted from the heated plastic material out of chips in computers when they are running, and be adsorbed on dust deposited on these components.

In summary, the analysis of organic contaminants in house particulate matter and settled dust should be performed in an effort to characterize human exposure in the indoor environment.

2 Sampling

A proper sampling device should fulfil the requirement of providing a representative air sample.

Active enrichment into solid sorbents is by far, the most widely used technique for sampling pollutants in air. In active sampling, a defined volume of air is pumped through an adsorbent tube packed with one or more adsorbents, where the pollutants are retained at a specific and controlled flow-rate. Active devices such as pumps and flow meters are required to force the flow of the sample through the trap, and to measure the sample volume or the flow rate. The adsorbent used for indoor air sampling must be carefully selected. By adding a proper filter into the sampling device, particles can also be collected. Glass fibre filters (Martin et al. 2002; Jahnke et al. 2007; Solbu et al. 2007; Shoeib et al. 2009; Toms et al. 2009), quartz fibre filters (Sasaki et al. 2003; Yoshida et al. 2004; Coscollà et al. 2008; Ramil Criado et al. 2002), or polycarbonate filters (Ormstad 2003) have been used. An interesting example is the collection of some perfluorinated compounds in high-volume environmental air samples enriched on glass-fibre filters (for the particle phase), and polyurethane foam/XAD-2 cartridges (for the gas phase) (Martin et al. 2002). Yoshida et al. have determined a wide range of SVOCs, including plasticizers, flame retardants, insecticides, fungicides and synergists in indoor air using a quartz fibre filter disk and Empore disk (Yoshida et al. 2004). These authors pointed out that a disk-type filter is more advantageous than a tube-type sorbent for determining trace amounts of compounds in air, because it does not restrict the flow rate of the pump. Other authors have described methods for determining organophosphorus compounds using a quartz fibre filter disk followed by an ODS filter disk (Saito et al. 2003; Matsumura et al. 1998).

It is worth to mention the use of membranes to collect actively both vapour phase and particles present in indoor air. Empore C_{18} solid phase extraction (SPE) membranes, able to collect even very fine particles, were used to collect organophosphate esters from different indoor environments (Tollbäck et al. 2006).

In a recent paper, particulate matter samples are collected using another type of high volume sampler; an impactor in which polyurethane foam (PUF) or polypropylene foam are used as the polymer substrates (Sun et al. 2009). To quantitatively extract organic tracer compounds from ambient particulate matter, a protocol of two extractions with isopropanol followed by three extractions with dichloromethane was developed for both substrates precleaning and analyte extraction.

The use of passive air samplers for indoor and workplace air is not as common as active sampling, although nowadays, they are playing an increasing role due to their ideal applicability for long-term on site monitoring providing time weighted average (TWA) estimations. Because of their simplicity, low prize and their ease of use, diffusive sampling devices became very popular the last few years. Nevertheless, their low sampling rates require long sampling times, from days to even several weeks for low concentrations, but their low cost facilitates simultaneous deployment in a large number of locations. The most relevant drawback for this type of sampling is that environmental conditions such as temperature, humidity, wind, and air velocity influence the quantification significantly. A further problem is the accumulation of artefacts. In addition, passive devices sample primarily the gas phase, and are therefore likely to underestimate concentrations of the highest molecular weight compounds like heptabrominated diphenyl ethers, which are preferentially associated with particles (Law et al. 2008).

A new promising passive sampler for TWA estimations is a needle trap device (NTD). The NTD consists of a needle and a sorbent positioned at a distance from the tip of the needle, and immobilized by a small quantity of epoxy glue. Samples are collected by drawing air across the NTD with a Luertip syringe. Particulates are trapped on the needle packing. The devices are introduced into a GC/MS injector for 5 min desorption. To aid the introduction of desorbed analytes, 10 μL of clean air are delivered by a gas-tight syringe. The needle trap technique has been shown to be convenient and useful for sampling and analyzing particulate matter (Koziel et al. 2001), although NTDs have been mostly tested to sample and determine VOCs (Eom et al. 2008; Demeestere et al. 2007).

Plants are typically "green" air samplers of natural environmental materials, and hence, they can also be used as passive biosorbent materials to retain semivolatile compounds. It was found that spruce needles can complement solid-phase membrane devices (SPMDs) in passive air sampling of PAHs, because the needles tend to uptake more of particle-bound PAHs in comparison to the SPMDs, which mainly sequester PAHs associated with the vapour phase (Zhu et al. 2008). In the light of using biomaterial as sorbents of pollutants for environmental biomonitoring, tree bark has been used as a passive sampling medium for atmospheric POPs (Meredith and Hites 1987; Hermanson and Hites 1990), playing an important role in identifying source/sink regions. This biological sampling medium has unique features, as it simultaneously accumulates both gas-phase and particle-phase POPs from the surrounding air, it can reflect time-integrated overall air pollution levels and conveniently reveals the history of air pollution by the so-called “tree-bark pocket” (Zhao et al. 2008).

A tapered element oscillating microbalance (TEOM) was extensively used for continuous real-time measurement of airborne particles by federal and state agencies. The TEOM measures the mass collected on an exchangeable filter cartridge situated at the end of the oscillating tapered element. As more mass is collected on the filter, the frequency of oscillation changes, so a direct relationship can be established between the change in frequency and the mass on the filter. Dust concentration is estimated as the ratio of the mass on the filter to the sampling air flow rate. This analyzer was used to determine 50 VOCs, including 5 hazard air pollutants (HAPs) associated with swine barn TSP, PM_{10}, $PM_{2.5}$ and PM_1 (Cai et al. 2006). It was found that a significant fraction of swine odour can be carried by particulate matter, and that the majority of VOCs and characteristic swine odorants were preferentially bound to smaller-size particulate matter.

An Inertial Spectrometer (Inspec) with membrane filters can also be used to collect different particle sizes on different locations of a filter (Molhave et al. 2000). In a study for the characterization of the indoor environment in a dental office, workday (6–8 h) integrated $PM_{2.5}$ samples were collected using a size-selective impactor (model 200″), and treated (hydrophobic) polyester membrane filters at a calibrated flow rate of 10 L min^{-1}. Filters were weighed before and after sampling using an appropriate conditioned electrobalance (Godwin et al. 2003).

To study the potential health effects of pollutants in crowded spaces for recreational activities, particle mass versus size distribution of an ambient aerosol have been measured using a 10-stage Quartz Crystal Microbalance cascade impactor system (Junker et al. 2000). This impactor system consists of a series of 10 aerodynamic inertial impactors capturing particles at a mid-point cut-off ranging from 0.07 to 35 mm, arranged in a cascade with jets, which segregate the larger aerosol particles on top.

In a study of the impact of printers as emission sources of VOCs, ozone and particulate matter on indoor air quality, ultrafine particles have been measured using Scanning Mobility Particle Spectrometer-Condensation Particle Counter (SMPS-CPC) (Kagia et al. 2007). SMPS distributes from 20 to 500 nm diameter particles and CPC counts ultrafine particles.

Cascade impactors have been used to collect e.g. perfluorinated octane sulfonate (PFOS) and perfluorinated octanoic carboxylic acid (PFOA) on particles by particle size distribution (Harada et al. 2006).

Glass electrostatic precipitators can also be utilized to collect particles. A photoelectric aerosol sensor was also used to determine the concentration of particle bound PAHs with the method of photoelectric charging of particles. Precipitators have been used as well e.g. to collect particles in swine barns (Shirey et al. 1998).

When assessing exposure to allergens and toxins, liquid impingement, where bioaerosols are directly collected into a liquid, is widely used. BioSampler, was designed to collect inhalable airborne particles while minimizing the problems associated with the AGI-30 impinger, and has a collection efficiency close to 90% when particles ≥ 0.5 μm are sampled. Biosampler collects bioaerosols through both impaction and centrifugation forces at a flow rate of 12.5 L min^{-1}.

In a very recent study, electrostatic collection was compared to liquid impinging methods to sample airborne house dust allergens, endotoxins and (1,3)-*β*-D-glucans (Yao et al. 2009). An electrostatic sampler, made of a plastic body and two copper sheets connected to high voltage supply was built. The air stream is drawn into the sampler by means of an external pump. Target compounds are subjected to an electrostatic field inside the sampler, and those negatively charged are deposited into walls. Compounds not charged exited the sampler without being collected. Results indicated that the concentrations of airborne allergens and toxins obtained by the electrostatic sampler were significantly higher than those obtained by Biosampler.

Regarding dust, some passive and active dust sampling techniques are available. Passive sampling techniques may involve setting out stationary "dust fall" jars or non-electrostatic plates, and simply let dust accumulate for a given period of time. Active sampling techniques include press sampling, sweeping, and vacuuming (Mannino and Orecchio 2008).

The most common method to collect dust is, by far, from conventional vacuum cleaners equipped with paper bags (Toms et al. 2009; Maertens et al. 2004; Molhave et al. 2000; Starr et al. 2008; Sjödin et al. 2008; Hwang et al. 2008; Canosa et al. 2007; Shoeib et al. 2005). The content of bags is passed through a suitable sieve (generally ~2 mm mesh size) to remove large pieces and obtain a high degree of homogeneity. A multistage filtering in the exhaust system of the vacuum cleaner can be added to avoid smaller particles passing through the cleaner, which may cause the (re)contamination of the air and surfaces at a site (Toms et al. 2009). Another sampler can be homemade using a vacuum cleaner and a crevice tool attachment (Allen et al. 2008; Stapleton et al. 2008). The dust is collected in a cellulose extraction thimble inserted between the crevice tool and the vacuum tube extender and secured using a rubber o-ring. Finally, between sample collections the equipment is carefully cleaned to avoid cross contamination between different samples. Although is not very common, lint e.g. from clothes dryer filters can also be collected (Schecter et al. 2009). Once the sample is collected, it has to be conveniently placed in a clean bag for shipping to the laboratory where it is going to be analyzed. Some comprehensive reviews on dust sampling techniques provide an overview to date (Butte and Heinzow 1994; Roberts and Dickey 1995; Lioy et al. 2002; Roberts et al. 1992).

From a scientific point of view, there is a great need to harmonize and standardize methods to make them more suitable for large-scale studies. For this reason, some standard methods have been developed. ASTM D5438 provides a method to collect particles greater than 5 μm using several cyclones, providing for the efficient capture of SVOCs associated with the dust (ASTM 2002). The test system can be fitted with special canisters downstream of the cyclone for the capture of specific SVOCs that may volatilize from the dust particles during collection. Part 8 of Guideline VDI 4300 describes the different sampling methods for sampling house dust such as wiping, vacuuming with flat filter systems, and vacuuming with commercial vacuum cleaners (VDI 2001). Restriction to a single method is not possible, the sampling must be optimized to the particular problem. In addition, operating instructions for sampling house dust are given in order to allow the highest possible reproducibility of the measurement data obtained for the sampling method specified in measurement planning. The guideline also distinguishes between "old dust" (of unknown age), and "new dust" (generally 1–2-week-old).

3 Sample Treatment

To extract the collected compounds, solvent extraction is usually employed. It is advantageous for relatively high boiling point or thermolabile analytes; it allows versatility for solvent selection, as well as successive analysis of the same sample. It does not need additional equipment, either. On the contrary, solvent extraction commonly requires the use of high solvent volumes, which in turn leads to time-consuming sample concentration and purification steps. Solvent extraction has been widely used to desorb pollutants from collected particulate matter (Martin et al. 2002; Razote et al. 2004; Fischer et al. 2000), or dust (Das et al. 2004), replacing more conventional techniques as Soxhlet extraction. However, this long and tedious technique is still in use nowadays, mainly as a reference method or in laboratories that do not perform method development, because the required instrumentation is very cheap, and it is available at any laboratory. For example, this technique has been used to extract PAHs from indoor dust matter to study their distribution and sources (Mannino and Orecchio 2008). Extractions were performed with a dichloromethane-pentane solvent mixture for 24 h. Then, the extracts were filtered through a Pasteur pipette filled with anhydrous sodium sulphate, previously rinsed with dichloromethane and concentrated in a rotary evaporator to get a final volume of 2 mL. Other examples are the papers by Shoeib et al. (2005, 2009), where perfluorinated alkylated substances (PFAS) and PBDE concentrations, as well as their occurrence, phase partitioning, and human exposure are investigated in indoor and outdoor air. Glass fibre filters and dust samples were Soxhlet extracted for 24 h using dichloromethane. In a very recent paper, Takigami et al. (2009) extracted brominated flame retardants, brominated dibenzo-p-dioxins/furans, organophosphate flame retardants and plasticizers in indoor dust of a hotel in Japan by Soxhlet using acetone for >6 h, and toluene for >16 h. In addition, chlordanes, DDTs, pyrethroids, phthalates, polychlorinated biphenyls (PCBs) and PBDEs were Soxhlet extracted from indoor dust with dichloromethane (Hwang et al. 2008).

Many procedures report the contribution of ultrasounds or microwaves to quantitatively extract the trapped compounds. For example, a low temperature microwave-assisted extraction method (MAE) was reported to determine PAHs in airborne particulate matter (Karthikeyan et al. 2006). The procedure requires a

20 mL mixture of acetone:n-hexane (1:1) and an extraction time of 20 min with no need of a clean-up step of the obtained extracts. The sum of indoor particulate-bound PAHs ranged from 27.6 to 75.7 ng m^{-3}. MAE was also employed to extract organophosphate flame retardants from indoor dust samples (García et al. 2007). In this case, the acetone extracts had to be subjected to exhaustive clean-up on a reversed-phase sorbent (OASIS), followed by purification using silica gel. Polychlorobenzenes, nitromusks and pyrethroids were recently extracted from house indoor dust by means of MAE followed by a single dispersive solid-phase clean-up step, avoiding other more complex multistep cleanup procedures (Regueiro et al. 2007). The use of an aqueous phase to promote microwave heating in combination with a non-polar organic solvent (*n*-hexane) allows achieving an efficient extraction while reducing the chromatographic background. The combination of MAE with an on-batch extract clean-up step, consisting on the addition of Florisil, subsequently shaking for 2 min, and filtration, allows increasing the throughput of the analysis while decreasing sample manipulation.

Pressurized liquid extraction (PLE) or accelerated solvent extraction (ASE) can be used e.g. to desorb PFOS bound to airborne particles collected on a quartz fibre filter (Sasaki et al. 2003). Nine pesticides were extracted from PM$_{2.5}$ by a rapid PLE procedure using acetone (Coscollà et al. 2008). Regarding indoor dust, different solvents have been chosen for PLE extraction of several compounds such as parabens and triclosan (Canosa et al. 2007), PCBs (Harrad et al. 2009), PAHs (Naspinski et al. 2008), PBDEs (Toms et al. 2009; Sjödin et al. 2008; Stapleton et al. 2008), and hexabromocyclododecanes (HBCDs) (Harrad et al. 2009).

Matrix solid-phase dispersion (MSPD) integrates extraction and clean-up in a single step, and greatly speeds-up sample throughput. It has also been proposed for the isolation of several organophosphate esters, mainly flame retardants and plasticizers in indoor dust samples (García et al. 2007).

The use of ultrasounds to aid the extraction is another possibility. Phthalates (Abb et al. 2009) and perfluorinated alkanoic acid (PFA) (Kato et al. 2009) determinations have been reported. Ethyl acetate (phthalates) or formic acid with methanol (perfluoroalkyl chemicals) was added to the dust sample, and extraction was performed in an ultrasonic bath at room temperature for 10 min. In the case of phthalates an enrichment step was not carried out to avoid the risk of contamination. Pyrethroids and their metabolites can also been extracted from indoor dust samples by adding methylene chloride followed by sonication for 10 min (Starr et al. 2008). Another option is the combination of Soxhlet extraction with an ultrasonic treatment (Schecter et al. 2009).

When a solvent extraction technique is used to desorb organic compounds, a further clean-up step of extracts, particularly for complex matrixes such as dust, must be usually performed. Thus, the extract is forced to pass through a SPE cartridge as C$_{18}$ (Starr et al. 2008), Florisil (Stapleton et al. 2008; Harrad et al. 2009), alumina (Hwang et al. 2008), silica (Harrad et al. 2009), silica and alumina (Gevao et al. 2006; Tan et al. 2007), or it can be filtrated through an appropriate filter like GHP (Coscollà et al. 2008). In certain cases, the extract is maintained in contact with sulphuric acid, and a subsequent centrifugation stage is carried out

(Sjödin et al. 2008; Harrad et al. 2009). Sample preparation prior to analysis generally implies a volume reduction, e.g. using a gentle stream of nitrogen, and the addition of an internal standard, which must be carefully selected taking into account the analytes of interest.

In addition to solvent extraction techniques, thermal desorption is an alternative, allowing compounds to be quantitatively transferred to the measuring equipment, usually a gas chromatograph, and leading to lower detection limits. Since it is solvent-free, it prevents overlapping of the analyte peaks with the solvent or solvent impurities peaks. Nevertheless, this technique only allows performing a single analysis by sample, and a focusing system to avoid the enlargement of the chromatographic band is much recommended. In addition to these drawbacks, many of the compounds under consideration are semivolatile, with relatively high boiling points, and thermally degradable, such as PBDEs. Thus, thermal desorption has been less used in the analysis of emerging pollutants in air and particulate matter. As an example of application, several VOCs have been thermally desorbed from house dust at 150°C for 4 min in a glass tube (Nilsson et al. 2005); then, the desorbed compounds were collected onto a solid-phase microextraction (SPME) fiber in an unheated zone assisted by a 1 mL min^{-1} nitrogen flow. This method eliminates the need for desorption onto an adsorbent, which in turn has to be desorbed before the analytes can be analyzed. Solid-phase microextraction can also be used as a sample preparation step. Interesting are the applications to extract atmospheric urban PAHs from Teflon-coated glass fibres and PM_{10} filters (Vaz 2003), atmospheric particulate matter from glass fibre filters (Odabasi et al. 2005), or swine barn particulate matter collected into TEOM or glass fibre filters (Cai et al. 2006; Razote et al. 2004).

4 Determination Techniques

Determination of contaminants in air is usually performed by gas chromatography (GC) using conventional capillary columns (30 m × 0.25 mm I.D., 0.25 μm film thickness) with common stationary phases, such as 5% phenyl substituted methylpolysiloxane and dimethylpolysiloxane. Mass spectrometry (MS) is the most extended detection technique and it is commonly operated in the electron impact (EI) mode either in the full scan mode or in the selected ion monitoring (SIM) mode. Used together with suitable preconcentration techniques, SIM mode allows achieving lower limits of detection (LODs). As an example, chlordanes, DDTs, pyrethroids, phthalates, PCBs, and PBDEs were analyzed in indoor dust samples by GC/MS, operating in the EI and SIM mode (Hwang et al. 2008). The negative chemical ionization mode (NCI) provides a very high sensitivity and selectivity for brominated compounds, mainly when the most abundant fragment, Br^- ($m/z = 79/81$) is selected. It has been used to analyze PBDEs in house dust (Toms et al. 2009). LODs and selectivity can also be improved in the tandem MS mode (MS–MS).

High resolution gas chromatography–high resolution mass spectrometry (HRGC/HRMS) also allows improving LODs. An example is PBDE determination in air, dust, and clothes dryer lint samples using this technique (Toms et al. 2009; Schecter et al. 2009). When ^{13}C-labeled internal standards are added, analysis can be carried out by the isotope dilution technique. For example, PBDEs were analyzed in house indoor dust of different countries by GC/isotope dilution-HRMS (Sjödin et al. 2008). When volatiles are analyzed, another possibility is to use multidimensional GC/MS-olfactometry in a system equipped with a non-polar precolumn and polar column in series. This system was used to determine VOCs from swine barn particulate matter (Cai et al. 2006).

Many emerging pollutants in air possess one or more halogenated atoms in their structure, which makes electron capture detection (ECD) selective and sensitive enough to analyze them. This is the case of PCBs (Ramil Criado et al. 2002), brominated flame retardants, pesticides, and nitromusks (Regueiro et al. 2009). Other detection techniques, such as nitrogen-phosphorus (NPD) or atomic emission detection (AED) are compatible with several groups of chemicals that can be found indoors, such as organophosphate flame retardants (García et al. 2007a, b).

Although it is not common in air monitoring, in some scarce cases, determinations can be carried out by spectrometric analysis. A combination of GC with UV spectrometry was proposed by Nilsson et al. (2005) to determine VOCs in house dust, using a diode array UV spectrophotometer. Altogether, 28 compounds were quantified in each sample, finding the highest concentrations for saturated aldehydes, furfuryl alcohol, BHT, 2-furaldehyde, and benzaldehyde.

Liquid chromatography is the determination technique generally selected for more polar compounds. When coupled with MS, selectivity can be noticeably improved. As an example, semi-volatile organophosphate esters have been analyzed by high-pressure liquid chromatography (HPLC)-MS (Tollbäck et al. 2006). The determination of pesticides in airborne fine particulate matter (Coscollà et al. 2008) or PFA chemicals in indoor dust (Kato et al. 2009) are some recent applications of HPLC–MS–MS. Hexabromocyclododecanes (Abdallah et al. 2008) or phthalates (Abb et al. 2009) have been determined in indoor dust using the same technique. It is also worth mentioning the case of carbonyl analysis. HPLC–UV is the most common method for the analysis of these compounds, even though the disadvantages of the UV detector such as its low resolution between carbonyls with similar properties and the difficulty to identify unknown compounds. HPLC–MS–MS can solve some co-elution problems, and greatly improves LODs, particularly for higher molecular weight compounds.

Although it is out of the scope of this chapter, it is worth mentioning that microanalysis of particles can be carried out too, e.g. using a transmission electron microscope (TEM) coupled to an energy dispersive X-ray spectrometer (Ormstad 2003). Scanning electron microscopy (SEM) can also be employed for particle identification and for the determination of sample size distribution (Molhave et al. 2000).

Regarding house dust allergens, endotoxin and (1,3)-β-D-glucans, they can be analyzed using the enzyme-linked immunosorbent assay (ELISA) method (Yao et al. 2009).

5 Method Quality Evaluation

Method performance in air analysis involves terms such as accuracy, storage stability, capacity, sampling rate, recovery, and sensitivity. To evaluate the performance of a developed method, certified reference materials for particulate matter, such as urban dust SRM 1649a particulate matter from NIST (Gaithersburg, MD, USA) can be purchased. In addition, a standard reference material has been recently developed for the determination of organic compounds in house dust; the SRM 2585 is intended for using in method validation for the analysis of PAHs, PCBs, chlorinated pesticides, and PBDEs (Poster et al. 2007).

Analysis of blank samples over a period of time can give an indication of whether the sampling medium contributes with artefacts or interferences to the analysis. Blanks of the sampling device or instrumental blanks of the determination system must be periodically run and checked to control interferences and/or contamination. In the case of dust, field blanks can be prepared using sodium sulphate powder as a surrogate for dust, and collected with the same procedure used for real samples (Stapleton et al. 2008). For example, the powder can be introduced into the bag of the vacuum cleaner, and then let it run for a while. The ubiquity of certain pollutants such as phthalates or synthetic musks, among others, constitutes a severe problem of contamination of the whole analytical system and hence, special attention should be paid to control the blank levels throughout the analysis. Analysing phthalates always bears the risk of lab- and cross-contamination. For that reason, during the extraction and analysis, particulate matter and dust samples should not come in contact with plastic materials, and unnecessary manipulation of the samples should be avoided.

As it was commented in the sampling section of this chapter, it is important to know the storage stability of the target analytes in the medium used for their collection. If analytes are decomposed into the device used for their collection during the sampling step or if some losses occur before being analyzed, the recovery of the compounds will decrease, leading to non-quantitative recoveries. Obviously, this is particularly important in the case of samples that must be collected far away from the laboratory where the analysis will be carried out. In addition, it must be considered that compounds strongly retained may not be further extracted quantitatively. Thus, this concept is deeply related to the recovery of the analyte from the medium, which is a quality parameter that must be determined. In general, and in order to avoid losses, storage at low temperatures, such as refrigeration at 4°C or even freezing, is much more preferable. For compounds that can be photodegraded, sample protection from sunlight using light-tight envelopes such as aluminium foil or amber vials are recommended.

Harrad et al. (2009) investigated the decomposition of HBCDs stored in a well homogenised indoor dust sample at different conditions: exposed to natural light, and kept in the dark. Calculated half-lives ($t_{1/2}$) showed that HBCD concentrations decay faster in light-exposed samples ($t_{1/2} = 12$ weeks), than in light-shielded dust ($t_{1/2} = 26$ weeks).

Recovery is another quality parameter that should be calculated and applied for correction of measurement results (recovery factor). It is defined as the recovered fraction of an analyte placed in or on a sampler, and it is calculated by dividing the amount recovered from a sampler by the amount of analyte fortified in or onto the sampler. The recovery of the analyte from the sampler should be $\geq 75\%$. Reanalysis of the samples on the day after initial analysis indicates if immediate analysis after sample preparation is required. Often when processing a large number of samples, it may be necessary to prepare the samples for analysis as a batch. In these instances, the last samples may not be analyzed for up to 24 h or more after preparation because of the time required for analysis. If samples prepared for analysis exhibit time dependent stability after desorption, analyses must be conducted within acceptable time constraints. Analysis and reanalysis results should agree within 5% of each other (Kennedy et al. 1995). The presence of particulate matter in air samples leads to more complex analyte distributions and increases the risk of inefficient recoveries. Thus, particulate matter may adversely affect the extraction efficiency in the desorption step (Tollbäck et al. 2006). Furthermore, it has to be taken into account that certain compounds cannot be sufficiently collected because they are decomposed by daylight during air sampling even in an indoor environment, obtaining very low recoveries and collection efficiencies (Strömvall and Petersson 1992; Zanella et al. 1999; Pellizzari and Krost 1984). Nevertheless, excessive recovery rates of even up to 150% can be sometimes obtained. This situation can be found when a high-level blank is monitored, or when interferences co-elute at the same retention time. Besides, very high recoveries can be encountered by the matrix enhancement effect, more precisely described as matrix-induced chromatographic response enhancement. It is explained by the blocking of active sites in the injection port due to sample matrix, resulting in reduced analyte losses during injection and higher response values of the measured components. Elflein et al. have overcome this problem using matrix-matched calibration when sampling household insecticides with a glass fibre filter and two PUF plugs.

To evaluate the linearity of the method, fortification of samples is feasible. Therefore, a viable solution is direct spiking of standard mixtures of the target compounds in an appropriate solvent on the sample. Then, the spike is left to homogenize with the sample, in suitable conditions depending on the tested compounds, e.g. at low temperatures for several hours.

Repeatability and reproducibility should also be estimated. IUPAC gold book defines repeatability as the closeness of agreement between independent results obtained with the same method on identical test material, under the same conditions (operator, apparatus, laboratory and after short intervals of time), and reproducibility as the closeness of agreement under different conditions (operators, apparatus, laboratories and/or after different intervals of time) (IUPAC 2009). Both are usually reported as a relative standard deviation or as a variation coefficient.

Sensitivity of the analytical method should also be determined by calculating LODs and limits of quantification (LOQs). LOD is the lowest mass that can be detected. It is defined as the mass of an analyte, which gives a mean signal $3\sigma_b$ above the mean blank signal, where σ_b is the standard deviation of the blank signal. LOQ is the lowest mass that can be quantified; this is that can be reported with acceptable precision. It is the largest of the mass corresponding to the mean blank signal + 10 σ_b, or the mass above which recovery is $\geq 75\%$ (Kennedy et al. 1995). LOD and LOQ can be determined as the concentration when signal to noise ratio (S/N) is 3 or 10, respectively.

Validation of the trueness of innovative methods for determining contaminant concentrations, such as mathematical models or new instruments, against measurements made with a reference method is essential. However, failure to consider the monitoring time necessary to characterize time-varying concentrations by reference methods may lead to differences between the reference concentration and the concentration estimated by the method being tested. Lee et al. (2008) developed a method to asses the minimum monitoring time required to estimate the mean concentration of an airborne contaminant in an enclosed space within a specified degree of precision, showing that monitoring time requirements substantially vary with location within a room and depend on airflow rates, which cause variation in airflow patterns and thus, in concentration.

6 Pesticides

Over the last decades, several hundreds of pesticides have been marketed for intensive farming and domestic use. The widespread use of these compounds has resulted in contamination of environmental compartments, such as surface water, groundwater, soil, and air (Tariq et al. 2004; Fernandez-Alvarez et al. 2008; Xue et al. 2005; Harner et al. 2005). Studies focussing on the assessment of pesticide exposure and on the adverse effects of pesticides on both human health and the environment are a matter of a growing scientific and public concern (Dorr et al. 2007; Ritter et al. 2006).

Pesticides are SVOCs that are known to be simultaneously present in the atmosphere both the gas and particulate phase. The distribution among these phases depends on the physico-chemical properties of the compound in question, such as vapour pressure and water solubility. It is also influenced by environmental factors, especially temperature, humidity, and the nature and concentration of suspended particulate matter (Coscollà et al. 2008). A comprehensive review, which summarizes sampling and analysis of pesticides in ambient air has been recently published by the same research group (Yusà et al. 2009).

Organophosphorus pesticides have been the insecticides most commonly used by professional pest control bodies and homeowners for the past three decades (Jeannot and Dagnac 2006). Nevertheless, the decision of the US Environmental Protection Agency (EPA) to phase out certain uses of the organophosphate insecticides because of their potentially toxic effects to humans has led to their gradual replacement by other pesticides. Among them, synthetic pyrethroids have been manufactured since 1950's based upon the structure of natural pyrethrins, which are chemicals with active insecticidal properties in the pyrethrum extract (a mixture of chemicals found in certain chrysanthemum flowers). Pyrethrins are very unstable in the environment, due to oxidation and UV-radiation.

Pyrethroids are widely applied as insecticides in households and greenhouses as well as for the protection of crops. Their advantageous properties like their non-persistence in the environment (most are degraded rapidly by sunlight or other compounds found in the atmosphere), excellent insecticidal activity against a wide range of insect pests, low dose of application needed and relatively low mammalian toxicity, have dramatically increased their use in recent years (ATSDR 2003; WHO 1986–1992). Therefore, they are effective substitutes of some traditional insecticides (e.g. organochlorine or organophosphate compounds) that are strongly or partially restricted by countries regulations. Nevertheless, laboratory tests showed that pyrethroids are toxic for fish, aquatic arthropods and honey-bees (Clark et al. 1989; Cotas et al. 1989).

Pyrethroids available today include allethrin, phenothrin, tetramethrin and cyphenothrin, usually for household insects control, and cypermethrin, deltamethrin, permethrin, γ-cyhalothrin and cyfluthrin, mainly for agricultural insects. Pyrethroids are often commercially combined with synergist compounds like piperonyl butoxide, which enhance their insecticidal activity, or mixed with fungicides such as 2-phenylphenol or other pesticides like propoxur (a carbamate pesticide).

Inhalation is an important route of exposure to pesticides, especially after spraying application indoors, and also for people living in agricultural areas. OSHA established the occupational exposure limit for an 8-h workday, 40-h workweek at 5 mg of pyrethrins and pyrethroids per cubic meter of workplace air ($5\ \mathrm{mg\ m^{-3}}$).

Common household pesticide levels are generally higher indoors, and are also present in dust and particulate matter. Several analytical procedures for the determination of pesticides in suspended particulate matter and dust are reported in Tables 1 and 2, respectively.

Rudel et al. (2003) identified endocrine disrupting compounds, including phthalates, alkylphenols, pesticides, and PBDEs, among other compounds, in dust samples obtained from 120 homes. In this study, 27 pesticides were detected in dust, the most abundant being permethrins and the synergist piperonyl butoxide. The 90th percentile concentrations for these pesticides ranged from 1.7 to $17\ \mu\mathrm{g\ g^{-1}}$ in dust. The prevalence indoors of pesticides that have been banned or restricted for many years, such as DDT, chlordane, heptachlor, methoxychlor, dieldrin and pentachlorophenol, suggests that degradation is negligible indoors.

Table 1 Analytical procedures for the determination of pesticides in air suspended particulate matter

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Permethrin and fenvalerate	Millipore filter (1–2 L min^{-1}, 60 min)	Solvent extraction with acetone	Partition between hexane and water	GC/ECD	1 µg m^{-3} (1–2 L min^{-1}, 60 min)	Kolmodin-Hedman et al. (1982)
Insecticides: pyrethrins, pyrethroids and a synergist	GFF (10 m^3, 3 m^3 h^{-1}). Also, an impactor was used.	Sonication with 10 mL ethyl acetate (×3)	Filtration through silanized glass wool and concentration to 1 mL by rotary evaporation	GC/ECD, GC/FID, HPLC/UV	0.5–250 ng m^{-3} (10 m^3)	Berger-Preiss et al. (1997)
Permethrin	GFF (2 L min^{-1}, 6 h)	Solvent extraction with 3 mL methanol	Dilution with phosphate buffer (1:20) for ELISA-optical detection	LC, ELISA-optical detection	2 ng mL^{-1} (ELISA), 300 ng mL^{-1} (LC)	Oepkemeier et al. (1999)
Pyrethroids	Pallflex filter (10 m^3, 2.6–3 m^3)	Sonication with 10 mL ethyl acetate (×3)	Filtration through sylanized glass wool and concentration to 1 mL by rotary evaporation	GC/EI-MS	1.0–3.0 ng m^{-3}	Leng et al. (2005), Berger-Preiss et al. (2002)

Table 1 (continued)

Analytes	Sampling	Desorption/ extraction	Extract treatment	Determination	LOD	References
Chlordanes	QFF (10 L min^{-1}, 29 m^3)	Addition of surrogate. Sonication with 25 mL dichloromethane (35 min, ×2)	Concentration with rotary evaporation and nitrogen. Clean-up on microcolumns of silicic acid followed by rinsing with 2 mL hexane-dichloromethane (9:1), concentration (nitrogen), addition of internal standard and concentration to 0.01 mL	GC/MS (SIM)	0.032–0.146 ng	Offenberg et al. (2004)
Pesticides	QFF (760 m^3, 30 m^3 h^{-1})	PLE with acetone. Purge of extracted analytes with pressurized nitrogen (125–150 psi, 1 min)	Concentration under nitrogen (40°C), redissolution in methanol and filtration (0.22 µm)	LC/MS/MS	LOQ = 6.5 pg m^3	Coscollà et al. (2008)

Table 2 Analytical procedures for the determination of pesticides in indoor dust

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Pesticides	Dust collected using a vacuum cleaner and homogenizated in a food processor	Solvent extraction with 5 mL acetone by shaking, 45 min	Filtration through a funnel containing glass wool and concentration to 1 mL (nitrogen). Addition of internal standard	GC/CI (with isobutene)-MS	25–100 ng g^{-1}	Roinestad et al. (1993)
Organophosphorous pesticides	HSV3 sampler (cyclone-equipped vacuum sampler, which collects small particles in a Teflon catch bottle, 5 g). Particles sieved through a 150-µm stainless steel mesh	Sonication with 50 mL acetone, 1 min	Concentration (nitrogen), solvent exchange into cyclohexane, filtration through PTFE membrane filters, GPC, and elution with cyclohexane. Concentration with Kuderna-Danish and final concentration to 2 mL (nitrogen)	GC/MS	LOQ = 11–40 ng g^{-1}	Simcox et al. (1995)
Insecticides, herbicides, fungicide	HVS3 vacuum cleaner (high volume small surface sampler, 4–180 g), sieving to a size fraction <53 µm, and resuspension using a fluidized bed generator	Addition of *p*-terphenyl-d_{14}. Soxhlet with diethyl ether in hexane (6%, 16–18 h)	Concentration to 20 mL by rotary evaporation (40°C, nitrogen)	GC/MS (SIM)	NR	Mukerjee et al. (1997)

Table 2 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Pyrethrins, pyrethroids	Dust collected using a modified vacuum cleaner where the usual dust bag was replaced by a Soxhlet filter tube	Soxhlet with 250 mL ethyl acetate, 15 h	Concentration, clean-up on a silica gel mini-column. Elution with 12 mL dichloromethane–hexane 20:80 for 2 pyrethroids, elution with 13 mL ethyl acetate–hexane 15:85, solvent exchange to acetonitrile (HPLC) or ethyl acetate (GC)	GC/ECD, GC/FID, HPLC/UV	LOQ = 0.05–0.5 μg g^{-1}	Berger-Preiss et al. (1997)
Permethrin, cyfluthrin	Dust collected with a vacuum cleaner (10–770 g) and sieved into two fractions; a fine fraction (<2 mm) and a coarse fraction (>2 mm)	Soxhlet with ethyl acetate, 15 h	Concentration, solvent exchange into hexane, clean-up with silica gel and elution with dichloromethane–hexane 30:70. Solvent exchange to ethyl acetate	GC/EI-MS	0.5 μg g^{-1}	Berger-Preiss et al. (2002)
Pesticides	Vacuum cleaner modified to collect dust into a cellulose extraction thimble (45–90 min, 4 g/sample)	Addition of a surrogate (*p*-terphenyl-d_{14}) and/or matrix spike solutions in hexane. Equilibration for 30 min, and Soxhlet with 6% diethyl ether in hexane, 16 h	Concentration to 10 mL, clean-up in a Florisil column, elution with 20 mL acetone–hexane (10%), concentration and elution with 2 mL diethyl ether–hexane (10%)	GC/MS (SIM)	0.2–1 μg g^{-1}	Rudel et al. (2003)

(continued)

Table 2 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Organophosphorous pesticides	Hi-vol surface sampler HVS3 with a Teflon catch bottle, sieving through a 150-µm stainless steel mesh	Sonication with 50 mL acetone, 1 min	Concentration, solvent exchange into cyclohexane, filtration through PTFE membrane filters, GPC, and elution with cyclohexane. Final concentration to 2 mL	GC/MS (SIM)	0.18–0.56 $\mu g\ g^{-1}$	Lu et al. (2004)
Pyrethroids	Dust collected using a modified vacuum cleaner where the usual dust bag was replaced by a Soxhlet filter tube	Soxhlet with ethyl acetate, 15 h	Concentration, solvent exchange into hexane, clean-up with silica gel and elution with dichloromethane–hexane 30:70. Solvent exchange to ethyl acetate	GC/EI-MS	0.5 $\mu g\ g^{-1}$	Leng et al. (2005)
Biocides	Manual wiping with Soxhlet-extracted paper towels (20 h toluene and 20 h acetone). Also, collection in a cleaned glass vial using metallic spoons.	Soxhlet or Sonication with acetone–hexane 50:50	NR	GC/ECD, GC/MS	LOQ $< 1\ \mu g\ g^{-1}$	Schieweck et al. (2007)

Table 2 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Pentachlorophenol, bisphenol-A, nonylphenol	HVS3 vacuum sampler	ASE with acetone	Concentration, addition of internal standard (dicamba-d_3), followed by methylation or silylation. Clean-up by SPE with Florisil and final concentration	GC/MS	2.0 ng g^{-1}	Wilson et al. (2007)
PCBs, pesticides	Dust collected from filters of air conditioning units or the blades of ceiling fan using a small pair of steel tweezers rinsed with *n*-hexane	Addition of internal standard (0.2 g dust), MAE with 25 mL *n*-hexane–dichloromethane (1:1) in the presence of sodium sulfate (2 g)	Acid silica gel column, elution with 100 mL *n*-hexane and subsequently with 50 mL *n*-hexane–dichloromethane (2:3). GPC packed with Biobeads (6 g) per column using *n*-hexane–dichloromethane (1:1) as a mobile phase. Concentration to 0.5 mL (nitrogen). Further concentration to 25 µL after addition of internal standard.	GC/MS/EI (SIM)	0.2–1.0 ng mL^{-1} (on column)	Tan et al. (2007)
Chlordanes, DDTs, pyrethroids, phthalates, PBDEs, PCBs	Dust from vacuum cleaners passed through a 100 µm metal screen	Soxhlet with dichloromethane, 8 h previous addition of surrogate (PCB 103, d_{10}-permethrin)	Concentration to 2 mL of hexane, clean-up with deactivated alumina, alution with dichloromethane–pentane (1:1), concentration to 1 mL hexane and addition of internal standard (PCB 140)	GC/MS	NR	Hwang et al. (2008)

This observation is further supported by the abundance of DDT in dust relative to its degradation product 1,1-dichloro-2,2-bis(*p*-dichlorodiphenyl)ethylene (DDE).

Leng et al. (2005) found positive correlations between pyrethroids in house dust and in airborne particles, especially one day after pest control operation. Concentrations of pyrethroids in indoor suspended particulate matter and household dust were also measured over a period of 25 months in an experiment simulating indoor pest control (Berger-Preiss et al. 1997). House dust was collected using a modified vacuum cleaner, where the usual dust bag was replaced by Soxhlet filter tubes, which were preferred as they allowed a quantitative transfer of the particles into de Soxhlet extractor. Moreover, it was found that the Soxhlet filter tubes retained (90%) smaller particles better than the usual dust bags (30%). Initial concentrations of deltamethrin and permethrin were 150–800 and 50 μg g^{-1}, depending on the commercial formulation applied. The concentration levels of both compounds decreased by a factor of about 10 within the first 12 months, but remained practically constant the following year.

Children of agricultural families are likely to be exposed to agricultural chemicals, even it they are not involved in farm activities. This can be concluded from a study involving household dust analysis in 59 residences (Simcox et al. 1995), in which dust concentrations for organophosphorous pesticides were significantly lower in reference homes (up to 820 ng g^{-1}) when compared to farmer homes (up to 17100 ng g^{-1}). A statistical comparison indicated that agricultural families had significantly higher concentrations of azinphosmethyl, chlorpyrifos, and parathion. In addition, Lu et al. (2004) estimated organophosphorus exposures of preschool children in agricultural and non-agricultural areas. Detectable levels of diazinon and azinphosmethyl in house dust were found in most of the agricultural homes, whereas only diazinon was found in the metropolitan homes in the summer.

Schieweck et al. (2007) analyzed biocides in dust samples in different rooms of a museum. A distinction between old and fresh dust was made. While the age of old dust is unknown, fresh dust was defined as dust whose age is determined by the measurement planning and it is known exactly, usually 1–2 weeks. The concentrations of pentachlorophenol (PCP) and lindane in a sample of old dust taken directly from a sculpture were exceptionally high with 117 and 14 μg g^{-1}, respectively. In the fresh dust samples taken from the floor, considerably high concentration up to 30 for PCP and 5 μg g^{-1} for lindane were also found, which probably resulted from the intensive treatment of the wooden sculpture for purposes of conservation. This result gave evidence for a possible exposure of museum staff and visitors.

Berger-Preiss et al. (2002) measured indoor pyrethroid exposure in 80 homes with woollen textile floor coverings. While permethrin concentrations in house dust were high (mean: 53.7 μg g^{-1}), the permethrin concentrations in suspended particles were very low (mean: 2.8 ng m^{-3}). Roinestad et al. (1993) identified 30 pesticides in household dust ranging from 80 (diazinon) to 15000 (chlorpyrifos) ng g^{-1}. Permethrin levels decreased from 2550–3850 (just after application) to 550–675 ng g^{-1} 8 weeks after pesticide application. However, dichlorvos and *o*-phenylphenol levels remained relatively constant suggesting that dust sampling may be a more appropriate method for determining chronic risk assessment of indoor pesticides than air.

7 Plasticizers

7.1 Phthalate Esters

Phthalate esters are extensively used as softeners in the production of polymeric materials such as polyvinyl chloride (PVC). Since phthalate esters are not chemically bound to the polymer, they can be easily released into the environment. PVC and other polymers are widely produced for building materials and thus, the surrounding environment can be polluted by phthalates.

Due to their high volume production and their widespread use, phthalates, as well as some other chemicals present in the domestic environment, are potentially important indoor contaminants. In addition, people working in industrial plants producing plasticizers or living near such plants may be exposed, via indoor air inhalation, to levels of these pollutants that could constitute a significant contribution to the total daily intake (Otaka et al. 2001).

Phthalates are so ubiquitous that can be found everywhere, including common laboratory equipment and reagents. In consequence, the main problem in phthalate analysis is external contamination coming from the sampling and sample preparation procedure and even the chromatographic analysis. This problem has been extensively studied by Frankhauser and Grob (2007). The analysis of blanks is of great importance, as are all the precautions in the treatment of the material and reagents used in any step of the analytical process. To minimize contamination, the use of plastic materials should be avoided, the sample preparation procedure should be as simple as possible with minimal extraction steps, and minimal glassware used (Gomez-Hens and Aguilar-Ceballos 2003; Tienpont et al. 2000). Glassware should be properly cleaned by solvent rinsing and thermal treatment at 400°C. Prior to use, it should be rinsed with blank tested organic solvent (cyclohexane or isooctane) to deactivate its surface. Organic solvents and laboratory grade water usually contain traces of phthalates, even the ones commonly available for trace analysis, and these must be checked to establish background levels. Also, reagents need to be checked. Additional contamination of material, water solvents, and reagents can occur due to the laboratory air. The material should be stored in a closed container or wrapped in aluminium foil to avoid adsorption of phthalates from the air. As previously commented, phthalates can be present in the chromatographic system. The most important contamination source is located in the inlet and gas supply system, inlet septa, liners and o-rings. Since the caps for autosampler vials also contain phthalates, as a general precaution, only one injection should be made from each vial (Llompart et al. 2007). Several procedures for the analysis of phthalates indoors are reported in Table 3.

Table 3 Analytical procedures for the determination of plasticizers in indoor dust

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Phthalate esters						
PAHs, phthalates, PCBs, pesticides	Dust (1.4–12.1 g) collected in a cellulose thimble	Soxhlet with 200 mL hexane–diethyl ether 94:6, 16 h, after addition of a deuterated surrogate	Treatment with anhydrous sodium sulphate, concentration to 2.5 mL cleanup with florisil, concentration to 2 mL in 10% diethyl ether in hexane and silylation	GC/EI-MS (SIM)	NR	Rudel et al. (2001)
DEP, DBP, BBP, DEHP, DCHP, DnHP, DiBP	Collection in cellulose extraction thimble placed in a PTFE holder inside a vacuum cleaner	Addition of the surrogate (*p*-terphenyl-d_{14}), equilibration at room T (30 min) and Soxhlet with 6% diethyl ether in hexane, 16 h	Concentration to 10 mL and 1-mL aliquot cleaned on a florisil column, elution with 20 mL 10% acetone in hexane, concentration to 2 mL with 10% diethyl ether in hexane	GC/MS	0.1–24 $\mu g\ g^{-1}$	Rudel et al. (2003)
DMP, DEP, DPP, DBP, DiBP, DCHP, BBP, DEHP, DOP, Musks	Collection in bags of vacuum cleaners (1 g dust)	Addition of deuterated surrogate, PLE with hexane diethyl ether 95:5	None	GC/EI-MS (SIM)	Determination limit = 0.5 $\mu g\ g^{-1}$	Fromme et al. (2004)

Table 3 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
DEP, DIBP, DBP, BBP, DEHP, DINP.	Cellulose membrane filters in holders of styrene-acrylonitrile polymer mounted on a sampler of polypropylene connected to a vacuum cleaner (>25 mg dust)	Solvent extraction with 2 mL dichloromethane (agitation 30 min) (×2)	NR	GC/MS, GC/FID	NR	Bornehag et al. (2005)
Phthalates	Dust from a vacuum cleaner with an inserted particle filter was sieved through 2 mm pore size	Solvent extraction with 10 mL hexane	Clean-up by SPE with silica gel	GC/ECD/FID	NR	Hutter et al. (2006)
Phthalates, PCBs, PCDDs, PCDFs, PBDEs, PFCs	Collection in special filter bags by slowly vacuum-cleaning the floor of the room during 10 min	NR	NR	GC/FID, GC/ECD	NR	Fromme et al. (2007)
Organotin compounds						
MBT, DBT, TBT, MOT, DOT, TPT	Dust (0.5–1.0 g) from vacuum cleaners	Sonication with ethanol	Buffering with sodium acetate (pH 4.5), derivatization with sodium tetraethylborate (STEB) and LLE with hexane	GC/EI-MS (SIM)	10 ng g^{-1}	Fromme et al. (2005)

Phthalates have been extracted from dust using the Soxhlet extractor (Llompart et al. 2007; Rudel et al. 2001), simple agitation with hexane (Hutter et al. 2006) or dichloromethane (De Boer and Wells 2006), sonication, as well as by PLE using a mixture of hexane and diethyl ether (95:5) (Fromme et al. 2004). Determination is usually performed by GC/MS. A typical procedure has been described by Rudel et al. (2003), consisting in the collection of dust samples using a mite vacuum cleaner modified to collect dust in a cellulose extraction thimble. Since phthalates are closely associated to the plastic materials, a custom crevice tool with a holder for the extraction thimble was constructed in PTFE to avoid dust contact with any plastic part of the cleaner. Prior to extraction, dust was weighed and sieved to <150 μm. Aliquots for the analysis (0.047–1.6 g) were spiked with the surrogate solution (*p*-terpenyl-d_{14}), let equilibrate at room temperature, and then Soxhlet extracted. After concentration and clean-up of the extract, the GC/MS determination of the phthalates was performed. Recoveries of the method ranged from 40 to 220% with RSD <20% and LOD values of 0.1–24 μg g^{-1}.

7.2 Organotin Compounds

The importance of organotins as environmental endocrine disrupters and their potential to adversely affect human health, has prompted the European Commission to identify tributyltin (TBT) as a priority hazardous substance. Organotin compounds are widely employed as stabilizers of polyvinyl chloride (PVC) polymers, and as industrial catalysts for polyurethane and silicone elastomers. Hence, they are present in water pipes, food packing materials, polyurethane foams and many other consumer products. The prominent toxicological feature of the organotins is their immunotoxicity, and the effect produced by di- and trialkyltins as well as triphenyltins.

Organotin compounds have been collected from indoor air by active sampling through quartz filters and an activated carbon-fibre filter (Kawata et al. 1993). A flow rate of 5 L min^{-1} was employed for 24 h periods, which yields to air volumes of approximately 7 m^3. Extraction was performed by sonication twice with 10 mL 1 M HCl in methanol for 10 min, and then twice with 2.5 mL benzene for 10 min. After derivatization with propyl magnesium and several clean-up steps, organotin compounds were analyzed by gas chromatography with flame photometric detection (FPD). Recoveries higher than 95%, and LODs in the range 0.2–0.4 ng m^{-3} were obtained. Measured concentrations of triphenyltin chloride (TPTC) ranged between 0.4 ng m^{-3} and 0.6 ng m^{-3}.

Organotin compounds have also been determined in house dust (Fromme et al. 2005) (see Table 3). Ultrasound-assisted extraction (USAE) was conducted with ethanol, followed by derivatization with sodium tetraethylborate (STEB) and liquid–liquid extraction with n-hexane. Extracts were analysed by gas chromatography/mass spectrometry. Recoveries higher than 70% and average LODs of 10 ng g^{-1} were obtained.

8 Flame Retardants

8.1 Organophosphate Esters

Organophosphate esters are manufactured on a large scale to be used as flame retarding agents and/or plasticizers in a variety of products such as electronic equipment, lubricants, plastics, glues, varnishes and furnishing fabrics. Several studies demonstrated the potential of these materials to emit phosphate flame retardants as well as their degradation products (Saito et al. 2007; Carlsson et al. 2000). Organophosphates may diffuse out at rates depending on their vapour pressures and the ambient temperature, and are thus emitted to the surrounding air (Hartmann et al. 2004). Consequently, there are abundant sources of organophosphates in both public and domestic buildings, including diverse building materials and consumer products. Several toxicological effects of organophosphate tri-esters have been reported, although very little is known about their health impact on humans. However, some reviews indicate that a number of these compounds, for instance tri-*n*-butyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP) and tris(2-chloropropyl) phosphate (TCPP), may negatively affect human health (WHO 1991, 1998). As well as for brominated flame retardants, indoor environment represents the main source of human exposure to these pollutants through inhalation of air and inadvertent ingestion of dust. The most volatile organophosphates are found in the gas phase, whereas the organophosphates with higher molecular mass are mainly associated to the suspended particulate matter and dust (Hartmann et al. 2004; Sjödin et al. 2001).

Table 4 summarizes the analytical procedures for flame retardants in dust and particulate matter. Tollbäck et al. (2006) used a single procedure for sampling and analysis of organophosphate esters in the gas phase and in particulate matter. An Empore SPE membrane is able to collect even very fine particles. The samples collected can be considered representative of the air being tested. Desorption is performed on-line with methanol in such a way that the extracts are directly introduced in the LC/MS. To assess if the presence of particulate matter may adversely affect the extraction efficiency in the desorption step, during the extraction of the esters associated with particulate matter, membranes containing 2 mg of NIST-certified urban dust were spiked with a standard solution. The relatively large amount was used in order to magnify any negative effects. Quantitative recoveries demonstrated that fair desorption is achieved in the experimental conditions used.

A personal sampling method for common organophosphate additives in hydraulic fluids in occupational air was developed with the aim of exposure assessment in working atmospheres potentially contaminated by hydraulic fluids, simultaneously collecting both the aerosols and the vapours. The described sampler combined a glass fibre filter with a Chromosorb 106 adsorbent tube. Desorption was performed with dichloromethane for GC/MS analysis (Solbu et al. 2007).

Table 4 Analytical procedures for the determination of flame retardants in indoor dust and particulate matter

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Organophosphate esters						
TCEP, TCPP	Dust from vacuum cleaners	Soxhlet with hexane/acetone (4:1) 8 h, previous addition of surrogate	Concentration to a small volume	GC/EI-MS (SIM)	100 ng g^{-1}	Ingerowski et al. (2001)
TMP, TEP, TCEP, TPP, TPhP, TBP, TCPP,TTP	Retention of particulate matter on Empore C8 SPE membranes (24 h sampling time)	On-line desorption with methanol (1.6 mL, 8 min × 0.2 mL min^{-1})	None	LC/MS	0.4–19 pg m^{-3}	Tollbäck et al. (2006)
TiBP, TBP, TCEP, TCPP, TDCPP, TPhP, TBEP	Dust from vacuum cleaners passed through a 60 µm mesh sieve	MSPD using 0.5 g dust mixed with Na_2SO_4 (0.5 g) and dispersed with florisil (0.5 g) in a glass mortar	Loading the blend in a cartridge containing alumina on the bottom, rinsing with 2 mL hexane, and elution with 3 mL acetone. Addition of 1 mL ethyl acetate, concentration to 0.5 mL and addition of internal standard (TPP)	GC/NPD	LOQ: 40–50 ng g^{-1}	García et al. (2007)
TiBP, TBP, TCEP, TCPP, TDCPP, TPhP, TBEP, TEHP, TPPO	Dust (0.5 g) from vacuum cleaners passed through a 60 µm mesh sieve	MAE with 10 mL acetone (130°C, 30 min)	Centrifugation (3000 rpm, 5 min), decantation, addition to 500 mL ultrapure water, SPE (Oasis HLB), elution with 2 mL ethyl acetate, clean-up on a silica cartridge, elution with 5 mL ethyl acetate and concentration to 1 mL	GC/NPD	LOQ: 40–50 ng g^{-1}	García et al. (2007)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
TBEP, TCEP, TCPP, TDCPP, TPhP, TEEdP, TEHP, TBP, DOPP, CLP1, TPhP, TMP	Dust (1–2 g) from vacuum cleaners	Sonication with 25 mL dichloromethane 20 min	Filtration through paper filters, concentration to a small volume and addition of internal standard (TEP)	GC/NPD	7–60 ng g^{-1}	Marklund et al. (2003)
Brominated compounds						
Tri-DecaBDE	Dust (0.25 g) from vacuum cleaners passed through a 150 μm mesh sieve	Soxhlet with dichloromethane, 15 h, previous addition of surrogate (BDE-35)	Concentration to 4 mL, solvent exchange to PE/isooctane up to 10 mL, a 5 mL aliquot concentrated to 3 mL, and treatment with 1–2 mL sulphuric acid (×2). Concentration to 1 mL in isooctane and addition of internal standard (Mirex)	GC/NCI-MS (SIM)	0.1–14 ng g^{-1}	Wilford et al. (2005)
Tri-DecaBDE, BTBPE, DeBDethane	Dust from vacuum cleaners	Soxhlet with toluene, 16 h, previous addition of ^{13}C-labeled surrogate	Clean-up on treated (KOH + sulphuric acid) silica column, elution with hexane, clean-up on GPC, elution with hexane/dichloromethane 65:35, concentration to a small volume, and addition of tetradecane and ^{13}C-labeled internal standard	GC/NCI-MS (SIM)	0.169–10.1 ng g^{-1}	Gevao et al. (2006)

(continued)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Tetra-Deca-BDE	Dust (10 g) from vacuum cleaners	Soxhlet with 300 mL toluene, 24 h	Addition of ^{13}C-labelled surrogate, clean-up on a multilayer (acidic, neutral, basic, neutral) silica column and elution with 150 mL hexane. Clean-up on alumina, elution with 100 mL hexane/dichloromethane 1:1, clean-up on a GPC column, elution with cyclohexane/ethyl acetate 1:1, clean-up on alumina, elution with 10 mL hexane/dichloromethane 1:1, addition of ^{13}C-labeled internal standard and concentration to 0.1 mL	GC/EI-MS (SIM)	NR	Knoth et al. (2002)
Tetra-penta-BDEs	Dust (0.047–1.6 g) from vacuum cleaners passed through a 150 μm mesh sieve	Soxhlet with hexane/diethyl ether 6%, 16 h, previous addition of deuterated surrogate	Concentration to 10 mL, clean-up on florisil of an 1 mL aliquot, elution with 20 mL acetone/hexane (10%), solvent exchange to diethyl ether/hexane (10%) and concentration to 2 mL	GC/EI-MS (SIM)	0.2–0.4 μg g^{-1}	Rudel et al. (2003)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Tri-Deca-BDE	Dust (0.1–0.5 g) from vacuum cleaners passed through a 1 mm mesh sieve	PLE (100°C, 2000 psi, 5 min, 3 cycles) with dichloromethane, previous addition of ^{13}C-labeled surrogate	Concentration to 0.5 mL, solvent exchange to hexane, clean-up on SPE cartridge (Silica Sep-Pak), elution with 20 mL hexane, and concentration to 0.5 mL	GC/NCI-MS (SIM)	1–6 ng g^{-1}	Stapleton et al. (2005)
Tri-Hexa-BDEs	Dust (1 g) from vacuum cleaners passed through a 500 μm mesh sieve	PLE (150°C, 1500 psi, 5 min, 1 cycle) with hexane and florisil on the bottom of extraction cell, previous addition of ^{13}C-labeled surrogate	Concentration to 2 mL, treatment with 2 mL sulphuric acid$_{(c)}$, LLE with DMSO, clean-up on florisil, elution with 20 mL hexane, concentration to a small volume, solvent exchange to 20 μL nonane, and addition of internal standard (PCB-29, PCB-129)	GC/EI-MS (SIM)	0.03 ng g^{-1}	Harrad et al. (2006)

(continued)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Tri-Deca-BDE	Dust (0.5–1 g) from vacuum cleaners (SRM 2585) passed through a 100 µm mesh sieve	(1) PLE (100°C, 2000 psi, 5 min, 3 cycles) with dichloromethane, previous addition of ^{13}C-labeled surrogate. (2) Soxhlet with dichloromethane, previous addition of ^{13}C-labeled surrogate	(1A) Concentration to a small volume, clean-up on SPE cartridge (Silica Sep Pak), elution with 20 mL hexane, concentration to 0.5 mL. (1B) Concentration to a small volume, clean-up on a SPE cartridge (alumina), elution with 10 mL dichloromethane/hexane (35%), clean-up on a GPC column, concentration and solvent exchange to 0.5 mL isooctane. (2) Concentration to a small volume, clean-up on alumina, elution with 20 mL PE, concentration to a small volume, solvent exchange to isooctane	GC/EI-MS (SIM), GC/NCI-MS (SIM)	NR	Stapleton et al. (2006)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Tetra-Hexa-BDEs	Dust (0.8 g) from vacuum cleaners passed through a 60 µm mesh sieve	MAE (80°C, 15 min) with a mixture of 8 mL hexane and 4 mL NaOH 10% (w/w), previous addition of ^{13}C-labeled surrogate	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min, and filtration. An aliquot of 2 mL concentrated to 0.2 mL	GC/EI-MS (MS/MS)	0.29–0.55 ng g^{-1}	Regueiro et al. (2006)
Tri-Deca-BDE	Dust (3.4 g) from vacuum cleaners passed through a 2 mm mesh sieve	Soxhlet with dichloromethane/ hexane (1:1), previous addition of surrogate (BDE-35, BDE-181)	Concentration to a small volume, solvent exchange, clean-up on a silica-alumina column 2:1, elution with 100 mL hexane/ dichloromethane (1:1), addition of 50 µL dodecane, concentration to < 0.1 mL, and addition of internal standard (Mirex)	GC/NCI-MS (SIM)	0.032–0.305 ng g^{-1}	Gevao et al. 2006
Tetra-Deca-BDE	Dust (0.8 g) from vacuum cleaners passed through a 60 µm mesh sieve	MAE (80°C, 15 min) with a mixture of 8 mL hexane and 4 mL NaOH 10% (w/w), previous addition of surrogate (PCB-30)	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min and filtration	GC/µECD	0.0439–1.44 ng g^{-1}	Regueiro et al. (2007)

(continued)

Table 4 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Tri-Deca-BDE	Dust (0.2 g) from air conditioning units	MAE (115°C, 15 min) with 25 mL hexane/ dichloromethane (1:1) in the presence of Na2SO4, previous addition of 1 3C-labeled surrogate	Clean-up on acidic silica (sulphuric acid) column, elution with 100 mL hexane and 50 mL hexane/ dichloromethane 2:3, clean-up on a GPC, elution with 30 mL hexane/ dichloromethane 1:1, addition of dodecane, concentration to 25 µL, and addition of ^{13}C-labeled internal standard	GC/NCI-MS (SIM)	0.02–40 ng g^{-1}	Tan et al. (2007)
HBCD (α,β,γ)	Dust (1 g) from vacuum cleaners passed through a 500 µm mesh sieve	PLE (90°C, 1500 psi, 5 min, 3 cycles) with hexane/ dichloromethane (1:1) and florisil on the bottom of extraction cell, previous addition of ^{13}C-labeled surrogate	Concentration to 0.5 mL, treatment with sulphuric acid, clean-up on florisil, elution with 30 mL hexane/ dichloromethane 1:1, concentration to a small volume, solvent exchange to methanol and addition of deuterated internal standard	LC/ESNCI-MS (MS/ MS)	0.1 ng g^{-1}	Abdallah et al. (2008)

Organophosphate flame retardants have been extracted from house dust by Soxhlet (Ingerowski et al. 2001), USAE (Marklund et al. 2003), MAE (García et al. 2007) and MSPD (García et al. 2007).

Marklund et al. (2003) carried out the US extraction of 12 organophosphate flame retardants with 25 mL dichloromethane for 20 min followed by a simple filtration and a volume concentration. An average recovery of 97%, and LODs ranging between 7 and 60 ng g^{-1} were obtained. MSPD has been recently applied for the extraction of these esters from house dust (García et al. 2007). An amount of 0.5 g dust was mixed with 0.5 g anhydrous sodium sulphate and dispersed with 0.5 g Florisil in a glass mortar. After loading the blend in a cartridge containing alumina on the bottom, compounds were eluted with acetone and finally volume reduced. Recoveries higher than 80% and RSD lower than 13% were achieved. Separation and quantification is typically performed by GC with NPD (García et al. 2007a, b; Marklund et al. 2003), although GC coupled to MS in the EI mode with SIM has also been used (Ingerowski et al. 2001).

8.2 Brominated Compounds

The widespread use of plastics and other synthetic materials in electrical appliances, construction materials and textiles has increased the flammability of these products and led to the extensive use of flame retardants to improve their flame resistance and to meet the fire safety standards. Measurements conducted in workplaces as offices, internet cafes, computer rooms and computers or electronic shops indicated significantly higher levels of brominated flame retardants compared to furniture stores, homes and outdoor air (Mandalakis et al. 2008).

In the last years, brominated compounds used as flame retardants have attracted great attention as emergent contaminants (Covaci et al. 2002). Most brominated flame retardants have been found to bioaccumulate in biota and humans (De Wit 2002). Their widespread production and use, together with the increasing contamination of the environment, wildlife and people, highlights the importance of identifying emerging issues associated with the use of brominated flame retardants, especially in indoor environments. The most used brominated flame retardants are polybrominated diphenyl ethers (PBDEs), hexabromocyclododecane (HBCD), tetrabromobisphenol-A (TBBPA) and polybrominated biphenyls (PBBs). Other less known brominated compounds like bis(2,4,6-tribromophenoxy)ethane (BTBPE) and decabromodiphenyl ethane (DBDPE) have an increasing interest due to their emerging use as substitutes of octaBDE and decaBDE commercial mixtures, respectively (Karlsson et al. 2007), as well as the brominated compounds of Firemaster550, 2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB) and (2-ethylhexyl) tetrabromo-phthalate (TBPH), the latter compound being a brominated analogue of di(2-ethylhexyl)phthalate (DEHP), which have been found in house dust (Stapleton et al. 2008).

Polybrominated diphenyl ethers constitute an important class of brominated flame retardants commonly added to a variety of consumer products. Their production began in the 1960 s and they were incorporated in building materials, electronic equipment, lighting, electric wiring, textiles, furniture, floor coverings, industrial paints, and in many other common products. Due to their persistent and bioaccumulative nature, penta- octa- and decabrominated commercial mixtures have been banned within the European Union and their use in North America has recently begun to be phased out (Sjödin et al. 2004). However, vast reservoirs of PBDEs remain in existing consumer products, potentially contributing to environmental and human burdens of PBDEs for decades (Harrad and Diamond 2006). PBDEs are incorporated into materials as additives and thus they may be released into air through volatilization during the product lifetime and, as a consequence, levels are expected to be elevated in indoor air.

Intake through food consumption is an undoubtedly important source of human exposure to PBDEs. However, the potential for exposure to PBDEs in the indoor environments is also real as inhalation and inadvertent ingestion of contaminated dust have been reported to be the largest contributors of PBDEs exposure of toddlers through to adults (Jones-Otazo et al. 2005). In addition, and because of higher concentrations, indoor air and dust likely represents a significant source to outdoor air (Currado and Harrad 2000). Regarding infant exposure, it is also worth mentioning that, as the level of bromination increased, the contribution of PBDE intake decreases via human milk and increases via dust e.g. by non-dietary ingestion or dermal contact (Toms et al. 2009).

The analysis of some brominated flame retardants, such as TBBPA, HBCDs and the higher brominated PBDEs, is a relatively new challenge for most analytical laboratories. Special emphasis must be given to the need of an adequate Quality Assurance/Quality Control (QA/QC) protocol, which is necessary for the reliable analysis of these environmental contaminants at trace levels (Päpke et al. 2004). Literature on the analysis of brominated flame retardants in different matrices, paying special attention to new analytical developments and quality assurance requirements, has recently been reviewed by Covaci et al. (2007). In addition, a recent paper of Kierkegaard et al. (2009) discusses the problems and challenges of the environmental analysis of the higher brominated compounds.

Polybrominated diphenyl ethers can be expected in any laboratory environment equipped with computers and other electronic devices. Significant concentrations of BDE47 and BDE99 have been identified in laboratory air by Thomsen et al. (2001). Thus, in order to avoid a high content of brominated flame retardants in the procedural blanks, it is important that all materials involved in the sample preparation are properly cleaned, and that direct exposure of the sample to the laboratory air is minimized. Proper glassware cleaning implies a thermal treatment at 450°C and solvent rinsing before being used. Polyurethane foam sorbents are usually precleaned by Soxhlet extraction with different solvents prior to sampling step. Moreover, the use of plastics should be reduced as possible in the determination of brominated flame retardants, since they can contain a wide range of these compounds. For the same reason, unnecessary electric appliances and upholstered furniture should be avoided as well as unpackaging of goods in the laboratory where extraction and clean-up take place.

Of special interest and concern is BDE209, the primary component in the decaBDE commercial mixture, actually the most important PBDE mix in production. This compound, as well as other highly brominated congeners, is photosensitive, so direct exposure to UV light should be avoided. Thus, incoming sunlight into the laboratory, as well as possible UV light from fluorescent tubes should be blocked by means of UV filters. Herrmann et al. (2003) reported up to 70% decomposition of BDE209 when stored for 24 h under light conditions. Wrapping glassware with aluminium foil during sample treatment, and using amber glassware are simpler preventive measures to minimize UV-degradation of the analytes. Additional recommendations regarding this issue can be found in de Boer and Wells (2006).

The procedures for the analysis of BFRs in dust are summarized in Table 4, and involve an extraction step with solvents (toluene, dichloromethane or different organic mixtures). The extraction using a Soxhlet extractor (Rudel et al. 2003; Karlsson et al. 2007; Knoth et al. 2002; Stapleton et al. 2006; Wilford et al. 2005) is the most common. An example of this kind of procedure has been reported by Wilford et al. (2005), who found mean recoveries of 99%, RSD values of 19%, and LODs in the range of 0.1–14 ng g^{-1}, for tri- to decaBDE, after extraction of 0.25 g dust with dichloromethane for 15 h and treatment with concentrated sulphuric acid. PLE has also been employed for the extraction of BFRs from house dust (Stapleton et al. 2005, 2006; Harrad et al. 2006; Abdallah et al. 2008). A PLE-based method was developed for Stapleton et al. (2005) for the analysis of PBDEs in house dust and clothes dryer lint. The extraction was carried out with dichloromethane at 100°C and 2000 psi for 5 min during 3 cycles. LODs ranged from 1 to 6 ng g^{-1} after a simple clean-up procedure on silica SPE cartridges and volume concentration. Harrad et al. (2006) reported recoveries from 45 to 67% for the PLE extraction from dust of tri- to hexaBDEs using n-hexane at 150°C and 1500 psi for 5 min. An in-cell clean-up with Florisil during the extraction and further purification with concentrated sulphuric acid and a Florisil column were used. Recently, the use of MAE has been demonstrated as a valuable alternative, providing satisfactory results for the extraction of PBDEs from indoor dust (Regueiro et al. 2006, 2007; Tan et al. 2007). Regueiro et al. (2006, 2007) performed the extraction of tetra- to decaBDE by MAE using 8 mL n-hexane in the presence of 4 mL 10% $NaOH_{(aq)}$ at 80°C for 15 min. Recoveries higher than 90%, RSD lower than 16% and LODs from 0.0439 to 1.44 ng g^{-1} were reported after a simple clean-up by dispersive SPE using a small amount of Florisil.

Determination of BFRs in particulate matter and dust is commonly carried out by GC/MS operating in the negative ionization with SIM (Gevao et al. 2006; Karlsson et al. 2007; Stapleton et al. 2005, 2006; Wilford et al. 2005; Tan et al. 2007), allowing obtaining LODs in the low ng g^{-1} level. Nevertheless, MS in the EI mode with SIM (Rudel et al. 2003; Knoth et al. 2002; Stapleton et al. 2006; Harrad et al. 2006), tandem mass spectrometry (MS/MS) (Regueiro et al. 2006), or even micro-electron capture detection (μECD) (Regueiro et al. 2007), have also been used. HBCD has been recently determined in house dust using LC coupled to ESI negative mode MS/MS (Abdallah et al. 2008). In contrast to GC, this technique is a versatile tool for the isomer-specific determination, enabling the separation and quantification of α-, β- and γ-HBCD.

9 Fragrance Components

There is an increasingly widespread use and exposure to scented products. Fragrances are complex mixtures of primarily volatile compounds that influence both indoor and outdoor air quality. In order to detect an odour, molecules of the substance must be airborne. Once in the air, they break down, mix with other pollutants, and form other compounds that often are more irritant or allergenic than the original substance (Bridges 2002). Fragrances such as air fresheners are used in products to scent the environment. They are added in large amounts to toiletries, cosmetics, household products, and a wide variety of other consumer products.

There are environmental concerns as synthetic musks, widespread components of many fragrances, contribute to both air and water pollution (Kallenborn et al. 1999). They have been measured in workplaces and other crowded indoor environments, although there is an important lack of information about their concentration levels in domestic indoor air.

Owing to their chemical structures, synthetic musks are classified in two main categories, nitromusks and polycyclic musks. Among them, the polycyclic musks Galaxolide (1,3,4,6,7,8-hexahydro-4,6,6,7,8,8- hexamethylcyclopenta-(g) 2-benzopyrane, HHCB) and Tonalide (7-acetyl-1,1,3,4,4,6-hexamethyl-tetraline, AHTN) are used in the highest quantities, being the latter included in the US EPA high production volume chemical list (US EPA 2003). In 1997, the nitromusks musk xylene (1-tert-butyl-3, 5-dimethyl-2, 4, 6-trinitrobenzene, MX) and musk ketone (4-tert-butyl-3,5-dinitro-2,6-dimethylacetophenone, MK) were added to the list of chemicals for priority action of the EU, and in 1998 MX was added to the corresponding list of the Oslo and Paris Commission (Kallenborn et al. 1999).

In spite of their vast use and exposure, there is limited information available related to their health effects. In addition, physical–chemical properties of synthetic musks have more in common with hydrophobic and semivolatile organic pollutants that are known to biomagnify through the food chain (Peck and Hornbuckle 2004). Fragrances can impact indoor air quality and there is suggestive evidence that may play an important role in respiratory diseases and long-term impact (Bridges 2002). Hence, synthetic musks present enough properties, which make them worth considering as a group of indoor air pollutants.

In addition, other fragrance components that are air sensitive may form peroxides, respiratory irritants, and particles that cause inflammatory responses in lungs. It is reported that when D-limonene, a common fragrance ingredient, was added to the air in an office environment, there was a 10× increase in sub-μm particles than measured in a comparable office without added limonene (Wainman et al. 2000).

Most of fragrance determinations in indoor environments have been focused on synthetic musks, and have been performed on dust (Table 5). Synthetic musk fragrances have been extracted from house dust by PLE (Gevao et al. 2006; Rudel et al. 2003). Fromme et al. (2004) carried out the PLE extraction of both polycyclic and nitromusk in indoor dust with n-hexane/diethyl ether (19:1) and further determination by GC/MS operating in the EI mode with SIM. Recently, Peck et al. (2007) reported the extraction of musk compounds from the indoor dust standard reference material SRM 2585 with dichloromethane at 100°C and 2000 psi. After clean-up on an alumina SPE cartridge, a GPC column and volume concentration, recoveries in the range 73–90% were obtained.

MAE has also been applied for the extraction of nitromusk compounds from house dust samples (Regueiro et al. 2007). Dust (0.8 g) was extracted at 80°C for 10 min using a mixture of 8 mL *n*-hexane and 4 mL sulphuric acid 1 M containing ascorbic acid 0.10%. Clean-up was performed by addition and shaking of partially deactivated Florisil. Extracts were further analyzed by GC/μECD. Under these conditions, recoveries between 88 and 97% and LODs from 1.03 to 3.26 ng g^{-1} were reported.

10 Fluorinated Alkyl Substances

Per- and Polyfluorinated alkyl substances (PFAS) are a group of organic chemicals used in a variety of consumer products for water and oil resistance, including surface treatments for fabric, upholstery, carpet, paper, and leather, in fire-fighting foams, and as insecticides (Giesy and Kannan 2002). Many of them combine bioaccumulative potential, toxic effects and extreme persistence; thus, they are considered as candidates for the Stockholm Convention list of persistent organic pollutants (POPs) and are regarded as a new and emerging class of environmental contaminants. Perfluorooctane sulfonate (PFOS), perfluorooctanoate (PFOA) and related compounds such as perfluoralkyl sulfonamides (PFASs) and fluorotelomer alcohols (FTOHs) figure among the most widespread PFAs (Shoeib et al. 2005; Jahnke et al. 2007).

Perfluoroalkyl sulfonamides have been collected in indoor environments using SPE cartridges (Jahnke et al. 2007) or a glass filter followed by polyurethane foam plugs (Shoeib et al. 2009). Air volumes sampled ranged between 20 and 200 m^3. These compounds have also been collected by means of polyurethane foam disk passive air samplers (Shoeib et al. 2005). Very recently, Shoeib et al. (2008) have developed a novel type of polyurethane foam disk impregnated with XAD-4 powder, which provides a higher sorptive capacity for organic and polar chemicals, such as the FTOHs and PFASs. Uptake rates for this sorbent-impregnated polyurethane foam disks from 1.4 to 4.6 m^3 day^{-1} were estimated for the studied compounds.

Table 5 Analytical procedures for the determination of fragrance components and fluorinated compounds in indoor particulate matter and dust

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Fragrance components						
HHCB, AHTN, ATII, ADBI, AHMI, DPMI, MX, MK	Fine dust fraction from vacuum cleaners (1 g)	PLE with hexane/diethyl ether (19:1), previous addition of deuterated surrogate	–	GC/EI-MS (SIM)	LOQ: 500 ng g^{-1}	Fromme et al. (2004)
MX, MK, MM	Dust (0.8 g) from vacuum cleaners passed through a 60 μm mesh sieve	MAE with a mixture of 8 mL hexane and 4 mL sulphuric acid 1 M containing ascorbic acid 0.10% (w/w) (80°C, 10 min), previous addition of surrogate (PCB-166, PCB-195)	Centrifugation, separation of organic phase, on-batch clean-up by addition of 100 mg florisil per mL extract, shaking 2 min and filtration	GC/μECD	1.03–3.26 ng g^{-1}	Regueiro et al. (2007)
HHCB, AHTN, ATII, ADBI, AHMI, MX, MK	SRM 2585 Organics in House Dust	Dust mixed with sulphuric acid and PLE (100°C, 2000 psi) with dichloromethane, previous addition of deuterated internal standard (Fluoroanthene-d_{10})	Concentration to a small volume, solvent exchange to 0.5 mL isooctane, clean-up on SPE cartridge (5% deactivated alumina), elution with 9 mL dichloromethane/hexane (35%), concentration to a small volume, solvent exchange to 1 mL dichloromethane, clean-up on GPC, elution with 5.5 mL dichloromethane, concentration to 1 mL	GC/EI-MS (SIM)	NR	Peck et al. (2007)

Table 5 (continued)

Analytes	Sampling	Desorption/extraction	Extract treatment	Determination	LOD	References
Fluorinated alkyl compounds						
PFOS, PFOA	Dust (0.5 g) from vacuum cleaners	Sonication with 10 mL methanol 60 min	Centrifugation (1500 rpm) 10 min, filtration, and addition of deuterated internal standard	LC/ESI–MS (MS/MS)	10–50 ng g^{-1}	Moriwaki et al. (2003)
PFOS, PFOA, PFBS, PFOSA, PFHS	Dust (0.5 g) from vacuum cleaners passed through a 150 μm mesh sieve	Sonication with 5 mL acetonitrile 5 min (×2)	Clean-up of a 2 mL aliquot on a SPE cartridge (C18 Waters), elution with 7 mL acetonitrile, concentration to dryness, reconstitution in 0.2 mL acetonitrile, and addition of ^{13}C-labled internal standard	LC/ESI–MS (MS/MS)	0.99–4.56 ng g^{-1}	Kubwabo et al. (2005)
MeFOSE, EtFOSE, EtFOSA, MeFOSEA	Dust (0.25 g) from vacuum cleaners passed through a 150 μm mesh sieve	Soxhlet with dichloromethane, 24 h	Concentration to 0.5 mL and addition of internal standard (Mirex)	GC/EI-MS (SIM)	NR	Shoeib et al. 2005
PFAS	GFF (+PUF/XAD2/PUF), 1160 m^3 12–15 m^3 h^{-1}	Solvent extraction with 50 mL ethyl acetate, mechanical shaker, 1 min (×3, 200 mL extract)	Concentration to 1 mL by rotary evaporation. Drying on sodium sulfate, filtration on cotton wool, concentration (nitrogen) to 0.200 mL, addition of internal standard	GC/CI-MS	LOQ = 0.2–2.5 pg m^3	Jahnke et al. (2007)

Extraction of perfluoroalkyl compounds has been carried out by both Soxhlet (Shoeib et al. 2005) and USAE (Moriwaki et al. 2003; Kubwabo et al. 2005) (see Table 5). Recoveries higher than 73% and LODs in the range 10–50 ng g^{-1} were reached. Soxhlet extraction with dichloromethane during 24 h was applied by Shoeib et al. (2005) for the extraction of perfluoralkyl sulfonamides (PFASs) in indoor dust. No further extract preparation than volume concentration was performed before analysis by GC/EI-MS in the SIM mode. Moriwaki et al. (2003) developed an US-based method for the determination of perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in indoor dust. Compounds were ultrasound extracted using methanol for 60 min and determined using LC coupled to ESI MS/MS. Analysis is usually carried out by GC/MS operated in the EI mode with SIM (Shoeib et al. 2009) or in the PCI mode (Jahnke et al. 2007; Shoeib et al. 2008).

Separation of PFASs can be performed with common stationary phases 5% phenyl substituted methylpolysiloxane (Shoeib et al. 2005), although more polar capillary columns are required for FTOHs (Jahnke et al. 2007; Shoeib et al. 2008). Shoeib et al. (2009) determined concentrations of PFAS in indoor air from homes and laboratories. *N*-methyl perfluorooctane sulfonamidoethanol (MeFOSE), widely used as a stain repellent on carpets, was the most abundant in both indoor and outdoor air, followed by *N*-ethyl perfluorooctane sulfonamidoethanol (EtFOSE). Mean indoor concentrations of MeFOSE and EtFOSE were 2589 and 772 pg m^{-3}, respectively. These concentrations were approximately 100 times higher than their outdoor values. PFAs in indoor air from office were evaluated by Jahnke et al. (2007), obtaining values for MeFOSE and EtFOSE of 727 and 305 pg m^{-3}, respectively.

Recently, two interesting reviews on this kind of substances and the recent methodologies developed for their analysis in several matrices have been published, one of them focused on extraction and clean-up strategies in environmental and human samples (van Leeuwen and de Boer 2007) whereas the other one included outdoor and indoor air as well as airborne particulate matter and dust (Jahnke and Berger 2009).

11 Conclusions

The concern about chemicals now characterized as emerging pollutants has led to a marked increase in the number of studies reporting contamination of indoor environments, underlining the significance of indoor dust and suspended particulate matter to human exposure. The constituents of the air are many more than we ever realized, and they need much more monitoring so that we develop a deeper understanding of them and hence ultimately produce healthier workplaces and homes for people. The characterization of pollutants related to dust and particulate matter requires efficient analytical tools. Last developments in sampling, sample preparation and determination have been reported in this chapter. To make methodology suitable for large-scale epidemiological studies, harmonization of methods would be very convenient. It would be also advantageous to establish quality assurance criteria for all the operations implied in the analytical process. In addition, new developments exploring the possibilities of miniaturization, solvent-saving or solvent-free sample preparation methods, which could improve sample throughput without loosing analytical performance, would be acknowledged.

Acknowledgments We want to acknowledge the Spanish Ministry of Science and Technology for funding (FEDER- project CTQ2006-03334).

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Application of Synchrotron X-ray Techniques for the Determination of Metal Speciation in (House) Dust Particles

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1 Introduction

The composition of indoor settled dust is influenced by outdoor soil and dirt, but there are many distinct differences between the two types of samples. A key difference is that many metals and metalloids, including lead, arsenic, cadmium, copper, nickel, zinc, antimony and mercury, accumulate to higher concentrations in indoor dust compared to exterior dust and soil in ordinary urban environments (Culbard et al. 1988; Kim and Fergusson 1993; Rasmussen et al. 2001; Rasmussen 2004a). Most studies of indoor/outdoor metal concentration ratios are based on "total concentrations"—determined using strong acid digestions which put all the metal compounds (species) from the dust or soil sample into solution. However, the total amount of an element is not necessarily a good measure of its potential health risk; rather it is the chemical and physical form (i.e. speciation) of the metal of interest which controls its bioaccessibility and toxicity.

Rasmussen (2004b) and Rasmussen et al. (2008) showed that differences in metal concentrations between indoor dust and outdoor soil may become magnified when metal bioaccessibility is considered, depending on the sources of the element and its speciation. Particularly in residential environments where anomalously high metal concentrations are encountered, it is important to elucidate metal speciation in order to refine risk assessments of metal contaminants. Advanced

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_9,

speciation techniques are needed to address the increasing demand by risk assessors and risk managers for information on the oral bioaccessibility of the metal compounds, their chemical identity and host matrix (e.g. carbonates, oxides, alloys, sulfides, organometallics), and their probable sources (e.g. consumer products such as paint, or external industrial pollution sources).

Due to the complexity of indoor particles (multiple sources, numerous matrices, and secondary transformations), analytical techniques must be able to determine metal speciation of dust particles at low parts-per-million concentrations in various phases (e.g. natural minerals, alloys, adsorbed onto organics, co-precipitated). Synchrotron radiation-based analytical techniques can be used to obtain molecular information at very high sensitivity and spatial resolution and are ideal for studying trace metal speciation in particles. The great advantage of these techniques is in their ability to investigate solid samples in situ, ideal for heterogeneous matrices such as dust samples as there are no pre-treatment steps which can disturb or destroy the sample and alter the original species distribution (Reeder and Schoonen 2006).

In this chapter we first provide an overview of commonly applied synchrotron radiation-based X-ray techniques for determining metal speciation in powdered samples, including X-ray absorption spectroscopy, micro X-ray fluorescence, and micro X-ray diffraction (XRD). The second part of this chapter will provide an example of the application of these techniques to an investigation of lead (Pb) speciation in a house dust sample, characterized by elevated total and bioaccessible Pb concentrations.

2 Overview of Synchrotron Radiation and X-ray Techniques for Metal Speciation in House Dust

2.1 What is Synchrotron Radiation?

While providing a complete physical description of the production of synchrotron radiation is beyond the scope of this chapter, a brief description is necessary. Interested readers are referred to more detailed reviews (e.g. Sham and Rivers 2002; Margaritondo 2002). Fundamental electromagnetic theory states that when a charged particle is accelerated through a magnetic field electromagnetic radiation is emitted (Giancoli 1985). Synchrotron radiation is electromagnetic radiation emitted from a charged particle (e.g. electron) undergoing centrifugal acceleration near the speed of light and is produced naturally in galaxies (Wielebinski 2006). The term synchrotron radiation was coined because this type of radiation was first observed in the electron accelerators called synchrotrons, used by particle physicists (Winick 1987). Initially, use of this unwanted energy loss was termed ‘parasitic’ by particle physicists working at the accelerators. Today, dedicated accelerators called “storage rings” are used to

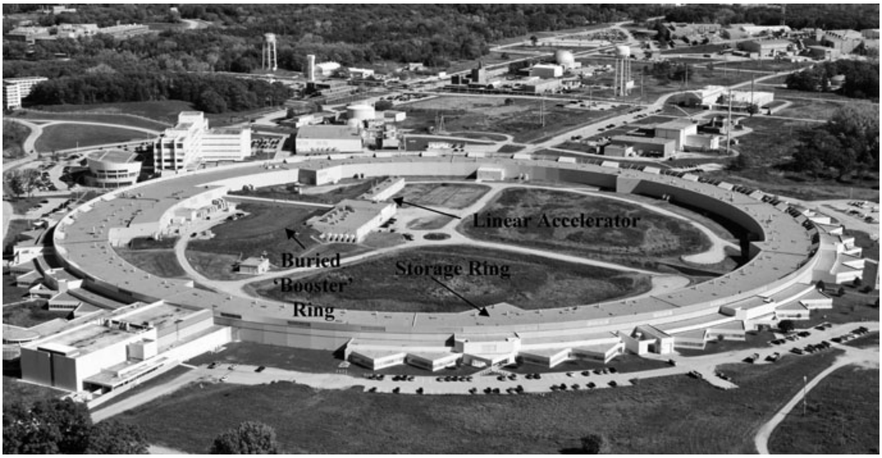


Fig. 1 Aerial view of the advanced photon source (APS) storage ring at Argonne National Laboratory, Argonne, IL. The storage ring, synchrotron booster and linear accelerator are *labeled*. Photo credit: Argonne National Laboratory

produce this type of radiation for experimental purposes (Fig. 1). To produce synchrotron radiation at these facilities charged particles (usually electrons) are first generated and accelerated by a linear accelerator. A booster synchrotron (Fig. 1) is then used to increase the electrons up to the desired energy. When the desired energy is reached the electrons are injected into the storage ring (Fig. 1) where they are kept in circulation, in vacuum, around the ring with magnets (Sham and Rivers 2002; Margaritondo 2002). As the magnets 'bend' the electrons around the curvature of the ring the charged particles undergo a centripetal acceleration—emitting a very bright, intense source of radiation (synchrotron radiation) tangential to the orbit (Sham and Rivers 2002). The end result is a source of electromagnetic radiation that possesses a higher intensity and smaller beam divergence than conventional laboratory-based sources. In addition, synchrotron radiation has a broad continuum of wavelengths (from ultra-violet to X-ray regions) that permits a user to choose the appropriate energy for a particular experiment or provide a continuous, tunable source of X-rays that is required in some experiments (Maginn 1998).

The storage ring is connected to the endstation (where the detectors and instruments are set up and samples analyzed) by a straight section called the beamline. The beamline is under high vacuum and houses the optical devices that are used to optimize the spectral and geometrical characteristics of the X-ray beam. As the X-rays leave the ring and travel down the beamline their energy is tuned using a crystal monochromator set-up that exploits Bragg's law of diffraction to choose the appropriate wavelength to pass through. The beam's geometry is then optimized for each specific experiment by optical devices, typically mirrors and diffraction gratings, before finally arriving at the end station for use in the experiment.

2.2 Why is Synchrotron Radiation Beneficial to the Study of Particle Composition?

To understand the properties of chemical compounds in dust particles we need to ultimately understand the compound's atomic-level structure in the sample. Wavelengths in the ultra-violet and X-ray regions are the most appropriate to study chemical bonds at the molecular level. Synchrotron radiation provides a continuum of wavelengths from the ultra-violet to X-ray regions of the electromagnetic spectrum. In addition, the high-intensity X-rays are required in samples of low absorbing element concentrations (<1 wt%) (Brown and Sturchio 2002) which are characteristic of many metals in household dust. In addition, the synchrotron radiation source provides a highly focused beam which enables chemical and mineralogical information to be collected at a very fine spatial resolution (in the micron to nm range). Thus, synchrotron radiation provides techniques that either cannot be done or are impractical on a laboratory-based X-ray source (e.g. spectroscopy, microprobe and surface scattering) (Sham and Rivers 2002).

Although there are numerous techniques that utilize the bright and intense beams generated by synchrotron radiation (see Brown and Sturchio 2002) we will focus in this chapter on three of the more common X-ray techniques most applicable to indoor dust (absorption, fluorescence, scattering). In particular, this chapter will provide more emphasis to describing the X-ray absorption fine structure (XAFS) spectroscopy over the more well-known XRD and X-ray fluorescence techniques.

2.3 X-ray Interactions with Matter

X-rays interacting with matter can be transmitted through the sample, scattered, and/or absorbed. When X-rays are transmitted they pass through the matter unchanged in energy. X-ray scattering provides information on the crystallographic structure and chemistry of materials based on measuring the intensity of the scattered radiation, the angle of scattering as well as changes in polarization and energy or wavelengths (Margaritondo 2002). X-ray scattering can be divided into two groups: (1) elastically scattered by the matter where there is no change in energy but a change in direction (e.g. small angle X-ray scattering, wide-angle X-ray scattering, X-ray reflectivity); and (2) inelastically scattered which results in a change in energy and direction (e.g. XRD).

X-ray absorption occurs when all the incoming X-ray's energy is transferred to an electron in the atom which is then ejected from its orbital into a higher energy, unoccupied orbital. The resulting empty electron orbital (termed a 'hole') is filled by a higher-energy electron which releases energy in the process in the form of fluorescence radiation, Auger electron production or secondary electron production (Kelly et al. 2008). If the incident energy is high enough the excited electron

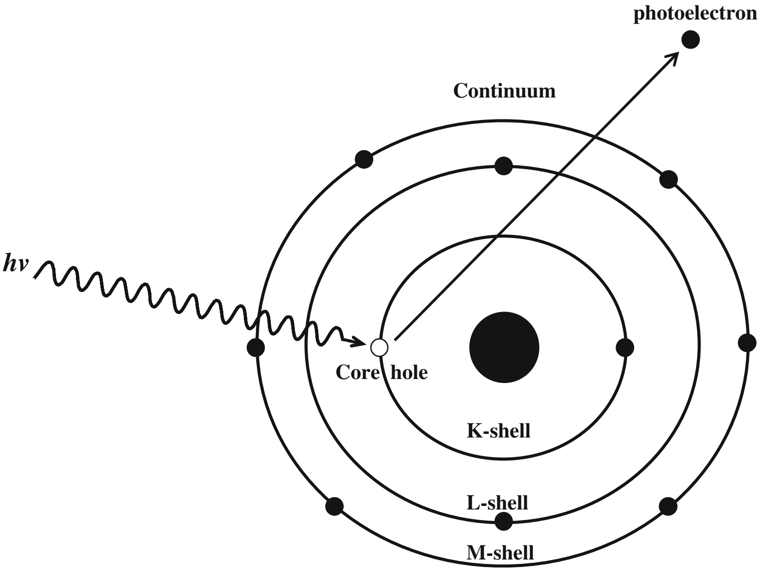


Fig. 2 The Bohr model of the atom demonstrating the absorption of an X-ray by a core-level electron and the production of a photoelectron

(called a photoelectron) will be ejected from the atom out into the continuum (Fig. 2). The energy at which a particular electron will be ejected from the atom is called the ionization energy (or binding energy). Because the binding energy of each electron orbital is a function of the type of atom, X-ray absorption and subsequent emission processes related to relaxation provide a powerful element specific probe.

2.4 XAFS Spectroscopy

The absorption of an X-ray by a core-level electron is characterized in an absorption spectrum by an increase in X-ray absorption, typically called an absorption edge (Fig. 3). The absorption of X-rays by electrons with different orbital energies gives rise to different X-ray absorption edges (K-edge for 1s and 2s core levels; L edges to 2p, 3s and 3p core levels, etc.). XAFS spectroscopy involves the measurement of X-rays absorbed by the element of interest at and above that element's characteristic absorption edge energy (Brown and Sturchio 2002). The importance of this absorption edge for speciation studies lies in the fine structure that is superimposed onto the absorption edge, from which we can extract information on the molecular environment surrounding the absorbing element. XAFS spectroscopic measurements can be collected in all sample phases (solid, liquid or gas) with little sample preparation, thereby minimizing any chemical or

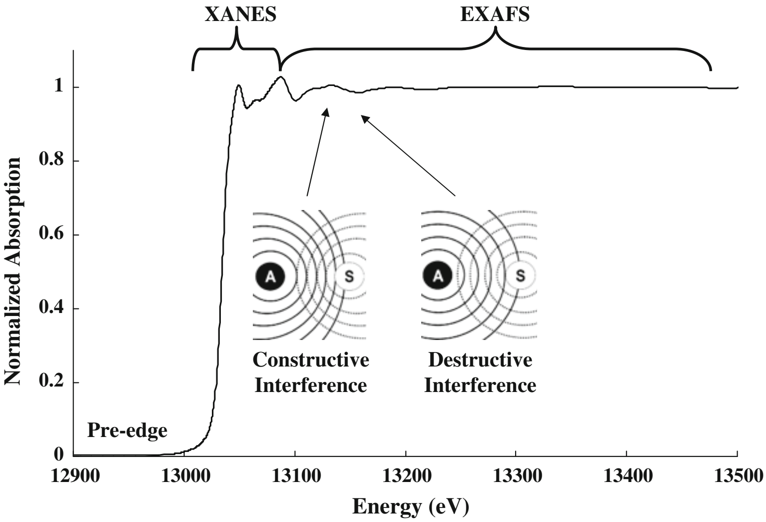


Fig. 3 Example of an XAFS spectrum (PbS) demonstrating both the different regions of the spectrum and the effects of backscattering interferences between the outgoing photoelectron and the backscattered waves on the EXAFS region of the spectrum. *A* absorber atom, *S* scattering atom

structural changes due to sample pre-treatment (Manceau et al. 2002). Another advantage of XAFS is that it does not rely on the species having crystallinity and long-range order like XRD, and therefore it can be used to determine the structural bonding environment of crystalline, non-crystalline and adsorbed molecular environments. Because of the need for a continuous, tunable range of X-rays to scan across an element's absorption edge XAFS spectroscopic experiments normally require the use of synchrotron radiation.

X-ray absorption is usually measured by: (1) transmission by counting the number of X-rays transmitted through the sample (and the difference between the incident number of X-rays and those transmitted is the amount absorbed); and/or (2) fluorescence whereby the energy released during the back-filling of the empty core hole after the electron has been excited is related to the number of X-rays absorbed by the atom. An example of an X-ray absorption spectrum is shown for PbS in Fig. 3. A full spectrum is typically collected from 200 electron volts (eV) below an absorption edge to 1,000 eV above the edge (Kelly et al. 2008).

To derive the structural and chemical information contained in the spectrum, the XAFS is broken down into two regions: the near-edge region, called the X-ray Absorption Near-Edge Structure (XANES) and the far region called the Extended X-ray Absorption Fine Structure (EXAFS). The XANES region includes the structures located close to the absorption edge that are created by electronic transitions and multiple scattering of the photoelectrons, while the EXAFS region is produced by the scattering of the photoelectrons off neighboring atoms.

2.5 X-ray Absorption Near-Edge Structure

The XANES spectrum ranges from −50 eV below the absorption edge to 100 eV above the absorption edge (Fig. 3) and contains features from two sources: (1) bound-state transitions—electronic transitions of excited electrons from lower-energy core states to unbound orbitals of higher energy—located on the absorption edge; and (2) multiple scattering features caused by the photoelectron wave scattering multiple-times from the surrounding atoms (Penner-Hahn 1999). These features are found on the high energy side of the absorption edge and are attributed to the low kinetic energy of the photoelectron wave just above the absorption edge. At this energy the photoelectron has a long mean free path which results in the photoelectron scattering multiple times off surrounding atoms. This multiple scattering leads to the production of prominent sinusoidal features near the absorption edge which are quickly damped out as energy increases. The XANES spectrum provides empirical information about the oxidation state and bonding environment of the element of interest as the absorption edge, which is characterized by the number of electrons present in an atom, will shift with changes in oxidation state of the atom. As an atom loses or gains an electron, the core-level electrons are, respectively, held more tightly or less tightly.

2.6 Extended X-ray Absorption Fine-Structure

The EXAFS is the structure located in the region of the absorption spectra beyond the absorption edge, from about 50 to 1,000 eV above the edge (Fig. 3). This portion of the spectrum is rich in information that comes from the constructive and destructive interferences of the photoelectron wave as it leaves the absorbing atom and scatters off atomic neighbors. As the photoelectron gains energy it is ejected out of the atomic and/or molecular orbitals and into the continuum where it can interact with the surrounding environment. In the continuum (Fig. 2) the photoelectron is scattered by the surrounding atoms (Fig. 4). The backscattered photoelectron waves interfere with the outgoing photoelectron waves at the absorbing atom which leads to modulations in the overall absorption (Fig. 4). When the backscattered photoelectron wave is in phase with the outgoing photoelectron wave, constructive interference between the two waves takes place and results in a maximum in the absorption spectrum (Fig. 3). When the backscattered photoelectron is out of phase with the outgoing photoelectron wave, the photoelectron waves undergo destructive interference which shows up as a minimum in the absorption spectrum (Fig. 3). These constructive and destructive cycles continue as the energy is scanned and generate oscillations which make up the EXAFS pattern. Thus, the EXAFS can be thought of as a scattering process that is measured spectroscopically (Penner-Hahn 1999). The characteristics of these oscillations are influenced by the molecular structure of the absorbing atoms out to

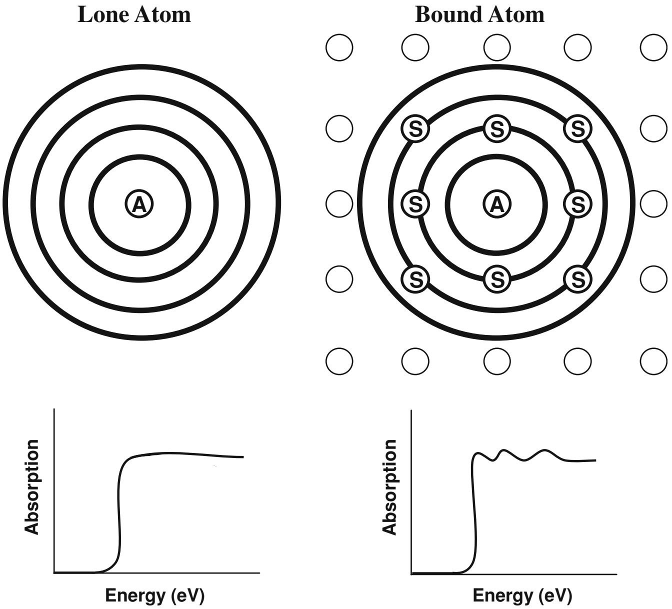


Fig. 4 Illustration demonstrating the effect of neighboring atoms (*numbered*) have on the X-ray absorption spectrum during an EXAFS experiment. *Solid circles* represent outgoing photoelectron waves. *A* absorbing atom, *S* scattering atom

about 6 Å (0.6 nm) (Kelly et al. 2008). The number of atoms at a particular distance from the absorbing atom (i.e. a shell; Fig. 4) and the type of atoms in the shell (atomic number) affect the amplitude of the EXAFS oscillations. The more atoms in a particular shell (coordination number) the higher the amplitude of the EXAFS. In the same way, the higher the atomic number of the backscatters in a shell, the higher the amplitude of the EXAFS. The frequency of the oscillations in an EXAFS spectrum is related to the distance between the absorbing atom and a particular coordination shell of atoms surrounding the absorbing atom.

2.7 XAFS Data Analysis

Normally, XAFS is considered a “bulk sample” technique which means that it averages the speciation of the element of interest across the sample as a whole; thus, multiple species can be present. In these mixed systems the average XAFS spectrum is additive in nature, i.e. it is a combination of XAFS spectra of each individual species detected (Kelly et al. 2008). Due to this additive nature a common approach in XAFS studies of natural samples involves modeling the unknown sample using computed fractions of representative standards which give the best fit to the unknown sample. The approach commonly used is linear combination fitting (LCF) which involves performing least-squares fits of the sample spectrum using linear combinations of spectra from known species. LCF is a fingerprinting technique and is limited by how well the set of standard species represents the actual species in the samples. However, natural samples usually possess a range of species from crystalline to amorphous and doped solids that would be difficult to reproduce exactly with pure standards (Kelly et al. 2008). Thus, LCF benefits from the use of additional information provided by other statistical approaches like principal component analysis and target transformation (Beauchemin et al. 2002) as well as complementary analysis of the sample (e.g. XRD, X-ray fluorescence, ion-coupled plasma mass spectrometry).

3 Synchrotron X-ray Fluorescence Spectroscopy

As discussed earlier, the interaction of X-rays with an atom leads to a relaxation process whereby energy is emitted in the form of fluorescence radiation, Auger electron production or secondary electron production. X-ray fluorescence occurs when an electron from a higher-energy orbital drops into the newly created core hole, releasing energy that is equal to the difference in energy between the two orbitals (Chang 1991). It is this energy difference that is measured in an XRF experiment. Since the transition energy and the orbital energy (and thus the energy difference) are unique to each element, X-ray fluorescence lines are characteristic of the element of interest based on the energy measured.

Synchrotron X-ray fluorescence (SXRF) is sensitive to trace element concentrations. In addition, the micro-focusing optics available at high-brightness synchrotron sources provide a small spot size. By raster scanning the sample stage in the X-ray beam, at a fixed incident energy, maps of X-ray fluorescence intensities can be generated for selected elements. Thus, synchrotron radiation allows one to collect maps of elemental distribution at high spatial resolution (μm range) and high sensitivity (sub-mg kg^{-1} range) (Sutton et al. 2002). In addition, the maps obtained by μSXRF can then be used to provide qualitative information on the elemental associations between two or more elements of interest. By using the μSXRF map, regions of interest can be chosen for additional analysis, such as XRD (see below).

3.1 X-ray Diffraction

X-ray diffraction is based on Bragg's law of diffraction which states that a set of lattice planes in a crystalline material diffracts a beam of X-rays at a certain incident angle that satisfies the Bragg equation (Cullity 1978):

$$n\lambda = 2d \sin\theta \tag{1}$$

where n is an integer, λ is the wavelength of the X-ray, d is the interplanar spacing and θ is the angle between the incident X-ray and a given lattice plane of atoms.

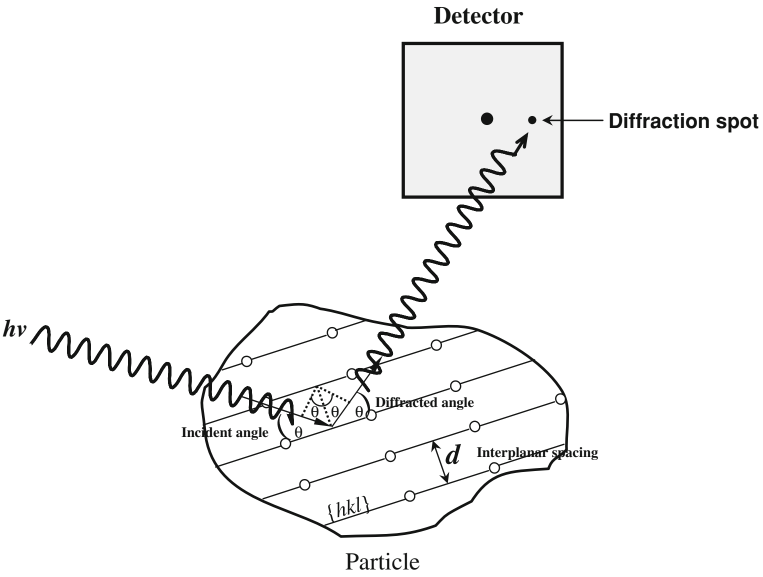


Fig. 5 A simple illustration describing the geometry of the Bragg condition of powder X-ray diffraction. Each unique set of lattice planes {*hkl*} in a crystal will diffract the X-ray at a certain θ angle that is characteristic to that set of planes. In a single crystal this would result in a diffraction spot on the X-ray detector. In a powder diffraction experiment the presence of numerous lattice planes diffracting in all orientations simultaneously results in a ring pattern on the X-ray detector

In a powdered or polycrystalline sample each unique set of diffracting planes {*hkl*} will produce a cone of diffracted rays that will be centered around the undiffracted X-ray beam with a radius of $2\theta_{\{hkl\}}$ (Fig. 5) (Flemming 2007).

The high intensity of X-rays generated at synchrotrons give synchrotron-based XRD techniques lower detection limits ($\sim$1 wt%) than traditional laboratory-based XRD instruments ($\sim$5 wt%) (Manceau et al. 2002). In addition, natural samples usually contain mixed, poorly crystalline and nano-crystalline phases in smaller concentrations (Manceau et al. 2002). It is these smaller particles that are often associated with trace metals (Utsunomiya et al. 2004). The high-collimation of the synchrotron X-ray beam allows XRD to be applied on the micron-scale length (μXRD) to reduce the heterogeneity in a natural sample. A two-dimensional μXRD pattern of a natural sample commonly has two characteristic patterns (Manceau et al. 2002): (1) spotty and discontinuous diffraction rings due to the presence of a finite number of micron to sub-micron crystalline particles in the diffraction volume (Figs. 2, 6a) rings of constant intensity due to the presence of nanocrystalline particles which diffract the X-rays in all directions due to the infinite (relative) number of diffracting planes, oriented in all directions, within the diffraction volume (Fig. 6b). Thus, μXRD can provide information on the crystal sizes present in the sample. In addition, the collection of diffraction patterns from specific regions of interest on a μXRF map can allow one to identify the mineralogy associated with trace elements of interest. While it is not certain that the

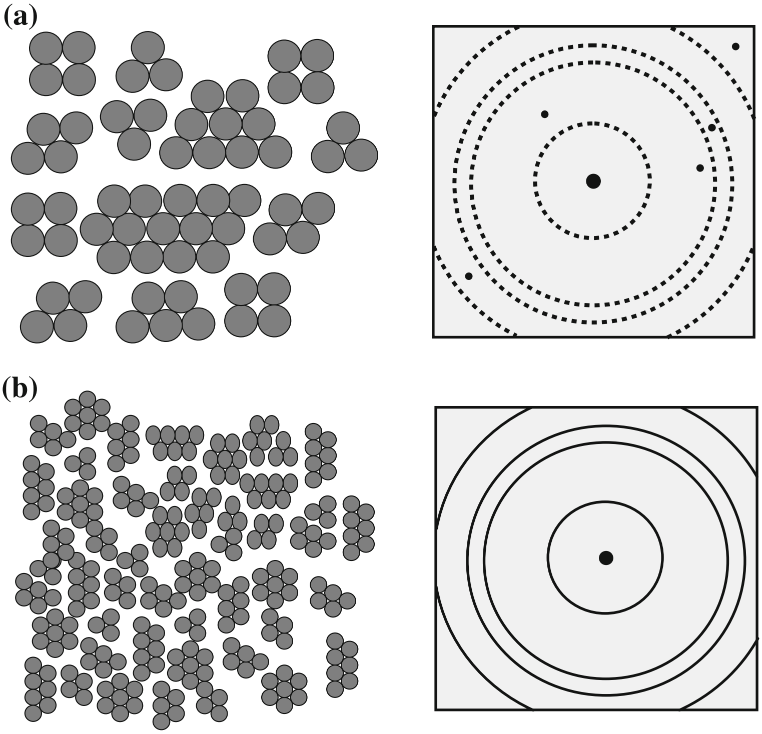


Fig. 6 Illustration of the common characteristics of powder diffraction patterns collected with micro-XRD. Notice that the *individual spots* are from larger, micron-sized crystallites while the *spotted rings* are indicative of micro-crystalline particles (**a**). The *spottiness* of the rings is an indication of insufficient number of grains in the diffraction volume of the sample. The *continuous rings* indicate that all lattice planes $\{hkl\}$ are simultaneously present in all orientations relative to the incident X-ray beam. In micro-diffraction with spot sizes on the micron-scale this usually occurs only with nanocrystalline particles (**b**)

diffracting mineral is the host of the trace element of interest, the identification of the dominant mineral phase can aid XAFS spectroscopy in determining the molecular environment of the element of interest.

4 Illustrated Application: Pb Speciation in a Household Dust Sample

4.1 Background

The objective of this synchrotron application was to determine the Pb speciation in the fine fraction (<80 μm) of an archived vacuum dust sample collected from a

Canadian urban single family dwelling. This sample is characterized by a potentially hazardous concentration of total Pb (1,670 mg kg^{-1}), of which 95% is bioaccessible. Health Canada required information about the solid sample Pb speciation to provide information about potential source(s) for the elevated Pb, and the reason for the high metal bioaccessibility. This was achieved using a combination of bulk XAFS, micro-XRF and micro-XRD analyses.

Lead (Pb) is a potent neurotoxin that can cause a lifetime of health impacts in exposed children, including impairment of intellectual and social-behavioral function (Ryan et al. 2004). Ingestion of house dust is widely regarded as a key pathway for childhood exposure to environmental Pb (Lanphear et al. 2002; Rasmussen 2004a). Although few studies have investigated the speciation of Pb in residential environments, isotopic studies have indicated that the main sources of Pb in house dust are deteriorating lead-based paints, tracking-in of soils and street dusts, and penetration of windblown dusts (e.g. Adgate et al. 1998a, b).

Over the last two decades there have been numerous examples of XAFS studies of Pb speciation, for example in: aerosol particles (Funasaka et al. 2008; Ishizaka et al. 2009; Pingitore et al. 2009); soils (Manceau et al. 1996; Morin et al. 1999, 2001; Welter et al. 1999; Nguyen and Manning 2003; Fernandez et al. 2007); clay minerals (Sipos et al. 2008); mine wastes (Morin et al. 1999; Courtin-Nomade et al. 2008); plants (Cotter-Howells et al. 1999; Marmiroli et al. 2005); and microorganisms such as biofilms (Templeton et al. 2003) and fungi (Sarret et al. 1998). However, to our knowledge there have been no XAFS studies on Pb speciation in household dust, and only one previous study used XAFS to investigate the speciation of other metals in residential indoor dust (Rasmussen et al. 2008).

5 Experimental

5.1 *Bulk XAFS*

5.1.1 Pb Reference Compounds

Various standards of Pb were purchased as reference compounds and previously checked by XRD for purity (data not shown): Pb oxide (PbO), Pb sulfide (PbS), Pb metal, Pb sulfate [mixture of $Pb_2O(SO_4)$ and $(PbSO_4)$], Pb carbonate ($PbCO_3$), Pb hydroxyl carbonate [$(PbCO_3)_2 \cdot Pb(OH)_2$] and Pb chromate [$Pb(CrO_4)$]. XRD analysis of Pb hydroxyl carbonate showed mainly Pb carbonate but EXAFS analysis revealed a distinct spectrum compared to Pb carbonate. Organic reference compounds of Pb acetate, Pb citrate and Pb oxalate were also obtained from commercial suppliers and included in the study. Three more Pb reference compounds were synthesized in our laboratory: pyromorphite ($Pb_5(PO_4)_3Cl$), Pb adsorbed on cysteine ($HO_2CCH(NH_2)CH_2SH$) and Pb adsorbed on goethite (FeOOH—as a representative species on Pb associated to Fe-oxyhydroxides).

The pyromorphite was synthesized as described in Fomina et al. (2005). Pb adsorbed on cysteine (pH 7.0) was obtained following a procedure similar to that described for Zn by Beauchemin et al. (2004). Goethite was synthesized according to the procedure of Schwertmann and Cornell (1991) and washed with ammonium oxalate, following the method described in Ross and Wang (1993), to remove non-crystalline Fe. A solution of 1 M KCl was used to remove the oxalate, followed by multiple washings with DI water to decrease the ionic strength (Alcacio et al. 2001). The goethite was finally resuspended in 10 mM KCl for the adsorption of Pb. Pb was adsorbed on the goethite at a final rate of 350 mmol Pb per kg goethite at pH 6.5.

5.1.2 Data Collection

The reference compounds were finely ground and diluted in boron nitride to achieve an optimized edge step of one for data collection in transmission mode. Two to four scans were collected and averaged for each Pb reference compound. The household dust samples were directly mounted behind Kapton tape in a 380 μm Teflon$^{\text{TM}}$ holder and analyzed in fluorescence mode using a solid-state germanium, multielement detector. Four to ten scans were collected and averaged for each dust sample. The analyses were conducted at beamline X-11A at the National Synchrotron Light Source, Brookhaven National Laboratory (New York). The Si(311) monochromator was calibrated to the Pb L-111 edge at 13,035 eV using the first peak of the first derivative XANES spectrum for the Pb metallic foil. The energy scale for each sample was referenced to the edge in the Pb metal spectrum collected in transmission mode simultaneously with sample data.

5.1.3 Data Analysis

The XAFS data were processed using Athena 8.054 (Ravel and Newville 2005). Pre-edge baseline subtraction and XANES normalization were performed by fitting a linear regression in the pre-edge region (−150 to −75 eV; relative energy) and a linear regression to a post-edge section typically chosen between 150 and 645 eV. Background removal for the EXAFS spectra (chi data) was done using a spline range from about 0.5 to 11 A^{-1}. The chi data were square weighted (k^2) for fitting analysis.

Least-squares LCF of Pb chi data ($k = 2$) was performed on the dust sample spectra using all possible binary and ternary combinations of the 13 Pb reference standards. LCF was done using Athena 8.054. No energy shift was allowed for the chi fitting and constraint to sum to 1 was imposed. The chi fitting ranged from 2 to 8 A^{-1}. R factor and reduced chi-squared values were adopted as goodness-of-fit criteria. The best combinations obtained on the chi data were then tested for reliability by fitting the normalized XANES spectra over the relative energy range −40 to 100 eV. Energy offset parameters were included in the fitting of XANES and constraints to sum to one and to have positive weighting factors were imposed. The fits for XANES were considered acceptable when the energy offset parameters were less than ±1.0 eV.

5.1.4 μXRF and μXRD

Samples were prepared by spreading the dust samples thinly on Kapton® tape and covering with ultralene. They were then placed in a cardboard slide-holder and attached to a vertical plastic sample holder oriented at 45° to the beam in the horizontal plane. Micro-XRF maps and μXRD patterns were collected on beamline 13-ID-C (GSECARS) at the Advanced Photon Source (APS) at Argonne National Laboratory (Illinois). The incident X-ray beam was focused using a pair of Kirkpatrick-Baez mirrors, and a monochromatic incident beam was achieved using a Si(111) double crystal monochromator. During μXRF map collection, the incident X-rays were tuned to 18,000 eV and focused to a spot size of 20 μm in the vertical direction by 20 μm horizontally. The motorized sample stage was translated in the *X* and *Y* directions through the beam path at 20 μm steps with a count time of 1 s per step. The emitted fluorescence X-rays of 13 elements (K Kα, Cl Kα, Ca Kα, Ti Kα, Cr Kα, Mn Kα, Fe Kα, Ni Kα, Cu Kα, Zn Kα, Br Kα, As Kα and Pb Lα) were collected simultaneously with a quad element Vortex detector (SII NanoTechnology USA Inc., Northridge, CA, USA), placed at 90° relative to the incident X-rays in order to minimize the interference from scattered X-rays.

Micro-XRD patterns were collected on selected areas of the μXRF map where Pb counts were either high or medium. Micro-XRD patterns were collected in transmission geometry using a MarCCD camera (Mar USA, Evanston, IL, USA) at 2,048 × 2,048 pixels and with the incident X-ray beam energy tuned to 18,000 eV ($\lambda = 0.6881$ Å). The distance between the sample and the X-ray detector and geometric corrections were calculated with FIT2D™ software (Hammersley 1998) using CeO_2 as the diffraction standard. Following these corrections the Kapton® tape and ultralene were subtracted from the data and the resulting 2D images were processed to produce 1D diffraction in the computer program, FIT2D (Hammersley 1998). The resulting diffraction patterns were imported into Jade 9.0, plotted as intensity versus *d* spacing, and phases were identified using the International Center for Diffraction Data (ICDD) database PDF-4 + (2008).

6 Results and Discussion

6.1 Sample Characterization

An archived vacuum sample of settled dust previously collected from an anonymous Canadian home was air-dried, homogenized, and sieved to the <80 μm size fraction. The sample was subjected to a total metal digestion and a simulated stomach acid extraction, with metal concentrations reported on a dry weight basis. Total elemental contents in the dust sample were determined using strong acid digestion followed by inductively coupled plasma mass spectrometry (ICP-MS), as follows: Ca 8.95 wt%; Fe 0.79 wt%; Al 1.16 wt%; Mn 156 mg kg^{-1}; Ni 45.5 mg kg^{-1}; Cu 260 mg kg^{-1}; Zn 1,220 mg kg^{-1}; and Pb 1,670 mg kg^{-1}. The bioaccessible content of Pb as determined by simulated stomach acid digestion was 1,586 mg kg^{-1}. Bulk powdered XRD analysis identified the presence of calcite and various alumino-silicates.

This study employs the Hamel et al. (1998) definition of "bioaccessibility", which is "the maximal amount of metal that is soluble in a synthetic gastric fluid, and therefore potentially available for transport across the intestinal lumen". The bioaccessible fraction was determined using a modification of the European Standard Toy Safety Protocol (described by Rasmussen et al. 2008): 25 mg test sample in 50 mL HCl solution (2,000:1 acid volume to sample mass ratio); 2 h in water bath at 37°C; 1 h agitation followed by 1 h no agitation; centrifuged at 3,500 RPM and diluted as required for ICP-MS. The pH of the extract was within the range 1.3–1.5 and met the requirement of the EN-71 protocol ($\text{pH} \leq 1.5$) without the addition of concentrated HCl. Thus a bioaccessibility of 95% was calculated for this sample (the concentration of the simulated stomach acid extraction divided by the total concentration, expressed as a percentage).

6.2 Pb Speciation

The Pb XANES and EXAFS spectra for few selected reference compounds are shown in Fig. 7 to illustrate that each species has a unique signature. Based on these specific features, the composite signal of mixed species in a complex matrix like dust can be modeled using the spectra of known species and LCF. Considering that the Pb EXAFS spectra carry more structural information and variation than does the XANES data, we relied first on the EXAFS data to allow for differentiation of Pb species in the house dust and the XANES data were used to test the reliability of the best fit derived from the EXAFS spectra.

The results from analysis of the EXAFS data (Fig. 8a) indicate that Pb is associated mainly with two phases: Pb-carbonate (45%) and Pb bound to an Fe phase (55%). However, the discrepancy in the XANES fit (Fig. 8b) and the large energy shift in the XANES data for the standard of Pb adsorbed on goethite (Fig. 8c) provide ambiguous data regarding the actual presence of a Pb species associated to Fe-oxyhydroxides in this dust sample and warrant further investigation. A combination of μXRF and μXRD was used for additional sample characterization, specifically to confirm the presence or absence of a Pb–Fe oxyhydroxide phase.

The Pb, Ca, Cr, Fe, Mn and Zn μXRF maps are shown in Fig. 9. Bright colors indicate areas with high concentration of the element of interest. From the XRF maps it can be seen that there is little correlation between Pb and the other elements

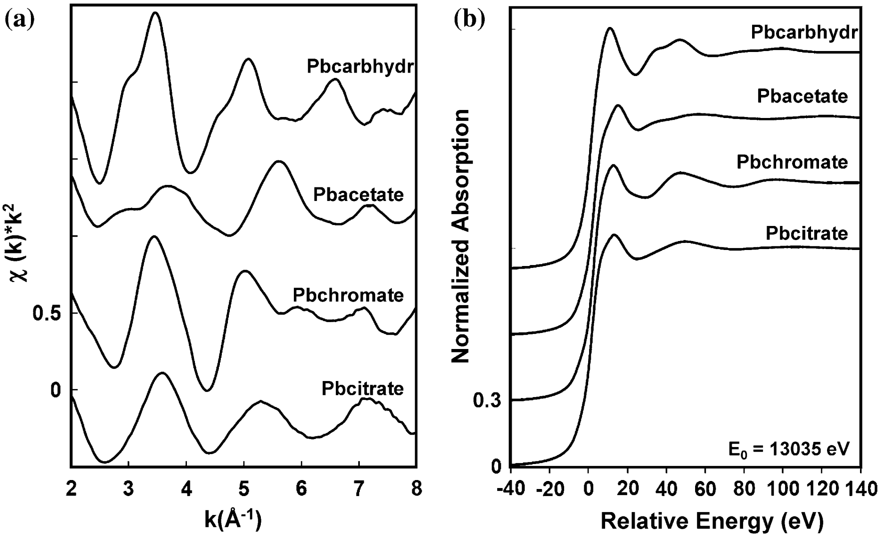
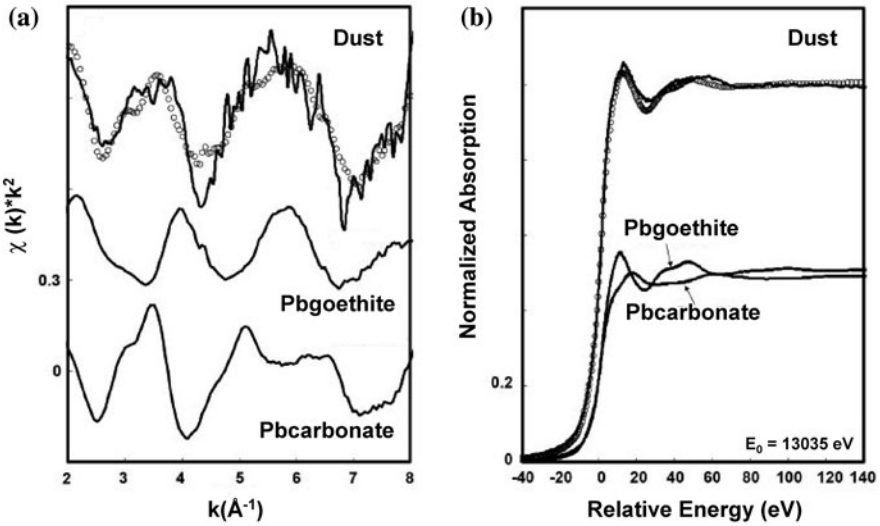


Fig. 7 Pb L-III edge EXAFS (**a**) and XANES (**b**) spectra for selected inorganic and organic Pb reference standards. *Pbcarbhydr* Pb hydroxyl carbonate, *Pbacetate* Pb acetate, *Pbchromate* crocoite, and *Pbcitrate* Pb citrate

of interest, except for some correlation with Fe in specific areas. This is consistent with the EXAFS results in that Pb is mostly present as a $PbCO_3$ (C and O were not measured in fluorescence) and as an adsorbed species on an iron oxide phase.

Micro-XRD patterns were collected from different regions of the Pb μXRF map, associated with various XRF counts of Pb, to determine the mineralogy associated with Pb. Two representative μXRD ring patterns and their corresponding 1D diffraction peak patterns are reported in Fig. 10. In a high Pb region with little iron present (Fig. 10b) the μXRD analysis identified hydrocerussite $(PbCO_3)_2{\cdot}(OH)_2$, calcite ($CaCO_3$), and quartz (SiO_2) as the major minerals while goethite (FeOOH) and a poorly crystalline iron oxide are likely present as a minor mineral species. No cerussite was identified. In another region of the μXRF map with both Pb and Fe present in moderate counts (Fig. 10c) Pb mineral species are absent and the spectrum is dominated by poorly crystalline iron oxides along with calcite, quartz, muscovite and an unidentified alumino-silicate. The discrepancy between the bulk EXAFS and μXRD data between cerussite and hydrocerussite is due to the similar EXAFS spectra of both at lower k-range. Significant structural differences occur only at higher k (Figs. 7 vs. 8) where the dust sample EXAFS data deteriorates. The slight discrepancy in the XANES fit and resulting energy shift (E_0) required to fit the data with the Pb-goethite spectrum (Fig. 8b, c) may indicate that the Pb-goethite standard is not the exact species present in the dust and that Pb may be adsorbed onto another iron oxide or on different mineral phase in this sample.

The presence of Pb hydroxyl carbonate suggests that a source of Pb in the house dust is derived from paint, since hydrocerussite has been widely used as a white



(c)

Sample concentration (mg kg^{-1})	Bioaccessible Pb† (mg kg^{-1}) (% of total Pb)	Pb standards‡	% of total Pb (± standard error) EXAFS	XANES	
1670	1586 (95%)		2 to 8 Å^{-1}	-40 to 100 eV	E_0 shift (eV)
		Pbcarbonate	45.0(±2.0)	51.0(±2.5)	-0.060
		Pbgoethite	55.0(±2.0)	49.0(±2.5)	-1.068
		Reduced χ^2	0.610	0.056	

† Pb bioaccessible content determined by the modified EN-71 method as described in Rasmussen et al. (2008).

‡ Pbgoethite: Pb adsorbed on goethite at 350 mmol Pb per kg goethite at pH 6.5; Pbcarbonate: cerussite ($PbCO_3$).

Fig. 8 Pb L-III edge EXAFS (**a**) and XANES (**b**) spectra for the house dust sample along with standards used to give the best fit. *Solid line* measured, *open circles* best LCF fit. Fitting parameters are shown in the table (**c**)

pigment in house paint (Van Alphen 1998; Hall and Tinklenberg 2003). When paint deteriorates it produces a powdery residue (chalking) that can contain Pb in significant amount in the case of old, Pb-based paints (Van Alphen 1998; Health Canada 2007). This powder eventually settles to surfaces and becomes part of the settled dust. The co-presence of both calcite and goethite with hydrocerussite in the sample could point towards indoor materials such as wall paint and/or wall boards often used in homes (Van Alphen 1998), although both calcite and goethite are also components of soils. Lead carbonates can also be present in soils but these Pb minerals have been mainly found in calcareous soils contaminated by mining wastes (Denys et al. 2007). Due to the high affinity of Pb for soil organic matter, it is likely that Pb adsorbed on humates would be the predominant Pb species in most soils. For example, in the top soil layers most likely to contribute to interior dust, Pb bound to humate has often been reported as the major phase in urban soils or soils contaminated by organo-metallics from gasoline (Pingitore et al. 2009; Manceau et al. 1996)

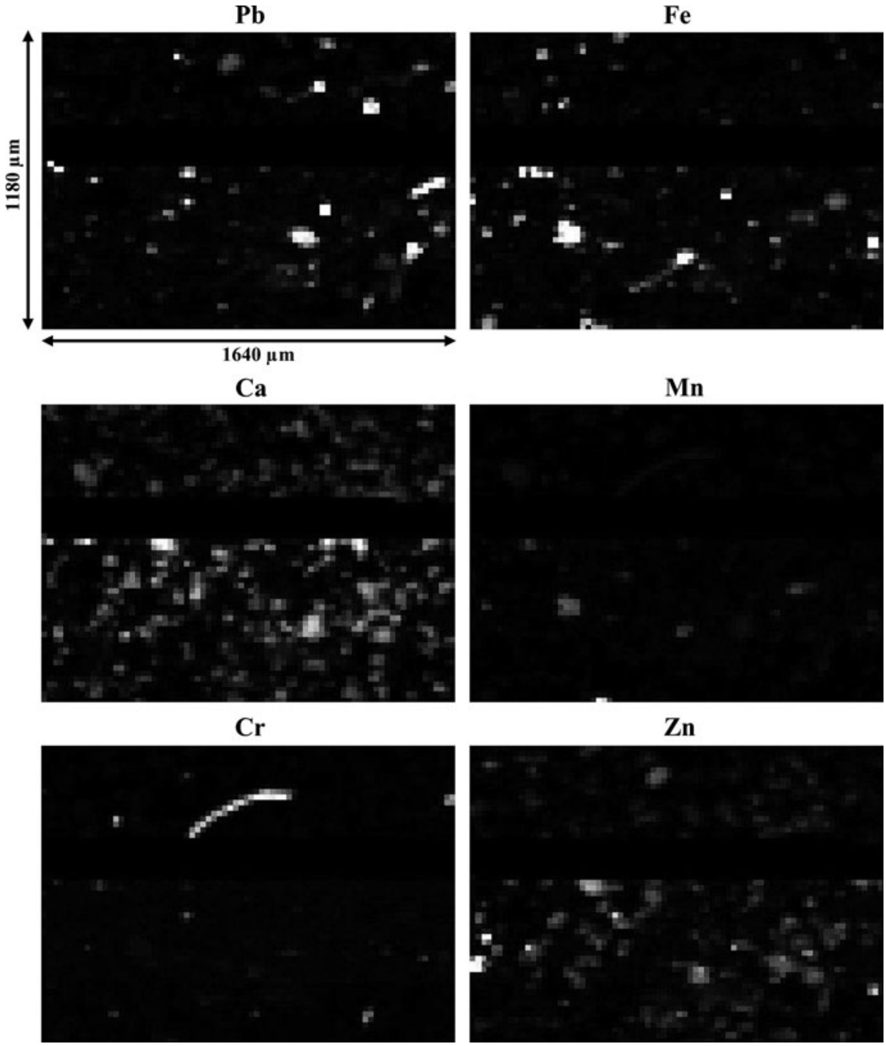


Fig. 9 Micro-XRF Pb Lα, Ca Kα, Cr Kα, Fe Kα, Mn Kα and Zn Kα maps collected from a surface of 1.64 mm × 1.18 mm of the dust samples at a step size of 20 µm. Pb and Fe maps show a small correlation in some areas between Pb and Fe. The bright spectral areas are regions with high concentration of the element of interest ($E = 18{,}000$ eV; count rate = 1 s/step)

as well as in soils contaminated by smelter (Morin et al. 1999) or in top soil layers developed on a Pb mineralized sandstone (Morin et al. 2001).

In the μXRF map at spot 2 both Pb and Fe are present; however, no Pb mineral species are identified in the μXRD pattern collected from that area. Instead, the μXRD pattern is dominated by muscovite, quartz, calcite, poorly crystalline iron oxides and peaks attributed to unidentified alumino-silicates. We attribute the absence of a Pb mineral phase in a region of the μXRF map where Pb XRF counts

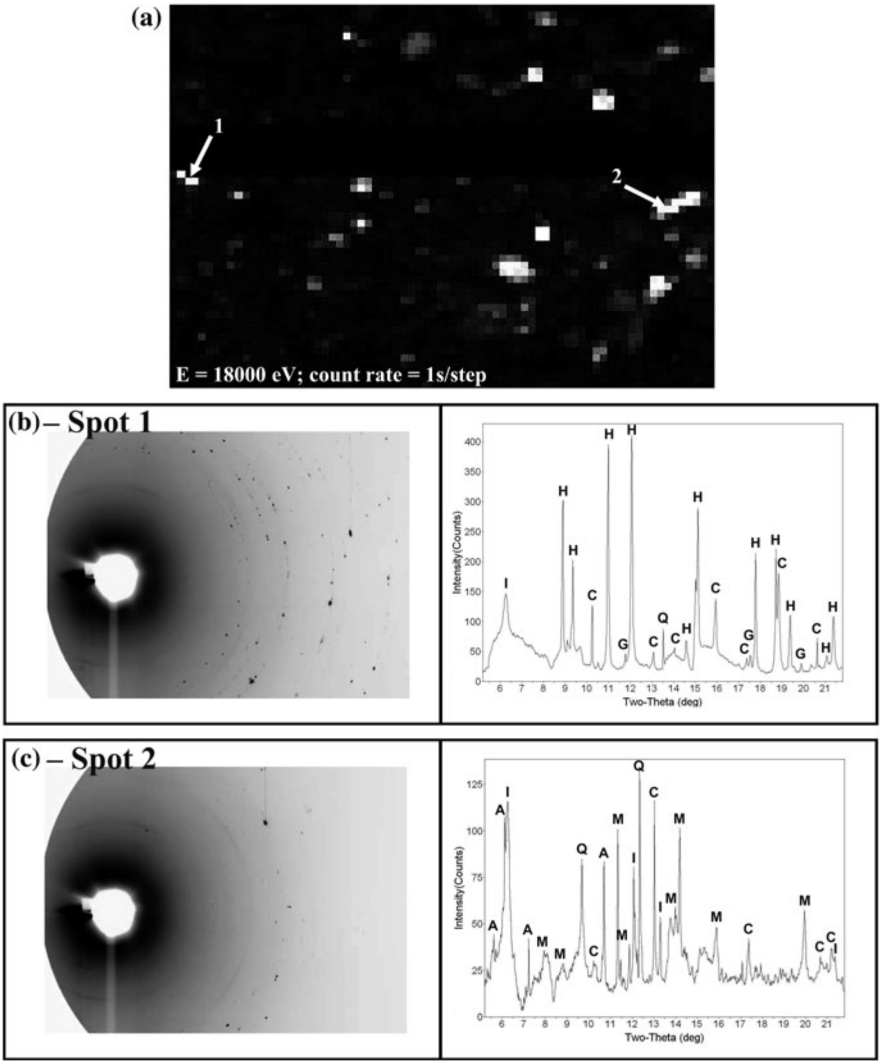


Fig. 10 **a** μXRF map (1.64 mm × 1.18 mm; 20 μm spot size) at Pb Lα showing areas where μXRD patterns (20 μm spot size) were collected; (**b**) 2D Debye rings and 1D diffraction patterns of spot 1 showing the major mineral phases of hydrocerussite (*H*; $(PbCO_3)_2 \cdot (OH)_2$) and calcite (*C*; $CaCO_3$), and the probable minor phase of goethite (*G*; FeOOH); and (**c**) 2D Debye rings and 1D diffraction patterns of spot 2 showing the major mineral phases as being muscovite (*M*; $KAl_2(AlSi_3O_{10})(F,OH)_2$), calcite (*C*; $CaCO_3$), quartz (*Q*; SiO_2), an unknown iron oxyhdyroxide (*I*), an unidentified alumino-silicate (*A*), and the broad humps likely associated with a poorly crystalline material

are moderate to be indicative of Pb present as an adsorbed phase which is likely why Pb-goethite gave a decent match in the LCF results. Pb adsorption to other mineral species such as alumino-silicates or calcite is another possibility that would require further investigation. The affinity of Pb for the silicate phase was reported by Manceau et al. (1996) who showed that Pb bound to silica was a predominant form in sandy soils contaminated by Pb acid batteries. Pb has also been demonstrated to adsorb to calcite (Rouff et al. 2005) and muscovite (Zhang and Bailey 1998). The Pb bound to a mineral phase (Fe-oxyhydroxide, aluminosilicate, calcite or muscovite) would likely indicate an outdoor source as these minerals are ubiquitous in soils (Schwertmann and Cornell 1991; Harris and White 2008), and can be tracked in on shoes (Roberts et al. 1996) or deposited by airborne particulate matter that was resuspended (Laidlaw and Filippelli 2008).

Thus, we conclude that the likely sources of Pb in this house dust originate from both indoor (Pb-based paint) and outdoor (soil) sources. These conclusions are similar to those of Adgate et al. (1998a, b) who used Pb isotopes to study the contributions from indoor versus outdoor Pb sources in New Jersey homes. Adgate et al. (1998a) estimated that around 35% of total Pb in house dust originated from lead-based paints compared to 50% coming from soil and street dust in an urban area.

6.3 Speciation as an Explanation of Sources and Bioacccessibility

The combined EXAFS, μXRF and μXRD characterization successfully answered the two main questions posed at the outset of the study. First, the methods identified that Pb in the dust mainly occurs as (1) the mineral hydrocerussite commonly used in indoor paint, and (2) adsorbed onto Fe-oxyhydroxides, which is commonly found in soil. This tells us that both indoor and outdoor sources contribute to the elevated Pb concentrations in the home from which this sample was collected. Second, the identification of these two soluble Pb compounds explained the observed high bioaccessibility of the Pb in this sample (95%), as both phases dissolve easily in a dilute HCl solution. Similarly, Casteel et al. (2006) reported that Pb carbonate, Pb carbonate hydroxide and Pb adsorbed onto goethite are readily bioaccessible in gastric juices. Thus, the in situ investigation to determine the Pb speciation by XAFS and μXRD explained the high Pb bioaccessibility in this sample, while identifying probable sources for the metal.

7 Summary

The synchrotron radiation-based X-ray techniques presented here are powerful tools for characterizing the speciation of metals in house dust samples because of the metal specificity, high spatial resolution and ability to examine elements of interest with little to no sample preparation or pre-treatment. Bulk XAFS analysis can be used to infer the chemical speciation of an element of interest in both moist and dry samples while μ-XRF and μ-XRD can determine the spatial relationship between trace metals and associated mineral particles.

The Pb dust analysis demonstrated the applicability of XAFS, μ-XRF and μ-XRD to determine the speciation of trace metals in heterogeneous samples. The X-ray techniques successfully identified the speciation and potential sources of Pb in house dust samples, and provided an explanation for the observed high bioaccessibility. Linear combination fitting of the EXAFS $\chi\ (k)\cdot k^2$ data of a Pb-elevated house dust sample show that Pb is complexed in two environments, as both a mineral (hydrocerussite) and an adsorbed species (adsorbed onto an iron oxide). The main findings from the Pb dust analysis can be summarized as follows: (1) The presence of Pb hydroxyl carbonate suggests that this portion of lead is from paint as hydrocerussite has been used as a white pigment in house paint; and (2) The source of Pb adsorbed to iron oxyhydroxide is likely to have an outdoor soil source, as iron oxyhydroxides are common in soil environments.

Ultimately this approach has the potential to fingerprint the various sources of Pb in houses (outdoor vs. indoor) and help determine any transformation processes that Pb compounds may undergo inside a building. Understanding these sources and processes will have important implications for risk management within the indoor environment.

Acknowledgments Funding for this project comes from Health Canada's Chemicals Management Plan Surveillance and Monitoring Fund (ref. no. CRRS/SDRC: 4500177216). XAFS spectroscopy was conducted at the beamline X-11A at the National Synchrotron Light Source, which is supported by the US Department of Energy, Division of Material Sciences and Division of Chemical Sciences, under contract number DE-AC02-98CH10886. The beamline X-11 is supported by the Office of Naval Research and contributions from Participating Research Team (PRT) members. The authors are very grateful to Dr. Kumi Pandya for her help with the set-up at the beamline. Micro-XRF and micro-XRD experiments were performed at GeoSoilEnviroCARS (Sector 13), Advanced Photon Source (APS), Argonne National Laboratory. GeoSoilEnviroCARS is supported by the National Science Foundation—Earth Sciences (EAR-0622171) and Department of Energy—Geosciences (DE-FG02-94ER14466). Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. In addition, Matt Newville and Nancy Lazarz are thanked for their help during the experimental runs at 13-ID. Sincere thanks are extended to Christine Lévesque and Marc Chénier for the chemical characterization of the selected samples (Health Canada, Ottawa). The contribution of Ted MacKinnon for sample preparation for XAFS analysis and Dr. John Wilson for part of the XRD analysis on the standards (CANMET-MMSL, Ottawa) are acknowledged.

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Ultra-Trace Analysis of Palladium: State-of-the-Art and Future Challenges

C. Puls, A. Limbeck and S. Hann

1 Introduction

Due to the introduction of the three-way catalytic converter (TWC) in Europe in the mid-eighties, determination of platinum group elements (PGE) in environmental compartments has received elevated interest over the past two decades. While improving air quality by converting hydrocarbons, carbon monoxide, and nitrogen oxides into the less harmful substances carbon dioxide, nitrogen, and water, the use of these devices constitutes a new source for the widespread emission of PGE into the environment.

Catalytic converters are composed of a monolithic support surrounded by a mat and tightly packed into a stainless steel housing. The monolith has a honeycomb structure traversed by straight, square channels and consists of a ceramic or sometimes metallic material, coated with the so called washcoat. To carry out the catalytic reactions, PGE are dispersed throughout the washcoat, which typically has a thickness of about 10–30 μm at the walls and 100–150 μm at the corners of the support channels and contains as major constituents alumina and other oxides.

While in the early years the classical Pt/Rh catalyst dominated the market, Pd was successively used to replace Rh and later Pt, leading finally to the development of the Pd-only catalyst. In 2008, 136.2 tonnes of Pd was used for catalytic converters, accounting for 63.9% of the worldwide demand (Johnson Matthey 2009).

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_10,

Washcoat particles containing PGE are emitted into the environment due to surface abrasion and deterioration of those catalytic converters, which is mainly caused by thermal stress and vibration of the catalytic material. These particles range in size from several micrometers down to sub-micrometers (Gomez et al. 2001; Zereini et al. 2001) and are emitted at rates in the ng km^{-1} range (Moldovan et al. 1999; Palacios et al. 2000; Limbeck et al. 2007).

As a consequence, accumulation of Pd and other PGE has been detected in road dust as well as soil and grass samples collected along highways (Barefoot 1999; Zereini and Alt 2000; Ravindra et al. 2004). Pd concentrations in airborne particulate matter (APM) samples (particulate matter <10 μm, PM10) were reported to be in the range of 2.6–32 pg m^{-3} on urban sampling sites (Gomez et al. 2003; Kanitsar et al. 2003; Zereini et al. 2005).

It has been assumed in the past that PGE contained in particulates from car exhaust are emitted primarily in their metallic form and are therefore rather inert. Nevertheless, recent studies have shown that significant portions of those PGE are soluble in diluted acid solutions (Zereini et al. 2001; Moldovan et al. 2002) or rain water (Limbeck 2006). Numerous publications have shown that the mobility of PGE into the environment, as well as the uptake of those elements into flora and fauna is increasing according to Rh < Pt < Pd (Schäfer et al. 1998; Moldovan et al. 2001; Sures et al. 2002; Ek et al. 2004; Turner et al. 2006).

In order to evaluate possible hazards for the environment and human health it is crucial to develop analytical strategies for fast and easy quantification of traces and ultra-traces of Pd in environmental matrices as well as biological tissues and fluids. Despite the efforts of numerous workgroups, a reliable method for the determination of Pd in all environmental matrices has yet to be developed. Up to date, the most important analytical methods for this task are electrothermal atomic absorption spectrometry (ETAAS), inductively coupled plasma-mass spectrometry (ICP-MS) and isotope dilution (ID)-ICP-MS, also strategies involving inductively coupled plasma-atomic emission spectrometry (ICP-AES), and electrochemical methods like anodic stripping voltammetry (ASV) have been described. Furthermore, total reflection X-ray fluorescence (TXRF) and instrumental neutron activation analysis (INAA) have been successfully employed for the determination of PGE in environmental matrices.

2 Palladium in Airborne Particulate Matter

Palladium analysis in APM poses additional challenges, since usually small sample sizes with very low analyte concentrations are involved. Additionally, information about the apportionment of Pd into the size fractions of APM is needed to assess the risk posed by Pd emissions and the occurring long-range transport of PGE contaminants, which are thereby polluting even background sites. Over the last years, several studies have focused on the determination of Pd in APM, employing various analytical methods for analyte enrichment, matrix elimination and quantification of Pd. Concentrations in urban environment usually varied from not detectable up to 150 pg m^{-3}, in heavily polluted areas even 2.1 ng m^{-3} could be determined (da Silva et al. 2008). Details about Pd determination in urban particulate matter are given in Table 1.

Since exhaust fumes of vehicles equipped with catalytic converters are believed to be the main contributor to Pd emissions into the environment, dynamometer studies have been carried out to evaluate the amount of PGE released into the environment by abrasion of the catalyst material (e.g. Moldovan et al. 1999). It has been pointed out that the tailpipe emission of PGE is strongly dependent of age and type of the respective catalytic converter, as well as of the driving conditions. In case of dynamometer studies conducted in the laboratory, standardized driving cycles under controlled conditions are employed. While guaranteeing the comparability of the achieved results, real-world driving conditions may be different (Fraser et al. 1999). Furthermore, results derived from tests of single vehicles cannot reflect the emissions caused by the existent car fleet, which is composed of a wide variety concerning age, type and maintenance conditions of vehicles. Additionally, dynamometer studies do not consider non-tailpipe emissions like wear of brakes, tires and asphalt or resuspension of road dust, which can lead to serious underestimation of the environmental impact (Sternbeck et al. 2002).

To determine emission data based on real-world conditions, tunnel studies involving large numbers of cars are an approach of choice. Simultaneous determination of the pollutant concentrations at the entrance and exit of the tunnel as well as monitoring of traffic density and speed, temperature, air pressure and wind speed are used for calculation of vehicle emission factors representative for the respective car-fleet-composition.

A tunnel study conducted in two tunnels in Milwaukee (WI, US) reported for Pd a mean PM10 emission rate of 150 ± 130 ng $vehicle^{-1}$ km^{-1} (Lough et al. 2005), while in Vienna, Austria Pd emission rates ranged from 4.6 to 24 ng $vehicle^{-1}$ km^{-1} (Limbeck et al. 2007). This discrepancy can be explained by the differing car fleet compositions of the US and Europe, since the percentage of diesel powered vehicles is distinctly higher in Europe.

To assess the potential health risks of the Pd content in APM, mainly the respiratory intake has to be considered. It has been shown that the intake of PGE through respiratory pathways is significantly higher than through the digestive tract (Colombo et al. 2008). The main parameter influencing the respiratory uptake of particulate matter is the aerodynamic diameter (aed) of the particle, as defined in Standard ISO 7708: 1995, but information about the size segregation of Pd in APM is still sparse. For the alveolar fraction smaller than 2.5 μm aed, Kanitsar et al. (2003) used a 6-stage impactor for sampling and reported a maximum in the fraction of 1–2.15 μm aed. In this study, Pd concentrations of individual fractions ranged from 0.1 to 1.4 pg m^{-3}. In order to achieve detectable amounts of Pd, sampling periods lasted seven days, which corresponded to sample sizes ranging from 566.4 to 640.7 m^3, depending on the respective weather conditions.

Table 1 Methods for determination of Pd in airborne particulate matter

Location	Separation	Determination	Detection limit	Sample type	Concentration range	References
Karlsruhe	NiS fire assay	ICP-QMS	0.4 ng g^{-1}	Road dust	<35 ng g^{-1}	Schäfer et al. (1999)
	Te coprecipitation			Urban APM	nd–27.2 ng g^{-1}	
Czech Republic	Modified silica C18 + Septonex	ICP-QMS ICP-AES	50 ng l^{-1} 5000 ng l^{-1}	APM	nd–280 pg m^{-3}	Vlasankova et al. (1999)
Berlin	FIAS DEBT	ETAAS	13 ng l^{-1}	Urban APM	<0.2–14.6 pg m^{-3}	Tilch et al. (2000)
Rome		HR-ICP-MS	2.5 ng g^{-1}	Road dust	11.8–504 ng g^{-1}	Petrucci et al. (2000)
			1 pg m^{-3}	Urban APM	2.1–98.6 pg m^{-3}	
Göteborg		ICP-QMS	0.9 pg m^{-3}	Urban APM	<0.9–151 pg m^{-3}	Rauch et al. (2001)
			0.6 pg m^{-3}	Urban PM10	1.3–9.7 pg m^{-3}	
				Urban PM2.5	0.7–2.2 pg m^{-3}	
Madrid	Te coprecipitation	ICP-QMS	0.6 pg m^{-3}	Urban PM10	5–32 pg m^{-3}	Gomez et al. (2003)
Graz		ID-ICP-QMS	1 ng g^{-1}	Road dust	26–75 ng g^{-1}	
				Tunnel dust	4.3–5.1 ng g^{-1}	
Vienna	FIAS DEBT	ETAAS	23 ng l^{-1}	Urban APM	4–16 pg m^{-3}	Limbeck et al. (2003)
Vienna	Anion exchange	ID-ICP-SFMS	0.22 pg m^{-3}	Urban APM	10.4–17.9 pg m^{-3}	Kanitsar et al. (2003)
			0.06 pg m^{-3}	Urban PM10	1.9–3.0 pg m^{-3}	
Frankfurt am Main	Hg coprecipitation	TXRF	170 pg g^{-1}	Urban APM	<0.6–44.3 pg m^{-3}	Zereini et al. (2004)
				Urban PM10	9.4–29.3 pg m^{-3}	
Salzburg	FIAS DEBT	ETAAS	23 ng l^{-1}	Urban PM10	7.1–31.2 pg m^{-3}	Limbeck et al. (2004)
Klagenfurt					2.9–5.0 pg m^{-3}	
Boston	NiS fire assay	ICP-SFMS		urban PM10	0.8–39 pg m^{-3}	Rauch et al. (2005)
Vienna	FIAS DEBT	ETAAS	25 ng l^{-1}	Urban APM	2–13 pg m^{-3}	Limbeck (2005)
Vienna	FIAS DEBT	ETAAS	21 ng l^{-1}	Tunnel APM	10–33 pg m^{-3}	Limbeck et al. (2007)
				Tunnel PM10	4–19 pg m^{-3}2.6–	
				Tunnel PM2.5	7.9 pg m^{-3}	
Rio de Janeiro		ICP-MS	0.92 ng g^{-1}	Urban PM10	60–2100 pg m^{-3}	da Silva et al. (2008)

Therefore, in order to gain further information on the Pd content of ambient PM2.5 or short term variation thereof or to conduct studies on various extractable fractions, e.g. the bioaccessible fractions extractable by gastric juice or lung fluid, accurate and sensitive analytical strategies accounting for the involved ultra-trace concentrations, small sample sizes and complex matrices are crucial.

3 Analytical Methods

3.1 Electrothermal Atomic Absorption Spectrometry

In electrothermal atomic absorption spectrometry (ETAAS), a small sample volume of typically 20–100 μl of liquid or 0.1–1.0 mg of solid sample is introduced into a graphite tube mounted in the optical path of a spectrometer. A temperature program, realized by electrothermal heating of the tube, ensures in a first step drying and pyrolysis of the sample, thus eliminating part of the matrix constituents. Afterwards, the remaining analytes are atomized to generate free atomic vapor within in the graphite tube, providing a 100- to 1000-fold increase of residence time of the analyte vapor in the optical pathway of the spectrometer compared to flame or ICP-excitation sources. Of course, remaining matrix constituents experience the same treatment, inducing gas-phase (chemical) interferences (Kántor 2001).

Commercially available ETAAS instruments providing transverse heating of the graphite atomizer (THGA) and Zeeman-effect background correction can compensate most of those interferences, making ETAAS an effective tool for determination of PGE. Nevertheless, an inherent drawback of this technique is the low productivity of most AAS systems, since usually ETAAS instruments are only able to perform single-element analysis, although some instruments show capability for multi-element measurements for up to six analytes (Radziuk et al. 1995).

Achievable detection limits for direct Pd quantification in solutions employing ETAAS are in most cases in the μg l^{-1} range, which is not sufficient for most environmental or biological sample digestions. Accordingly, preconcentration of analytes is necessary to reach adequate sensitivity.

3.2 Inductively Coupled Plasma-Mass Spectrometry

Of all atomic spectroscopic methods, ICP-MS is unrivalled concerning its detection power (Bencs et al. 2003). Its capability to process fast transient signals is crucial for the combination with sample preparation methods that generate impulse signals, like e.g. ablation techniques or most on-line preconcentration systems.

However, due to the sample introduction into the plasma and the thereby occurring spectral and non-spectral interferences, the determination of palladium is not straightforward. The formation of molecular or doubly charged ions of matrix constituents or the plasma argon poses a considerable impediment.

As quadrupole ICP-MS (Q-ICP-MS) usually has a mass resolution of approximately 300 $m/\Delta m^{-1}$, it is advantageous to employ high resolution (HR) sector field (SF)-ICP-MS since it is without argument better suited for eliminating spectral interferences ($m/\Delta m < 9{,}000$). Additionally, its enhanced sensitivity yields detection limits improved by a factor of 50–100. But even HR-ICP-MS does not allow the separation of all occurring interferences. An overview of possible spectral interferences on Pd isotopes and the mass resolution required for

Table 2 Isotope abundances and main potential interferences for Pd determination

Isotope	Abundance (%)	Interference	Abundance (%)	Required resolution (m/Δm)
^{102}Pd	1.02	^{86}Sr^{16}O	9.84	71,700
		^{204}Hg^{2+}	6.85	1,257
		^{204}Pb^{2+}	1.37	1,261
		^{102}Ru	31.60	80,780
^{104}Pd	11.14	^{40}Ar^{64}Zn	48.61	8,300
		^{88}Sr^{16}O	82.36	29,800
		^{104}Ru	18.7	74,400
		^{208}Pb^{2+}	52.38	1,234
^{105}Pd	22.33	^{40}Ar^{65}Cu	30.71	7,042
		^{89}Y^{16}O	99.76	24,370
		^{88}Sr^{17}O	0.03	330,000
		^{87}Sr^{18}O	0.01	35,260
		^{87}Rb^{18}O	0.01	32,100
		^{88}Sr^{16}O^{1}H	82.37	31,980
		^{68}Zn^{37}Cl	4.5	7,320
		^{36}Ar^{69}Ga	0.20	92,000
		^{70}Zn^{35}Cl	0.45	9,615
		^{35}Cl^{35}Cl^{35}Cl	43.5	72,044
^{106}Pd	27.33	^{40}Ar^{66}Zn	27.79	7,033
		^{90}Zr^{16}O	51.34	27,492
		^{89}Y^{17}O	0.037	58,800
		^{88}Sr^{18}O	0.16	70,600
		^{106}Cd	1.25	35,468
^{108}Pd	26.46	^{40}Ar^{68}Zn	18.72	6,474
		^{38}Ar^{70}Ge	0.014	8,600
		^{92}Zr^{16}O	17.07	27,386
		^{92}Mo^{16}O	15.01	49,724
		^{108}Cd	0.89	369,535
^{110}Pd	11.72	^{40}Ar^{70}Ge	20.44	5,927
		^{94}Mo^{16}O	9.33	21,265
		^{40}Ar^{70}Zn	0.62	6,300
		^{94}Zr^{16}O	17.36	27,929
		^{110}Cd	12.49	50,834

separation is given in Table 2. High concentrations of matrix constituents can lead to non-spectral interferences, leading to suppression or enhancement of the analyte signals, but mostly spectral interferences, originating from metal oxides, metal-argon cluster ions or isobaric metal species, are dominating.

Apart from high resolution mode, which is not able to eliminate all those interferences, further possibilities to overcome these interferences are mathematical correction procedures, which can be applied to rectify results, but they have to be specifically modeled for each sample matrix (Krachler et al. 1998; Barbante et al. 2001; Caroli et al. 2001) and are prone to errors due to the relatively high abundance of interferents. By employing membrane desolvation for the reduction of oxide formation, spectral interferences can be significantly reduced, but in case of road dust mathematical correction still had to be applied to compensate for Sr interference (Köllensberger et al. 2000). To further minimize the risk of interferences, pretreatment routines have to be employed, entailing additional risks of analyte losses.

For poly-isotopic elements like Pd, ID constitutes a further option for quantification. For ID, an isotope enriched spike is added to the sample, allowing the determination of the analyte content by measuring the isotope ratio of the spiked sample. One of the key features of the method is that the result is unaffected by instrumental signal drifts or analyte losses occurring after ID. Since total or reproducible analyte recovery is often problematic in trace and ultra trace analysis, ID is well suited for this task, especially if extensive sample pretreatment is employed (Heumann 2004).

On the other hand, ID requires the interference free measurement of two isotopes for accurate quantification. In case of Pd, the necessity for matrix elimination is even more evident if ID-MS is used. The accurate determination of Pd in soil and road dust by ID-ICP-MS employing multi-stage sample pretreatment including microwave digestion, matrix elimination by cation exchange and solid phase preconcentration, has been described (Rudolph et al. 2006).

3.3 Inductively Coupled Plasma-Atomic Emission Spectrometry

In the past, ICP-AES has also been employed for determination of PGE, but use of this technique is limited due to its lower sensitivity when compared to ICP-MS (Rao and Reddi 2000). Furthermore, abundance of PGE in most samples is several magnitudes lower than that of transition metals, which cause considerable spectral interferences of the analytical lines. Therefore, not only the selection of applicable spectral lines is crucial, but in most cases, adequate matrix removal is a precondition for PGE-quantification.

In case of road dust, quantification of Pd using the 340.458 nm line could only be performed after removal of interfering elements (Ce and Zr), whereas the 363.47 nm line was completely overlapped by Ar (Kovacheva and Djingova 2002).

3.4 Anodic Stripping Voltammetry

Although a sensitive anodic stripping voltammetry (ASV) method for the determination of Pt based on accumulation of a Pt^{2+}–formazone complex on a hanging mercury drop electrode (Zhao and Freiser 1986) has been applied to a variety of biological and environmental samples, measurement of Pd by electrochemical methods remains, due to the irreversibility of electrode processes, rather difficult. Often ligands containing oxime-groups are used for adsorptive accumulation of Pd on Hg electrodes, since in complex forming media reduction of Pd is accelerated. A method employing dimethyl-glyoxime for enrichment of Pd on a hanging mercury drop electrode with a detection limit of 20 ng l^{-1} has been described (Wang and Varughese 1987) and applied to the measurement of some spiked environmental and biological materials (Georgieva and Pihlar 1997).

The method is extremely sensitive to the presence of organic matrix constituents, e.g. surfactants. Hence, for the determination of PGE in complex organic matrices adequate matrix decomposition or removal procedures are required.

3.5 X-ray Fluorescence Spectrometry

Generally, the sensitivity of X-ray spectrometric methods is not sufficient for direct measurement of PGE in environmental samples. However, adequate total reflection X-ray fluorescence (TXRF) methods have been developed to enable, after adequate sample preparation and analyte enrichment via Hg-coprecipitation, PGE-determination in various samples like road dust, airborne particles or liver and kidney tissue of exposed European eels (*Anguilla anguilla*) (Messerschmidt et al. 2000; Sures et al. 2001).

4 Sample Pretreatment

Especially for environmental samples, pretreatment is crucial to prepare the sample for analysis. Depending on the employed analytical technique, sample digestion, removal of interfering matrix constituents and preconcentration of the analytes are required to allow accurate measurement.

Several methods have been proposed for digestion of samples of differing origin. With respect to the sample composition and the intended analytical technique, acidic dissolution, microwave assisted digestion, chlorination and fire assays have been proposed. Generally, these procedures allow removal of matrix as well as simultaneous enrichment of analytes.

In case of APM, special attention has to be given to the filter substrate, which mostly has to be dissolved completely prior to analysis.

4.1 Dissolution Techniques

4.1.1 Fire Assays (Docimasy)

Fire assay techniques have been developed predominantly for the processing of geological samples. It uses rather large sample sizes (4–100 g), which are mixed with a fluxing agent (consisting of $Na_2B_4O_7$, Na_2CO_3 and SiO_2) and a collector. For Pd, the NiS fire assay, using Ni and S as collector substances, has proven to be most effective for quantitative recovery, as well as the approach using PbO and starch (Balcerzak 2002).

The blend is molten in a fireproof crucible at temperatures up to 1100°C. The fusion leads to the production of a NiS-button containing the precious metals, while most matrix elements react with the flux components to form slag, which is discarded. The NiS-button is cut up and dissolved with HCl, while Pd and other insoluble noble metal sulphides remain in the residue to be filtered off and dissolved with diluted HNO_3 or HCl and H_2O_2. PGE-recovery is reported to improve if Te-coprecipitation is used after the digestion of the NiS-button with HCl (Shazali et al. 1987).

Although fire assay procedures are able to preconcentrate the analyte and to remove part of the interfering matrix and have been successfully applied to environmental samples like road dust (Zischka and Wegscheider 2000; Jarvis et al. 2001) or fluvial sediments (de Vos et al. 2002), a drawback is that the selection of type and amount of the fluxing agent as well as the furnace condition is subjective. Therefore, fire assay procedures require an experienced operator to achieve good results. Another disadvantage of fire assays is the high amount of reagents added to the sample, leading to a high procedural blank of low ng g^{-1} levels (Ely et al. 1999), precluding analysis of ultra trace levels of Pd. For APM, fire assay techniques are not applicable, since APM sample amounts tend to be limited to approximately 1 to 10 mg, even if high volume samplers are employed.

4.1.2 Digestion Methods

Wet digestion procedures for a multitude of sample types using various acid mixtures consisting of HNO_3, HCl, HF, $HClO_4$ or H_2O_2 have been widely examined. The most common method is dissolution in *aqua regia*, with additional HF for decomposition of silica matrix constituents. For a variety of matrices, e.g. road dust, APM, soil, blood and urine, various combinations of open vessel treatments, high pressure bombs and microwave assisted methods are employed.

Although accurate results were also reported for leaching road dust with *aqua regia* under high-pressure and temperature without HF (Müller and Heumann 2000), addition of HF is mostly required for siliceous samples. Efficient HF digestion procedures have been recommended to dissolve strongly bound Pd from silicates (Limbeck et al. 2003). Excess HF is evaporated in open vessels or masked by addition of a H_3BO_3 solution (Boch et al. 2002). To avoid the necessity to evaporate large amounts of oxidants after digestion of samples containing dissolved organic matter, UV-assisted microwave digestion involving only small amounts of H_2O_2 has been proposed (Limbeck 2006). To decompose the organic matrix in biological materials, such as blood samples, UV-photolysis is recommended (Begerow et al. 1997). APM usually requires microwave-assisted digestion with *aqua regia* and HF for total decomposition.

As the formation of anionic PGE-chloro-complexes during mineralization is often a prerequisite for subsequent enrichment or matrix separation procedures, mineralization is in some cases followed by one or multiple open vessel evaporation treatments with *aqua regia* or HCl.

4.2 Enrichment and Matrix Separation

4.2.1 Coprecipitation

For preconcentration and matrix elimination, reductive coprecipitation involving a suitable collector can be applied. For airborne and road dust, a method for ICP-MS measurement using Te^{4+} as carrier has been demonstrated (Gomez et al. 2003). Generally the coprecipitation procedure consists of the reduction of added Te^{4+} by stannous chloride, triggering the precipitation of Pd, which is equally reduced in an acid medium. Boiling the solution breaks down the occurring $(Pd^0Sn_4Cl_4)^{4+}$ complex (Amosse 1998). The precipitate is filtered off and dissolved in HNO_3 or *aqua regia*.

Often Te-coprecipitation is used to reduce analyte losses occurring during the dissolution of the NiS-button in fire assays (Sun et al. 1998; de Vos et al. 2002). For environmental samples like APM however, Te-coprecipitation is often employed as sole preconcentration procedure (Schäfer et al. 1999; Gomez et al. 2003).

Another coprecipitation procedure, using Hg as collector and formic acid as reducing agent, has been optimized for Pd measurement employing TXRF (Messerschmidt et al. 2000; Sures et al. 2001). Since reduced Pd, unlike Pt, exhibits high solubility in Hg, it can be effectively enriched in the resulting Hg bead. After transferring the collector to a sample carrier, it can be removed afterwards by evaporation at 300°C with assistance of a Hg-absorber.

4.2.2 Liquid–Liquid Extraction

Another technique for separation from the matrix and preconcentration of Pd is complexation of the analyte with organic ligands and extraction of the neutral product with an organic solvent. Various combinations of ligand and solvent have been proposed, like dimethylglyoxime and chloroform (Brzezicka and Szmyd

1999), formation of a Pd(II)–$SnCl_3$–*N*-butylacetamide complex and extraction with 1-pentanol (Patel et al. 2000). Ion pairing involving $Pd(SCN)_4^{2-}$ and a crown ether with subsequent extraction into chloroform and re-extraction as $Pd(NH_3)_4^{2+}$ has also been proposed (Hossain and Honjo 2000).

Cloud point extraction, using a surfactant to form micellar structures which associate with metal chelates and achieving phase separation through elevation of temperature, has also been evaluated for analysis of noble metals in digested biological samples (da Silva et al. 2001).

Nevertheless, due to the necessity for extensive and time consuming manual operation, liquid–liquid extraction still bears increased risk for sample contamination or analyte loss.

4.2.3 Solid Phase Extraction

The use of solid phase extraction (SPE) techniques in sample preparation is widely spread, since a wide variety of substrates interacting variously with different metal species or organic compounds is available (Fritz 1999). Furthermore, SPE procedures are well suited for automatization and usually require less organic solvents than liquid–liquid extraction techniques.

Accordingly, many different SPE sorbents have been employed for Pd analytics. Due to the fact that Pd forms highly stable anionic chloro-complexes in hydrochloric solutions while other metals are mostly present as weaker anionic or stable cationic species, ion exchange methods can be employed for separation of these compounds. To eliminate cationic species, various cation exchange sorbents have been employed (Lesniewska et al. 2006). In this case, it is necessary to use an excessive mass of cation exchange sorbent to ensure the retention and to prevent breakthrough of the large amounts of base metals usually present in environmental samples. Other studies used on-line coupled cation exchanger systems like packed Dowex AG50W ×8 columns (Meisel et al. 2003) or silica capillaries, modified with 2-(4-chlorosulfophenyl)ethyltrichlorosilane to gain cation exchange functionality, to eliminate metals interfering with the subsequent ICP-MS measurements.

A potential difficulty of these methods is that several elements occur as anionic species and are therefore not retained by cation exchange sorbents. Among these are Y, Zr and Mo, which form oxide interferences impeding Pd quantification (Jarvis et al. 1997).

The high affinity of Pd-chloro-complexes to strong anion exchange materials enables the use of various anion exchange sorbents for preconcentration of Pd with simultaneous elimination of cationic interferents. Especially styrene or acrylic polymers cross-linked with divinylbenezene can be applied for enrichment of PGE from large sample volumes (Matsubara et al. 2000; Kovacheva and Djingova 2002; Lesniewska et al. 2006).

However, several other anionic compounds are also retained by those materials and are thereby preconcentrated, causing spectral interferences of Pd determination by ICP-MS. Among those elements retained on anion exchange resins are Fe, Sr, Cu, Mo and Zr (Hann et al. 2001; Kovacheva and Djingova 2002). Furthermore, elution of the strongly bound Pd-complexes proves to be quite difficult, even if high amounts of hot acids are used. This leads to diminished recoveries and also causes memory effects, necessitating the use of fresh SPE-sorbent for each analysis (Müller and Heumann 2000; Hann et al. 2001).

Sorbents based on cellulose modified with weak anion exchange groups were also used for preconcentration of PGE. Since the analytes are more weakly retained by these materials, they can be elueted more easily with mineral acids or thiourea solution (Godlewska-Zylkiewicz et al. 2000). The method worked well for determination of Pd with ETAAS, but an unidentified interference, probably caused by deteriorating resin, prohibited Pd-quantification with ICP-MS.

Activated alumina can function as cation or anion retaining sorbent, depending on pH. Accordingly its acidic form is suitable for enrichment of anionic PGE-chloro-complexes from water samples stabilized with 2% (v/v) HCl (Moldovan et al. 2003). Elution was carried out on-line with 300 μl 0.3 M KCN solution for ICP-MS determination.

To enhance the selectivity of the preconcentration procedure and thereby avoid quantification errors caused by simultaneously eluted interferents, adsorption on chelating sorbents was used for sample treatment prior to ICP-AES detection. Complete recovery of Pd could be achieved by eluting with 2 ml of 1 M thiourea and 1 M sodium perchlorate in 4 M HCl (Muzikar et al. 2006).

Preconcentration of Pt and Pd by ion-pairing of the respective chloro-complexes with a cationic surfactant (*N*(1-carbaethoxypentadecyl)-tri-methylammonium bromide, $C_{21}H_{44}ONBr$/Septonex) with subsequent adsorption on C18 silica gel and elution with ethanol was employed for both ICP-AES and ICP-MS quantification, although the eluent had to be evaporated and the residue transferred into a 0.1 M HCl solution before measurement (Vlasankova et al. 1999).

Instead of combining Pd- or PGE-selective reagents and adsorbing the emerging complexes on conventional SPE-sorbents, functionalization of those materials by binding the complexing agent onto the sorbent prior to sample loading is an option. Using the strong complex forming agent *N*,*N*-diethyl-*N*′-benzoylthiourea (DEBT) loaded reversibly onto a microcolumn filled with a C18 material; elution could be accomplished with 60 μl of ethanol, which was directly transferred into a graphite tube for ETAAS determination. Thereby, preconcentration factors up to 200 could be achieved from 5 ml of sample solution (Schuster and Schwarzer 1996). Covalent binding of isodiphenylthiourea to silicagel was employed for a preconcentration routine intended for flame atomic absorption spectrometry (F-AAS) (Liu et al. 2002).

It has to be mentioned that most preconcentration or matrix elimination procedures require the analyte to occur in a definite species, in most cases as anionic chloro-complex. Hence, adequate decomposition and mineralization methods are a prerequisite for accurate quantification of PGE from environmental or biological samples.

4.3 Flow Injection Systems

To minimize manual sample preparation and the entailed risks of sample contamination or handling errors, automatization of various sample preparation steps has been a principal topic to improve the reliability and reproducibility of these procedures. The use of flow injection (FI) is widely spread due to the modular nature of the systems and the possibility for miniaturization, entailing reduced sample and reagent consumption and costs. Furthermore, it is feasible to couple FI-systems on-line to various detection systems, thus enabling conjoined sample preparation and measurement. If detection systems able to record transient signals are employed, on-line coupling of FI-sample preparation and measurement has proven to be advantageous to off-line methods, since undesirable dilution of the preconcentrated analyte is avoided. If blank samples yield no detectable peak, blank correction can be carried out using baseline subtraction before peak integration (Hann et al. 2001).

For matrix separation and analyte enrichment purposes, especially FI-systems with integrated SPE are popular. Various schemes are employed for switching differing SPE columns, e.g. modified silica C18, alumina, chelating sorbent or knotted PTFE reactors, between an analyte enrichment position and on-line elution into F-AAS, ICP-MS or ICP-AES, respectively (Liu et al. 2002, Moldovan et al. 2003, Muzikar et al. 2006).

The FI-manifold for Pd preconcentration designed for ETAAS measurement presented by Schuster and Schwarzer (1996) included a sample loop for enhanced reproducibility as well as automatized loading of a ligand solution onto the sorbent before each enrichment, thereby providing a newly functionalized sorbent for each analysis. Further refinement of this procedure introduced flow segmentation to prevent longitudinal diffusion of the preconcentrated analyte in the carrier flow (Limbeck et al. 2003). It was feasible to adapt the method for ID-ICP-MS quantification, but to prevent interferences an additional cation exchange matrix elimination procedure was required (Rudolph et al. 2006, Falta et al. 2007). Employing this most sensitive analytical procedure, a limit of detection (3σ) of 15 ng l^{-1} for the digested sample or 0.24 ng g^{-1} for the solid sample could be achieved.

5 Conclusion and Outlook

Due to the increased importance of palladium as catalyst metal and the continuously occurring release of the element into the environment, assessment of the ensuing ecological impact is of great importance, requiring reliable data on amount and species of existing Pd contaminations and occurring Pd emissions. Furthermore, for determination of biological availability and mobility of Pd in miscellaneous environmental compartments, e.g. segregation of Pd in APM or Pd uptake and accumulation by plants growing on contaminated soil, the physicochemical behavior of Pd has to be studied.

Although much effort has been invested into the development of analytic strategies for determination of Pd in various environmental and biological matrices, many are hampered by insufficient selectivity or sensitivity. Hence, reliable sample preparation routines are needed for accurate quantification, involving analyte preconcentration for improved sensitivity as well as elimination of interfering matrix compounds. Automatization of those procedures would be advantageous, since usually this implies a reduction of costs and reagent consumption as well as less risk of sample contamination and/or handling errors than manual preparation procedures.

Especially with regard to future investigations involving smaller or less contaminated samples, e.g. inhalable aerosol fractions or determination of background concentrations, or speciation studies, the existing strategies for Pd analysis have to be further improved.

Acknowledgments The authors gratefully acknowledge the financial support from the Austrian Science Fund-FWF (Project Nr.: P20838-N17).

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Direct Determination of Metals in PM_{10} Filters by Laser Ablation-ICP-MS

Sebastien Rauch, Gabriele Carugati and Ying Cao

1 Introduction

The concentration of airborne particles has dramatically increased since the onset of the industrial revolution. Exposure to airborne particles has been demonstrated to cause effects is humans and animals, including asthma, lung cancer and cardiovascular problems (Lave and Seskin 1970, 1973; Pope et al. 1995). Premature deaths have been attributed to exposure to airborne particles. Particle size is believe to be the main determinant of toxicity because only particles smaller than 10 μm penetrate into the lungs and the smaller the particles the deeper they can penetrate. The finding that exposure to PM_{10} may result in health effects has sparked the initiation of monitoring programs. While particle concentrations are typically determined, there is a widespread interest in the composition of particles because it may partly be linked to health effects and inhalation of airborne particles is a source of exposure to metallic and organic compounds. In addition, the composition of airborne particles provides information relevant to source apportionment.

In this paper, we present a procedure for the direct quantification of metal concentrations on PM_{10} filters using laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS). This technique combines the high sensitivity of ICP-MS direct solid sampling by laser ablation (Durrant 1999; Gunther and Hattendorf 2005). LA-ICP-MS has previously been used for the determination of trace element and their distribution in airborne particulate matter collected on

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_11,

filters (Wang et al. 1998; Chin et al. 1999; Rauch et al. 2001; Tanaka et al. 1998; Okuda et al. 2004). Wang et al. proposed a calibration method using standard filters prepared by collecting a standard reference material onto a filter in a specially designed sampling chamber (Wang et al. 1998; Chin et al. 1999) or a filter standard reference material (Gligorovski et al. 2008). A simpler calibration consisting of spiking a filter with standard solutions was assessed by Tanaka et al. (1998). A similar calibration strategy has also been applied to the analysis of solutions by LA-ICP-MS (Yang et al. 2005). The work presented here assesses the use of use of LA-ICP-MS for the analysis of PM_{10} samples with calibration based on standard solution spikes.

2 Materials and Methods

2.1 *Filters and Sample Collection*

Cellulose filters (Whatman 41, Whatman, USA) were selected for this study because of their low intrinsic metal content and hygroscopic character (Dams et al. 1972). These filters are widely used in a range of applications including filtering of solutions and airborne particulate matter collection. The cellulose filters used for this work have a dimension of 20 × 25 cm^2; 2 × 1 cm^2 sections were cut using stainless steel scissors to fit in the sample cell of the LA system.

Airborne particles were collected on Whatman 41 filters at two urban sites in Boston, MA, USA. The first sampler was located on the roof of a trailer with the inlet at a height of approximately 5 m at Kenmore Square at the intersection of three high-volume roadways. The second sampler was located on a roof top at a height of approximately 15 m on Columbus Avenue, near the intersection with Berkeley Street. Both sampling sites are located in the urban area and have similar PM_{10} concentrations with an annual arithmetic mean between 20 and 30 $\mu g\ m^{-3}$ for 1989–2001. Sampling was performed for approximately 24 h starting at 09:00 using a high-volume PM_{10} impactor (Thermo Andersen, USA) at a flow of approximately 67 $m^3\ h^{-1}$, resulting in sample volumes of approximately 1,500 m^3. The flow rate was continuously monitored, and sampling time was recorded.

2.2 *Preparation of Filter Standards*

Filter standards used for calibration and method assessment were prepared by adding 2 μL drops of standard solutions with concentration of 0–100 mg L^{-1} onto blank filters. The solutions were prepared in 100 mL acid washed flasks by dilution of a multi-element standard (Merck CertiPUR, 1,000 mg L^{-1}) in 18 MΩ cm^{-1} water obtain from a Milli-Q Gradient system (Millipore, Bedford, MA) with 7 mL concentrated nitric acid (65% HNO_3, suprapure grade) and 2 mL of a Rhodamine B dye solution (prepared by dissolution of 0.125 g Rhodamine B

Table 1 Operation conditions for LA-ICP-MS measurements

Parameters	Setting
ICP-MS	
RF power	1,200 W
Plasma Ar gas flow rate	16 L/min^{-1}
Auxiliary Ar gas flow rate	0.9 L/min^{-1}
Nebulizer Ar gas flow rate	1 L min^{-1}
Scanning mode	Peak hopping
Dwell time	20 ms
Reading per replicate	10
Laser ablation	
Energy	2.2 mJ
Size of laser beam	300 μm
Repetition rate	20 Hz
Scanning speed	100 μm s^{-1}
Isotopes recorded for sample analysis	^{27}Al, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{114}Cd, ^{208}Pb

($C_{28}H_{31}O_3N_2Cl$) flacky crystal in 100 mL Milli-Q water). The drop was added using a 1–10 μL pipette (Thermo Scientific). Optimisation of the procedure is presented in the result and discussion section.

2.3 Analysis

Analysis was performed using a Cetac LSX-200 laser ablation system (Cetac, Omaha, NE, USA) coupled to an Elan 6000 quadrupole ICP-MS (Perkin Elmer Sciex, Toronto, ON, Canada). Ablation is performed using a Nd:YAG laser with a frequency output at the fourth harmonic wavelength of 266 nm and a pulse width of <6 ns. The sample is placed in a cylindrical cell (internal diameter 5.4 cm, volume of 98 cm^3) flushed with Ar and ablated particles are transported to the ICP-MS in an Ar stream (1 L min^{-1}) through a 3 m long Tygon tube (internal diameter 4 mm). Optimum conditions for filter analyses are provided in Table 1. Instrumental parameters were optimized for maximum signal intensity. Laser penetration through the filter material was considered important because standard drops and sampled airborne particles penetrate into the filter mesh.

3 Results and Discussion

3.1 Preparation of Standard Filters

Method assessment and calibration were performed using blank filters with single drop spikes of standard solutions in the concentration range 0–100 mg L^{-1}.

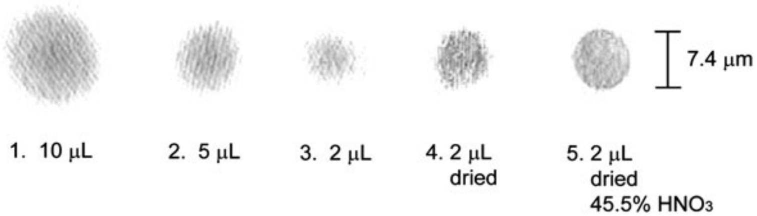

Fig. 1 Comparison of drop size, drying and acid content for the preparation of filter standards

A colorant was added to the spike solutions to visualise the spikes on the filters and the procedure was optimised in order to obtain reproducible spots with well-defined edges. Several colorants were tested, including Rhodamine-B, iodine and potassium permanganate. Rhodamine-B was selected on the basis of its pink/violet colour and insignificant analyte concentrations. However, we found that Rhodamine-B may react with some of the analytes to form a precipitate, and the solutions were therefore acidified with HNO_3. Drop sizes of 2, 5 and 10 μL were tested and a drop size of 2 μL was found to be optimal. Increasing the acid content was also found to limit the spread of the solution absorbed in the filter and well-defined, reproducible spots were obtained with 45.5% HNO_3. The reproducibility of the spike was determined by measuring the diameter of 18 drops using the optics of the LSX-200. The average diameter was 7.4 ± 0.2 mm with a range of 7.0–7.8 mm.

3.2 Calibration and Method Performance

Calibration was performed using solutions of 1, 10, 20, 50, 100 mg L^{-1}, resulting in densities of approx. 5, 50, 100, 250, 500 ng cm^{-2} on the filter. Blank signal intensities were obtained by analysing new, unspiked filter material. Three sets of standard were prepared on separate days (Fig. 1). Calibration plots for Cr, Cu and Pb are presented in Fig. 3. Correlations (R^2) between analyte density on the filter and signal intensity was better than 0.98 for all elements, except Al (0.95) and Fe (0.85). The observed variability for the two highest concentrations (Fig. 2) indicates the need to prepare a set of standards to ensure an accurate calibration.

Detection limits were determined using the 3σ criterion based on the analysis blank filter material (Table 2). Detection limits are below 1 ng cm^{-2} for all elements except Fe. Detection limits estimated for a 24-h collection using a high volume sampler (62.5 m^3 h^{-1}) range from 0.001 ng m^{-3} for Cd to 1 ng m^{-3} for Fe. Detection limits are largely dependent on the sampler used with important specifications including sampled volume and filter size. The method presented here provides an improvement of at least 10-fold over the method described by Tanaka et al. (1998).

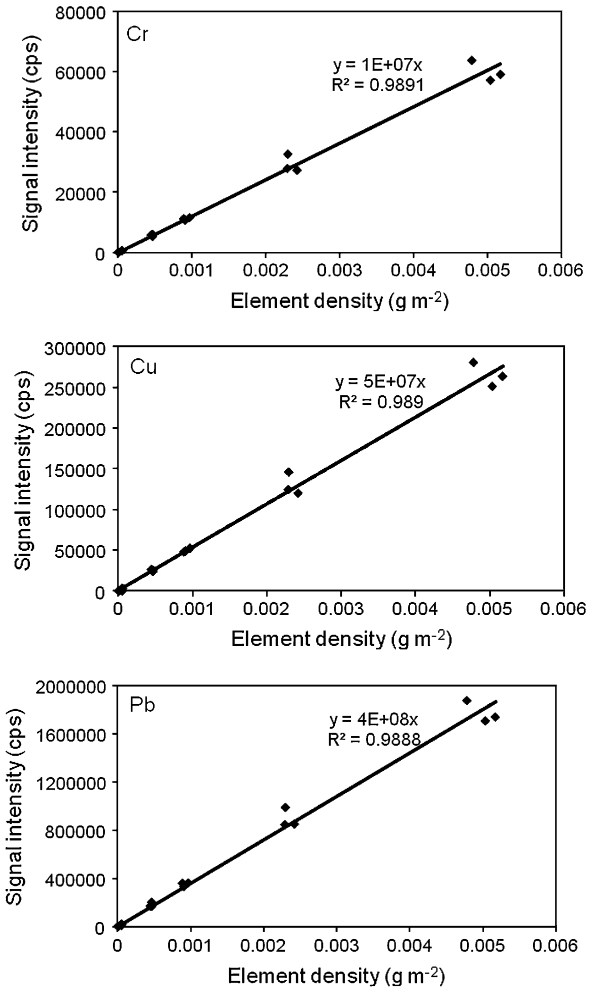

Fig. 2 Calibration of Cr, Cu and Pb performed by LA-ICP-MS analysis of spiked filters. Filters standards were prepared on three different days

3.3 *Application to PM_{10} Sample Analysis*

PM_{10} samples collected at two sites in Boston, USA were analysed by LA-ICP-MS with quantification based on the analysis of spiked filters.

3.3.1 Signal and Element Distribution

Signal intensity profiles obtained for these samples present well defined plateaus and average signal intensity for this plateau was estimated for the determination of analyte concentrations (Fig. 3). The observed signal variability corresponds to the heterogeneity in analyte distribution on the filter, as well as analytical variability.

Table 2 Detection limits for the analysis of spiked filters and airborne particulate matter

Elements	Detection limits for standards (ng cm^{-2})	Estimated detection limit for air samples[a] (ng m^{-3})	Detection limit reported in Tanaka et al. (1998) (ng cm^{-2})
Al	0.7	0.2	22
Cr	0.02	0.006	4.4
Mn	0.05	0.01	18
Fe	4	1	33
Co	0.006	0.002	0.7
Ni	0.05	0.01	1.1
Cu	0.1	0.03	155
Zn	0.2	0.04	33
Cd	0.004	0.001	0.04
Pb	0.02	0.004	0.5

[a] Estimated assuming a collection of 1,500 m^3 (24 h collection at a flow rate of approximately 62.5 m^3 h^{-1})

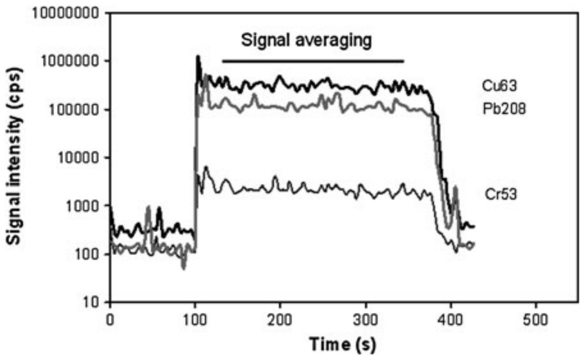

Fig. 3 Signal profile for the analysis of Cu, Pb and Cd on a PM_{10} filter collected in Boston, USA

To assess the importance of analyte distribution, 10 sub-samples were obtained from a single filter and analysed. The standard deviation of the analysis of the 10 sub-samples ranged from 15% for Cd, Pb and Ni to 33% for Al and 35% for Cu.

3.3.2 Interference Contribution

Interferences caused by spectral overlap were studied by spiking blank filters with 100 ppm single element solutions of potential interferents. Interefered elements were subsequently analysed to assess the extent of the interference. Non-oxide polyatomic and double charged species were considered (Table 3). Oxides are limited when using laser ablation and were therefore not considered. Isobaric interferences were corrected based on their natural abundances. Interfering elements caused an elevated analyte signal relative to the signal for the filter blanks.

Table 3 Potential spectral interferences considered in this study

Analyte	Potentially interfering species	Observed interferences in samples
Al27	$^{53}Cr^{2+}$, $^{54}Cr^{2+}$, $^{54}Fe^{2+}$, $^{55}Mn^{2+}$	
Cr53	$^{106}Cd^{2+}$, $^{107}Ag^{2+}$	
Mn55	$^{111}Cd^{2+}$	
Fe57	$^{114}Sn^{2+}$, $^{114}Cd^{2+}$, $^{115}Sn^{2+}$	($^{114}Sn^{2+}$, $^{115}Sn^{2+}$) (<5%)
Co59	$^{117}Sn^{2+}$, $^{118}Sn^{2+}$, $^{119}Sn^{2+}$	
Ni58	$^{115}Sn^{++}$, $^{116}Sn^{++}$, $^{116}Cd^{++}$, $^{117}Sn^{2+}$	
Cu63	$^{25}Mg^{38}Ar$, $^{27}Al^{36}Ar$, $^{117}Sn^{2+}$	
Zn64	$^{127}I^{2+}$, $^{28}Si^{36}Ar$, $^{26}Mg^{38}Ar$, $^{24}Mg^{40}Ar$	$^{127}I^{2+}$ (<5%), $^{28}Si^{36}Ar$ (<20%)
Cd114	$^{76}Se^{38}Ar$, $^{78}Se^{36}Ar$, $^{74}Se^{40}Ar$	
Pb208		

[a] Contribution of interference to measured signal in brackets

Table 4 The results of concentration (ng m^{-3}) of metals in the airborne particulate samples collected at two sites in Boston

Sample	Concentrations (ng m^{-3})									
	Al	Cr	Mn	Fe	Co	Ni	Cu	Zn	Cd	Pb
K1	95	1.7	4.9	294	0.7	8.3	48	31	0.7	5.0
K2	173	3.3	11	770	0.8	20	157	57	0.6	8.9
K3	159	2.5	6.9	544	0.4	10	65	29	0.8	5.6
K4	176	4.4	11	698	0.7	20	56	42	1.0	7.9
$K_{average}$	151	3.0	8.5	577	0.7	15	82	40	0.8	6.9
C1	183	2.8	9.4	531	1.3	9.6	38	54	0.6	5.0
C2	142	1.9	5.1	363	0.5	7.1	18	22	0.3	3.9
C3	219	1.8	7.3	460	0.5	7.3	48	25	0.3	4.7
C4	226	2.0	7.2	522	0.7	6.8	23	24	0.4	4.9
$C_{average}$	193	2.1	7.2	469	0.8	7.7	32	32	0.4	4.6

K Kenmore square; *C* Columbus avenue)

However, the concentrations of these elements are often too low to have a significant impact on the determination of selected analytes. The analysis of spiked filter enables the estimation of interference formation and the contribution of interference to the measured signal in the samples (Rauch et al. 2001). Interferences were found to represent <2% of the measured signal for all elements, except for Zn and Fe for which interferences represent <5 and <25%, respectively. Interferences were corrected mathematically following the method described by Rauch et al. (2001).

3.3.3 Element Concentrations in PM$_{10}$ Filters

Concentrations of selected elements in 8 PM$_{10}$ filters collected in Boston are presented in Table 4. All elements had concentrations above detection limits

Table 5 Concentrations in airborne samples obtained by LA-ICP-MS ($n = 8$) and ICP-MS ($n = 10$) analysis after digestion

Element	Concentrations (ng m^{-3})	
	LA-ICP-MS	ICP-MS[a]
Cu	57 ± 44	55 ± 8
Pb	6 ± 2	7 ± 2
Zn	32 ± 15	25 ± 6
Cd	0.6 ± 0.3	0.2 ± 0.1

[a] Data from Rauch et al. (2005)

(Table 2). Cd and Co were found to have the lowest concentrations with typically <1 ng m^{-3}. In contrast, Fe and Al concentrations were typically >100 ng m^{-3}. The higher concentrations observed at the Kenmore Sq. site are likely due to lower sampling inlet and higher traffic compared with the Columbus Ave. site.

Obtained concentrations were compared with previous measurements on samples collected at the same sites and performed by ICP-MS after sample digestion (Table 5). Cu, Pb and Zn concentrations were found to be in good agreement, but differences were observed for Cd. These differences are possibly due to the fact that the samples were collected on different days. Measured concentrations are also in good agreement with concentrations reported for other urban areas (e.g. Limbeck et al. 2009; Moreno et al. 2006).

4 Conclusion

LA-ICP-MS combined with a simple calibration strategy was found to enable the determination of metal concentrations in airborne particulate matter. Calibration was performed using blank filters spiked with standard solution and detection limits estimated using these standards were ≤1 ng cm^{-2}. The method was successfully applied to the determination of Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in urban airborne particulate matter collected in Boston, USA using a high volume impactor. The capability to determine trace elements at ambient concentrations without samples digestion makes LA-ICP-MS an attractive technique for the elemental characterization of airborne particulate matter. Potential applications of this technique include monitoring and source tracing.

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Chemical Composition of Subway Particles in Seoul, Korea, Determined Using Quantitative Single Particle Analysis

Hae-Jin Jung, Sunni Kang, Hye Kyeong Kim and Chul-Un Ro

1 Introduction

People spend most of their time indoors, either at home, in the workplace, or in transit, and concern over air quality of indoor microenvironments and its influence on public health is increasing. Among the various types of indoor microenvironments, underground subway stations have some unique characteristics in that they are somewhat closed spaces with strong indoor particle emission sources. Aerosol particles in underground subway stations can be generated mainly by the movement of trains and passengers. The aerosol particles can accumulate in this closed environment, resulting in high concentrations of indoor particulate matter (PM). Many people within the worldwide metropolitan areas commute using underground subway transportation and spend considerable time in the underground subway environment on a daily basis. Therefore, there has been increasing attention to air quality in the underground subway system because of its possible adverse influence on public health (Chillrud et al. 2004; Karlsson et al. 2005, 2006; Seaton et al. 2005).

Up until now, several studies on air quality of worldwide underground subway systems have reported that the concentrations of PM in subway systems are generally much higher than those in outdoor environments. In Prague, PM_{10} concentrations in underground subway stations are reported to be about 30–70% higher than those in outdoor environment (Branis 2006). The concentrations of daytime $PM_{2.5}$ collected at two underground subway stations in Helsinki were 3–6 times higher that those at urban background and street canyon monitoring sites

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_12,

(Aarnio et al. 2005). A similar observation was also made for PM_{10} and $PM_{2.5}$ samples collected in an underground station in central Stockholm, in which the PM concentrations are 5–10 times higher than those measured at a busy street in Stockholm (Johansson and Johansson 2003). Higher PM concentrations in underground subway stations in Tokyo than in the aboveground were observed throughout the seasons (Furuya et al. 2001). In addition to the elevated PM concentrations observed in underground subway stations, personal exposures to particulate matter were also reported to be more for commuters using underground subway systems than for those using other aboveground transportation systems. In the research performed in London, it was observed that personal exposure levels to $PM_{2.5}$ were 3–8 times higher for commuters using the underground subway system than for those using a bicycle, bus, or car (Adams et al. 2001a, b). Similar observations were also made in other studies carried out in Toronto (Pellizzari et al. 1999) and London (Pfeifer et al. 1999; Sitzmann et al. 1999), where the personal exposure levels to PM for commuters using the underground subway system could be up to 40 times higher. Since PM emission sources in the underground subway stations are very different from those in aboveground urban environments, the chemical composition of PM collected at worldwide underground subway systems are unique. Major chemical elements in PM in underground subway systems are Fe and Si, with Mn, Cr, Cu, Ca, and K elements also abundantly observed (Sitzmann et al. 1999; Birenzvige et al. 2003; Chillrud et al. 2004; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007). In particular, concentrations of Fe, Mn, and Cr in $PM_{2.5}$ samples collected in underground subway stations of New York City were found to be more than 100 times higher than those in aboveground ambient samples, which especially raises concern over the potential adverse health effect of long-term exposures to Mn and Cr (Chillrud et al. 2004). Indeed, a study reported that particles collected at a subway station were about eight times more genotoxic and four times more likely to induce oxidative stress in cultured human lung cells than urban street particles (Karlsson et al. 2005). When the genotoxicity of different particle types collected from wood and pellet combustion, tire–road wear, an urban street, and a subway station was compared, the particles from the subway station were the most genotoxic among all particles tested (Karlsson et al. 2006). Another genotoxicity test for particles collected at underground stations in London showed that subway particles are comparable in toxicity to welding fume particles, although the concentrations at subway stations are below allowable workplace concentrations for iron oxide and thus a significant cumulative risk to the health of workers or commuters is improbable (Seaton et al. 2005).

As summarized in a recent review article (Nieuwenhuijsena et al. 2007), some characteristic features of underground subway particles such as PM concentrations have been investigated by a significant number of previous studies. However, detailed information on the chemical composition of subway particles is still scarce, with just a few of chemical elemental bulk analyses having been performed (Furuya et al. 2001; Birenzvige et al. 2003; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007). The chemical composition of subway particles can be more clearly elucidated by the application of single particle analysis, since atmospheric subway particles are chemically and morphologically heterogeneous and the average composition and aerodynamic diameter obtained from bulk analyses do not adequately describe the population of the particles. The single particle analysis can provide detailed information on the sources of subway particles as well as their chemical composition. Up until now, just one single particle analysis study on the chemical composition of subway particles has been published (Sitzmann et al. 1999). In this work, subway particle samples were analyzed using computer-controlled scanning electron microscopy and energy dispersive X-ray detection, showing that the most abundant particles are Fe/Si-rich particles.

Herein, results on the characteristics of subway particles collected in underground subway stations in Seoul, Korea, obtained by the application of a novel single particle analytical technique, called low-*Z* particle electron probe X-ray microanalysis (low-*Z* particle EPMA) are presented (see also Kang et al. 2008). The low-*Z* particle EPMA allows the determination of the concentration of low-*Z* elements such as carbon, nitrogen, and oxygen, as well as elements observed using conventional EPMA, in individual particles of micrometer size. Further, by the application of a quantification method, which employs Monte Carlo simulation combined with successive approximations, quantitative specification of the chemical compositions can be performed, and thus this technique can perform molecular analyses of individual particles (Ro et al. 1999, 2000, 2003, 2004; Khan et al. 2008). By the combinational use of morphological and chemical information obtained from the low-*Z* particle EPMA, it was observed that particles collected at subway stations in Seoul are mostly from wear processes at rail-wheel-brake interfaces and indoor emission sources predominate in the underground subway microenvironments.

2 Experimental

2.1 Samples

Subway particle samples were collected at a platform of the Hyehwa subway station in Seoul, Korea. Seoul, the capital of Korea, is a densely populated megacity (population: 10.3 million, area: 605 km^2). The Seoul subway system contains eight lines with a total of 327 stations. According to statistics provided from the Seoul metro transportation center (http://www.seoulmetro.co.kr), approximately 6.7 million commuters use the Seoul subway system on a daily basis. The Hyehwa station is one of the busiest subway stations with 58,000 commuters per day. Ambient annual PM10 concentrations in Seoul were 58.0 μg/m^3 in 2005, with overall PM10 concentrations at subway stations and the Hyehwa station reported to be 110.9 and 121.5 μg/m^3 in 2004, respectively. This indicates that PM10 concentrations at subway stations are much higher than in the outdoor environment (http://www.seoulmetro.co.kr). Sampling was done twice every season during 2004–2005: Dec. 16 and 17, 2004; May 3 and 5, July 4 and 6, and Nov. 23 and 25, 2005. Particles were sampled on Ag foil using a 7-stage May cascade impactor (May, 1975). The May impactor has, at a 20 L/min sampling flow, aerodynamic cutoffs of 16, 8, 4, 2, and 1 μm for stages 1–5, respectively.

To clearly identify local sources of subway particles, samples were collected at four different areas in two subway stations; namely the Jegi and Yangjae stations in Seoul. The four sampling sites are in the tunnel, at the platform, at the waiting room, and outdoors. The outdoor aerosol samples were collected nearby the subway stations. In many subway stations of Seoul (the Yangjae station is one of them), screen doors are installed between the tunnel and the platform, which effectively limit air-mixing between the platform and the tunnel. Sampling was done using a 3-stage Dekati PM_{10} sampler on Feb. 10, 2009 in the Jegi station and on Feb. 25, 2009 in the Yangjae station. The sampler has cut-off diameters of 10, 2.5 and 1 μm for stages 1–3. Particle samples collected on stage 2 and 3 were analyzed by the low-*Z* particle EPMA technique, where the particle sizes on stage 2 and stage 3 are in the ranges of 10–2.5 and 2.5–1.0 μm, respectively. Sampling durations varied in order to obtain a good loading of particles at the impaction slots. Since the number concentration of smaller particles in the air is higher than that of larger particles, it is necessary to collect smaller particles within a shorter sampling duration to avoid the collection of agglomerated particles. The collected samples were put in plastic carriers, sealed, and stored in a desiccator.

2.2 EPMA Measurements

The measurements were carried out using a Hitachi S-3500 N environmental scanning electron microscope equipped with an Oxford Link SATW ultrathin window EDX detector. The resolution of the detector is 133 eV for Mn–Kα X-rays. X-ray spectra were recorded under the control of EMAX Hitachi software. To achieve optimal experimental conditions, such as a low background level in the spectra and high sensitivity for low-*Z* element analysis, a 10 kV accelerating voltage was chosen. The beam current was 1.0 nA for all measurements. In order to obtain statistically enough counts in the X-ray spectra while limiting beam damage effects on sensitive particles, a typical measuring time of 10 s was used. A more detailed discussion on the measurement conditions is given elsewhere (Ro et al. 1999). Computer-controlled X-ray data acquisition for individual particles was carried out automatically in the point analysis mode, whereby the electron beam was focused at the center of each particle and X-rays were acquired while the beam remained fixed on this single spot. The localization of the particles was based on inverse backscattered electron contrast. Morphological parameters, such as diameter and shape factor, were calculated by an image processing routine. These estimated geometrical data were set as input parameters for the quantification procedure.

2.3 Data Analysis

The net X-ray intensities for the elements were obtained by non-linear least-squares fitting of the collected spectra using the AXIL program (Vekemans et al. 1994). The elemental concentrations of individual particles were determined from their X-ray intensities by the application of a Monte Carlo calculation method combined with reverse successive approximations (Ro et al. 2001, 2003). The quantification procedure provided results accurate within 12% relative deviations between the calculated and nominal elemental concentrations when the method was applied to various types of standard particles such as NaCl, Al_2O_3, $CaSO_4$ 2H2O, Fe_2O_3, $CaCO_3$, and KNO_3 KNO_3 (Ro et al. 2000, 2003, 2004). The low-*Z* particle EPMA can provide quantitative information on the chemical composition, and particles can be classified based on their chemical species. The classification procedure takes a substantial amount of time if done manually, since analysis of tens of thousands of pieces of particle data is required. Thus, an expert system that can determine chemical species from the elemental concentration data has been applied to these underground subway sample data. By applying the expert system, the time necessary for chemical speciation becomes significantly shorter, and detailed information on particle data can be saved and extracted when more information is needed for further analysis (Ro et al. 2004).

3 Results and Discussion

3.1 Chemical Composition of Subway Platform Particle Sample

Overall, some 10,400 particles for eight seasonal samples (1,300 particles for each sample) collected at the Hyehwa subway station platform were analyzed and classified on the basis of their chemical species. Four major particle types are significantly encountered in the subway platform samples: Fe-containing; soil-derived; carbonaceous; and secondary nitrate and/or sulfate particles. In Table 1, the overall relative abundance of those particle types encountered in the subway platform samples are shown. The overall relative abundance is calculated by dividing the number of the specific type of particles by the total number of analyzed particles. A typical secondary electron image for a sample collected on July 4, 2005 is shown in Fig. 1, where the chemical species of each particle is notated with the particle number. In subway platform samples, Fe-containing particles are the most abundantly observed with the relative abundance of 61–79%. Previous studies have reported that Fe-containing particles are the most prevalent in subway particle samples. For example, in London underground subway system, it was reported that Fe/Si-rich particles constituted 53% (in number fraction) of subway particles (Sitzmann et al. 1999), and iron oxide particles were the majority

Table 1 Overall relative abundance of particle types encountered in Hyehwa subway station particle samples (in %) (Kang et al. 2008). (Reproduced by permission of American Chemical Society)

Particle types	Dec. 16, 2004	Dec. 17, 2004	May 3, 2005	May 5, 2005	July 4, 2005	July 6, 2005	Nov. 23, 2005	Nov. 25, 2005
Iron-containing	60.5	71.5	70.8	71.4	79.1	78.0	71.1	74.6
Carbonaceous	13.2	7.7	9.0	9.2	10.5	8.6	5.4	7.4
Soil-derived (sum)	(14.0)	(11.4)	(10.7)	(11.5)	(6.0)	(7.5)	(13.1)	(9.4)
Aluminosilicates	5.1	4.6	3.8	3.8	2.0	2.6	4.6	2.5
Aluminosilicates/C	2.8	1.5	2.2	1.8	1.0	1.3	2.0	1.1
$CaCO_3$	0.8	1.0	0.1	0.7	0.5	0.7	1.5	1.0
$CaCO_3$/C	1.2	0.8	0.4	0.6	0.5	0.4	1.3	0.8
SiO_2	1.8	1.3	2.7	2.8	0.8	1.4	1.5	2.5
SiO_2/C	2.5	2.2	1.5	1.8	1.2	1.1	2.2	1.5
Secondary nitrates/ sulfates (sum)	(8.0)	(6.8)	(5.1)	(4.0)	(1.3)	(2.7)	(6.0)	(4.1)
$Ca(NO_3,SO_4)$	4.2	2.5	1.5	2.2	0.8	1.1	2.6	1.2
$(Na,Mg)(NO_3,SO_4)$	1.5	1.0	3.6	1.8	0.5	1.2	3.2	2.7
$(NH_4)_2SO_4$	2.3	3.3	–	–	–	0.4	0.2	0.2
Others	4.2	2.6	4.5	3.9	3.1	3.3	4.3	4.5
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

(67% in weight fraction) of $PM_{2.5}$ subway samples (Seaton et al. 2005). Subway samples collected in New York, Helsinki, Tokyo, and Budapest also contained very high concentrations of iron, i.e., 42% of $PM_{2.5}$, 88–92% of $PM_{2.5}$, 74% of SPM, and 40–46% of PM_{10}, respectively (Furuya et al. 2001; Chillrud et al. 2004; Aarnio et al. 2005; Salma et al. 2007). Indeed, as shown in Fig. 1, Fe-containing particles (29 among 36 particles) are the most. The summer samples show the highest population of Fe-containing particles (see Table 1). Since whole areas of the subway system in Seoul are air-conditioned in the summer, the limited air-exchange between indoor and outdoor areas might result in the higher population of Fe-containing particles of indoor origin. Other works have also reported the higher concentration of Fe-containing particles in the summer than in the winter (Adams et al. 2001a, 2001b). Fe-containing subway particles are likely to be generated from mechanical wear and friction processes at rail-wheel-brake interfaces. The composition and origin of Fe-containing particles will be discussed in detail later.

Carbonaceous particles are significantly encountered with their relative amount ranging from 5.4 to 13.2%. Since hydrogen cannot be detected with EPMA measurement, the low-*Z* particle EPMA has a limitation on the speciation of organic particles. Thus, particles are simply classified as carbonaceous particles when the sum of the carbon, nitrogen, and oxygen contents of the particles is larger than 90% in atomic fraction. It was suggested that carbonaceous species in subway particles could originate from carbon contained in cast iron (Sitzmann et al. 1999). In this case, it is expected that carbonaceous species should be combined with

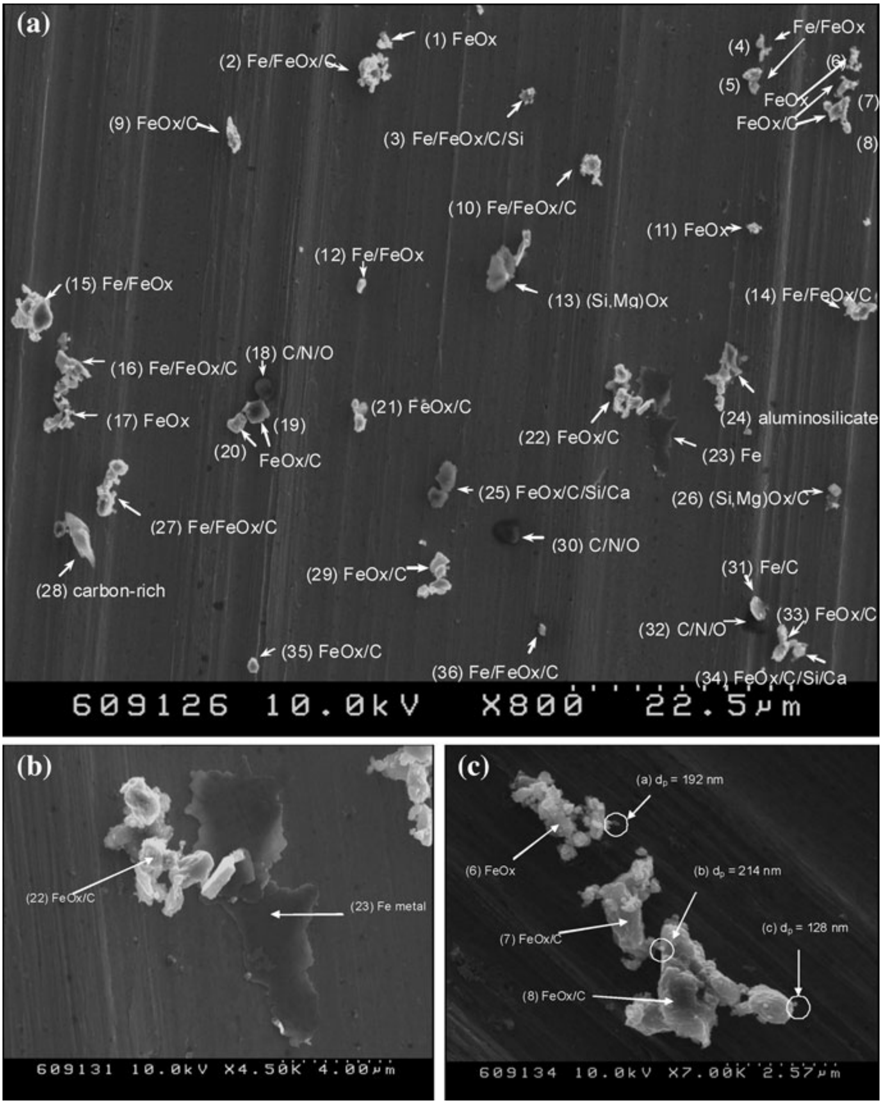


Fig. 1 **a** A typical secondary electron image of subway particles. **b** The enlarged image of subway particles, **c** The enlarged image of agglomerated Fe-containing particles (Kang et al. 2008). Reproduced by permission of American Chemical Society

Fe-containing particles. Actually, it was found that many Fe-containing particles contain carbon, however, these particles were classified as Fe-containing. Here, the particles classified as carbonaceous are mostly composed of carbon, nitrogen, and oxygen without iron. These carbonaceous particles might be from outdoor sources, since it is well known that anthropogenic carbonaceous particles are one of the major chemical species in urban atmosphere.

Soil-derived particles, such as aluminosilicates, SiO_2, and $CaCO_3$ are the second most abundant particles encountered in subway platform samples, with relative amounts in the range of 6.0–14.0% (Table 1). Also, some of the soil-derived particles exist as internally mixed with carbonaceous species (denoted as Aluminosilicates/C and SiO_2/C). Soil-derived particles are one of the most abundant aerosol types in ambient urban atmosphere, especially in the coarse fractions, whereby soil-derived particles might be from an outdoor environment. Most of these soil-derived particles were found at stages 1–3 ($d_p > 4$ μm) of May impactor. Such soil-originated particles were detected in considerably lower amounts in July samples (Table 1), reflecting the limited air-exchange between indoor and outdoor environments in the summer.

Nitrate- and sulfate-containing particles are also significantly encountered in subway aerosol samples, and exist mostly in the chemical forms of $Ca(NO_3, SO_4)$, $(Na,Mg)(NO_3, SO_4)$, and $(NH_4)_2SO_4$. Particles internally mixed with $Ca(NO_3)_2$ and $CaSO_4$ are denoted as $Ca(NO_3, SO_4)$, and are reaction products of $CaCO_3$ with nitrogen and sulfur oxide species (Krueger et al. 2004; Ro et al. 2005; Hwang and Ro, 2006). Similarly, sea-salts can react with nitrogen and sulfur oxide species in the air to produce nitrate and sulfate combined with Na and Mg, denoted as $(Na,Mg)(NO_3, SO_4)$ (Laskin et al. 2003; Ro et al. 2005; Hwang and Ro, 2006). These secondary particles containing nitrates and/or sulfates are likely from the outdoor environment. Since gaseous nitrogen and sulfur oxides are abundant in the indoor subway microenvironment, it is possible that such nitrate and sulfate can be formed by the reaction of $CaCO_3$ and sea-salts from the outdoor with indoor gaseous nitrogen and sulfur oxides. $(NH_4)_2SO_4$ particles are a major chemical species in urban aerosols, especially in fine fractions. In our work, the $(NH_4)_2SO_4$ particles are encountered only at stage 5 that collects particles with the size range of 1–2 μm. Somewhat lower amounts of nitrate- and sulfate-containing particles detected in the summer samples (Table 1) might be mainly owing to a limited air-exchange with outdoor air. Some studies suggest that subway particles are well correlated with the outdoor environment, implying that air-exchange between underground and aboveground environments is well established (Aarnio et al. 2005; Branis (2006)), whereas others indicated that they are not correlated (Sitzmann et al. 1999; Salma et al. 2007). In our work, the relative abundance of particles of outdoor origin varies somewhat among seasonal samples, and yet those variations are not apparent.

3.2 Iron-Containing Subway Particles

Fe-containing particles encountered in the Hyehwa station samples are mainly oxidized iron, although some iron metal particles are also encountered. Fe-containing subway particles might be produced from the friction at rail-wheel-brake interface. It is likely that wear and friction processes on the rail initially produce the iron metal flakes, and yet the active iron surface can easily react with oxygen, resulting in the formation of iron oxides. In mineralogy, iron oxide minerals are known to exist as FeO (wüstite), Fe_2O_3 (hematite, maghemite), or Fe_3O_4 (magnetite). When the iron particles are fully oxidized, these three types of oxides can be distinguished as a result of low-*Z* particle EPMA analysis. But most of Fe-containing particles were found to be partially oxidized. Therefore, Fe-containing particles were classified into three different types: iron metal (denoted as "Fe" in Fig. 1), partially oxidized (denoted as "Fe/FeO_x"), and fully oxidized (denoted as "FeO_x"). In the secondary electron image, iron metal particles are clearly distinguishable from oxidized iron particles due to their irregular shape with dark color. Iron metal particles were observed mostly as flakes, implying that they are scraps broken off from train wheels or rails (see Fig. 1b). In the image, the iron metal particles look darker than iron oxides due to the difference in the secondary electron yields between conducting iron metal and insulating iron oxide. The insulating oxide particles can develop a negative voltage by the accumulation of primary electrons, and it results in a bright contrast due to a larger emission of secondary electrons by repulsion (Goldstein et al. 2003). Most of the iron oxide particles were found as an agglomerate of fine particles (see Fig. 1). Particles with various sizes, including very small nano-sized particles, make an agglomerated lump on the surface of large Fe-containing particles (see Fig. 1c). Those nano-sized iron oxides are most probably formed by the condensation of gaseous iron species from the sparking between the third rail and the electricity guide of subway trains. An attractive magnetic force between the iron oxide particles may form agglomerate. Although a study reported that some of iron oxide particles in subway system were found as magnetic Fe_3O_4 (Karlsson et al. 2005), more studies need to be done on the oxidation state of iron and the magnetic properties of Fe-containing particles in the subway system.

Many Fe-containing particles include other elements such as C, N, Mg, Al, Si, S, and/or Ca. When the atomic concentrations of those elements are larger than 10%, the elements are regarded as a major constituent of the particle. For example, the notation of "FeO_x/C/Si/Ca" for particles #25 and #34 in Fig. 1 indicates that the particles are iron oxides internally mixed with C, Si, and Ca elements. In our study, various internally mixed Fe-containing particles were found. For the eight subway aerosol samples, the most abundant particle type is FeO_x/C (ranging in 29–45%), followed by Fe/FeO_x/C (10–16%), FeO_x (2.8–6.9%), FeO_x/Si/C (1.8–4.8%), Fe/FeO_x (1.8–4.1%), and FeO_x/Ca/C (1.4–3.3%). Using single particle analysis, Sitzmann et al. (1999) discussed in depth the sources of Fe particles containing C, Si, and/or Ca: (a) particles containing both Fe and Si are generated from the friction between the brake block composed of iron and glass fibers and train wheels, (b) particles containing both Fe and Ca are also generated in the same way because brake blocks contain $CaCO_3$, and (c) C element is from cast iron used for wheels and rails. Also in our study, these elements are very frequently encountered in Fe-containing particles. For example, among 29 Fe-containing particles shown in Fig. 1, 22 particles contained Si (0.7–3.4% in atomic fraction) and 12 particles contained Ca (0.6–5.0% in atomic fraction), and 25 particles contained C element with >3% in atomic fraction. According to Korean Standard

Database (http://www.standard.go.kr), cast irons used for rails and wheels contain C (0.5–0.7%), Si (0.1–0.35%), Mn (0.6–0.95%), P (<0.045%), and S (<0.05%). The higher content of carbon in Fe-containing particles compared to that in cast iron might be due to the heterogeneous oxidation of volatile organic carbons (VOCs) on the active surface of Fe-containing particles. Also the reaction of VOCs with Fe-containing particles explains why C element is contained in almost all Fe-containing particles. A few studies reported that transition metals such as Mn, Cr, Ni, and Cu, as well as Fe, are enriched in subway particles when compared to those in outdoor atmospheric particles (Furuya et al. 2001; Birenzvige et al. 2003; Chillrud et al. 2004; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007). In general, all the reports showed that Fe, Mn, Cu, and Cr were enriched in the subway particles, but other elements showed different characteristics. For example, Ni and Ti were enriched in Helsinki subway samples (Aarnio et al. 2005), but Ni was not enriched in New York samples (Seaton et al. 2005) and Ti was hardly found in Budapest samples (Salma et al. 2007). In addition, Ba was uniquely reported to be enriched in Tokyo subway samples (Furuya et al. 2001). These differences might be due to the difference in chemical composition of wheels, rails, and brake blocks. In our study, some subway particles are observed to include several transition metals, such as Ti, Cr, Mn, Ni, Cu, and Zn, and Ba. Among them, Ti, Cu, and Ba elements are significantly encountered; of which, the overall relative amounts are 4.4%, 1.6%, and 1.0%, respectively. Since rails, wheels, and brake blocks do not contain Ti, the somewhat abundant presence of Ti in subway particles is likely due to the erosion of painting material. Cu is originated from the wear of the third rail. In our study, minor amounts of Ba in Fe-containing single particles are always observed together with minor amounts of S, indicating that Ba originates from $BaSO_4$, which was reported to be a major constituent of brake block used in Tokyo subway system (Furuya et al. 2001). Many studies reported significant amounts of Mn and Cr elements in subway samples (Furuya et al. 2001; Birenzvige et al. 2003; Chillrud et al. 2004; Aarnio et al. 2005; Seaton et al. 2005; Salma et al. 2007); whereas in our work, just few particles containing Cr, Ni, and Zn were detected. Since our study is for supermicron subway particles, the possibility of the presence of these elements in submicron subway particles cannot be excluded.

3.3 Chemical Composition of Subway Particles Collected at Various Locations in Subway Stations With/Without Screen Doors

To clearly identify indoor sources of subway particles, samples were collected at different locations of two subway stations, i.e., in the tunnel, at the platform, at the waiting room, and outdoors. The two subway stations are the Jegi and Yangjae stations. In the Yangjae station, screen doors are installed between the tunnel and the platform, resulting in limited air-mixing between the platform and the tunnel.

Tables 2 and 3 show the relative abundance of particle types observed in the Jegi and Yangjae station samples, respectively. Four major particle types are encountered: Fe-containing; soil-derived; carbonaceous; and secondary nitrate and/or sulfate particles. Among them Fe-containing particles are the most prevalent with a relative abundance of 30–80%. However, the distributions of the particle types are different between samples collected at different locations. Particularly, the relative amounts of Fe-containing particles in samples collected in tunnels are about 80% both for the two stations, indicating that Fe-containing particles produced by the friction between the rail and wheel brake interface accumulate in tunnels with limited ventilation. The relative abundance of Fe-containing particles at the platforms is still high, ranging between 50 and 70%. However, it is obvious that the relative abundance of Fe-containing particles at the Yangjae station platform (about 50%) is much lower than that at the Jegi station platform (about 70%). The difference is due to the presence of screen doors in the Yangjae station. The screen doors all the time separate the platform region from the tunnel except when trains arrive at the platform, resulting in limited inflow of Fe-containing particles from the tunnel to the platform area. In addition, PM_{10} concentrations at the platforms in the Jegi and Yangjae stations were 160 $\mu g/m^3$ and 85 mg/m^3, respectively, for the sampling days, indicating that the platform in the Yangjae station is effectively separated from a strong indoor source, i.e., the tunnel. A proper loading of particles on collecting substrate is necessary for the single particle analysis, i.e., particles should be seated on the substrate individually without agglomerates, therefore, sampling time depends on PM concentration at sampling site. Due to its lower PM_{10} concentrations, the sampling time

Table 2 Relative abundance of particle types observed in samples collected at various locations in Jegi subway station (in %)

Jegi station	Tunnel		Platform		Waiting room		Outdoor	
	st2	st3	st2	st3	st2	st3	st2	st3
Iron-containing	80.9	78.3	74.0	71.0	62.2	35.1	16.0	3.7
Carbonaceous	4.5	4.7	2.0	9.0	5.4	35.1	13.0	72.9
Soil-derived (sum)	(11.8)	(7.5)	(17.0)	(12.0)	(28.8)	(15.3)	(28.0)	(11.2)
Aluminosilicates	0.0	0.0	0.0	1.0	1.8	3.6	10.0	2.8
Aluminosilicates/C	3.6	1.9	1.0	0.0	0.9	2.7	6.0	3.7
$CaCO_3$	3.6	0.0	8.0	5.0	9.0	5.4	4.0	2.8
$CaCO_3/C$	1.8	3.8	7.0	5.0	14.4	2.7	4.0	0.0
SiO_2	0.9	0.9	1.0	0.0	0.0	0.0	3.0	0.9
SiO_2/C	1.8	0.9	0.0	1.0	2.7	0.9	1.0	0.9
Secondary nitrates/sulfates (sum)	(2.7)	(7.5)	(6.0)	(6.0)	(3.6)	(12.6)	(42.0)	(12.1)
$Ca(NO_3,SO_4)$	1.8	2.8	6.0	0.0	1.8	5.4	12.0	5.6
$(Na,Mg)(NO_3,SO_4)$	0.9	4.7	0.0	6.0	1.8	3.6	30.0	6.5
$(NH_4)_2SO_4$	0.0	0.0	0.0	0.0	0.0	3.6	0.0	0.0
Others	0.0	1.9	1.0	2.0	0.0	1.8	1.0	0.0
Total	100	100	100	100	100	100	100	100

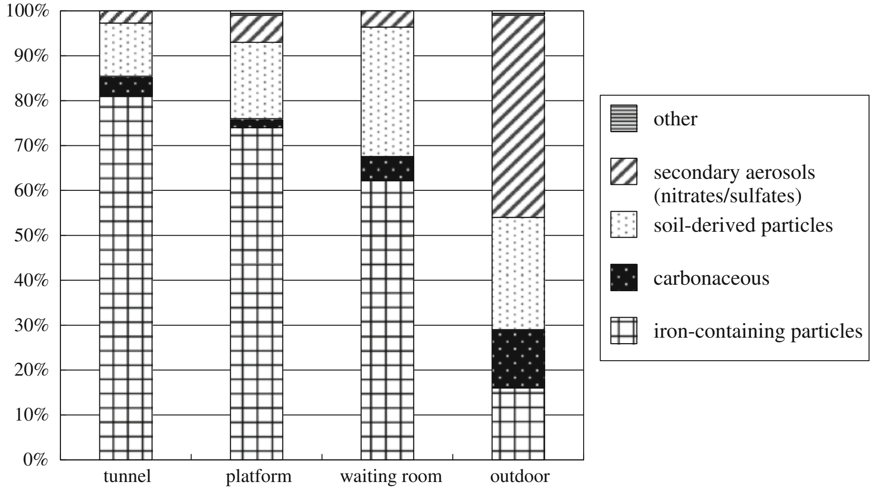
Table 3 Relative abundance of particle types observed in samples collected at various locations in Yangjae subway station (screen door installed) (in %)

Yangjae station	Tunnel		Platform		Waiting room		Outdoor	
	st2	st3	st2	st3	st2	st3	st2	st3
Iron-containing	78.4	81.1	53.2	48.6	29.9	35.0	11.0	13.7
Carbonaceous	12.6	2.8	6.3	25.2	16.2	15.0	11.0	38.2
Soil-derived (sum)	(1.8)	(13.2)	(35.1)	(6.5)	(32.5)	(21.0)	(51.0)	(25.5)
Aluminosilicates	0.9	0.9	1.8	1.9	7.7	2.0	23.0	9.8
Aluminosilicates/C	0.0	0.0	7.2	1.9	6.0	3.0	5.0	0.0
$CaCO_3$	0.0	5.7	12.6	1.9	6.8	5.0	11.0	5.9
$CaCO_3$/C	0.0	3.8	9.9	0.9	6.0	6.0	6.0	5.9
SiO_2	0.0	0.0	3.6	0.0	2.6	2.0	3.0	2.9
SiO_2/C	0.9	2.8	0.0	0.0	3.4	3.0	3.0	1.0
Secondary nitrates/sulfates (sum)	(3.6)	(2.8)	(2.7)	(16.8)	(17.9)	(23.0)	(21.0)	(16.7)
$Ca(NO_3,SO_4)$	0.9	2.8	1.8	8.4	7.7	10.0	14.0	4.9
$(Na,Mg)(NO_3,SO_4)$	2.7	0.0	0.0	5.6	10.3	12.0	7.0	11.8
$(NH_4)_2SO_4$	0.0	0.0	0.9	2.8	0.0	1.0	0.0	0.0
Others	3.6	0.0	2.7	2.8	3.4	6.0	6.0	5.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

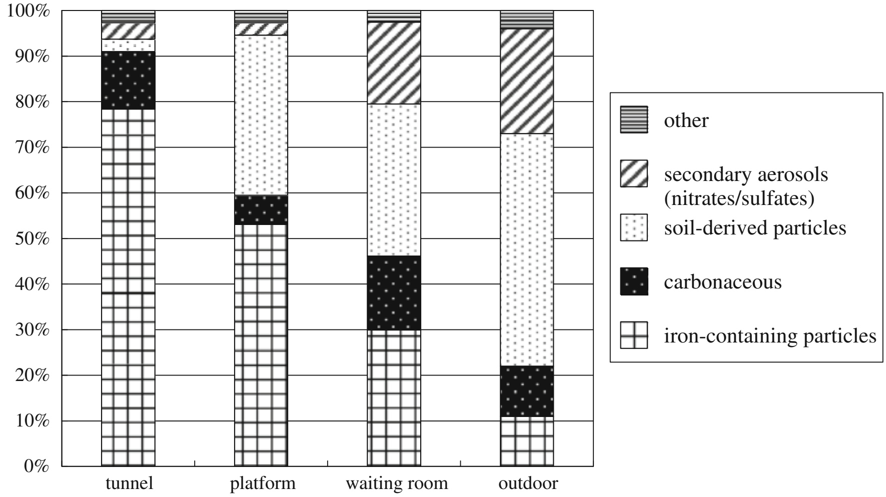
(60–100 min) at the platform in the Yangjae station was longer than that (5–10 min) in the Jegi station. The relative amounts of Fe-containing particles detected in samples from the waiting rooms are still high, but those for the Yangjae station sample are much lower (30–35%) than those for the Jegi station sample (35–62%). The indoor micro environment in the Yangjae station with screen doors not only has a lower PM concentration overall but also has a lower content of Fe-containing particles than that in the Jegi station without screen doors.

In order to compare the difference in aerosol composition between indoor and outdoor environments, outdoor aerosols were collected nearby the subway stations and analyzed by the use of the low-*Z* particle EPMA (see Tables 2, 3). For the outdoor aerosol sample collected close to the Yangjae station, soil-derived particles are the most abundant in the coarse fraction (2.5–10 μm in diameter) and carbonaceous particles are major particle types encountered in fine fraction (1–2.5 μm in diameter). For the outdoor aerosol sample collected nearby the Jegi station, secondary nitrates and sulfates which are reaction products of sea-salts with nitrogen oxide and sulfur oxide species, respectively, are the most abundant species in the coarse fraction. As Seoul is located 30–40 km away from the Yellow Sea coast, airborne particles of sea origin occasionally outnumber soil-derived particles in coarse fraction. The outdoor atmosphere nearby the Jegi station on the sampling day is likely influenced by the air mass from the Yellow Sea, resulting in the high population of secondary nitrates and sulfates.

In Fig. 2 shown are the variations of the relative abundance of major particle types encountered on stage 2 ($2.5\ \mu m < d_p < 10\ \mu m$) of Dekati impactor which were collected at different locations in the Jegi and Yangjae stations. The relative



(a) Jegi station



(b) Yangjae station

Fig. 2 Relative abundance of major particle types encountered on stage 2 (2.5 μm $< d_p <$ 10 μm) of Dekati PM10 sampler collected at various locations in **a** Jegi and **b** Yangjae (screen doors installed) subway stations

amounts of Fe-containing particles decrease as the distance of sampling locations from the tunnel increases. The extent of the decrease of Fe-containing particles in the Yangjae station is larger than that in the Jegi station, clearly indicating that Fe-containing particles predominating in the indoor microenvironment of subway stations originated from the tunnel and the screen doors play a significant role in reducing Fe-containing particles at the platform and the waiting room.

Soil-derived particles such as aluminosilicates, $CaCO_3$, and SiO_2 are the second most abundant particle type in indoor environment of subway stations. The relative abundance of the soil-derived particles in subway stations are the lowest in the tunnel and the highest at the waiting room. Also secondary particles such as nitrates and sulfates are more abundantly encountered in the waiting room than in the platform area. The soil-derived and secondary aerosol particles are likely from the outdoor atmosphere. Therefore, the contents of those particles are higher for the samples collected at the locations closer to the outdoor.

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Analysis of Palladium Concentrations in Airborne Particulate Matter with Reductive Co-Precipitation, He Collision Gas and ID-ICP-Q-MS

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1 Introduction

Platinum group elements (PGE) are used as catalysts in a variety of industrial, chemical and pharmaceutical applications, such as in the production of pesticides and dye stuffs and in the processing of polymers. These rare noble metals, notably platinum (Pt), rhodium (Rh) and palladium (Pd), are also used as catalysts in automobile catalytic converters to reduce the emission of carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC) in exhaust fumes. This application, in fact, accounts for the largest consumption of the global supply of these metals on a per weight basis. In 2008, for instance, catalytic converter producers consumed a total of 52, 47 and 86% of the world's Pt, Pd and Rh, respectively (Matthey 2008). Pd use by the catalyst industry increased by a factor of six from 1993 to 2008 (Matthey 1996, 2008).

While the noxious by-products of fossil fuel combustion are significantly reduced in automotive exhausts, PGE are also released in small amounts together with particles from the wash coat of the converters, due to fast changing oxidative and reductive conditions, high temperatures and mechanical abrasion of the catalytic material (Schlögl et al. 1987; Artelt et al. 2000). This has led to increasing concentrations of these metals in the environment since the introduction of catalytic converters in Europe in the 1980s and elsewhere, as has been documented in a number of studies (e.g. Zereini et al. 1997, 2007; Whiteley and Murray 2003;

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_13,

Limbeck et al. 2004; Rauch et al. 2005; Figueiredo et al. 2006; Jarvis et al. 2001; Gómez et al. 2003). It has generally been assumed that the concentrations of these metals in the environment are too low to pose a real risk to human health (Wiseman and Zereini 2009; Colombo et al. 2008). For instance, Pd concentrations in airborne PM sampled in various cities have generally been found to be present in the low pg/m^3 range (Zereini et al. 2004, 2005; Limbeck et al. 2007; Iavicoli et al. 2008). Recent evidence suggests, however, that the environment and health risks of exposures to these metals are greater than once thought (Wiseman and Zereini 2009). In particular, there are concerns regarding significant increases in the concentrations of Pd in the environment during the last decade due to the introduction of a three-way catalytic converter as an alternative to the conventional ones using Pt and Rh. Pd may pose a greater environmental and human health risk given its apparent greater solubility (Jarvis et al. 2001) and increased bioavailability and uptake by organisms (Colombo et al. 2008; Turner and Price 2008).

The development of reliable methods for the quantitation of PGE at low and ultra low levels (i.e. ppb range) typical for environmental samples is a primary focus of attention. Inductively coupled plasma mass spectrometry (ICP-MS) has become the most common method for the determination of PGE in environmental and biological samples (Gómez et al. 2003; Fritsche and Meisel 2004; Hann et al. 2006; Kanitsar et al. 2003; Meisel et al. 2003; Vanhaecke et al. 2004; Bencs et al. 2006; Ravindra et al. 2004). However, the application of ICP-MS is critical since other elements present in the sample matrix can cause molecular interferences during the measurement of PGE. This problem is particularly strong in the case of Pd and its measurement in airborne PM samples. As such, it has been suggested that the use of ICP-MS to measure Pd should be limited to those instances where little interferences are expected (Schuster et al. 1999). Mathematical corrections concerning the molecular interferences with Pd have also been recommended but can be problematic. Molecular interferences have been shown to be minimized when the PGE are pre-concentrated and separated from the sample matrix using validated methods prior to analysis such as chromatographic separation (Müller and Heumann 2000), ion exchange (Hann et al. 2006; Meisel et al. 2003; Ely et al. 2001) and co-precipitation with tellurium (Te) (Gómez et al. 2003; Gómez-Gómez and Palacios-Corvillo 2006) or mercury (Hg) (Iavicoli et al. 2008; Messerschmidt et al. 2000). Some methods such as Te co-precipitation have been demonstrated to be more effective in the analysis of Pt and Rh but not for Pd at low concentrations (Gómez et al. 2003). Measurement reliability using ICP-MS can also be enhanced with the use of isotope dilution, which involves the addition of an enriched isotope of the element of analysis as a form of internal standard. For this though, at least two isotopes must be free from interferences. If complete matrix separation is not achieved for Pd, argides, oxides and hydroxides from copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr) and strontium (Sr) can form in the plasma and interfere with the measurement of Pd isotopes.

The application of collision gas techniques in combination with ICP-MS have also been found to minimize molecular interferences by transforming interfering elements into other species with different mass-to-charge ratios (Koppenaal et al. 2004;

Moldovan et al. 2006). For instance, Simpson et al. (2001) used oxygen as an oxidizing reaction gas to remove oxide interferences on different noble metals such as Pd, silver (Ag), Pt and gold (Au) by formation of higher oxides leaving the mass free from interference.

A standardized method which successfully combines the aforementioned methods to improve the Pd determination in the very low concentration range typical for most environmental media has yet to be systemically developed, evaluated and applied. As indicated, there is a need to focus on the development of a reliable method for the analysis of Pd in media such as PM, as the quantitation of this metal has proven to be particularly problematic. The aim of this study was to evaluate Hg and Te co-precipitation procedures and the application of ID-ICP-Q-MS with He as a collision gas to measure Pd in airborne PM samples. For verification, the road dust certified reference material BCR723 was analyzed, as well as the CANMET CCRMP reference material TDB-1 and WPR-1.

2 Experimental

2.1 Reagents and Apparatus

The 69% nitric acid (HNO_3) and 37% hydrochloric acid (HCl) used for sample dissolution in a high pressure asher (HPA-S, Anton Paar, Austria) were supra grade quality purchased from Roth (Karlsruhe, Germany). The 40 % hydrofluoric acid (HF) used to remove silicates was of suprapure grade from Merck (Darmstadt, Germany).

The Hg (150 mg mL^{-1}) solution was prepared by dissolving 15 g of Hg (suprapure grade 99.99%, Merck, Darmstadt, Germany) in 22.5 mL diluted HNO_3 (12.5 mL of 69% HNO_3 diluted in 10 mL de-ionized water) and then filled up to 100 mL with water purified using an Astacus analytical system (membraPure GmbH, Bodenheim, Germany). Concentrated formic acid (HCOOH) (100 %; supra pure grade) used for the reduction of the Pd-salts in the digestion product to Pd(0), was also purchased from Merck (Darmstadt, Germany).

The calibration and working standards used for Pd in diluted HNO_3 (2–3%) and the interfering elements (e. g. Cu, Y, Zr and Rh) were prepared daily by diluting 1,000 mg L^{-1} standard solutions (Merck, Darmstadt, Germany) in 0.5% HNO_3. For the co-precipitation of samples using Te, a solution with a concentration of 10 mg Te/mL (in 20% HCl) was obtained from Alfa Aesar (Karlsruhe, Germany). The tin(II) chloride solution needed to induce the precipitation of Pd was prepared by dissolving 10 g tin(II) chloride dihydrate (analytical grade; Merck, Darmstadt, Germany) in 8 mL 37% HCl diluted up to 50 mL with pure water in a volumetric flask. Indium (^{115}In) was used as an internal standard for correction of the instrumental drift.

Enriched ^{105}Pd (97% ^{105}Pd) standard material for ID was obtained from Cambridge Isotope Laboratories (Woburn, Ma, USA) and dissolved in *aqua regia* (HCl:HNO_3, 3:1).

Table 1 Instrumental operation conditions of the ICP-Q-MS

Plasma conditions	
Argon plasma gas flow	17.5 L/min
Auxiliary gas flow	1.63 L/min
Nebulizer Flow	0.98 L/min
Solution uptake rate	0.22 mL min^{-1}
ICP RF power	1.40 kW
Dwell time	50 μs
Replicates	5
Scans	15
Scan mode	Peak hopping
Oxide formation rate $^{140}\mathrm{Ce}^{16}\mathrm{O}/^{140}\mathrm{Ce}$	1.8%
Intensity for $^{115}\mathrm{In}$ in a 1 ng/mL solution	4.2×10^5 counts*s^{-1}

Table 2 Important molecular interferences of Pd isotopes with other elements (Simpson et al. 2001)

Isotope	Abundance (%)	Interference	Abundance (%)
$^{104}\mathrm{Pd}$	11.14	$^{40}\mathrm{Ar}^{64}\mathrm{Zn}$	48.61
		$^{88}\mathrm{Ar}^{16}\mathrm{O}$	82.36
		$^{104}\mathrm{Ru}$	18.70
		$^{208}\mathrm{Pb}^{2+}$	52.38
$^{105}\mathrm{Pd}$	22.33	$^{40}\mathrm{Ar}^{65}\mathrm{Cu}$	30.71
		$^{88}\mathrm{Sr}^{16}\mathrm{O}^{1}\mathrm{H}$	82.37
		$^{89}\mathrm{Y}^{16}\mathrm{O}$	99.76
$^{106}\mathrm{Pd}$	27.33	$^{40}\mathrm{Ar}^{66}\mathrm{Zn}$	27.79
		$^{106}\mathrm{Cd}$	1.25
		$^{90}\mathrm{Zr}^{16}\mathrm{O}$	51.34
$^{108}\mathrm{Pd}$	26.48	$^{40}\mathrm{Ar}^{68}\mathrm{Zn}$	18.72
		$^{38}\mathrm{Ar}^{70}\mathrm{Zn}$	0.014
		$^{92}\mathrm{Zr}^{16}\mathrm{O}$	17.07

An ICP-Q-MS (Varian 820-MS, Darmstadt, Germany) with a concentric nebulizer (MicroMist) and a double-pass Scott-type spray chamber cooled by a Peltier system was used for analysis of Pd. Table 1 details the ICP-Q-MS operating conditions. Maximal intensity was optimized for In^{+} and minimal values for $\mathrm{CeO}^{+}/\mathrm{Ce}$ and $\mathrm{Ba}^{2+}/\mathrm{Ba}$. For ID calculations three isotope ratios ($^{105}\mathrm{Pd}/^{104}\mathrm{Pd}$, $^{105}\mathrm{Pd}/^{106}\mathrm{Pd}$, $^{105}\mathrm{Pd}/^{108}\mathrm{Pd}$) were used (Table 2).

2.2 Sample Collection and Digestion

A total of 143 airborne PM samples were collected at three sampling stations in Germany: Deuselbach (Rhineland-Palatinate, south-western Germany), Neuglobsow (Brandenburg, north-eastern Germany) and in the city of Frankfurt am Main (Hesse, Germany). The former two locations are geographically situated in more rural areas, with predicted Pd concentrations to be more reflective of background levels. The third sampling location in Frankfurt am Main has a high traffic volume with expected higher airborne metal concentrations (i.e. a major street, four lanes, speed limit 50 km/h, traffic load approximately 32,500 vehicles/day).

Airborne PM samples with an aerodynamic equivalent diameter of less than 10 microns (PM_{10}) were collected with a high-volume sampler (DHA-80, Digitel) on cellulose nitrate filters with a diameter of 150 mm and a pore size of 3 μm. The total volume of air sampled for the collection of PM was about 4,500 m^3 for the rural locations and 1,400 m^3 for the sampling location in the city of Frankfurt am Main.

Filters were weighed three times at minimum on a microbalance (Satorius BP 210S) both before and after sampling under constant humidity and temperature conditions to check for constant weight. The blank and sampled filters were conditioned for about 48 h before weighing in this room. Following sample collection, the cellulose nitrate filters were digested in a sealed 90 mL quartz vessel with 4.5 mL of 37% HCl and 1.5 mL of 69% HNO_3. The samples were spiked with 1.2 ng to 15 ng of a ^{105}Pd enriched Pd solution before digestion.

The samples were then digested in a high pressure asher for 1 h at a temperature of 320 °C and a pressure up to 130 bar, which has been found to be the most effective way to achieve the full dissolution of environmental samples (Messerschmidt et al. 2000; Meisel and Moser 2004; Meisel et al. 2003). Following digestion, the sample volume was reduced to approximately 1 mL by evaporation and treated with 40% HF to eliminate silicates. Then, the solution was heated to near dryness; 69% HNO_3 was added and then the solution was again evaporated to remove the fluorides (this step was repeated twice) (Gómez et al. 2003). Finally, the sample solution was diluted to 10 mL with 0.5% HNO_3 in a volumetric flask.

Ten samples of the road dust reference material BCR723 and the CANMET CCRMP reference material TDB-1 and WPR-1 were analyzed equivalent to the method described above. Prior to analysis, 0.5 g of the road dust reference material BCR723 and 0.2 g of the CANMET CCRMP reference material were mixed with 1.5 mL of 69% HNO_3 and 4.5 mL of 37% HCl.

2.3 Precipitation of Palladium with Mercury and Tellurium

Co-precipitation of Pd with Hg was carried out following a procedure previously described by Messerschmidt et al. (2000), which is recommended elements that are more electropositive than Hg. Therefore, only Pd and Au can be scavenged and collected by Hg under the reaction conditions (Messerschmidt et al. 2000).

Using a 15 mL centrifuge tube, 0.5 mL HCOOH and 0.2 mL of an Hg solution (150 mg/mL^{-1} in diluted HNO_3) were added to 2 mL of the sample solution.

This solution was heated to 80 °C for about 10 min, during which a black precipitate appeared. Another 0.5 mL of HCOOH was added to complete the reduction step. Samples were held at a constant temperature of 80 °C for 30 min, during which Hg formed droplets at the bottom of the centrifuge tube. The solution was then heated to weak boiling for 10 min to finish the reduction.

The Hg droplets were filtered via a glass frit (pore size 16–40 μm), washed with 5 mL of 0.3 M HCl, and then with 3 mL of purified water. Finally, the droplets were dried with a small amount of acetone. To isolate the Pd, the droplets were transferred to an evaporating dish and heated to 350 °C to remove the Hg. The residue was suspended in 0.1 mL of concentrated HNO_3, which dissolves the Pd and brings it into solution, and then diluted up to 10 mL with 0.5% HNO_3. The Pd standard was also obtained in diluted form (with HNO_3) from Merck (Darmstadt, Germany).

For co-precipitation of Pd with Te, previously described by Gómez et al. (2003), 3 mL of the sample solution were evaporated in a 100 mL Teflon vessel to eliminate the HNO_3. After adding 2 mL of 37% HCl dissolved in 50 mL purified water, the solution was evaporated again. This step was repeated once. Afterwards, the solution was treated with 5 mL of 37% HCl diluted in 45 mL purified water. As a reductive reagent, tin(II)chloride was added to a solution of 10 mg/mL Te in diluted HCl. The solution was then heated until it reached a weak boil for a total of 10 min to induce the coagulation of a black precipitate which contains the Pd. The black precipitate was filtered through a 0.45 μm PTFE filter and rinsed with 1 mol L^{-1} HCl. The precipitate was then dissolved in a few ml of *aqua regia* and evaporated to near dryness. The residue was transferred with small amounts of 0.5% HNO_3 into a volumetric flask which was finally filled up to 10 mL with 0.5% HNO_3.

3 Results and Discussion

3.1 Co-Precipitation Using Mercury and Tellurium

Several steps were undertaken to assess the applicability and effectiveness of the Hg co-precipitation method for the reliable measurement of Pd in environmental samples using ID-ICP-Q-MS. In a first step, *aqua regia* digestion solutions of airborne PM were analyzed directly without any prior treatment. In a second step, these samples were co-precipitated with Hg to minimize matrix elements. For comparison, a co-precipitation method using Te was also used (Gómez et al. 2003; Moldovan et al. 2006).

With Hg co-precipitation, the concentration of Cu was reduced in the analytical solution by a factor ranging between 2.6×10^6 and 2.9×10^7 (Table 3). In contrast, Te precipitation depleted the concentration of Cu in the analytical solution by 1×10^5 to 1×10^6 fold. After Hg co-precipitation, the concentration of Zn was 100 times lower than that achieved by Te co-precipitation. Sr was

Table 3 Concentration differences for interfering elements between tellurium (Te) and mercury (Hg) co-precipitation obtained from four airborne PM samples from Deuselbach (b.dl. below detection limit)

Sample	Isotope	Before precipitation (μg/g)	After Te-precipitation (ng/g)	After Hg-precipitation (ng/g)
1	^{65}Cu	50.1	0.05	0.004
2		87.9	0.18	0.003
3		39.3	0.35	0.015
4		15.2	0.13	0.003
1	^{66}Zn	416.1	2.65	0.016
2		423.6	1.02	0.005
3		794.8	3.30	0.01
4		347.7	2.12	0.03
1	^{88}Sr	108.7	0.07	b. dl.
2		96.3	0.05	b. dl.
3		74.2	0.2	0.002
4		72.1	0.02	0.004
1	^{89}Y	40.2	9.34	0.32
2		27.3	6.35	0.15
3		51.1	11.9	0.28
4		18.5	4.3	0.16
1	^{90}Zr	3100	1100	12.9
2		3200	1100	18.4
3		2600	890	10.0
4		830	290	8.5
1	^{106}Cd	12.6	89.7	b. dl.
2		7.2	8.3	b. dl.
3		9.8	17.1	0.04
4		2.0	3.4	b. dl.

reduced by Te co-precipitation by a factor of 3.7×10^2 up to 1.5×10^3. With Hg co-precipitation, the concentration of Sr was reduced by as much as 3.8×10^4 fold or to below the detection limit. Oxides of Y ($^{89}Y^{16}O$) also disturb the determination of ^{105}Pd. Figure 1 shows the concentration of Y [μg/L] in airborne PM samples from Deuselbach before any treatment of the solution (diamond-dotted line) and after Te- (line with filled circles) and Hg co-precipitation (line with filled triangles). Te co-precipitation reduced Y levels by a factor of 6–8.5, compared to the untreated samples. Hg co-precipitation was more efficient, reducing the amount of Y by as much as 370 fold (Fig. 1).

The same effect was observed for Zr, which causes molecular interferences in the measurement of ^{106}Pd as the oxide $^{90}Zr^{16}O$ (see Fig. 2). The concentration of Zr in the *aqua regia* digestion solutions of the PM samples of Deuselbach reached levels in the μg/L range. This is not surprising given the fact that automotive

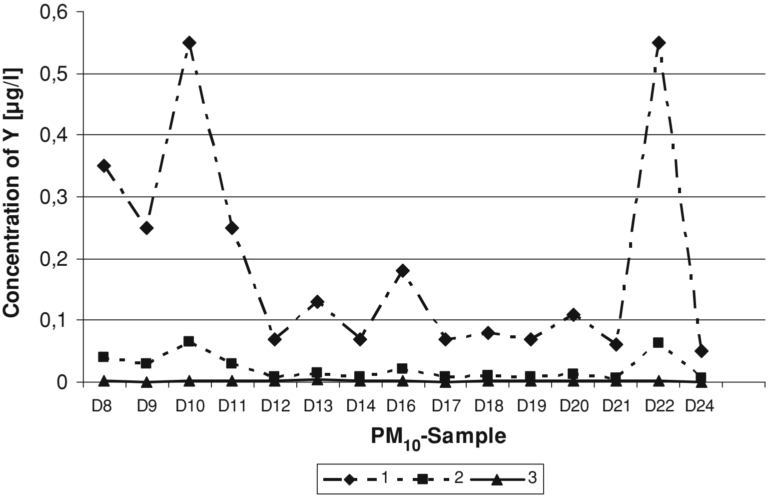


Fig. 1 Concentration of Y in airborne particulate matter (PM_{10}) samples after Hg- and Te-precipitation measured by ICP-Q-MS (samples collected in Deuselbach).The concentration of Y (µg/L) in the digestion solution before precipitation with Hg or Te (1); the Y concentration after Te co-precipitation (2); the concentration of Y after Hg precipitation (3)

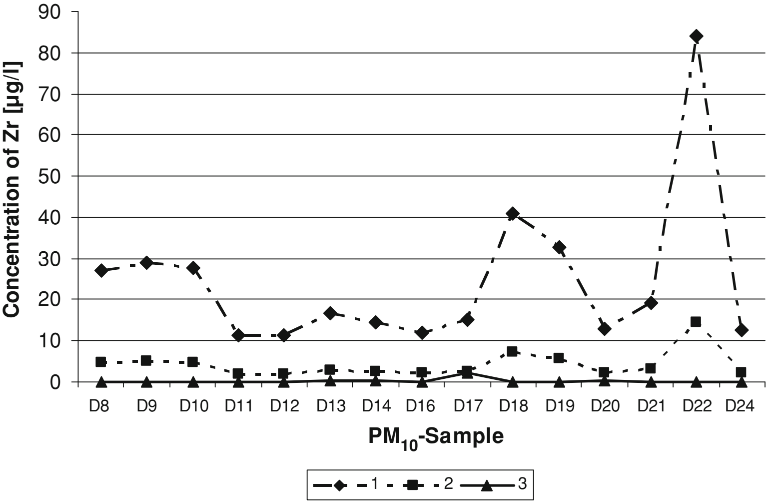


Fig. 2 Concentration of Zr in airborne particulate matter (PM_{10}) samples from Deuselbach after Hg- and Te-precipitation using ICP-Q-MS. The concentration of Zr (µg/L) in the digestion solution before precipitation with Hg or Te (1); the concentration of Zr after Te precipitation (2); the concentration of Zr after Hg precipitation (3)

catalytic converters have been found to contain as much as 50 g ZrO_2 per litre volume of the catalytic converter (Abdelnour and Murphy 2004).

As shown, Hg co-precipitation (line marked with filled triangles) proved to be much more effective than Te co-precipitation (a line with filled diamonds). With Te co-precipitation, the Zr level was reduced by a factor of 4.5 (untreated sample shown as a line with filled diamonds). In comparison, Hg co-precipitation reduced concentrations by as much as 150 fold. Other isobaric interferences which can originate from cadmium (Cd) and ruthenium (Ru) were determined to be insignificant or non-existent.

3.2 Optimisation of Helium Gas Flow

Different gases such as CH_4, NH_3 and H_2 have be used in collision cells to reduce isobaric or polyatomic molecular interferences (Niemelä et al. 2003). H_2 or He is typically used with the ICP-Q-MS employed in the present study (i.e. a Varian 820 ICP-MS). In this instrument, the flow of gas is introduced into the plasma with a double-walled skimmer cone. While the collision/reaction takes place in the plasma, high amounts of electrons are available for electron-ion dissociative recombination to attenuate molecular interferences (Abdelnour and Murphy 2004). All samples were measured both in standard mode (without He) and with the aid of He as a collision gas in conjunction with the ID-ICP-Q-MS for comparative purposes.

To identify the optimal He gas flow, a test solution containing 1µg/l Rh and 10µg/l of Cu, Y and Zr as interferents was used. Rh was chosen as a surrogate standard for Pd. The counting rates for all ions ($CuAr^+$, YO^+, ZrO^+, Rh^+) were examined as a function of the gas flow rate. The flow of the collision gas (He) into the plasma was increased from 0 to 130 ml/min and the counts of the ions Rh^+, $CuAr^+$, YO^+ and ZrO^+ were plotted versus the He gas flow (Fig. 3). The results show, that with increasing gas flow the counts for Rh^+, $CuAr^+$ YO^+ and ZrO^+ are decreasing. The counts of Rh^+ decreased from 270,000/s (without a collision gas

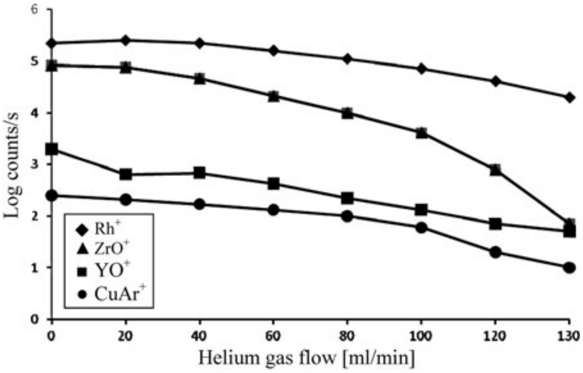


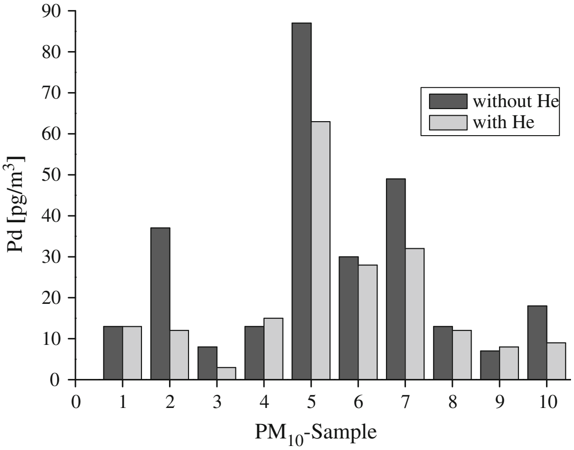
Fig. 3 Optimization of collision gas flow for Pd determination using 1 µg/L Rh as a surrogate standard and 10 µg/L of interfering elements Cu, Y and Zr. The counts per second in logarithmic scale are displayed for masses 103 (Rh), 105 ($CuAr^+$,YO^+) and 106 (ZrO^+)

flow) to 36,000/s at a helium gas flow of 130 mL/min. The counting rate for YO^+ was determined to 43,000 counts/s at a collision gas flow of 0 mL per minute. The rate decreased to 80 counts/s for a gas flow of 130 mL/min. The same effect was observed for the counting rate of ZrO^+ which interferes with ^{106}Pd. The counting rate for ZrO^+ decreased from 46,000 to 150 counts/s. For $CuAr^+$ a counting rate of 250 counts/s was determined without using He as a collision gas. With a gas flow of 130 mL/min, only 10 counts/s remained. The formation rate of $CuAr^+$ was very low, so that interferences from Cu can be neglected. The corresponding decreases in counts for all ions together with a increasing collision gas flow is a result of higher collision rates. The blank values for the three molecular ions were 155 counts/s for 105Pd, 160 counts/s for 106Pd, whereas Rh had a blank value of only 20 counts/s.

At a He gas flow of 120 mL/min, with a stabilization delay of 60 s, the counts of YO^+ (with mass 105) and ZrO^+ (with mass 106) were both below their blank values, while the counts for Rh^+ were still much higher. Based on these results, a He gas flow of 120 mL/min was determined to be the optimal flow rate to reduce molecular ion interferences from YO^+ and ZrO^+. In comparison, Moldovan et al. (2006) used 1% NH_3 in He as a collision gas with a flow rate of 1 mL/min to reduce YO^+ interferences in the measurement of ^{105}Pd using ICP-Q-MS.

Airborne PM_{10} samples collected in Frankfurt/Main ($n = 10$) were analyzed both with and without the use of He as a collision gas, in combination with the ID-ICP-Q-MS, to evaluate its effectiveness in minimising molecular interferences. The results are shown in Fig. 4. In seven of these samples, the Pd concentrations were determined to be higher when analysed without He collision gas compared to the results obtained with use of He collision gas. In three of the samples, the concentrations of Pd were with use of He collision gas equal or slightly lower than without use of He collision gas. According to the overall mean value of the determined Pd concentrations, the use of He as a collision gas provides Pd values which are 22% lower than without use of He collision gas. This indicates that the

Fig. 4 Palladium concentration in different samples from Frankfurt/Main determined after mercury co-precipitation by ID-ICP-Q-MS using helium as collision gas (gas flow 120 mL/min) and measured without helium



use of He collision is an effective way to reduce molecular interferences from YO^+ and ZrO^+, yielding values that more accurately reflect actual Pd concentrations in environmental samples.

3.3 Quality Control

The effectiveness of Hg co-precipitation to minimise molecular interferences in measuring Pd with ID-ICP-Q-MS and He as collision gas was verified using the road dust reference material BCR723. A value of 4.2 ± 1.4 μg Pd/kg (standard deviation ±) was determined. This value is lower than the certified value of 6.1 ± 1.9 μg Pd/kg for BCR723 (Table 4).

Sutherland (2007) reviewed literature data from 2001 to 2006 concerning PGE contents in the reference material BCR723. In this review, 29 different studies were evaluated with respect to the reported concentration of Pt, Pd and Rh; 16 studies focused on Pd. The concentrations of Pd in the reference material BCR723 ranged from 3.7 to 8.0 μg Pd/kg with values ranging from 4.2 to 7.9 μg/kg Pd in the 95 % confidence band. In nearly 50 % of the reviewed studies, concentrations lower than the certified value of 6.1± 1.9 μg Pd/kg were detected.

In the present study, a concentration of 7.2 ± 2.5 μg Pd/kg was determined for BCR723 when He was not used as a collision gas. This value is slightly higher than the certified value of 6.1± 1.9 μg Pd/kg.

Table 4 Palladium concentration (mean values with standard deviation) in different samples determined after mercury co-precipitation by ID-ICP-MS using helium as collision gas

	(*N* = number of samples)	Concentration
Procedural blank		0.01 pg/m^3
Limit of detection Pd		0.05 pg/m^3
BCR723 Measurement without helium as collision gas	10	7.2 ± 2.5 μg/kg
BCR723 Measurement with helium as collision gas	10	4.2 ± 1.4 μg/kg
Certified value for Pd in road dust reference material BCR723		6.1 ± 1.9 μg/kg
CANMET CCRMP TDB-1	5	22.3 ± 1 μg/kg
Certified value for Pd in CANMET CCRMP reference material TDB-1		22.4 ± 1.4 μg/kg
CANMET CCRMP WPR-1Certified value for Pd in CANMET CCRMP reference material WPR-1	5	235.6 ± 3.1 μg Pd/kg235 ± 9 μg Pd/kg
Air dust (PM$_{10}$) Neuglobsow (Brandenburg) background concentration	45	mean: 0.3 (0.06–7.4) pg/m^3
Air dust (PM$_{10}$) Deuselbach (Rhineland-Palatinate) background concentration	49	mean: 0.6 (<0.05–9.7) pg/m^3
Air dust (PM$_{10}$) Frankfurt am Main High traffic road	49	mean: 20.7 (1.3–102.8) pg/m^3

The Pd concentration in BCR723 obtained with He collision (4.2 ± 1.4 μg Pd/kg) is in the lower range of previously reported values and the value obtained without He collision (7.2 ± 2.5 μg Pd/kg) is in the higher range of the values reported previously. Due to the reduction of molecular interferences by He collision, the lower concentration range of 4.2 ± 1.4 μg Pd/kg appears to be more likely. The method was also verified by analyzing the CANMET CCRMP reference material TDB-1 and WPR-1. A mean concentration of 22.3±1.0 μg/kg was measured with He as a collision gas for theTDB-1 sample, which is in good accordance with the certified value for Pd (22,4±1.4 μg Pd/kg). The mean value calculated for this reference material without the use of He as a collision gas was 22.9±3.8 μg Pd/kg. The calculated mean value of the Pd concentration in the CANMET CCRMP reference material WPR-1 was 235.6±3.1 μg Pd/kg, determined with He as a collision gas. This value is close to the certified value of 235±9 μg Pd/kg. The close similarity of the measured concentrations with the certified values demonstrates that the described analytical method is reliable for the determination of Pd in environmental samples.

3.4 Blank Level and Limit of Determination

The results show that Pd can be effectively and accurately measured in airborne PM using Hg reductive co-precipitation to isolate and pre-concentrate samples and isotope dilution ICP-MS with He as a collision gas. The method proved to be effective for the determination of Pd in airborne PM for background samples at very low concentrations in the pg/m^3 range. The procedural blank was determined to be 0.01 pg Pd/m^3, while the limit of determination (LOD) was calculated to be 0.05 pg Pd/m^3 (Table 4).

3.5 Concentration of Pd in Airborne Particulate Matter (PM$_{10}$)

The described method was used for the analysis of 49 samples of airborne PM from Deuselbach, 45 samples of airborne PM from Neuglobsow and 49 samples of airborne PM from the City of Frankfurt am Main (total n = 143). The Pd concentrations varied significantly from the rural to the urban sampling locations, which was to be expected. PGE concentrations in environmental media have been found to be heavily dependent on proximity to traffic-emitting sources, with the highest levels to be found along major roadways (Zereini et al. 2005, 2007; Wichman et al. 2007). The lowest mean concentration of Pd was detected in samples from Neuglobsow with 0.3 pg/m^3. The observed Pd concentration ranged from 0.06 to 7.4 pg/m^3. In Deuselbach, the median concentration was 0.6 pg/m^3, with a Pd concentration that ranged from <0.05 pg/m^3 (below LOD) to 9.7 pg/m^3. This compares to that found by Zereini et al. (2005) and Gómez et al. (2002) for samples collected in rural areas. The mean concentration of samples collected in

Frankfurt am Main was 20.7 pg Pd/m^3, with a minimum concentration of 1.3 pg Pd/m^3 and a maximum concentration of 102.8 pg Pd/m^3 (Table 4). This falls in the same range as that reported elsewhere for a high traffic area (Limbeck et al. 2004; Rauch et al. 2005), but is slightly lower compared to concentrations reported by Zereini et al. (2004). The highest concentration of 102.8 pg Pd/m^3 measured in samples collected in Frankfurt am Main is of particular concern. This is almost twice that reported by Gómez et al. (2002) in PM$_{10}$ samples collected in Rome, who measured as much as 54.9 pg Pd/m^3. As discussed by Wiseman and Zereini (2009), observed Pd concentrations found in airborne PM highlights the need for continued monitoring and research.

3.6 Conclusion

Hg co-precipitation was demonstrated to be a considerably more effective method to pre-concentrate and isolate Pd from the matrix of airborne PM prior to analysis using ID-Q-ICP-MS, compared to Te co-precipitation. For all relevant elements, Hg co-precipitation reduced the concentrations of interfering matrix constituents by at least one order of magnitude more compared to Te co-precipitation (Table 3). The use of He as a collision gas was demonstrated to further increase the reliability of the measurements by minimizing molecular interferences. Pd concentrations measured for airborne PM samples collected in Frankfurt am Main demonstrate that they are significantly higher relative to those collected in more rural areas with a lower traffic density. Future levels of Pd in urban airborne PM need to be monitored to ensure they will not pose a human health risk, especially to vulnerable populations such as children.

Acknowledgments Financial support of the study by the Umweltbundesamt in Dessau, Germany under grant no. 351-01-049 is gratefully acknowledged. R. Schleyer, E. Bieber and M. Wallasch of the Umweltbundesamt Langen Branch, Air Monitoring Network are thanked for the cooperation and support.

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Part III
Airborne Particulate Matter: Environmental Pathways, Behaviour and Fate

Clare L. S. Wiseman and Fathi Zereini

The environmental transport, behaviour and fate of airborne particulate matter (PM) generated through primary or secondary sources is highly complex and can involve a number of physicochemical, thermodynamic, hydrological, meteorological and aerodynamic processes. Knowledge regarding how PM and its various components move between environmental compartments, and the physicochemical changes they may undergo, is critical to allow for an adequate assessment of human exposures and related health risks. For example, a contaminant may be emitted in a form which is toxic to humans but may not necessarily pose a risk if transport and/or transformation mechanisms serve to reduce its environmental bioaccessibility. An understanding of the environmental fate of PM and its chemical components is fundamental to the development of sound environmental and public health policy measures and regulations, which are protective of human health. Part III contains six chapters which address various important aspects and issues related to the transport, behaviour and fate of airborne PM in the environment. These are detailed below.

In the first chapter, Balasubramanian and He review the environmental transfer and fate of semivolatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). These compounds are of concern due to their toxicity and ability to bioaccumulate and biomagnify in the environment. In the context of studies conducted in Singapore, they specifically review environmental distribution processes such as gas/particle partitioning, precipitation scavenging and air–sea exchange, which strongly govern the fate of SVOCs upon their release into environment. Kalaiarasan et al. discuss the vertical distribution of airborne PM in a tropical urban environment in the second chapter. In particular, they focus on traffic-generated, fine PM and its vertical distribution in naturally ventilated, high-rise residential buildings in Singapore, a highly dense urbanized area with little available land space for new developments to house its growing population. In the third chapter, Wei and Li discuss the gas-particle partitioning behaviour of SVOCs. In addition to examining the partitioning behaviour of PAHs and PCBs, like Balasubramanian and He, they also discuss the fate of polybrominated diphenyl ethers (PBDEs), flame retardants which have become ubiquitous in the urban environment. Bonn details the steps and processes involved in the generation of secondary particles in urban environments in the fourth chapter. In particular, he focuses on how atmospheric trace gases (precursors) react in the gas-phase to yield particles of varying volatility and reactivity. In the fifth chapter, Ma discusses the effects of Asian dust on urban air quality in Japan, a country which receives significant airborne particulate inputs from other regions such as in China in the Spring. Using a combination of techniques to characterize the elemental composition of airborne PM and rainwater collected in Fukuoka in 2005, Ma demonstrates the importance of precipitation in the scavenging of aerosols. To conclude this chapter, Dahmani et al. detail the impacts of a pyrometallurgical facility operating in the coastal city Ghazaouet in Algeria in the sixth chapter. They describe the application of a method involving the use of sodium tetrachloromercurate to track the emission and fate of sulphur dioxide from this pyrometallurgical complex.

Fate and Transfer of Semivolatile Organic Compounds in a Multi-Compartment Environment

Rajasekhar Balasubramanian and Jun He

1 Introduction

Semivolatile organic compounds (SVOCs) comprise many priority pollutants such as polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs). These pollutants can be introduced into the environment via the atmosphere, for example, in the emissions of incomplete combustion of fossil fuels (e.g. PAHs), out-gassing from pollutant-containing media such as paints, transformers and capacitors etc. (e.g. PCBs) and by spraying onto soils and vegetation (e.g. OCPs). They are of significant concern due to their carcinogenicity and mutagenicity, and are subject to bioaccumulation in the lipid fraction of biological tissues, thus leading to their biomagnification in the environmental system (Holsen and Noll, 1992). Once released into the atmosphere, these pollutants can be transported by atmospheric movement over the Earth's surface and can be found far from any sources in media such as waters, soils, biota or even ice-cores (Kawamura et al. 1994; Wania 1994; Muir et al. 1996). In order to assess potential risks of these pollutants for the natural environment and human health, it is important to understand the fate and distribution of these pollutants after they are introduced into the environment.

An important aspect with regard to the atmospheric fate of SVOCs is their partitioning between the gas and particle phases. Once released into the atmosphere, generally SVOCs would be partitioned in these two phases and reach a partitioning equilibrium according to temperature dependences and the vapor pressure of the chemicals (Pankow and Bidleman 1992; Cotham and Bidleman 1995). The particulate-bound SVOCs could be transferred from the atmosphere to

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_14,

other compartments of the environment by dry deposition and wet deposition (washed out by rain or snow). The gas-phase concentrations of SVOCs could also be reduced by dissolution in rain droplets or degraded by exposure to ultraviolet rays. After SVOCs are deposited into the bulk seawater, partitioning in the water column can affect the distribution of pollutants between the dissolved aqueous and the solid phases and eventually impact the fate of these compounds in oceans (Luo et al. 2004). Other than the above-mentioned processes, SVOCs can diffuse across the air–water interface; the molecules in the vapor phase of air and the "truly" dissolved molecules in water participate in this diffusive transport which is driven by a deviation from chemical equilibrium between the air and water phase. Chemical equilibrium between two phases does not necessarily mean that the concentrations are equal, rather that the escaping tendency, or fugacity, is equal in both phases. This process is reversible and counteracts any fugacity gradient which may arise from precipitation scavenging, dry particle deposition, and air mass changes over a water body, and temperature gradients.

This chapter aims to provide a comprehensive review of the abovementioned environmental distribution processes such as gas/particle partitioning, precipitation scavenging and air-sea exchange, which are of significant progress in recent years. The relevant studies conducted in Singapore are discussed to provide more insights into the fate of these pollutants.

2 Gas-Particle Partitioning

2.1 Single Parameter Approach

The behavior and fate of SVOCs in the atmosphere greatly depends on the distribution of compounds between different sub-compartments of the atmosphere such as atmospheric gaseous and particulate phases. It has been summarized that gas-particle partitioning is controlling the relative importance of different deposition pathways for SVOCs from the atmosphere to the terrestrial and aqueous surface (Bildleman 1988).

Pankow (1987) consolidated, and subsequently refined early approaches (Pankow and Bidleman 1991, 1992) to describe the equilibrium partitioning between gas and particles based on adsorption theory (Junge 1977; Yamasaki et al. 1982). Much attention has also been paid to the effect of relative humidity (RH) (Thibodeaux et al. 1991; Pankow et al. 1993; Storey et al. 1995) and non-exchangeable matter (Pankow 1988). Pankow (1988) defined the gas-particle partitioning coefficient, K_P ($m^3\ \mu g^{-1}$), which can be related to measured fractions/concentrations of gas ($C_{A,G}$—retained by adsorbent) and particulate phase concentrations ($C_{A,P}$—retained by the filter) and the total suspended particle concentration (TSP), in $\mu g\ m^{-3}$:

$$K_P = \left(C_{A,P}/\mathrm{TSP}\right)/C_{A,G} \tag{1}$$

For adsorption mechanism, neglecting every process except adsorption was proposed by Junge (1977) (Junge 1977) and later critically reviewed by Pankow (1987) (Pankow 1987), the Junge–Pankow model (Eq. 2) is the most common method for estimating adsorption of SVOCs to aerosols and it can be simplified as Eq. 3.

$$K_P = \frac{N_s A_{TSP} T e^{(Q_L - Q_V)/RT}}{16 P_L^o} \tag{2}$$

where N_s is the surface concentration of sorption sites, A_{TSP} is the specific surface area of the TSP, p_L^o is the vapor pressure of the subcooled liquid, Q_L is the enthalpy of desorption from the surface and Q_V is the enthalpy of vaporization of the subcooled liquid, respectively.

$$\Phi = c\theta / \left(p_L^o + c\theta\right) \tag{3}$$

Equation 3 relates the mass fraction of chemical adsorbed to particles (Φ) to the subcooled liquid vapor pressure of the pure compound (p_L^o, Pa) and the particle surface area per unit volume of air (θ, m^2 of aerosol per m^3 of air). The parameter c (unit, Pa·m) is based on the heat of desorption from the particle surface, the heat of vaporization of the compound, and the moles of adsorption sites on the aerosol. The particle mass fraction Φ could be calculated by:

$$\Phi = K_p TSP / \left(1 + K_p TSP\right) \tag{4}$$

A value of $c = 0.172$ Pa·m is often used, although Junge (1977) and Pankow (1987) suggested that this may vary with the class of SVOCs. Values for the surface area parameter, θ, are often assumed to be 1.1×10^{-3} for urban air and $(4.2–35) \times 10^{-5}$ for rural air (Bidleman 1988; Jaenicke 1988).

Similar to the partitioning in the water column, SVOCs can also partition through an absorption process in addition to physical adsorption onto the surface of particles. SVOCs would "dissolve" in the organic matter (OM) in the atmosphere, which exists both as primary (POA) and as secondary organic aerosols (SOA) (Lohmann and Lammel 2004). K_{OA} absorption model has been proposed by Pankow (1994) and Finizio et al. (1997). The octanol–air partitioning coefficient (K_{OA}) can be used to predict K_p with the assumption that the predominant distribution process is absorption (Harner and Bidleman 1998). The relationship between K_p and K_{OA} is

$$K_p = K_{OA} f_{OM} M_{W_{OCT}} \zeta_{OCT} / \left(\rho_{OCT} M_{W_{OM}} \zeta_{OM} 10^{12}\right) \tag{5}$$

where f_{OM} is the fraction of organic matter (OM) phase on TSP; $M_{W_{OCT}}$, and $M_{W_{OM}}$ are the mean molecular weights of octanol and the OM phase (g mol^{-1}), respectively; ρ_{OCT} is the density of octanol (0.820 kg L^{-1}); ζ_{OCT} is the activity coefficient of the absorbing compound in octanol; ζ_{OM} is the activity coefficient of the compound in the OM phase. With the assumptions that $\zeta_{OCT} = \zeta_{OM}$ and $MW_{OCT}/MW_{OM} = 1$, Eq. 5 can be simplified as Eq. 6.

$$\log K_P = \log K_{OA} + \log f_{OM} - 11.91 \tag{6}$$

For equilibrium partitioning the slope is expected to have a value of near +1 in log K_P–log K_{OA} correlations. The intercept equals log $f_{OM} - 11.91$, depending on the organic matter content of aerosols which determines the absorptive capacity.

Values of K_{OA} have to be corrected as a function of temperature for several PCB congeners and PAHs using the following Eq. 7 with the regression parameters (A and B) given by Harner and Bidleman (1996, 1998) and Kömp and McLachlan (1997)

$$\log K_{OA} = A + B/T \tag{7}$$

For adsorption and absorption, the dependence of K_P on the subcooled liquid vapor pressure of different compounds has been demonstrated by plotting log K_P vs. log $p_L{}^{\circ}$ (Pankow 1987; Pankow and Bidleman 1991, 1992; Cotham and Bidleman 1995). The correlation could be shown as

$$\log K_P = m_r \log p_L^o + b_r \tag{8}$$

This regression of log K_P against the temperature corrected log p_L^o of the compound could potentially yield useful information on the distribution from the slope, m_r and the y-intercept, b_r, of the trendline. If equilibrium was established, m_r is expected to have a value of near -1 (Pankow and Bidleman 1992).

2.2 Poly Parameter Approaches

The abovementioned models use single-parameter linear free energy relationships (spLFERs) to describe sorption to aerosol particles. Generally, spLFERs relate the gas-particle partitioning coefficient to the subcooled liquid vapor pressure, $p_L{}^{\circ}$, or the octanol-air partitioning coefficient, K_{OA}, of the chemical. An alternative conceptual model for sorption to aerosol particles has been developed by Goss and co-workers (Goss 1997; Abraham 2004; Roth et al. 2005a, b). It has been advocated to describe gas-particle partitioning with polyparameter linear free energy-relationships (ppLFERs). A ppLEFR describing the gas-particle partitioning coefficient has the general form

$$\log K_P = w \cdot W + x \cdot X + y \cdot Y + \cdots + C \tag{9}$$

Each multiplicative group on the right side of the equation describes an interaction between the chemical and the sorbent such as van der-Waals interactions or hydrogen bonding. The multiplicative groups are composed of a term representing the chemical's ability to participate in an interaction (W, X, Y …). To calculate K_P for a chemical, one needs Abraham salvation parameters for the chemical (Achemical = $\{W, X, Y, \ldots\}$), a set of complementary sorbent parameters (Asorbent = $\{w, x, y, \ldots\}$), and the constant, C (Abraham 2004). In principle, the ppLFER approach can describe any surface adsorption or bulk phase absorption interactions that are possible between gas molecules and suspended particles. In laboratory and field studies, ppLFERs have been developed to describe the distribution of volatile organic compounds between the gas phase and various surfaces and bulk phases (Goss and Eisenreich 1996; Nguyen et al. 2005; Roth et al. 2005a, b; Arp et al. 2006).

In 2007, a more general model of gas-particle partitioning for semivolatile organic compounds has been developed (Götz et al. 2007), which combines existing ppLFERs for sorption to fine aerosols and components of coarse aerosols into a model that is applicable to aerosols with defined size distribution and composition. The new model is applicable to organic non-ionic polar and nonpolar chemicals (including PCBs, dichlorodiphenyltrichloroethane (DDT), and polar pesticides), and can describe a wide range of aerosol properties. A comparative evaluation was made between the spLFER and ppLFER models by (1) comparing the sorption models for a reference aerosol to identify compound classes where K_P is sensitive to which model is used, and (2) investigating the variability of K_P among different aerosols. Practical application of the general ppLFER model to a wide range of substances and surfaces is currently still limited by data gaps in measured Abraham salvation parameters and uncertainties in estimation methods.

A different tool depending on quantitative structure–property relationship (QSPR) can be utilized to predict K_P values for SVOCs. QSPR studies are widely used in chemistry, biochemistry and recently environmental problems (Gramatica et al. 1999; Gramatica et al. 2001). The main idea of QSPR is to construct the correlationship by expressing a special physicochemical property of organic compounds in terms of appropriate molecular descriptors (Karelson et al. 1996). Wei et al. (2007) have explored the relationship between molecular descriptors and gas/particle partitioning of PCBs. In their study, overall 14 molecular descriptors of each compound calculated using semi-empirical method parametric model 3 (PM3) were tested against log K_P of selected PCBs to determine the best ones governing partitioning. Eight descriptors, namely, molecular weight (M_W), molecular volume, total energy, electronic energy, squared atom electron densities on carbon, hydrogen and chlorine atoms in a given molecule and average molecular polarizability were found to be highly correlated with log K_P compared to other molecular descriptors. Using Partial Least-Squares Regression method (PLS), two-, three- and four-descriptor QSPR models with good fitting characters were successfully developed.

2.3 A Case Study of Gas/Particle Partitioning

The present study was carried out to measure gaseous and particulate concentrations of PAHs and PCBs in Singapore urban air. The data were then applied to make an assessment of the Junge–Pankow absorption model (Junge 1977; Pankow 1987), the octanol–air partitioning coefficient (K_{OA}) absorption model (Pankow

1994) and the combined K_{OA}–$K_{soot-air}$ (adsorption coefficient to soot) (Lohmann and Lammel 2004) for gas/particle partitioning of PAHs and PCBs in the tropical and coastal atmosphere of Southeast Asia.

2.4 Experimental

2.4.1 Sampling

All the air samples were collected between November and December 2006 at the National University of Singapore (NUS) Atmospheric Research Station which is located 67 m above sea level. The site is approximately 1 km away from the open sea, influenced by emissions from urban vehicular traffic, chemical industries, major power plants as well as oil refineries situated in a group of small islands on the west coast of the Singapore Island. Particulate and gaseous SVOCs in air were collected using a high volume sampler (Model: TE-1000PUF, Tisch Environmental, Inc. USA) at ca. 250 l min^{-1}. Particles were collected by two pre-combusted (at 450°C for 24 h) circular quartz filters of 4 in. diameter in series loaded onto the filter holder; an adsorbent cartridge filled with three pieces of 1-in. PUF plugs in series (7.62 cm) were used to trap gas phase compounds. PUF plugs were pre-cleaned with hexane followed by acetone in 33 ml stainless steel vessels of a Dionex ASE 200 under optimized conditions described below. Average sampling time was 12 h periods (successive daytime 8.00 am–8.00 pm and nighttime 8.00 pm–8.00 am) and average sampling volumes were 180 m^3. The filter and PUF samples were stored −20°C prior to extraction.

2.4.2 Material

The standard mixture USEPA 610 includes 16 native PAHs (naphthalene (Naph), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (B(a)A), chrysene (Chr), benzo[b]fluoranthene (B(b)F), benzo[k]fluoranthene (B(k)F), benzo[a]pyrene (B(a)P), indeno[1,2,3-cd]pyrene (Ind), dibenz[a,h]anthracene (DB(ah)A) and benzo[ghi]perylene (B(ghi)P)), in methanol: methylene chloride. The standard mixture of PCBs (C-QME-01) was obtained from AccuStandard (New Haven, USA). $13C_{12}$-PCBs congeners CB 77, 101, 141, 178 (Cambridge Isotope Laboratories, MA, USA) and anthracene-d_{10}, fluoranthene-d_{10} and benzo[e]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA) were used as surrogates; $13C_6$-Tetrachlorobenzene and $13C_{12}$-PCBs congeners CB 8 and 206 (Cambridge Isotope Laboratories, MA, USA) and phenanthrene-d_{10}, pyrene-d_{10} and benzo[a]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA) were used as internal standards. Silica gel, florisil and anhydrous sodium sulfate were of GR analysis grade (Merck, Germany), heated at 600°C for 24 h to remove any organic contamination.

2.4.3 Sample Preparation and Analysis

Both gaseous and particulate samples were extracted by Dionex ASE 200 under the following conditions developed in our lab: 3:1 (HEX and ACE) n-hexane and acetone combination at 100°C for 30 min. Extractions were performed with 40 ml of solvent at a high pressure (100 atm) by two static cycles. The extracted analytes were purged from the sample cell using pressurized nitrogen at 100 atm as well and concentrated to 3 ml by rotary evaporator. All extracts were further cleaned using silica gel (for PAHs) or florisil (for PCBs) columns. The extract in each fraction was then concentrated to approximately 3 ml at room temperature and further to 50 μl by nitrogen gas stream. Labeled PAHs (Phenanthrene-d_{10}, pyrene-d_{10} and benzo[a]pyrene-d_{12}) and PCBs ($13C_6$-Tetrachlorobenzene, $13C_{12}$-PCBs congeners CB 8, 206) were added to the extracted samples or blanks or calibration standards as internal standards to quantify and account for the loss of these SVOCs during analysis. All extracts were then kept in sealed vials at −20°C prior to GC–MS analysis.

Chemical analysis was performed using a QP2010 GC–MS equipped with a Shimadzu AOC-5000 auto injector and a DB-5 fused silica capillary column (30 m length and 0.25 mm I.D; film thickness 0.25 μm) with purified helium as carrier gas. 4 μl of the sample was injected into the GC–MS in splitless mode with a sampling time of 1.5 min using high-pressure injection mode (pressure 2.47 atm maintained for 2.0 min, initial column flow 3.17 ml min^{-1}), as recommended in the GC–MS manual (Shimadzu). PAHs and PCBs standards as well as extracted samples were analyzed separately in selective ion monitoring mode (SIM) with a detector voltage 700 V. For PAHs, GC temperature program was as follows: 70°C for 2 min; 15°C min^{-1} to 200°C, held for 4 min; 5°C min^{-1} to 300°C, held for 5 min; for PCBs, GC temperature program was as below: 170°C for 11 min; 3°C min^{-1} to 250°C; 10°C min^{-1} to 300°C, held for 5 min.

Organic carbon (OC) and elemental carbon (EC) were determined by using a laboratory two-step thermal procedure (Zappoli et al. 1999). Carbon contents were obtained by means of the 2400 series II CHNS/O analyzer (Perkin–Elmer Life and Analytical Sciences Inc.), which was operated in CHN mode with acetanilide (71.09% C, 6.71% H, 10.36% H) as a calibration standard and with helium plus 8% oxygen as carrier gas. When the combustion furnace temperature was set at 450°C, the content of OC in a sample aliquot put in a combustion boat could be determined directly; when the combustion temperature is set as high as 950°C, the total of OC and EC was determined. Prior to analysis, carbonates are removed by adding diluted HCl. EC content can then be obtained by subtracting OC from the total of OC and EC. All the OC and EC contents with total suspended particle (TSP) concentrations and ambient temperature (Temp) are listed in Table 1. The fraction of organic matter (OM) phase on TSP, f_{OM}, was in general

Table 1 Summary OC, EC, TSP data and f_{OM} for this study (μg m^{-3})

Date	OC	EC	TSP	f_{OM} (%)	Temp (K)
17.11.2006	21.8	9.8	42.1	77.8	301.4
17.11.2006	15.6	7.0	40.5	57.9	298.9
19.11.2006	11.3	5.1	33.0	51.2	302.1
19.11.2006	9.5	4.3	29.3	48.6	298.5
23.11.2006	17.0	7.6	40.0	63.6	301.5
23.11.2006	13.9	6.3	36.2	57.7	297.7
04.12.2006	15.7	7.1	34.5	68.4	301.7
04.12.2006	12.7	5.7	30.5	62.5	299.7
06.12.2006	26.6	10.2	46.1	86.7	302.2
06.12.2006	18.4	8.3	37.6	73.6	298.6
11.12.2006	8.0	3.6	29.3	40.9	301.0
11.12.2006	6.2	2.8	24.9	37.5	298.7
13.12.2006	10.6	4.8	28.3	56.4	301.9
13.12.2006	8.9	4.0	25.4	52.8	297.8
15.12.2006	8.6	3.9	23.8	54.1	302.5
15.12.2006	5.4	2.4	19.6	41.3	299.6
20.12.2006	2.3	1.0	14.3	23.8	300.8
20.12.2006	2.5	1.1	18.5	20.4	298.1
22.12.2006	23.9	10.7	45.0	79.6	300.7
22.12.2006	19.6	8.8	41.8	70.4	298.7
Mean	12.9	5.8	32.0	56.3	300.1
S.D.	6.9	3.1	9.2	17.7	1.6

obtained by multiplication of the fraction of OC on TSP with factor 1.5 for urban aerosols (Dachs and Eisenreich 2000; Turpin et al. 2000; Turpin and Lim 2001).

2.4.4 Weather Station in NUS

The relevant meteorological parameters (air temperature, total rainfall, solar incoming radiation, wind speed, etc.) were obtained from an automated NUS weather station located in the same building where the atmospheric station is housed. This meteorological station has been in operation to provide real-time meteorological data to the NUS community. Ambient temperature, wind speed, incoming solar radiation and rainfall were measured by CS 500 T sensor (Vaisala, Helsinki, Finland), cup anemometer 03001 (R.M. Young, Michigan, USA), LI-200X pyranometer (LI-COR, Nebraska, USA) and CS700 rainguage (Hydrological Services, Sydney, Australia) by mm of rainfall per 5 min, respectively.

2.4.5 Quality Control

The analytical quality of the data was determined using limit of detection (LOD), recovery, linearity, and by checking sampling artifacts, etc. During each set of extractions, a filter field blank and a PUF plug field blank were included. Detection limits were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks, based on 12 h sampling at 250 l min^{-1} (180 m^3 per sample). No PCBs congeners were detected in both the filter and PUF blanks, while trace amounts of PAHs were detected on both filter and PUF blanks, ranging from 1.2 ± 0.8 pg m^{-3} (B(k)F, filter blank) to 0.15 ± 0.07 ng m^{-3} (Naph, PUF blank). Sample quantities exceeding the LOD were quantified and blank-corrected. The whole analytical procedure was assessed by using $13C_{12}$-PCBs congeners CB 77, 101, 141, 178 for PCBs and anthracene-d_{10}, fluoranthene-d_{10} and benzo[e]pyrene-d_{12} for PAHs as surrogate standards, respectively. The procedural recoveries of surrogates ranged from $78.6 \pm 6.8\%$ (anthracene-d_{10}) to $97.2 \pm 13.9\%$ ($13C_{12}$-PCB141). Since the recoveries were generally high, sample amounts were not corrected for procedural recoveries. The linearity of calibration standards was calculated by regression analysis with values ranging from 0.99 to 1.00 (r^2) for SVOCs (PAHs and PCBs). Standards used for calibration spiked with internal standards were analyzed regularly to check instrument performance during analysis.

Examination of the suitability of the data set for detailed analyses of gas-particle partitioning is necessary because there are a number of potential sampling artifacts that can lead to over- and under-estimations of the gas and aerosol phase concentrations of SVOCs such as organochlorine compounds (Mader and Pankow 2001). A potential sampling artifact occurs when gaseous SVOCs sorb to filter and particle surfaces, thus leading to an over-estimation of particle-phase SVOCs (Dachs and Eisenreich 2000). Our sampling strategy here consisted of 12 h samples (diurnal and nocturnal samples, 180 m^3 per sample). Considering the ambient temperature variations were small and relative humidities were uniform and high, backup filters have been used to correct for gas adsorption of SVOCs to a front filter (Hart and Pankow 1994; Dachs and Eisenreich 2000; Turpin et al. 2000). According to the method by Mader and Pankow, 2001, the $V_{\text{min,f}}$ (the volume that can deliver the gas phase mass amount required to achieve gas/filter adsorption equilibrium on filters) under the climate conditions similar here was close to 180 m^3; in addition, it was found that less than 5% of mass recovered from the primary filter was sorbed on a secondary filter.

Breakthrough of SVOCs from the PUF can lead to under-estimated SVOCs gas phase concentrations. In this study, breakthrough was evaluated under field conditions by connecting three-one-inch plugs in series and analyzing them separately. For 12 h samples, measured SVOCs at the third plug were in the range of blank values. Three-one-inch plugs in series used in high-volume PUF sampler therefore could trap gas-phase target compounds effectively.

2.5 Comparison of Adsorption and K_{OA} Absorption Models

Figure 1 compares the percent of mass ($\Phi \times 100$) on particles as predicted by the Junge–Pankow adsorption model (using $c = 0.172$ Pa m and $\theta = 1.1 \times 10^{-3}$)

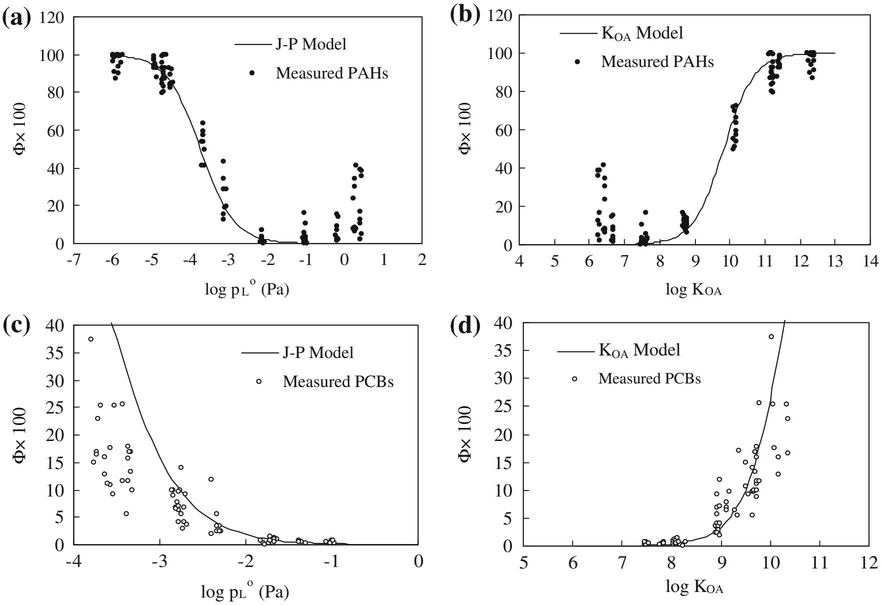

Fig. 1 Comparison of predicted and measured particle percentage (Φ) for both PAHs and PCBs

and K_{OA} absorption model with the average experimental values for PAHs and PCBs from all the sampling events. The K_{OA} absorption model was applied using the average measured f_{OM} value (0.563). It can be seen that the gas-particle distribution of low molecular weight (LMW) PAHs with vapor pressure $<10^{-3}$ Pa or $K_{OA} < 10^8$ was under-predicted by both models, while the predicted values agreed better with those observed ones for high molecular weight (HMW) PAHs (Fig. 1a, b). As hypothesized before, this may be related to the possibility that more volatile PAHs easily become bound within the particles during their formation in combustion and not exchangeable with the atmosphere.

In K_{OA} absorption model, the organic matter fractions in general for urban aerosols between 10 and 20% (Viana et al. 2006; Callén et al. 2008), but the measured average f_{OM} value in this study was much higher than those typically expected. The higher f_{OM} could result from the local heavy traffic emissions and also from oil refinery and petrochemical industries, which are the primary contributors to the organic aerosols. From Fig. 1c, one can see that the Junge–Pankow model over-predicted PCBs sorption; however, in Fig. 1d, the K_{OA} absorption model using the measured f_{OM} value fits the PCB data much better under tropical climate conditions with uniform ambient temperature and high humidity, indicating the f_{OM} might vary much in different areas. Hence, it is preferable to use the field-measured organic matter fraction, f_{OM}, of urban aerosols instead of the standard values (0.1–0.2) while studying the gas-particle partitioning of SVOCs. In addition, high RH in this coastal area might be another important factor for this absorption predominance since the K_P values of organo-chlorine compounds have been reported to be dominated by OM absorption for RH between 50 and 90% while adsorption to elemental carbon (EC) becomes the major sorption mechanism under dry conditions ($RH < 40\%$) (Götz et al. 2007). Based on the investigations made in this study, it appears that the sorption of nonpolar chemicals, for example, PCBs to "environmental lipids" such as aerosols with high OM content might be dominated by absorption into organic matter under the warm and humid conditions in this highly industrialized area.

2.6 Influence of Soot Carbon

Soot particles are byproducts of the combustion of liquid and gaseous fuels and their production depends strongly on the ratio of carbon to oxygen during combustion (Mader and Pankow 2001). PAHs are formed concurrently with soot particles and also play an important role in soot formation and particle growth (Seinfeld and Pandis 1998). It has been found that PAHs have a high affinity for carbonaceous materials as discerned from adsorption experiments with carbon black and activated carbon (Walters and Luthy 1984). The overall gas-particle partitioning coefficient that accounts for both the organic matter and the soot phases is given by the following equation (Lohmann and Lammel 2004):

$$K_P = 10^{-12}\left(K_{OA} f_{OM} MW_{OCT} \zeta_{OCT} / (\rho_{OCT} MW_{OM} \zeta_{OM}) + f_{EC} a_{EC} / (a_{soot} \rho_{EC}) K_{soot-air}\right) \tag{10}$$

where f_{EC} is the fraction of atmospheric elemental carbon (EC); α_{EC} is the specific surface area of elemental carbon and α_{soot} is the specific surface area of diesel soot derived from NIST SRM 1650; ρ_{BC} is the density of EC and 1 kg l^{-1} has often been assumed (Dachs and Eisenreich 2000; Lohmann and Lammel 2004); as assumed, the EC can be used as a surrogate for the soot carbon (Dachs and Eisenreich 2000), $\alpha_{EC}/\alpha_{soot}$ is equal to one; $K_{soot-air}$ is the partitioning coefficient between soot and air. To avoid the controversy over the calculation of $K_{soot-air}$ from soot–water and air–water partitioning coefficients, this study employed the approach used by Van Noort (2003) that estimated $K_{soot-air}$ from the subcooled liquid vapor pressure (p_L^o) and the soot specific area (α_{soot}):

$$\log K_{soot-air} = -0.85 \log p_L^o + 8.94 - \log(998/\alpha_{soot}) \tag{11}$$

The specific surface area of soot or soot-like material has been reported in the range between 3.6 (wood soot) (Jonker and Koelmans 2002) and 998 $m^2\ g^{-1}$ (activated carbon) (Walters and Luthy 1984); 100 $m^2\ g^{-1}$ was used for α_{soot} (Bucheli and Gustafsson 2000), which was derived from diesel particulate matter SRM-1650; the temperature-dependent vapor pressures were corrected as stated above.

The overall K_p values, derived from the Eq. 10, are presented for most of the PAHs characterized in this study and compared to measured K_p values and those predicted from the K_{OA} model (Fig. 2). As discussed above, the K_{OA}-derived

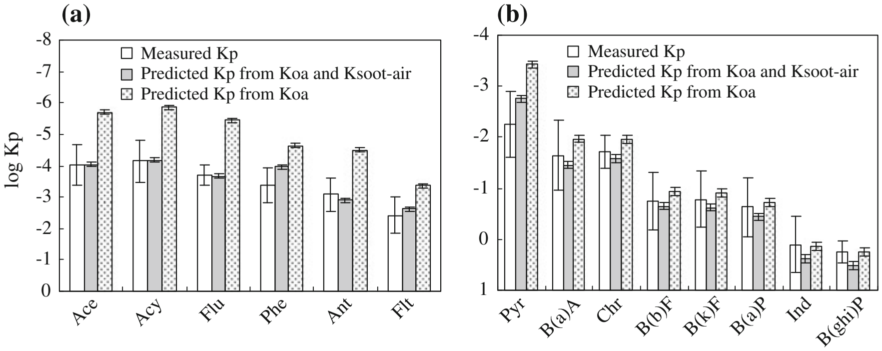

Fig. 2 Measured and predicted values of K_p ($\mu g\ m^{-3}$) by K_{OA} and the combined K_{OA} + $K_{soot-air}$ models in Singapore for PAHs (error bar for standard deviation)

K_p generally under-predicted the observed K_p values, while the combined K_{OA}–$K_{soot-air}$ model predicted results that were in agreement with the observed ones. The gas-particle partitioning coefficients increased by the combined model for LMW PAHs by 0.8–1.8 log units. However, for HMW PAHs, these coefficients increased only by 0.3–0.6 log unit. In this case, the gas-particle partitioning process of lighter PAHs was more affected by soot carbon than their heavier counterparts, indicating the lesser influence of soot sorption on predominantly particle-bound PAHs. A similar result was reported by Prevedouros et al. (2008) for solid-air and solid-water partitioning of PAHs with inclusion of soot sorption. These results differ from those of Helm and Bidleman (2005) who found that the combined K_{OA}–$K_{soot-air}$ model over-predicted the measured K_p by 0.3–1.4 log units and 1.2–2.2 log units for penta-chlorinated naphthalene-50 (CN-50) and hexa-chlorinated naphthalene-66/67 (CN-66/67), respectively. However, the partitioning behavior of PAHs in this area is consistent with observations in the literature (Dachs and Eisenreich 2000; Fernández et al. 2002; Lohmann and Lammel 2004) that elemental or soot carbon dominates in the partitioning of PAHs to PM in some circumstances, especially for LMW compounds.

The f_{EC} (7–24% with average of 17 ± 5%) used for Eq. 10 was directly determined from measurements of field samples, and the particulate elemental carbon ranged from 1.0 to 10.2 $\mu g\ m^{-3}$ with an average of 5.8 ± 3.1 $\mu g\ m^{-3}$. The elemental carbon concentrations (f_{EC} values) in this study are relatively higher than those in other urban areas such as Baltimore (1.3 $\mu g\ m^{-3}$, 2.8%) (Brunciak et al. 2001), Chesapeake Bay (1.5 $\mu g\ m^{-3}$, 5.1%) (Dachs and Eisenreich 2000), Washington (2.2 ± 0.1%) (Roth et al. 2005b) and Chur urban aerosols in USA (2.1 ± 0.1%) (Roth et al. 2005b), respectively.

The high content of EC of local aerosol might be associated with the human activities taking place in and around Singapore (heavy traffic emissions, dense oil/gas industries, etc.). Consequently, once the fresh PAHs have been emitted into the atmosphere, phase transfer may be limited by diffusion for particles coated with thick elemental carbon (Strommen and Kamens 1999; Dachs and Eisenreich 2000).

3 Precipitation Scavenging

3.1 Theoretical Approach

The washout ratios of SVOCs can be described by standard equations (Ligocki et al. 1985a, b):

$$W_T = W_P\Phi + W_G(1-\Phi) \tag{12}$$

where W_T, W_P and W_G are unitless total, particle and gas scavenging ratios, respectively. W_P is defined as $C_{R,P}/C_{A,P}$ where $C_{R,P}$ is the particle-associated concentration in rainwater (ng m^{-3} rain) and $C_{A,P}$ is the particulate concentration of SVOCs in air (ng m^{-3} air). Likewise, W_G is defined as $C_{R,D}/C_{A,G}$ where $C_{R,D}$ is the dissolved concentration of SVOCs (ng m^{-3} rain) and $C_{A,G}$ is the gaseous concentration in air (ng m^{-3} air); at equilibrium the gas scavenging ratio W_G equals the dimensionless air–water partitioning coefficient K_{aw} ($1/K_{aw} = RT/H$) where R is the universal gas constant (8.21×10^{-5} m^3 atm K^{-1} mol^{-1}), and H is the Henry's law constant (atm m^{-3} mol^{-1}).

Due to the observational evidence that submicron particles (non-filter retained particles) do exist in the filtrate and influence the partitioning behavior of SVOCs in rainwater (Gschwend and Wu 1985; Glotfelty et al. 1990). Equation 12 was modified considering the scavenging of submicron particles (Poster and Baker 1996a):

$$W_T = \frac{C_R}{C_A} = W_{P,F}\Phi_{P,F} + W_{P,NF}\Phi_{P,NF} + W_G(1-\Phi_T) \tag{13}$$

where $\Phi_{P,F}$, $\Phi_{P,NF}$, Φ_T are the fractions of SVOCs bound to filter-retained particles, nonfilter-retained particles, and all particles. Offenberg and Baker (2002) then expanded Eq. 13 to include a broader range of particle sizes:

$$W_T = \frac{C_R}{C_A} = W_{P,1}\Phi_{P,1} + W_{P,2}\Phi_{P,2} + \cdots + W_{P,X}\Phi_{P,X} + W_G(1-\Phi_T) \tag{14}$$

where each particle size's washout ratio is exhibited and all sizes are summed to the total aforementioned W_P as in Eq. 12.

Although the supersaturation could occur when the gaseous SVOCs from the air enter into rainwater partly due to the colloidal association of submicron particles as stated above, an additional mechanism requiring consideration is the adsorption of gaseous phase SVOCs to the surface to raindrops, either to an organic film or to pure water (Simcik 2004). In addition, the ice/snow scavenging effect has to be considered in Frigid Zone and during the winter time in temperate zone (Daly and

Wania 2004); however, since this study took tropical area as a case study as discussed below, the ice/snow scavenging is not considered. Simcik (2004) redefined the gas-phase scavenging equation as follows:

$$\mathrm{W_G = W_{G,DISS} + W_{G,ADS} = \frac{1}{K_{aw}} + K_{ia}\frac{6 \times 1000}{d_R}} \qquad (15)$$

where $\mathrm{W_{G,DISS}}$ refers to the washout by dissolution involving only Henry's law partitioning (including, eventually, subsequent dissociation or complexation) to the rainwater, defined as $1/\mathrm{K_{aw}}$; $\mathrm{W_{G,ADS}}$ is the equilibrium adsorption gas-phase scavenging ratio; $\mathrm{K_{ia}}$ the air–water interface adsorption constant, used to describe the adsorption of SVOCs to the surface of water, defined as mass of SVOCs per m^2 of water surface/mass of SVOCs per m^3 of air; $\mathrm{d_R}$ is the diameter of raindrops (mm) and 1,000 converts millimeters to meters. To transform the air–water interface adsorption constant into a unitless gas-phase washout parameter, one must normalize to the surface to volume ratio of a sphere, 6/d (assuming spherical raindrops).

Therefore, a comprehensive model could be developed with inclusion of all the factors affecting the total scavenging ratio of SVOCs as given below:

$$\mathrm{W_T = \frac{C_R}{C_A} = \sum_{i=1}^{X} W_{P,i}\Phi_{P,i} + \frac{(1-\Phi_T)}{K_{aw}} + K_{ia}\frac{6000}{d_R}(1-\Phi_T)} \qquad (16)$$

Offenberg and Baker (2002) explained the difficulty in the application of Eq. 14 due to the complexities in attributing particles of various sizes to their original atmospheric diameter and inefficiencies in separating small particles in rainwater. As such, Eq. 16 could be simplified as Eq. 17 and applied to assess the precipitation scavenging of SVOCs on those samples collected in Singapore.

$$\mathrm{W_T = \frac{C_R}{C_A} = W_P\Phi_T + \frac{(1-\Phi_T)}{K_{aw}} + K_{ia}\frac{6000}{d_R}(1-\Phi_T)} \qquad (17)$$

where the parameters such as $\mathrm{F_T}$, $\mathrm{K_{aw}}$ and $\mathrm{K_{ia}}$ can all be correlated to the supercooled liquid saturated vapor pressure, $\mathrm{P_L^o}$ (Pa), of the compound of interest; the diameter of the raindrop, $\mathrm{d_R}$, could be derived from the rain drop size distribution (DSD) described by log-normal distributions (Feingold and Levin 1986; Mircea et al. 2000), or gamma distributions (Cerro et al. 1998).

Henry's law constants are temperature-dependent and they have to be corrected to the ambient air temperatures during the sampling period by using published enthalpy and entropy data for PAHs (Hulscher et al. 1992; Bamford et al. 1999b; Monte et al. 2006) and correlation between H and temperature for OCPs (Sahsuvar et al. 2003; Cetin et al. 2006). Equilibrium gas scavenging ratios ($\mathrm{W_{G,DISS}}$) were calculated for PAHs and OCPs using the temperature-corrected Henry's law constants.

For the calculation of $\mathrm{W_{G,ADS}}$, rain droplet size distributions have to be considered because they determine the geometric mean diameter $\mathrm{d_{gm}}$ (mm) and the total number of raindrops for a rain event by precipitation rate p_o (mm h^{-1}) (Calderón et al. 2008). In this study, the log-normal distribution (Mircea et al. 2000) was chosen to derive d_{gm} which could be used as d_R for Eq. 15.

$$d_{gm} = 0.72p_o^{0.23}(\mathrm{mm}) \tag{18}$$

The relationship among water-to-air equilibrium constant K_{aw}, air to interfacial water equilibrium constant K_{ia} and interfacial water to bulk water equilibrium constant K_{iw} is as follows:

$$K_{ia} = K_{iw}/K_{aw} \tag{19}$$

where K_{aw} is the air–water partitioning coefficient, K_{iw} could be calculated by using Eq. 20 (Kelly et al. 2004):

$$\log K_{iw} = -8.58 - 0.769\log\left\{\frac{P_L^o}{P^o}e^{\frac{-\Delta G_S^o(aq)}{RT}}\right\} \tag{20}$$

where P_L^o is the subcooled vapor pressure of the compounds of interest, corrected to the ambient temperature during the sampling period by using the correlations between P_L^o and temperature for SVOCs (Hinckley and Bidleman 1990; Lei et al. 2002; Xiao et al. 2004; Odabasi et al. 2006); P^o is the pressure (24.45 atm) of an ideal gas at 1 M concentration and 298 K; $\Delta G_S^o(aq)$ is the standard-state aqueous free energy of solvation of the compounds of interest, of which the data calculated by Thompson et al. (2003) could be used for SVOCs.

3.2 Particle Scavenging Versus Gas Scavenging

3.2.1 Experimental

Sampling

Both the atmospheric and precipitation samples were collected simultaneously at the National University of Singapore (NUS) atmospheric research station. Altogether, 37 atmospheric samples (pairs of PUF and filter) and 32 rainwater samples were collected and studied under different weather conditions between June 2007 and May 2008 to get fundamental understandings of precipitation scavenging processes in the tropical environment; gaseous and particulate-phase distributions of PAHs and OCPs were also measured concurrently. Particulate and gaseous SVOCs in the atmosphere were collected separately using a medium volume sampler (Model: TE-1000 PUF, Tisch Environmental, Inc. USA) by drawing air through 4″ circular quartz microfiber filters (Whatman, Tisch Environmental, Inc. USA) and polyurethane foam plugs (PUF, TE-1012, Tisch Environmental, Inc. USA) in series at ca. 250 l min^{-1}. The rainwater samples were collected by an automated wet-dry sampler (Model US-330, Ogasawara Keiki Seisakusho, Tokyo, Japan), which collects only rainwater with no interference from dust fall. All rainwater samples were stored in an internal refrigerator at 4°C by the automated sampler immediately after a rain event. The rainwater samples were collected from the field site within 24 h after each rain event. After collection, rainwater samples were filtered with pre-cleaned (heated at 450°C for 24 h) Whatman GF/F filters (0.7 μm, 47 mm i.d.). The actual volume of each sample collected was measured and recorded after filtration. Before and after filtration, GF/F filters were conditioned in a dry box under the same condition as for quartz filters, and then weighed to calculate the mass of suspended particles. The relevant meteorological parameters (air temperature, total rainfall, etc.) were obtained as described in Section *Weather Station in NUS*.

Material

All solvents used for this study were of pesticide grade: n-hexane (HEX), acetone (ACE), dichloromethane (DCM) and methanol (METH) (Tedia, USA). The standard mixture USEPA 610, including 16 priority PAHs, the same as used for gas-particle partitioning case study, and the standard mixture of OCPs included in Kit 608-S were purchased from Supelco (USA). Anthracene-d_{10}, fluoranthene-d_{10} and benzo[e]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA) and $13C_{12}$-PCB 8 and $13C_6$-Hexachlorobenzene (Cambridge Isotope Laboratories, MA, USA) were used as surrogate standards; phenanthrene-d_{10}, pyrene-d_{10} and benzo[a]pyrene-d_{12} (Sigma-Aldrich, St. Louis, MO, USA) and $13C_{12}$-4,4′ DDT (Cambridge Isotope Laboratories, MA, USA) were used as internal standards. Silica gel and florisil, obtained from Merck (Germany), were heated at 600°C for 24 h to remove any organic contamination.

Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. All water filters, aerosol filters and PUF samples were extracted separately as described previously. All filtered water samples were extracted on the same day as collection via liquid–liquid extraction using 3 × 50 ml DCM aliquots in a two liter separatory funnel (EPA method 3510C). All extracts were evaporated, cleaned using silica gel (for PAHs) or florisil (for OCPs) columns, then evaporated and finally blown by gentle nitrogen stream, and reduced to 50 μl with internal standards for PAHs and OCPs, respectively, and kept in sealed vials at −20°C prior to GC–MS analysis. All extracts were then kept in sealed vials at −20°C prior to GC–MS analysis. Sample analysis was conducted using a Shimadzu QP2010 GC–MS. For PAHs, the same temperature program was used as in Section "*Sample Preparation and Analysis*"; for OCPs, GC temperature program was as below: 4°C $\min^{-1}$ from 125 to 300°C.

Quality Control

The analytical quality was guaranteed by the same protocol as described in Section "*Quality Control*". In this study, detection limits were derived from the blanks and quantified as the mean plus three times the standard deviation of the concentration in the blanks, ranging from 0.05 ± 0.08 pg m^{-3} (4,4′-DDE, filter blank) to 0.15 ± 0.07 ng m^{-3} (Naph, PUF blank).

The reliability of the whole analytical procedure was assessed by using surrogate standards for both PAHs and OCPs. The procedural recoveries of surrogates ranged from 86.7 ± 6.8% (anthracene-d10) to 97.2 ± 13.9% (benzo[e]pyrene-d12).

3.3 Results and Discussion

A comprehensive mathematical model has been developed as above by taking into consideration various factors such as particle scavenging, dissolution (Henry's law), and surface adsorption and used to gain insights into the wet removal of PAHs and OCPs in the tropical environment such as in Singapore. The particle and gas scavenging ratios by precipitation have been calculated based on the extensive dataset containing the distribution of PAHs and OCPs in gas- and particulate-phases and also in rainwater. Relative contributions of various factors mentioned above to precipitation scavenging were evaluated. In addition, effects of chemical properties of PAHs and OCPs and meteorological conditions on scavenging processes were also investigated.

Particle scavenging is highly complicated and is determined by several factors such as meteorology, size of particles and rain droplets, etc. (Offenberg and Baker 2002). On the other hand, gas scavenging ratios (W_G) are suggested to be near equilibrium as predicted by temperature-corrected H values ($W_{G,DISS}$, operationally truly dissolved phase), or are supersaturated due to the adsorption of contaminants to the rain droplets ($W_{G,\ ADS}$) or even the presence of non-filterable submicron particles in the filtrate. Therefore, the relative importance of gas and particle scavenging on the total removal of contaminants from the atmosphere depends on the relative magnitudes of the terms $W_P\Phi$, $W_{G,DISS}(1-\Phi)$ and $W_{G,ADS}(1-\Phi)$ as shown in Table 2.

From Table 2 it can be seen that particle scavenging is an extremely efficient mechanism of removal of SVOCs from the atmosphere; gas scavenging ($W_{G,DISS}(1-\Phi)+W_{G,ADS}(1-\Phi)$) has much less relative importance as a scavenging mechanism for all individual compounds of interest. The particle scavenging contribution to the total scavenging accounts for 86–99% for PAHs and 98–99% for OCPs. This observation that the efficiencies of washouts from the atmosphere by precipitation are much higher in the particulate phase than in the gas phase is also supported by those reported by Ogura et al. (2001), Offenberg and Baker (2002) and Sahu et al. (2004).

In addition, it can also be seen that particle scavenging ratios W_P for the more volatile compounds were generally larger than those for less volatile ones.

Table 2 Relative contributions of particulate-bound, gaseous (Henry's law) and adsorbed SVOCs scavenging to the total scavenging process

Fraction % compound	$W_P\Phi/W_T$	$W_{G,DISS}(1-\Phi)/W_T$	$W_{G,ADS}(1-\Phi)/W_T$
Naph	99.99	0.01	0.00
Acy	99.92	0.08	0.00
Ace	99.96	0.04	0.00
Flu	99.84	0.16	0.00
Phe	99.41	0.57	0.02
Ant	99.42	0.56	0.02
Flt	99.82	0.17	0.00
Pyr	98.65	0.99	0.36
B(a)A	94.25	0.64	5.11
Chry	99.37	0.33	0.30
B(b)F	99.58	0.06	0.35
B(k)F	99.36	0.05	0.59
B(a)P	98.79	0.40	0.81
Ind	86.35	0.05	13.60
B(ghi)P	86.84	0.04	13.12
α-HCH	99.58	0.41	0.01
β-HCH	98.94	1.03	0.03
γ-HCH	99.46	0.53	0.02
4,4′-DDD	98.95	0.92	0.13
4,4′-DDE	98.70	1.01	0.29
4,4′-DDT	98.39	1.19	0.42

For PAHs, W_P range from 1.8×10^5 to 2.7×10^7, relatively more scattered compared to those for OCPs which vary only within one order of magnitude. The particle fraction Φ of SVOCs in the atmosphere described by Junge–Pankow adsorption model or $K_{\text{octanol–air}}$ absorption model, which is a function of P_L^o and affected by meteorological condition such as ambient temperature (Pankow 1987; Harner and Bidleman 1998). Since the particle scavenging by rain dominates wet deposition, the effect of the yearly uniform ambient temperature in this tropical area on gas/particle partitioning might reduce the variation of precipitation scavenging ratios. The larger W_T and W_P values found for more volatile compounds may be due to their preferential sorption to larger particles (Poster and Baker 1996b; Sahu et al. 2004); the below-cloud scavenging rates increase with particle size (Sahu et al. 2004), indicating the consistency of the increase in W_T and W_P for contaminant associated with larger particles with the particle scavenging mechanism.

Relationships between particle fraction (Φ), subercooled vapor pressure (P_L^o), rainfall intensity Φ, and W_P have been investigated as shown in Fig. 3 and the correlations for all data were significant ($P < 0.05$). It can be observed that particle scavenging decreased with particle fraction because the relationships for both PAHs and OCPs were with shallow negative slopes. The latter suggests that the particle scavenging by rain is less efficient for higher molecular weight SVOCs,

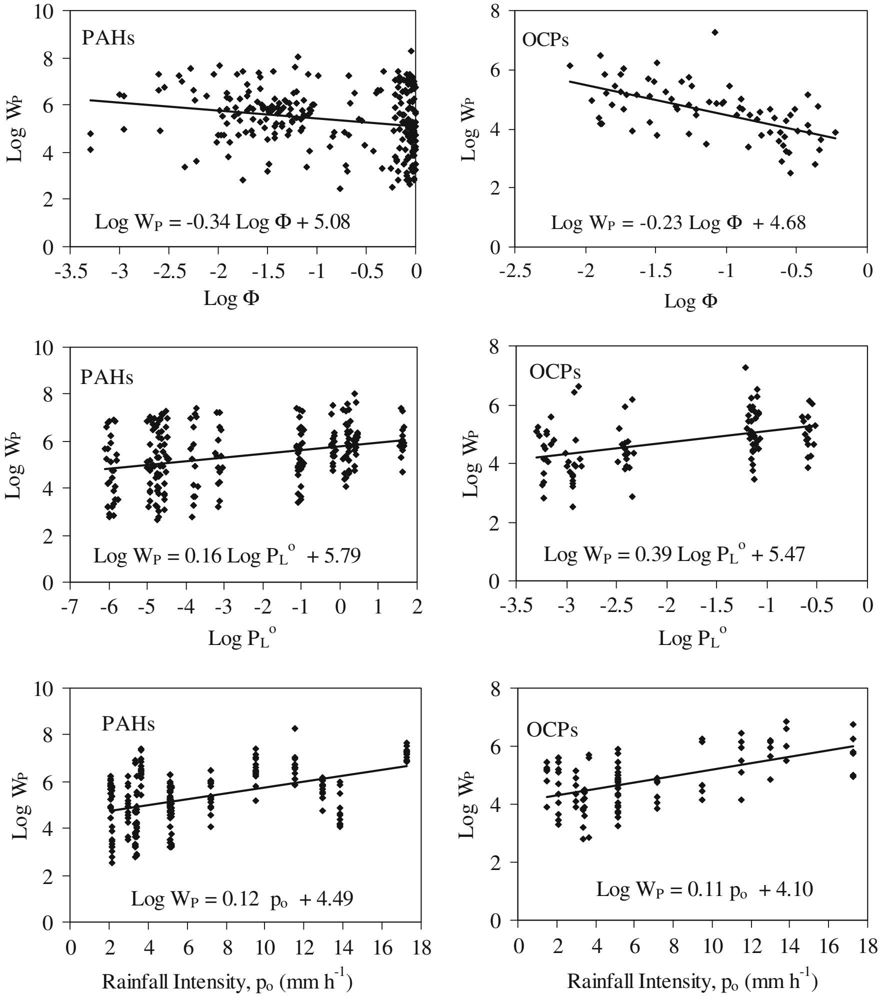

Fig. 3 Relationship between particle scavenging ratio W_P and particle fraction Φ, subercooled vapor pressure P_L^o and rainfall intensity p_o

which in the ambient atmosphere prefer to distribute into submicron atmospheric particles. This observation is supported by the reports published by Poster and Baker (1996b) and Franz and Eisenreich (1998). A similar behavior was shown by the relationship between log W_P and log P_L^o. Although the slopes were slightly positive, particle scavenging increased with P_L^o, implying that lower molecular weight SVOCs with more volatility may have been associated with larger particles that were scavenged more efficiently as stated above. In addition, W_P and p_o were positively correlated, signifying an increased efficiency for particle scavenging from the atmosphere with rainfall intensity. The role of other factors such as rain droplet size distributions and collision efficiency between particles and rain droplets for particle scavenging can not be disregarded (Seinfeld 1986). Theoretical analysis of the Marshall–Palmer rain droplet size distribution shows that the number of rain-droplets increases with increasing rain intensity (Marshal and Palmer 1948), which might lead to more removal of particles through more collision interaction between rain droplets and particles.

In Eq. 17, the gas scavenging is modified to include SVOCs dissolution into bulk rainwater and adsorption to the surface of raindrops, both of which are strong functions of particle fraction Φ. Since Φ is highly dependent on subercooled vapor pressure and ambient temperature, a relationship between dissolution ($W_{G,DISS}$) or adsorption ($W_{G,ADS}$) might be expected as plotted in Fig. 3. As subercooled vapor pressure decreased, the gas scavenging ratios for both adsorption and dissolution increased. In this study, $W_{G,DISS}$ ranges from ~ 20 to as high as 10^4, and the $W_{G,ADS}$ ranges from <1 to as high as 10^5. Since the slopes of log $W_{G,DISS}$ versus log P_L^o and log $W_{G,ADS}$ versus log P_L^o are different, both trends intersect as shown in Fig. 3. At a subercooled vapor pressure of approximately $10^{-3.5}$–10^{-4} Pa, the relative importance shifted from dissolution dominated scavenging to adsorption dominated scavenging with decreasing of P_L^o. This observation was supported by the theoretical simulation of adsorption and dissolution scavenging for PAHs at assumed rainfall intensity (10 mm h^{-1}) and full range of particle fraction (Φ: 0–100%) (Simcik 2004). SVOCs of interest with subercooled vapor pressures between $10^{-3.5}$ and 10^{-4} Pa used in this study mainly include PAHs with five or more aromatic rings. From Table 1, it can be observed that for B(b)F, B(k)F, B(a)P, Ind and B(ghi)P, the relative of contributions of $W_{G,ADS}$ to W_T were more dominant than those of $W_{G,DISS}$ to W_T. In the case of Ind and B(ghi)P, their $W_{G,ADS}$ contribution to the total scavenging can account for $\sim 13\%$. As mentioned above, this study cannot distinguish the contribution of nonfilterable submicron particles to the gas scavenging**.** Particle size distribution analysis might need to be considered in the future study.

4 Air–Sea Diffusive Exchange

4.1 Background

As discussed above, SVOCs are removed from the atmosphere and transported to the waters by precipitation scavenging of atmospheric vapors and particles, which are incorporated into the rain within or below the clouds. After SVOCs are deposited into the bulk seawater, partitioning in water column can affect the distribution of pollutants between the dissolved aqueous and the solid phases and eventually impact the fate of these compounds in oceans (Luo et al. 2004). In addition, air–sea exchange can make SVOCs diffuse across the air–sea interface; however, the sea surface microlayer (SML), a unique compartment at the air–sea boundary defined operationally as the upper millimeter (1–1,000 μm) of the sea surface, has large storage capacity to delay the transport of SVOCs across the interface. This interfacial effect has been reported as the enrichment of contaminants with different physicochemical properties, i.e., the nature of polar groups, architecture of the hydrophobic chain, and ionic strength, etc. (Hardy 1982; Chernyak et al. 1996; Gašparović et al. 1998; Wurl et al. 2006b).

In the aqueous environment, those SVOCs sorbed onto colloidal matter (DOC) are not available for air–water exchange. The partitioning between truly dissolved and colloidal phases has to be investigated in order to obtain the truly dissolved concentrations of SVOCs. The apparent dissolved concentrations (non-filter retained fraction) of SVOCs ($c_{d,a}$) is the sum of the truly dissolved (C_{truly}) and colloidal (C_{DOC}, DOC-dissolved organic carbon, mg l^{-1}) phases, onto both of which the fractions of SVOCs partitioned can be estimated as described in Eq. 5 by Totten et al. (2001) and Wurl et al. (2006a)

$$C_{d,a} = C_{truly} + C_{DOC} = C_{truly}\left(1 + K_{OW} \times DOC \times 10^{-7}\right) \tag{21}$$

A classical two-layer model, which has been previously applied to the air–sea exchange of SVOCs (Achman et al. 1993; Zhang et al. 2007; Li et al. 2009), assumes that the rate of gas transfer is controlled by the pollutant's ability to diffuse across the air layer and sea surface water on either side of the air–water interface. The molecular diffusivity of the pollutant, dependent on the amount of resistance encountered in the liquid and gas films, describes the rate of transfer while the concentration gradient drives the direction of transfer (Totten et al. 2001). The flux F (ng m^{-2} day^{-1}) is calculated by

$$F = K_{OL}\left(C_{truly} - \frac{C_{A,G}}{K_{aw}}\right) \tag{22}$$

where K_{OL} (m day^{-1}) is the overall mass transfer coefficient, and (C_{truly} − $C_{A,G}/K_{aw}$) describes the concentration gradient (ng m^{-3}) where $C_{A,G}$ is the gas-phase concentration of the compound in air that is divided by the dimensionless Henry's law constant ($\acute{H}$) corrected by the temperature and salinity. A positive flux indicates net volatilization out of the seawater and a negative flux indicates net absorption into the seawater. The overall mass transfer coefficient (K_{OL}) comprises resistances to mass transfer across the air layer and the water layer.

$$\frac{1}{K_{OL}} = \frac{1}{K_W} + \frac{1}{K_a K_{aw}} \tag{23}$$

where K_a and K_w (m day^{-1}) are the mass transfer coefficients across the air layer and water layer, respectively. The mass transfer coefficient $K_{a,comp}$ (cm s^{-1}) for a compound in air was calculated using the following equation (Schwarzenbach et al. 2003):

$$K_{a,comp} = K_{a,H_2O}\left(\frac{M_{H_2O}}{M_{comp}}\right)^{-0.5\times0.67} \tag{24}$$

where $K_{a,H_2O} = 0.2 \times u_{10} + 0.3$ and M (g mol^{-1}) is molar mass of the compound. Wanninkhoff's quadratic equation (Wanninkhof 1992) for the mass transfer coefficient K_w has been applied in a number of studies (Totten et al. 2001; Wanninkhof et al. 2004; Wurl et al. 2006a), but this relationship was a semi-empirical estimation with low correlation ($r^2 = 0.66$) only at steady winds. A more robust model was thus used in this study to calculate $K_{w,comp}$ (cm s^{-1}) for compounds of interest (Schwarzenbach et al. 2003):

$$K_{w,comp}=\begin{cases} 0.65\times10^{-3}\left(\frac{Sc_{comp}}{600}\right)^{-0.67} & \text{for } u_{10}\le4.2\text{ms}^{-1}(\text{smoothsurfaceregime}) \\ (0.79u_{10}-2.68)\times10^{-3}\left(\frac{Sc_{comp}}{600}\right)^{-0.5} & \text{for } 4.2<u_{10}\le13\text{ms}^{-1}(\text{roughsurfaceregime}) \\ (1.64u_{10}-13.69)\times10^{-3}\left(\frac{Sc_{comp}}{600}\right)^{-0.5} & \text{for } u_{10}>13\text{ms}^{-1}(\text{breakingwaveregime}) \end{cases} \tag{25}$$

where the Schmidt number, Sc, is the ratio of kinematic viscosity ν_{kin} (cm^2 s^{-1}) and diffusivity D (cm^2 s^{-1}) by $Sc = \nu_{kin}/D$. The kinematic viscosity of seawater is obtained using the method recommended by Chen et al. (1973). The diffusivities of compounds of interest in seawater were calculated using the Eq. 26 developed by Wilke and Chang (1955).

$$D = 7.4 \times 10^{-8}\frac{(2.6M_{comp})^{0.5}T}{\eta V_{comp}^{0.6}} \tag{26}$$

where T is the average temperature during each sampling event, V_{comp} is the molar volume of compound investigated (Mackay et al. 1992, 1996) and η is equal to the kinematic viscosity of solution (here referring to seawater).

4.2 The Exchange of SVOCs Across Air–Sea in the Tropical Marine Environment

A study was conducted in Singapore's Southern coastline during the Northeast monsoon season to evaluate if this coastal area is a sink or source for selected SVOCs via air–sea diffusive exchange as well as to investigate the SML enrichment effect.

4.3 Experimental

4.3.1 Sampling

Sea Subsurface Water (SSW) and Sea Surface Microlayer (SML) Sampling. The SSW samples were collected at the depth of 1 m at a southern coastal area of

Singapore with a 2 l glass amber bottle inserted in a stainless-steel sampling device. The SML samples (approximately 1 l) were collected simultaneously using the glass plate technique (Harvey and Burzell 1972) and stored in an amber glass container. Eight samples were collected for SSW and SML, respectively.

Air Sampling. Atmospheric samples were collected simultaneously with SSW by a high volume sampler (Model: TE-1000PUF, Tisch Environmental, Inc. USA) with quartz microfiber filters (Whatman, Tisch Environmental, Inc. USA) to capture particles and polyurethane foam plugs (PUF, TE-1012, Tisch Environmental, Inc. USA) in series (7.62 cm) at ca. 250 l min^{-1} to collect gaseous phase. Particles were collected by a pre-combusted (at 450°C for 24 h) circular quartz filter of 4 inches diameter, followed by a combination of 3 PUF plugs connected in series (7.62 cm) to trap gas phase compounds. Eight paired samples (SSW + atmospheric gas) were collected.

Meteorological Conditions. The relevant meteorological parameters (air temperature, rainfall, wind speed, etc.) were obtained from an automated NUS weather station located in the same building where the atmospheric station is located. More details could be referred to Section "*Weather Station in NUS*".

After collection, all water samples were filtered with pre-cleaned (heated at 450°C for 24 h) Whatman GF/F filters (0.7 μm, 47 mm i.d.). The actual volume of each sample collected was measured and recorded after filtration. Before and after filtration, GF/F filters were conditioned in a dry box (maintained at 22°C and 30% RH), and then weighed to calculate the mass of suspended particles.

4.3.2 Sample Preparation and Analysis

Prior to extraction, surrogate compounds were added to all samples. Water filters, aerosol filters and PUF samples were extracted separately by Dionex ASE 200 All filtered water samples were extracted on the same day as collection via liquid–liquid extraction using 3 × 50 ml DCM aliquots in a two liter separatory funnel (EPA method 3510C). Details of extraction for both air and water samples could be referred in Section "*Sample Preparation and Analysis*". After purification by the protocol in Section "*Sample Preparation and Analysis*" and "*Sample Preparation and Analysis*", all extracts were finally blown by gentle nitrogen stream and reduced to 50 μl with internal standards, and kept in sealed vials at −20°C prior to GC–MS analysis. Chemical analysis was performed using a QP2010 GC–MS equipped with a Shimadzu AOC-5000 auto injector and a DB-5 fused silica capillary column (30 m length and 0.25 mm I.D; film thickness 0.25 μm) with purified helium as carrier gas. Organic carbon (OC) and elemental carbon (EC) were determined as described in Section "*Sample Preparation and Analysis*". DOC was measured in the filtrate of the SSW using a TOC-5000 Shimadzu instrument by measuring total dissolved carbon and dissolved inorganic carbon to obtain DOC by subtraction.

4.3.3 Quality Control

The analytical quality was guaranteed by the same protocol as described in Section "*Quality Control*".

4.4 Truly Dissolved SVOCs

In this study, DOC concentrations are in the range of 0.6–7.8 mg l^{-1}. The predicted mean fractions adsorbed to DOC for individual PAH varied in the range of 0.1–40%. It clearly showed that HMW PAHs are more readily adsorbed to DOC (10–50%) than those LMW compounds (below 10%). α-, β-, and γ-HCH were adsorbed to DOC at a mean fraction of 0.26, 0.25 and 0.20%, consistent with the values (~0.4%) reported by Wurl et al. (2006b), while the DOC fraction for DDXs was much higher in the range of 30–40%. This distribution pattern confirms the anticipation that the sorption of SVOCs onto DOC in the seawater is correlated with the chemical's K_{OW}, namely, pollutants with higher K_{OW} are more easily sorbed onto DOC (Schwarzenbach et al. 2003).

4.5 Air–Water Gas Exchange Flux

The fluxes (average ± SD) of the individual PAH compound were in the range of -21.7 ± 20.2 and -1608.4 ± 869.6 ng m^{-2} day^{-1} and $\sum$ PAH flux reached up to -5884.0 ± 4040.7 ng m^{-2} day^{-1}. All PAHs showed by average negative fluxes indicating the tendency to transfer these contaminants from air to water (net absorption). The magnitude and direction of PAH fluxes varied widely on temporal and spatial scales. In Chesapeake Bay, individual fluxes ranged from 14,200 ng m^{-2} $year^{-1}$ net volatilization of Flu to 11,400 ng m^{-2} day^{-1} net absorption of Phe on different sampling events (Bamford et al. 1999a). Both New York harbor and Raritan Bay systems exhibited net volatilization fluxes for the majority of PAHs (Gigliotti et al. 2002), while LMW PAHs showed positive fluxes and HMW PAHs showed negative values in Mumbai harbor of India (Pandit et al. 2006). The magnitudes of net PAH fluxes are comparable to the reported values (-0.01 to -21.2 μg m^{-2} day^{-1}) in an urban lake in Guangzhou of China (Li et al. 2009). The large net absorption fluxes in this island were likely a result of high gaseous concentrations of PAHs, attributed to the highly uniform ambient temperature and the strong terrestrial sources such as island-wide vehicular traffic, chemical industries, major power plants and oil refineries.

Air–water gas exchange fluxes were estimated in the range from -44.4 ± 37.8 to -73.7 ± 31.3 ng m^{-2} day^{-1}, and from -0.74 ± 0.67 to -2.9 ± 1.8 ng m^{-2} day^{-1} for HCHs and DDXs, respectively (Table 3), indicating Singapore's south coastal line as a sink for both HCHs and DDXs. The fluxes estimated here were comparable

Table 3 Annual mean air–sea exchange fluxes of selected SVOCs over Singapore's coastal area in 2009

Compound	Air-sea exchange (mean ± SD) (ng m^{-2} day^{-1})
PAHs	
Naph	−1608.4 ± 869.6
Acy	–
Ace	−36.5 ± 8.0
Flu	−27.3 ± 22.0
Phe	−457.7 ± 489.7
Ant	−210.6 ± 53.9
Flt	−394.5 ± 283.5
Pyr	−674.4 ± 359.3
B(a)A	−192.2 ± 137.4
Chry	−825.1 ± 669.0
B(b)F	−383.1 ± 131.7
B(k)F	−405.6 ± 386.8
B(a)P	−630.0 ± 563.0
Ind	−21.7 ± 20.2
DB(ah)A	–
B(ghi)P	−17.0 ± 6.6
ΣPAHs	−5884.0 ± 4040.7
OCPs	
α-HCH	−73.7 ± 31.3
β-HCH	−44.4 ± 37.8
γ-HCH	−48.4 ± 30.4
δ-HCH	–
4,4′-DDD	−2.9 ± 1.8
4,4′-DDE	−0.74 ± 0.67
4,4′-DDT	−1.1 ± 0.85
Σ OCPs	−171.3 ± 102.8

to those for the Johor strait located between Singapore and Malaysia with −8.2 to −66.8 ng m^{-2} day^{-1} (Wurl et al. 2006a). It has been reported that air–water gas exchange of SVOCs is a dynamic process that is especially sensitive to fluctuations in concentrations of both air and water phases (Wilkinson et al. 2005). Even though the Henry's law constants of DDXs are larger than those of HCHs, their net absorption was still much lower than that of HCHs, most likely due to much higher occurrence levels of gaseous HCHs, driving more HCHs transferred across the air–sea interface.

4.6 Sea-Surface Microlayer Enrichment

SML can have an enrichment effect of SVOCs, most likely due to their hydrophobic character and great affinity for surfactants collected at the air–water interface (Hardy 1982; Chernyak et al. 1996; Wurl et al. 2006a). This effect can be quantified by the enrichment factor EF, calculated as the ratio between SML and

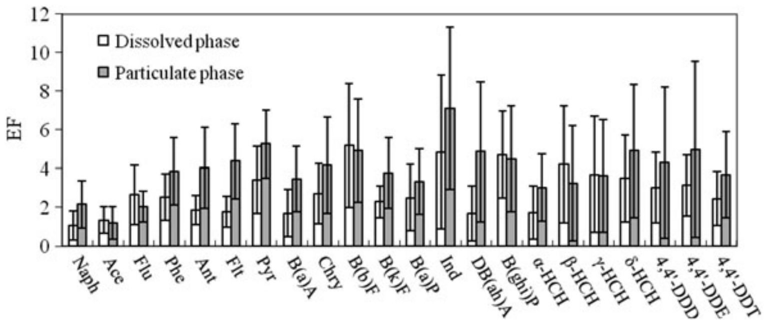

Fig. 4 Enrichment factors (EF) of PAHs and OCPs in the sea-surface microlayer of Singapore's coastal line (error bar for standard deviation)

SSW concentrations (Manodori et al. 2006) as shown in Fig. 4. EFs in the SML of particulate phase were 1.2–7.1 and 3.0–4.9 for PAHs and OCPs, and those of dissolved phase (non-filter retained fraction) were 1.1–4.9 and 1.6–4.2 for PAHs and OCPs, respectively. EFs in the SML for HCHs found in this study were relatively higher than those reported for the Johor Strait between Malaysia and Singapore (EF = 1.1–1.4 for particulate phase and EF = 3.3–4.4 for dissolved phase) by Wurl and Obbard (2006) (Wurl et al. 2006b). Similar profiles were found in the SML that EFs generally increased with an increase in molecular weight for both particulate and dissolved phases. In addition, the individual components exhibited similar trends in both phases, with relatively higher enrichments for particulate than for dissolved SVOCs. It is known that the major harbor, one of the busiest harbors in the world, is in the south coastal line of Singapore, and chemical industries as well as oil refineries situated in a group of small islands on the southwest coast of Singapore Island. It is plausible that more organic film float in the south coastal surface than in the north area (Johor Strait), resulting in more SVOCs enriched in the SML of the south coastal area. It also indicated that SML really has larger storage capacity (per volume) and may be able to delay the transport of SVOCs across the interface to SSW. In addition, the SML is a relatively dynamic compartment, highly influenced by changes of the meteorological and hydrographical conditions (Guitart et al. 2007). This may be the reason for high variation of EFs obtained in this study.

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Vertical Distribution of Airborne Particulate Matter in a Tropical Urban Environment: Changes in Physical and Chemical Characteristics

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1 Introduction

Air pollution has become a subject of great interest on the global scale from both the regulatory and the scientific points of view. This is a result of the expanding economies, increasing population and urbanization. Particulate matter pollution has become a serious concern in urban areas due to its adverse impacts on human health (US EPA 2009). Most of the previous studies reported in the literature on particulate air pollution deal with its temporal and spatial distributions as part of routine air quality monitoring (Hitchins et al. 2000; Wu et al. 2002; Levy et al. 2003; Morawska et al. 1999; Zhu et al. 2002), but little work has been done on its vertical distribution in the vicinity of buildings. The horizontal distribution of particles is of interest because it helps town planners to decide on the location of buildings and amenities considering the degree of exposure of occupants to fine and ultra fine particles. In addition to those studies, the vertical distribution of particles also merits consideration because it provides an understanding how particles are distributed with respect to the height of a building so that one can decide on the location of the natural air intake of the building, or the building orientation based on the source of particulate matter pollution.

Several studies in urban areas show that motor vehicular emissions constitute the most significant source of ultrafine (particle's aerodynamic diameter less than

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_15,

0.1 μm) and fine particles ($PM_{2.5}$) in urban environments (Zhu et al. 2002; Shi et al. 2001; Charron and Harrison 2003). It was found that the daily concentrations of inhalable particles have been linked with cardio-respiratory health effects and even with mortality (Le Tertre et al. 2002; Schwartz 1994; Dockery et al. 1993); Pope et al. (2002) reported the correlation between long-term exposures to combustion related fine particulate matter and health effects. Long term exposure has been found to be an important environmental risk factor for cardiopulmonary and lung cancer mortality. A study reported that ultra fine particles in motor vehicle emissions have the largest surface area and the highest content of potentially toxic hydrocarbons among all particulate matter sources (Oberdörster and Utell 2002). Studies show the majority of particles from the vehicle exhausts were found to be in the range 0.02–0.13 μm diesel and 0.04–0.06 μm petrol vehicles (Morawska et al. 1998; Ristovski et al. 1998). A small fraction of the total emissions is in the coarse mode which is generally less than 30% (Rogak et al. 1994 and Weingartner et al. 1997). Thus, a large number of the emitted particles have a high chance of depositing in the vulnerable parts of the respiratory system of human. The particles present in diesel engine exhaust are composed mainly of elemental carbon (EC), adsorbed organic material and traces of metallic compounds. The particles emitted from gasoline engines are composed primarily of metallic compounds, elemental carbon and adsorbed organic material. Soluble organic fractions of the particles contain primarily polycyclic aromatic hydrocarbons, heterocyclic compounds, phenols, nitroarenes and other oxygen- and nitrogen-containing derivatives (IARC 1989).

Most of the studies and ongoing research on vertical distribution of fine particles in buildings are mainly done in the United States of America, Europe, Australia and Asian countries like Hong Kong and China (Morawska et al. 1999; Wu et al. 2002; Rubino et al. 1998; Chan and Kwok 2000). Generally, the buildings are air-conditioned or partially air-conditioned and the studies were done in temperate, semi tropical or in dry climatic conditions. However, no systematic studies have been conducted on vertical distribution of fine particles in buildings, influenced by the urban traffic in the tropics. A study on the vertical distribution of fine particles in buildings was conducted in Singapore which has tropical climate, characterized by hot and moist conditions year-round. Results obtained from this study are discussed in this book chapter. Changes in the physical as well as the chemical characteristics of the particles were measured at these buildings as described in Sect. 3. The physical characteristics of particles determine in which part of the respiratory system the particles are likely to be deposited. Particles smaller than 10 μm are inhalable. Coarse particles and part of the fine particles in the size range 0.5–2.5 μm are usually deposited in the extra-thoracic and trachea-bronchial parts of the lung system. Particles smaller than 1 μm can penetrate into the pulmonary alveoli of the lungs, and end up in the interstitial spaces of the alveolar lung tissue. Chemical characterization of particles helps to identify its toxicological constituents and provides as indication of the origins of $PM_{2.5}$ since certain compounds are characteristic of specific sources.

2 Motivation of Study

Currently, Singapore has a population of 4.84 million and is the fourth most densely populated country in the world. With a very high population density of 6,489 persons/km^2 as at 2009 and a land area of 707.1 km^2, Singapore can be considered a land scarce country. The projected resident population is 6.5 million by 2020. Currently, almost 83% of the residents live in high-rise residential buildings which are mostly naturally ventilated (Department of Statistic Singapore 2009). Due to the lack of land space, residential buildings are usually high-rise and in close proximity to each other. Some of these buildings are located very close to busy expressways and major roads which have very high traffic volume. To cater for the 894,682 vehicles owned (Department of Statistic of Singapore 2009), Singapore has a comprehensive transport infrastructure with roads occupying 12% of the total area (Tai and Chong 1998). Diesel vehicles make up of about 20% of Singapore's motor vehicle population.

With the expected increase in the population growth and in the motor vehicle numbers in Singapore, there is an increasing concern over both ambient and indoor air quality in the urban areas, especially in naturally ventilated high-rise residential buildings located near expressways and major roads as on-road vehicles are main sources of fine traffic-generated particles in urban areas (Gupta et al. 2003; Weingartner et al. 1997; Kittelson et al. 2000; Wehner et al. 2002; Shi et al. 2001; Palmgren et al. 2003). The fine traffic-generated particles could be inhaled by the residents of the buildings, and thus affect their health over time. A study has shown that about 1 out of 5 children in Singapore are asthmatics and Singapore ranks number one in the Asia Pacific region in terms of the number of asthmatic kids between the ages 13–14 (ISSAC 1998).

To safeguard the health of its citizens, the government of Singapore has taken various steps to ensure the particulate matter exposure be kept to the minimum. In an attempt to curb the increasing motor vehicle pollution, the government has implemented various policies and measures such as improved public transport system, restricted car ownership, decentralization to get people to live nearer their work place, and having green belts to absorb some of the polluted air. Unleaded petrol was introduced in 1991 to replace leaded petrol which was eventually phased out in 1998. The National Environmental Agency (NEA) tasked by the Singapore government introduced Euro IV emission standards for new diesel vehicles such as taxis, buses and commercial vehicles, in an attempt to lower concentrations of $PM_{2.5}$ to acceptable standards. This was put in force as of 1st October 2006. NEA also encourages its citizen to adopt Compressed Natural Gas (CNG) vehicles by providing incentive package such as substantial tax rebates for purchasing new CNG vehicles(NEA of Singapore Annual Report 2005). These measures show a growing concern of the government in keeping particulate matter level to the minimum.

To date, there is however a lack of comprehensive data on the vertical distribution of fine traffic-generated particulate matter in naturally ventilated high-rise residential buildings located in close proximity to busy expressways in the tropics. To fill this knowledge gap, this research study was initiated with a focus on the vertical distribution of fine traffic-generated particulate matter in several typical naturally ventilated high-rise public residential buildings of point and slab block configurations at different parts of Singapore for the first time. The point block selected is generally 'H' shaped and has four apartments in each horizontal storey with two of them facing the expressway and the other two facing away from the expressway. The slab block selected is rectangular and has normally 18–20 apartments, in each horizontal storey with their living rooms facing the expressway.

3 Site Characterization and Sampling Strategy

3.1 Scope of Study

The main focus of the study was to quantify the mass concentration exposure levels of fine traffic-generated particles ($PM_{2.5}$) at the various heights of typical high-rise naturally ventilated residential buildings located in close proximity, i.e., within 30 m and along a busy major expressway in a tropical climate. In addition, chemical characterization of the traffic-generated particles was also performed using the samples collected at each of the floors. Chemical analysis included the determination of organic carbon (OC), EC, water soluble (WS) inorganic ions, water soluble (WS) trace metals and particulate polycyclic aromatic hydrocarbons (PAH) mass concentrations at the floors.

3.2 Site Characterization

The Central Expressway (CTE) is one of the most highly utilized expressways which link many residential towns to the Central Business District of Singapore. The expressway is a dual carriageway with each carriageway having three lanes. Two typical naturally ventilated high-rise residential buildings from the same prescint, one point block and the other of slab block configuration were selected due to their close proximity to the CTE. The end elevations of the buildings are shown in Figs. 1 and 2. The schematic illustration of the locations and characteristics of sampling sites is shown in Fig. 3. The ground on which both buildings stood was reasonably flat. The actual dimensions of the point and slab blocks were 23.82 m(L) × 23.71 m(W) × 52.87 m(H), and 126.90 m(L) × 12.57 m(W) × 42.40 m(H), respectively. Each storey height is about 2.80 m for both the buildings. The living rooms of both the buildings were facing the expressway. The number of occupants in each apartment varied from 3 to 5. The only obstacle for airflow towards the buildings was the trees and hedges planted along the

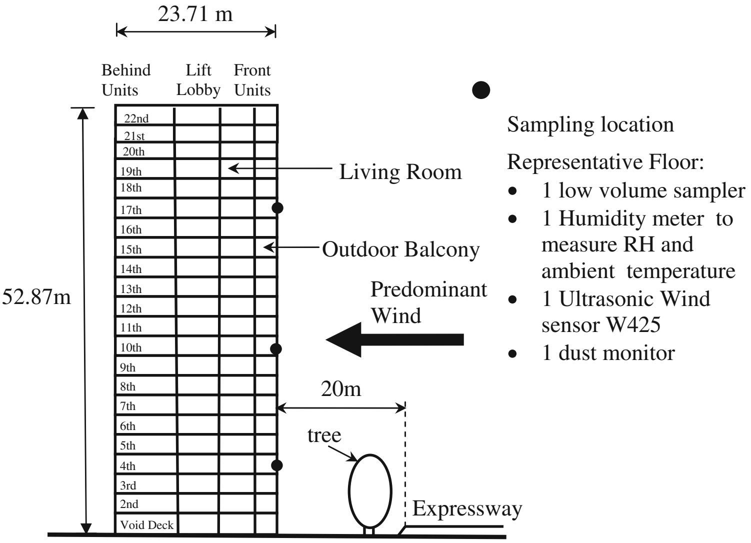


Fig. 1 End elevation of point block

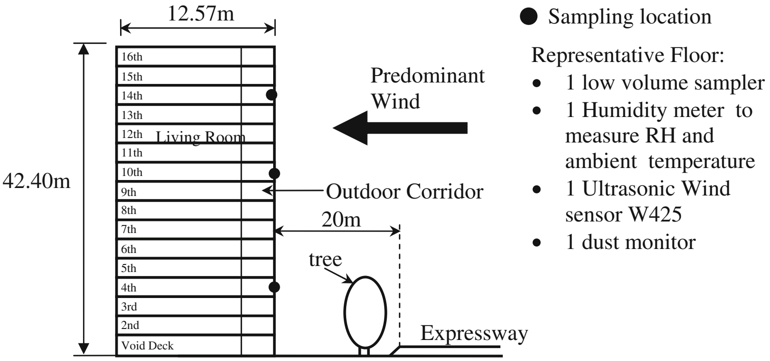


Fig. 2 End elevation of slab block

expressway. The trees are planted in a single row and have drooping branches with dense and complex canopy structure. The average tree canopy spans up to about 3½ to 4 storey high. Fronting the tree canopy is 1 m tall hedges which is about 0.7 m wide. This type of green belt has become a unique feature for the naturally ventilated high-rise residential buildings that are in close proximity to expressways. The predominant wind was blowing in the south-east direction, nearly perpendicularly towards the building facades where the living rooms were. On the opposite side of the expressway, the nearest high-rise building is about 500 m away from the measurement site and in the north-west direction, and the other buildings are some distance away from the measurement site. This building

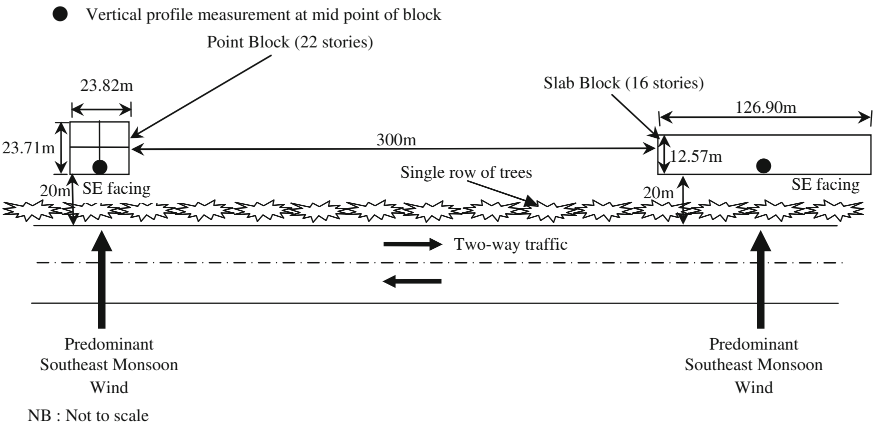


Fig. 3 Schematic illustration of the locations and characteristics of measurement sites

location provided an opportunity to study the effects of unobstructed airflow on the concentration level of fine traffic-generated particles at the various floors of the buildings, i.e., these experiments can be considered as being conducted in an open street geometry and street–canyon effect is negligible.

3.3 Sampling Strategy

For both the blocks, the mass concentration and particulate samples for chemical analysis were collected in the middle of each building on three representative floors, i.e., low, mid and high floors and at the upstream of the measurement sites to determine the background concentration levels. The instruments were placed about 1.5–1.8 m high from the floor (Li et al. 2005; IDEM 2009; Quackenboss et al. 1986) in the building's outdoor balcony/corridor to simulate the breathing zone, at least 1 m away from the parapet wall of the building and away from lighting heat sources as recommended by the manufacturer. All these measurements were made at the windward face of the buildings and strategically located to allow free flow of outdoor air laden with particulate matter which subsequently penetrates into the homes of the buildings.

Outdoor measurements were taken because the previous studies in Singapore (Gupta and Cheong 2007) reported that the I/O ratio in naturally ventilated building was close to unity indicating that pollution migration was from outdoors into indoors rather than its emission from internal sources. During the course of field measurements, the intense indoor activities such as candle burning, incense burning were minimum. Key meteorological parameters such as wind speed, wind direction, ambient temperature, and relative humidity were also concurrently measured at the same sampling locations. The frequency of measurement was

5 min average readings in the case of meteorological parameters while it was 24 h for the chemical and particulate mass concentration levels. Wind speed and direction were measured from 10 a.m. to 10 p.m. daily while ambient temperature and relative humidity were measured for 24 h daily. The measurements were conducted for one month continuously (2 July to 27 July 2007). All the measurements were taken on hot and sunny days and no measurements were made during the weekends. Also, all the measurements were conducted simultaneously in the six floors of both the buildings.

3.4 Instrumentation

3.4.1 Samples

Filter-based gravimetric measurements were made using portable, battery-operated MiniVol® low volume samplers which draw air continuously for 24 h through Teflon (PTFE) filters with 2.0 μm pore size or Whatman high quality quartz microfibre filters (47 mm diameter) at a pre-calibrated flow rate of 5 l/min via a $PM_{2.5}$ inlet. The PTFE samples were subsequently used for chemical analysis including WS inorganic ions and WS trace metal concentration determination whilst the Whatman high quality, pre-combusted quartz microfibre filter samples were used for the determination of EC, OC and PAHs. The air flow rates were checked before and at the end of each measurement to ensure that a constant flow rate was maintained throughout the sampling period. Field blanks were collected in all the representative floors to determine any potential contamination during sampling, transport and storage. A total of 80 PTFE samples (60 samples from the building and 20 samples from the background location) and 80 Whatman high quality quartz microfibre filter samples (60 samples from the building and 20 samples from the background location) were collected for each block. The filters were weighed using MC-5 microbalance with 1 μg sensitivity before and after sampling. For the chemical analysis, all exposed filters and field blanks were conditioned for a minimum of 24 h in a dry box maintained at a constant temperature of 25°C and a relative humidity (RH) of 30%. The filters were stored in the dark at 4°C until further extraction and chemical analysis to minimize possible degradation and volatilization losses.

3.5 Chemical Analysis

3.5.1 Carbonaceous Species

The total carbon (TC) can be categorized as the sum of OC and EC.

$$\mathrm{TC} = \mathrm{EC} + \mathrm{OC} \tag{1}$$

To investigate the two different forms of carbonaceous species, two circular punches of 6 mm diameter were taken from one quarter of the filters. One of the pieces was pre-combusted in the furnace at 350°C for 24 h to remove OC (Zappoli et al. 1999). Both uncombusted and combusted pieces were then weighed with the microbalance and analyzed for carbon using the 2400 Series II CHNS/O Analyzer (PerkinElmer Life And Analytical Sciences Inc., MA, USA), which was operated in the CHN mode with acetanilide (71.09% C, 6.71% H, 10.36% N) as calibration standard.

3.5.2 Particulate PAHs

The remaining three-quarters of the Whatman high quality quartz microfibre filters were extracted and analyzed for PAHs using the method developed by Karthikeyan et al. (2006). The filters were treated with 20 ml of 1:1 v/v acetone and n-hexane in the MLS 1200 MEGA microwave digestion system (Milestone S.r.l., Bergamo, Italy) for 20 min at 150 W. The extract was then concentrated to below 1 ml by carefully blowing a gentle stream of dry nitrogen above it to minimize evaporative losses of the semi-volatile PAHs. The final volume was then brought back to exactly 1.0 ml with the extraction solvent. The extracted samples were analyzed for the 16 U.S. EPA priority PAHs, namely naphthalene (Nap), acenaphthene (Ace), acenaphthylene (Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]-fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3,cd]pyrene (Ind), dibenz[a,h] anthracene (DBA) and benzo[g,h,i]perylene (BPe).

3.5.3 WS Trace Metals

One half of the PTFE filters were used for the WS trace metal analysis. The WS metals were extracted by ultrasonicating for an hour at room temperature with 20 ml of ultrapure water. The extracts were passed through a 0.45 mm pore size filter before analysis. Both extracts were analyzed for 14 metals, i.e., Al, Co, Cr, Cu, Fe, Mn, Pb, Cd, Ni, As, Ag, Ti, Zn and V, with the ELAN 6100 Inductive Coupled Plasma Mass Spectrometer (ICP-MS, PerkinElmer, Inc., MA, U.S.A.). Prior to each analytical batch, the ICP-MS was calibrated with multi-element standards at different concentrations, prepared from serial dilution of 1,000 mg/l of individual standard solutions, and its response was regularly verified by a calibration standard. The instrumental settings used for the analysis were similar to those recommended by the manufacturer.

3.5.4 WS Inorganic Ions

The other half of the PTFE filters were analyzed for WS inorganic ions. For the ions analysis, a pair of forceps was used to place all the Teflon filter samples in 50 ml conical flasks. About 0.1 ml of iso-propanol was added into each conical flask, using an auto pipette, onto each filter surface so as to wet the filter surface completely since PTFE filters are hydrophobic in nature. Next 15 ml of ultra pure deionized water (resistivity > 17.8 M_cm) was added into the conical flask. The conical flasks were then capped and place into an ultrasonic bath (ULTRAsonik, 57X, ITS Science & Medical Pte Ltd), at a temperature of 60°C for about 1 h after which the solutions were transferred into 20 ml volumetric flasks. About 5 ml more ultra pure deionized water was added to the solutions and they were filtered through a special Whatman filter with 0.45 μm PTFE membrane in order to remove any particles present, so as not to clog up the Ion Chromatography (IC) system.

For the separation and quantification of the cations and anions, a Metrohm AG ion chromatograph (IC), was utilized. The ions analyzed were lithium (Li^+), sodium (Na^+), ammonium (NH_4^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), fluoride (F^-), chloride (Cl^-), nitrite (NO_2^-), nitrate ($_3^-$), phosphate (PO_4^{3-}) and sulphate (SO_4^{2-}). The instrument was equipped with a 733 IC analytical separation systems, a 732 IC detector, 709 IC pump, 753 Suppressor module and a 750 Auto sampler. A Metrosep Anion Dual 2 column is used for anion detection with the suppressor module at a flow rate of 0.8 ml min^{-1} while Metrosep C2-100 is used for the cation detection without the suppressor unit at a flow rate of 1.0 ml min^{-1}. Before doing the ion analysis, the IC was calibrated using a series of standard solutions of different concentrations containing the same ion.

3.5.5 Non-Sea-Salt (nss) Sulphate

The nss-sulphate over the total sulphate was calculated using the below formula:

$$\mathrm{nss} - \mathrm{SO}_4^{2-} = \left[\mathrm{SO}_4^{2-}\right] - [\mathrm{Na}^+] \times 0.2516\ldots \qquad (2)$$

(Source: Millero and Sohn 1992).

4 Results and Discussion

4.1 *Traffic Count*

The contribution of the various types of motor vehicles to the total fine traffic-generated particulate matter was not quantified in this study. The traffic composition analysis indicated that petrol-driven passenger cars fitted with catalytic converters were the major contributor to traffic counts (about 60%). The daily traffic count ranged from 14,000 to 17,000 vehicles/h (15,500 ± 1,200 vehicles/h). Results showed that traffic pattern on all days of a week had similar trend. Traffic count started to rise between 0700 and 1,300 h (mean 15,000 vehicles/h), before reaching maximum traffic count during 1,300–1,700 h (15,000–17,000 vehicles/h). Traffic counts then decreased between 1,700 and 2,000 h due to the diversion of vehicles towards other alternative routes as the Electronic Road Pricing (ERP) gantry operates from 1,800 to 2,000 h. Traffic counts then started to increase again between 2,000 and 2,200 h. Approaching the end of the day, the traffic condition worsens, leading to congestion with cars moving at low speed. The mean traffic count during 1,700–2,200 h was about 13,500 vehicles/h.

4.2 Wind Direction and Wind Speed

The wind direction measurements showed that the southeastern monsoon winds were the dominant winds blowing at right angles towards the building façade where the living room was located. These prevailing weather conditions facilitated the transport of the fine traffic-generated particulate towards the residential apartments. The overall mean wind speed was 1.75 ± 0.45 and 1.36 ± 0.42 m/s for the point block and slab block, respectively, which showed a slab block tend to slow down the wind speed compared to the point block. Also, the wind data show the buildings experience a low wind environment similar to those in other urbanized regions (Fung et al. 2009; Ng et al. 2004). For the point block, the mean wind speed at the low floor was 1.65 ± 0.49, 1.73 ± 0.32 m/s for the mid floor and 1.91 ± 0.47 m/s for high floor and for the slab block, the mean wind speed at the low floor was 0.68 ± 0.37, 1.49 ± 0.40 m/s for the mid floor and 1.72 ± 0.39 m/s for the high floor. Generally, the wind speed increased with height of the building. It has been accepted that the wind velocity is low at the surface, and increases with height (Calvert 2004).

4.3 Ambient Temperature and RH

Many previous studies have discussed the influence of meteorological parameters on the spatial distribution of particle concentration, but very little information exists on the vertical distribution of ambient temperature and RH in buildings and how they influence on the particle concentration levels. For example, in Turkey Cuhadaroglu and Demirci (1997) found that the airborne particle concentration increased with increasing temperature and decreased with decreasing RH. A study in Hong Kong showed that the indoor–outdoor ratios of particle concentrations tend to increase with increase of temperature and humidity (Chan 2002). In Hanoi, Vietnam, Hien et al. (2002) reported that the most important determinant of $PM_{2.5}$ concentration levels was air temperature while RH mainly influenced the daily variations of $PM_{2.5-10}$. Latini et al. (2002) reported that temperature and RH affect the chemical transformations of particles and hence the type of particles entering the indoor environment.

In the study, the overall mean ambient temperature was 29.9 ± 2.7°C and 30.2 ± 3.1°C for the point block and slab block, respectively. For the point block, the mean temperature at the low floor was 30.2 ± 3.5°C, 29.7 ± 2.5°C for the mid floor and 29.4 ± 3.2°C for high floor while for the slab block, the mean temperature at the low floor was 30.5 ± 2.7°C, 30.1 ± 2.9°C for the mid floor and 29.8 ± 3.6°C for high floor. The temperature difference between any two floors did not exceed 0.8°C for both the blocks. The overall mean RH was 71.7 ± 4.7% and 69.1 ± 4.1% for the point block and slabs, respectively. For the point block, the mean RH was 69.2 ± 3.9% at the low floor, 72.8 ± 4.2% at the mid floor and 73.4 ± 3.2% at the high floor and for the slab block, the mean RH was 65 ± 4.6% at the low floor, 68.1 ± 4.9% at the mid floor and 70.3 ± 4.4% at the high floor. The difference in RH between any two floors did not exceed 5% for both the blocks. For both the blocks, the vertical temperature and RH distribution profiles showed very little stratification between the three representative floors. The insignificant RH and temperature stratifications observed between the three floors could be due to rapid mixing of air near the boundary layer of the building. The insignificant temperature stratification between the floors reduced the buoyancy effect on the vertical transportation of fine traffic-generated particulate matter.

4.4 Vertical Distribution of Traffic-Generated Fine Particles

Experimental results from this study revealed that $PM_{2.5}$ mean particle mass concentration was highest at the mid floors of both buildings when compared to those measured at low and high floors during a typical day as shown in Table 1. Although the low floors were closest to traffic emissions, the mean particle mass concentration was lower there than that at the mid floors, which could presumably be due to the interception of $PM_{2.5}$ particles by tree leaves (Beckett et al. 2000; Impens and Delcarte 1979) or the inflow of clean and drier air from higher altitude with lower aerosol burden mixing with the traffic-polluted air at the lower levels or both. The high floors had the least fine particulate matter mass concentration due to dilution following pronounced mixing of traffic-polluted air with ambient air. The vertical distribution profile of $PM_{2.5}$ mass concentration in this study is different from those of several studies reported in the literature which found that

Table 1 $PM_{2.5}$ mass concentration in point block (pb) and slab block (sb) for a typical week

Day		Upstream background level (μg/m^3)	Low floor (μg/m^3)	Mid floor (μg/m^3)	High floor (μg/m^3)
1	pb	22.11 ± 4.92	45.63 ± 5.31	62.17 ± 6.12	33.36 ± 3.99
	sb	24.25 ± 3.96	58.49 ± 4.46	73.87 ± 5.08	45.32 ± 5.42
2	pb	23.67 ± 5.24	48.75 ± 4.06	61.48 ± 5.03	35.63 ± 4.28
	sb	22.98 ± 4.53	60.28 ± 5.51	75.91 ± 4.96	50.01 ± 4.67
3	pb	20.78 ± 4.15	36.80 ± 4.92	49.33 ± 4.41	26.97 ± 3.36
	sb	23.67 ± 4.99	52.67 ± 4.95	65.39 ± 4.15	41.33 ± 5.06
4	pb	22.98 ± 3.96	37.25 ± 4.76	53.91 ± 5.63	28.36 ± 4.14
	sb	24.01 ± 5.07	51.76 ± 5.19	66.83 ± 4.29	40.03 ± 3.93
5	pb	23.96 ± 4.53	39.11 ± 5.77	54.14 ± 4.19	30.69 ± 4.58
	sb	22.83 ± 4.45	53.55 ± 5.77	68.76 ± 4.07	39.95 ± 4.98

airborne particulate matter concentration levels usually decreased with increasing building height. For example, Morawska et al. (1999) found no significant height dependence of particle number concentration for an office block from 3rd to 25th floor which was located 80 m from the motorway in Brisbane, Australia. However, for a building located 15 m from motorway, they found the particle number concentration at the building envelope was very high comparable to those in the immediate vicinity of the motorway and suggested that for a building in very close proximity to motorway, the air flow around the building envelope was such that it drew air directly from the motorway. Wu et al. (2002) observed at the building height of 79 m, the mass concentration levels of PM_1, $PM_{2.5}$ and PM_{10} decreased to about 80, 62 and 60%, respectively, of the maximum concentration level occurring at 2 m from the ground in Macau, China. Other investigators including Rubino et al. (1998) of Italy, Hitchins et al. (2001) of Australia, Chan and Kwok (2000) of Hong Kong have also found that particle mass/number concentrations decreased with increasing height of a building. The only difference between both blocks is that at corresponding floors, the mass concentration levels for slab block is much higher than those of point block. This could be attributed to the configuration of the blocks under similar traffic and meteorological conditions. The observational data show the slab block tends to slow down the approaching wind, thus allowing the accumulation of the fine traffic-generated particulate matter in front of the building.

4.5 Health Impacts due to Traffic-Generated Fine Particles

4.5.1 Physical Characteristics

The daily mean $PM_{2.5}$ mass concentration levels at the various floors of both the buildings exceeded either the $PM_{2.5}$ National Ambient Air Quality Standard (NAAQS 2009) annual average of 15 $\mu g/m^3$ or the 24 h value of 35 $\mu g/m^3$. This exceedance is of major concern since the health of residents including the health of "sensitive" populations such as asthmatics, children, and the elderly will be affected. Both the blocks showed that $PM_{2.5}$ particle counts consisted of about 94% of the particles below the size range of 0.65 μm while the rest 6% of the particles fell in the size range 0.65–1.6 μm. Of the 94% particles, about 75% of the particles were in the size range of 0.3–0.4 μm, 15% in the size range of 0.4–0.5 μm and 4% in the size range of 0.5–0.65 μm at all the floors. The size distribution of both the cases showed that the majority of the traffic-generated particles have a very high chance of penetrating deeper into the lungs. Toxicological studies have reported that fine and ultra fine particles have considerably enhanced toxicity per unit mass and their toxicity increased as particle size decrease. Figures 4 and 5 show the size distribution of the traffic-generated particles at both the blocks.

Fig. 4 Size distribution of $PM_{2.5}$ at the various floors of the point block

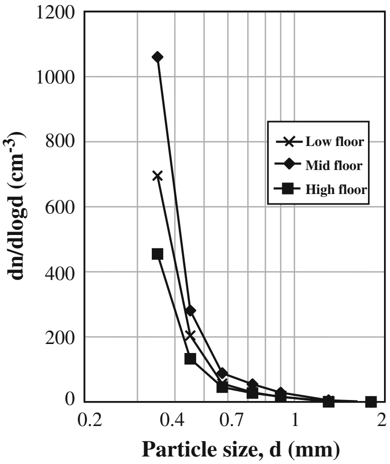
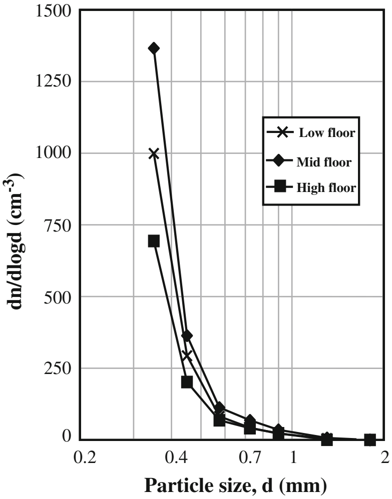


Fig. 5 Size distribution of $PM_{2.5}$ at the various floors of the slab block



Based on the health risk model used by Pandey et al. (2005), the inhalation of fine particles is of serious concern for the residents in the point block and slab block. For the point block, the health risk (HR) values at the mid and low floors suggest that residents living in these floors have 1.81 and 1.34 times more risk, respectively, in terms of developing respiratory diseases when compared to residents living at the high floors for all the age categories (new born babies, one year old children, children between ages 8 and 10 years and adults). Similarly, for the slab block, the HR values at the mid and low floors indicated that residents living in these floors have 1.62 and 1.28 times more risk, respectively, in terms of developing respiratory diseases when compared to residents living at the high floors for all the age categories. The dose rates and HR values for both the blocks are shown in Tables 2 and 3.

4.6 Chemical Characteristics

4.6.1 Carbonaceous Species

The daily mean upstream background levels for EC and OC were 5.8 ± 2.6 and 6.7 ± 1.8 $\mu g/m^3$, respectively. The EC and OC mass concentrations at the various floors of point and slab blocks are shown in Table 4. There was a significant difference between upstream and those EC and OC values measured at the various floors of both the blocks ($P < 0.05$ for OC and EC for both the blocks). This indicated most of the particulate matter measured at the floors was from the traffic since motor vehicle emissions mainly consisted of elemental and organic carbon particles.

For point block and slab block, the overall mean OC/EC ratio for the various floors was 1.59 ± 0.23 (1.20–1.81) and 1.67 ± 0.31 (1.04–1.73), respectively. Values in bracket indicate the range of OC/EC ratio values for all days at the different floors of the buildings. This was within the expected value of 3.7 for traffic emissions (Cabada and Pandis 2002) and the lower values obtained in this study suggested that the expressway was dominated by vehicles with catalytic converter (Giugliano et al. 2005). EC is toxic and can cause acute and chronic effects and even premature death. Studies have shown the relative risk of premature death increases with 1% per 1 $\mu g/m^3$ of EC. This is 5–10 times larger than the relative risk of PM_{10}. For both the buildings, the correlation coefficient (r) of OC and EC at the various floors of the block are 0.92–0.94 for the low floor, 0.90–0.96 at the mid floor and 0.89–0.95 at the high floor. The good correlation suggested that OC and EC came from the same anthropogenic sources.

4.6.2 WS Inorganic Ions

Among the 12 inorganic ions, tested in this study, Na^+, NH_4^+, Ca^{2+}, K^+, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-} were detected in PM samples collected from both the point and slab blocks. SO_4^{2-} accounted for most of the ionic mass followed by NH_4^+ and NO_3^- ions at all the floors. The results generally showed that the total mass concentrations of anions were slightly higher than that of cations. A recent study reported that the relatively high concentrations of anions are associated with urban particulate matter (Talebi and Adedi 2005). The highest total cation and anion mass concentrations were observed at the mid floor of both the buildings.

For the point block, cationic species accounted for about 17% at the low floor, 14% at the mid floor and 20% at the high floor whilst anionic species accounted for

Table 2 Dose rates and HR values for point block

Floor	$n = 80$							
	Dose rate (μg kg^{-1})				HR (dimensionless)			
	New born	Children (1 year)	Children (8–10 years)	Adult	New born	Children (1 year)	Children (8–10 years)	Adult
Low floor	7.68 ± 1.00	10.95 ± 1.42	9.61 ± 1.24	8.24 ± 1.06	0.51 ± 0.06	0.52 ± 0.07	0.36 ± 0.04	0.54 ± 0.05
Mid floor	10.41 ± 1.02	14.83 ± 1.45	13.01 ± 1.27	11.15 ± 1.09	0.70 ± 0.07	0.72 ± 0.04	0.47 ± 0.05	0.71 ± 0.06
High floor	5.74 ± 0.66	8.18 ± 0.94	7.18 ± 0.82	6.15 ± 0.70	0.39 ± 0.04	0.38 ± 0.05	0.26 ± 0.03	0.40 ± 0.04

n = number of samples collected and analyzed for mass concentration

Table 3 Dose rates and HR values for slab block

Floor	$n = 80$							
	Dose rate (µg kg^{-1})				HR (dimensionless)			
	New born	Children (1 year)	Children (8–10 year)	Adult	New born	Children (1 year)	Children (8–10 year)	Adult
Low floor	10.25 ± 0.70	14.61 ± 1.00	12.81 ± 0.88	10.98 ± 0.75	0.70 ± 0.04	0.69 ± 0.05	0.47 ± 0.03	0.68 ± 0.07
Mid floor	12.99 ± 0.84	18.51 ± 1.20	16.24 ± 1.05	13.92 ± 0.90	0.88 ± 0.06	0.86 ± 0.04	0.59 ± 0.04	0.89 ± 0.03
High floor	8.02 ± 0.80	11.43 ± 1.14	10.03 ± 1.00	8.60 ± 0.86	0.55 ± 0.05	0.53 ± 0.07	0.36 ± 0.05	0.56 ± 0.04

n = number of samples collected and analyzed for mass concentration

Table 4 EC and OC mass concentration in point block (pb) and slab block (sb) for a typical week

Day		$n = 80$					
		EC			OC		
		Low floor ($\mu g/m^3$)	Mid floor ($\mu g/m^3$)	High floor ($\mu g/m^3$)	Low floor ($\mu g/m^3$)	Mid floor ($\mu g/m^3$)	High floor ($\mu g/m^3$)
1	pb	16.58 ± 2.17	21.58 ± 3.02	11.79 ± 2.94	19.31 ± 3.31	30.98 ± 3.68	15.98 ± 2.10
	sb	19.63 ± 3.12	26.65 ± 2.17	16.53 ± 1.75	27.37 ± 2.43	36.31 ± 3.91	21.26 ± 3.18
2	pb	17.39 ± 3.21	20.89 ± 2.56	12.33 ± 1.89	20.87 ± 2.26	29.98 ± 3.01	16.96 ± 2.66
	sb	21.71 ± 2.97	27.32 ± 1.95	18.01 ± 2.26	28.79 ± 3.85	37.56 ± 3.77	23.27 ± 2.89
3	pb	12.54 ± 2.16	17.60 ± 2.92	8.98 ± 1.71	16.42 ± 2.02	22.67 ± 2.36	12.24 ± 1.95
	sb	17.37 ± 3.09	22.53 ± 2.44	14.49 ± 2.22	24.49 ± 1.99	32.61 ± 2.55	19.24 ± 1.95
4	pb	12.96 ± 2.11	18.96 ± 3.09	9.21 ± 2.54	17.63 ± 1.98	25.63 ± 3.44	13.91 ± 2.82
	sb	17.85 ± 2.82	22.87 ± 2.81	13.91 ± 3.17	23.55 ± 2.48	32.83 ± 2.09	20.42 ± 2.09
5	pb	13.16 ± 1.57	18.23 ± 2.54	9.86 ± 1.39	18.42 ± 2.75	26.96 ± 3.08	15.03 ± 2.17
	sb	18.87 ± 2.33	23.30 ± 3.02	12.85 ± 2.48	26.03 ± 3.32	34.45 ± 2.67	20.11 ± 3.02

n = number of samples collected and analyzed for mass concentration

about 21% at the low floor, 17% at the mid floor and 20% at the high floor of the $PM_{2.5}$ mass concentration. The daily concentrations of cations and anions are presented in Tables 5 and 6 for the point block. The contribution of nss-sulfates to the total sulfate in $PM_{2.5}$ samples was over 93% at the three different floors indicating a substantial anthropogenic origin. For the SO_4^{2-} and NH_4^+ ions, the highest concentration was observed at the low floor while for NO_3^-, K^+, Na^+, Cl^- and Ca^{2+} ions, the highest concentrations were observed at the mid floor of the building. The highest concentration of PO_4^{3-} ion was found at the upper floor of the building. Na^+ and Cl^- mass concentrations correlated very well ($r = 0.993$), suggesting that their origin may be due to sea spray.

For the slab block, cationic species account for about 13% at the low floor, 13% at the mid floor and 15% at the high floor whilst anionic species account for about 16% at the low floor, 13% at the mid floor and 18% at the high floor of the $PM_{2.5}$ mass concentration. The daily concentrations of cations and anions of the slab block are presented in Tables 7 and 8, respectively. The contribution of nss-sulfates to the total sulfate in $PM_{2.5}$ samples was over 95% at the three different floors indicating a substantial anthropogenic origin. For the SO_4^{2-}, NO_3- and NH_4^+ ions, the highest concentration was observed at the low floor while for K^+, Na^+, Cl^-, PO_4^{3-} and Ca^{2+} ions, the highest concentration was observed at the mid floor of the building. Correlation analysis of Na^+ and C^- showed both the mass concentrations correlated well ($r = 0.995$) suggesting that their origin may be due to sea spray.

Table 5 Daily mass concentration of cation at point block

Cation	Low floor (μg/m^3)	Mid floor (μg/m^3)	High floor (μg/m^3)
Sodium	0.53 ± 0.28	1.16 ± 0.34	0.38 ± 0.26
Ammonium	2.95 ± 1.02	2.45 ± 0.89	2.04 ± 0.96
Calcium	1.36 ± 0.37	1.88 ± 0.43	1.70 ± 0.51
Potassium	1.26 ± 0.63	2.38 ± 0.57	1.93 ± 0.49
Total mean	7.10	7.87	6.05

Table 6 Daily mass concentration of anion at point block

Anion	Low floor (μg/m^3)	Mid floor (μg/m^3)	High floor (μg/m^3)
Chloride	0.43 ± 0.12	1.03 ± 0.39	0.32 ± 0.23
Nitrate	2.62 ± 0.86	3.15 ± 1.76	1.61 ± 1.49
Sulfate	5.60 ± 1.28	4.79 ± 1.51	3.85 ± 0.67
Phosphate	0.21 ± 0.09	0.29 ± 0.11	0.31 ± 0.05
Total mean	8.86	9.26	6.09

Table 7 Daily mass concentrations of cation at slab block

Cation	Low floor ($\mu g/m^3$)	Mid floor ($\mu g/m^3$)	High floor ($\mu g/m^3$)
Sodium	0.68 ± 0.13	1.21 ± 0.57	0.51 ± 0.36
Ammonium	3.61 ± 0.79	3.24 ± 0.64	2.80 ± 0.88
Calcium	1.65 ± 0.45	2.01 ± 0.55	1.43 ± 0.23
Potassium	1.42 ± 0.81	2.38 ± 0.70	1.67 ± 0.37
Total mean	7.36	8.84	6.41

Table 8 Daily mass concentration of anion at slab block

Anion	Low floor ($\mu g/m^3$)	Mid floor ($\mu g/m^3$)	High floor ($\mu g/m^3$)
Chloride	0.51 ± 0.26	1.06 ± 0.44	0.43 ± 0.15
Nitrate	2.93 ± 2.15	2.47 ± 1.26	2.34 ± 1.83
Sulfate	5.27 ± 2.09	5.32 ± 2.33	4.89 ± 1.97
Phosphate	0.24 ± 0.18	0.29 ± 0.07	0.26 ± 0.12
Total mean	8.95	9.14	7.92

4.6.3 Vertical Distribution Profile of PAHs

The distribution of the mass concentrations of particulate PAH species at the point block is presented in Table 9. The mean concentration levels of total particulate PAHs ranged from 2.70 to 4.54 ng/m^3 for the different floors the block. The overall total mass concentrations of particulate PAHs for the block is 3.32 ± 1.76 ng/m^3 (0.56–7.2 ng/m^3). The highest total mean PAH mass concentration occurred at the mid floor followed by the high floor of the building. The low floor had the least total mean PAH mass concentration. The dominant particulate PAHs measured at the point block were Nap, Acy, BbF and BPe. Many studies have reported the mutagenic and or carcinogenic effects of PAHs. IARC (2002) has identified BaA, BaP, DBA, BkF, Ind, including BbF and Nap to be carcinogenic compounds.

PAH species with four or more ring structures (i.e., BPe, DBA, Ind, BaP, BkF, BbF, Chr, BaA and Pyr), are less volatile than those PAHs with two or three rings (Nap, Ace, Acy, Flu, Phe, Ant and Flt) which mainly exist in gaseous state (Beak et al. 1991). The vertical distribution of more volatile PAHs to total PAHs (sum of Nap–Flt as a % of total PAH) remained almost the same from the low to mid floors and increased from mid to the high floors as shown in Table 10. PAH concentration ratios can be used to identify possible emission sources (Kakimoto et al. 2002; Venkataraman et al. 1994). Li and Kamens (1993) used the BPe/Ind ratio to distinguish emission of PAHs from different engine types. The study reported a ratio over the range of 3.5–3.8 for petrol engines and a ratio of 1.1–1.2 for diesel engines. Based on the results shown in Table 10, the ratio values suggested a mixture of both diesel and petrol engine type of vehicles contributed to the

Table 9 Profile of particulate PAHs at point block

PAH	Concentration (ng/m^3)		
	Low floor	Mid floor	High floor
Naphthalene (Nap)	0.08 ± 0.03 (0.08–0.23)	0.35 ± 0.15 (0.21–1.04)	1.15 ± 0.37 (0.24–3.47)
Acenaphthene (Ace)	0.08 ± 0.02 (0.08–0.29)	0.55 ± 0.25 (0.03–1.69)	0.05 ± 0.02 (0.01–0.08)
Acenaphthylen (Acy)	0.66 ± 0.33 (0.22–1.17)	0.81 ± 0.37 (0.11–1.34)	0.81 ± 0.41 (0.61–1.44)
Fluorene (Flu)	0.32 ± 0.10 (0.16–0.47)	0.37 ± 0.16 (0.03–0.57)	0.33 ± 0.18 (0.21–0.53)
Phenanthren (Phe)	0.22 ± 0.12 (0.07–0.41)	0.30 ± 0.18 (0.14–0.55)	0.22 ± 0.18 (0.03–0.49)
Anthracene (Ant)	0.06 ± 0.02 (0.01–0.07)	0.21 ± 0.09 (0.01–0.61)	0.06 ± 0.02 (0.01–0.10)
Fluoranthene (Flt)	0.09 ± 0.04 (0.02–0.11)	0.15 ± 0.05 (0.09–0.43)	0.16 ± 0.06 (0.01–0.46)
Pyrene (Pyr)	0.13 ± 0.06 (0.09–0.24)	0.19 ± 0.08 (0.05–0.31)	0.12 ± 0.04 (0.04–0.24)
Benz[*a*]anthracen(BaA)	0.06 ± 0.03 (0.02–0.10)	0.11 ± 0.03 (0.03–0.58)	0.07 ± 0.03 (0.01–0.15)
Chrysene (Chr)	0.09 ± 0.04 (0.01–0.25)	0.08 ± 0.03 (0.02–0.33)	0.09 ± 0.03 (0.01–0.13)
Benzo[b]fluoranthene (BbF)	0.30 ± 0.13 (0.04–0.93)	0.51 ± 0.15 (0.02–1.74)	0.10 ± 0.03 (0.05–0.25)
Benzo[k]fluoranthene (BkF)	0.07 ± 0.03 (0.03–0.11)	0.13 ± 0.05 (0.06–0.27)	0.06 ± 0.02 (0.03–0.11)
Benzo[a]pyrene (BaP)	0.14 ± 0.08 (0.05–0.26)	0.11 ± 0.04 (0.07–0.22)	0.09 ± 0.03 (0.03–0.14)
Indeno[1,2,3,cd]pyrene (Ind)	0.13 ± 0.06 (0.11–0.50)	0.08 ± 0.04 (0.04–0.13)	0.07 ± 0.02 (0.06–0.22)
Dibenz[a,h]anthracene (DBA)	0.10 ± 0.04 (0.01–0.16)	0.23 ± 0.13 (0.05–0.41)	0.18 ± 0.05 (0.03–0.47)
Benzo[g,h,i]perylene (BPe)	0.17 ± 0.10 (0.06–0.36)	0.36 ± 0.26 (0.06–0.89)	0.11 ± 0.04 (0.01–0.30)
ΣPAH	2.70 ± 1.23	4.54 ± 2.06	3.67 ± 1.53

Table 10 Proportion of Nap–Flt species sum as a % of total PAH, ratio of BPe/Ind and BaP_{eq} values at Point Block

Floor	Nap–Flt (% of total PAH)	BPe/Ind	BaP_{eq} (ng/m^3)
Low floor	54	1.36 ± 0.2	0.69 ± 0.33 (0.14–1.21)
Mid floor	56	1.63 ± 0.6	1.34 ± 0.63 (0.59–2.17)
High floor	78	1.57 ± 0.4	1.15 ± 0.78 (0.17–2.45)
Overall total			1.06 ± 0.64 (0.14–2.45)

Values in bracket are minimum and maximum values

particulate PAH concentrations, with diesel engine vehicles contributing a higher percentage of particulate PAHs to the different floors of the building.

Using the TEF values proposed by Nisbet and LaGoy (1992), for particulate PAH inhalation, the mean BaP_{eq} value for the point block slightly exceeded the maximum permissible risk level of 1 ng/m^3 of benzo(a)pyrene. Based on the BaP_{eq} values, mid floor residents have the highest potential cancer risk compared to those residing in the low and high floors of the building. The high floor residents had the second highest potential cancer risk followed by the low floor residents. The BaP_{eq} value of the lower floor was about 69% of maximum permissible risk level.

For the slab block, the mean concentration levels of total particulate PAHs ranged from 4.67 to 6.79 ng/m^3. The overall total concentrations of particulate PAHs for the block is 6.0 ± 1.88 ng/m^3 (3.19–10.26 ng/m^3). For the block, the highest mean total PAH concentration occurred at the lower floor which did not vary significantly up to the mid floor and thereafter gradually decreased all the way to the upper floor of the building. The dominant particulate PAHs measured at the block are Nap, Phe, Flt and BPe. The distribution of the mass concentrations of particulate PAH species at the slab block is presented in Table 11. The vertical distribution profile of more volatile PAHs to total PAHs (sum of Nap–Flt as a % of total PAH) remained almost the same from the low floor to mid floor and increased from the mid floor to the high floor as shown in Table 12. Based on the BPe/Ind ratio values shown in Table 12, the results suggested a mixture of both diesel and petrol engine type of vehicles contributing to the particulate PAH concentrations, with diesel engine vehicles contributing a higher percentage of particulate PAHs concentrations to the different floor levels of the building.

For the slab block, the overall mean BaP_{eq} value was slightly below the maximum permissible risk level of 1 ng/m^3 of benzo(a)pyrene. Based on the BaP_{eq} values, low floor residents have the highest potential cancer risk compared to those residing in the mid and high floors of the building. The BaP_{eq} values at the mid and high floors were about 72 and 64% of maximum permissible risk level, respectively. For floors whose BaP_{eq} values fall below the maximum permissible risk level of 1 ng/m^3 of benzo(a)pyrene, the maximum permissible risk level is most likely to be exceeded since the vehicle counts and the number of trips per vehicle in Singapore keep on increasing over the years. The World Health Organization (WHO 1987) suggested that exposure to BaP at a concentration of 1 ng of BaP per m^3 of air, throughout life, carried a risk of lung cancer of 1 in 10,000 or 0.0001%.

Table 11 Profile of particulate PAHs at slab block

PAH	Mean concentration (ng/m^3)		
	Low floor	Mid floor	High floor
Naphthalene (Nap)	1.54 ± 0.81 (0.69–2.60)	1.16 ± 0.68 (0.56–2.16)	0.93 ± 0.46 (0.50–1.76)
Acenaphthene (Ace)	0.21 ± 0.18 (0.03–0.54)	0.06 ± 0.03 (0.01–0.11)	0.05 ± 0.02 (0.01–0.11)
Acenaphthylen (Acy)	0.35 ± 0.25 (0.02–0.58)	0.52 ± 0.17 (0.01–2.17)	0.19 ± 0.04 (0.06–0.42)
Fluorene (Flu)	0.38 ± 0.19 (0.18–0.64)	0.56 ± 0.10 (0.16–1.96)	0.23 ± 0.07 (0.08–0.31)
Phenanthren (Phe)	0.76 ± 0.34 (0.38–1.23)	0.68 ± 0.23 (0.42–0.98)	0.52 ± 0.14 (0.35–0.73)
Anthracene (Ant)	0.03 ± 0.01 (0.01–0.08)	0.09 ± 0.02 (0.01–0.13)	0.06 ± 0.02 (0.01–0.11)
Fluoranthene (Flt)	0.98 ± 0.17 (0.76–1.28)	0.95 ± 0.12 (0.71–1.10)	0.98 ± 0.16 (0.73–1.15)
Pyrene (Pyr)	0.23 ± 0.10 (0.01–0.33)	0.21 ± 0.11 (0.02–0.38)	0.14 ± 0.05 (0.01–0.38)
Benz[*a*]anthracen(BaA)	0.31 ± 0.25 (0.02–0.70)	0.47 ± 0.12 (0.14–0.81)	0.27 ± 0.10 (0.01–0.64)
Chrysene (Chr)	0.40 ± 0.19 (0.13–0.69)	0.28 ± 0.09 (0.01–0.65)	0.31 ± 0.09 (0.01–0.72)
Benzo[b]fluoranthene (BbF)	0.23 ± 0.09 (0.02–0.50)	0.13 ± 0.05 (0.02–0.30)	0.18 ± 0.06 (0.02–0.48)
Benzo[k]fluoranthene (BkF)	0.17 ± 0.05 (0.01–0.52)	0.43 ± 0.15 (0.03–1.74)	0.08 ± 0.03 (0.04–0.32)
Benzo[a]pyrene (BaP)	0.20 ± 0.07 (0.02–0.46)	0.22 ± 0.07 (0.02–0.38)	0.11 ± 0.05 (0.01–0.57)
Indeno[1,2,3,cd]pyrene (Ind)	0.35 ± 0.10 (0.01–0.97)	0.39 ± 0.16 (0.03–1.38)	0.30 ± 0.11 (0.02–0.62)
Dibenz[a,h]anthracene (DBA)	0.20 ± 0.06 (0.01–0.84)	0.11 ± 0.04 (0.01–0.31)	0.10 ± 0.04 (0.01–0.25)
Benzo[g,h,i]perylene (BPe)	0.45 ± 0.13 (0.03–1.13)	0.45 ± 0.22 (0.02–1.22)	0.22 ± 0.08 (0.01–0.61)
ΣPAH	6.79 ± 2.99	6.71 ± 2.36	4.67 ± 1.52

Table 12 Proportion of Nap–Flt species sum as a % of total PAH, ratio of BPe/Ind and BaP_{eq} values at slab block

Floor	Nap–Flt (% of total PAH)	BPe/Ind	BaP_{eq} ng/m^3
Low floor	62	1.36 ± 0.3	1.36 ± 1.86 (0.17–3.49)
Mid floor	60	0.92 ± 0.2	0.72 ± 0.54 (0.33–1.83)
High floor	65	1.41 ± 0.4	0.64 ± 0.67 (0.10–1.57)
Overall total			0.94 ± 1.22 (0.10–4.59)

Values in bracket are minimum and maximum values

Table 13 Daily mass concentration of WS trace metals at point block

Metals	Low floor	Mid floor	High floor
Al	662.43 ± 10.32	936.56 ± 15.16	711.24 ± 16.84
Co	3.65 ± 0.81	2.04 ± 0.21	4.74 ± 0.56
Cr	13.47 ± 3.42	14.63 ± 4.02	12.36 ± 2.48
Cu	201.62 ± 25.53	160.95 ± 28.74	101.89 ± 15.35
Fe	230.84 ± 11.06	202.52 ± 17.32	254.98 ± 20.95
Mn	43.67 ± 5.40	31.26 ± 5.39	13.54 ± 3.87
Pb	144.24 ± 13.17	87.77 ± 8.52	28.43 ± 4.49
Cd	4.35 ± 1.05	6.84 ± 0.98	3.79 ± 1.25
Ni	5.12 ± 1.17	4.93 ± 0.55	3.82 ± 0.38
As	6.08 ± 2.46	5.16 ± 1.91	3.75 ± 1.16
Ag	4.82 ± 1.76	3.58 ± 0.94	4.05 ± 0.69
Ti	143.51 ± 13.48	162.49 ± 16.53	177.81 ± 18.36
Zn	9.86 ± 3.61	5.51 ± 1.44	4.80 ± 1.68
V	3.02 ± 0.52	2.67 ± 0.48	1.94 ± 0.67
Total	1476.68	1620.07	1327.14
Total in μg/m^3	1.477	1.620	1.327

All values in ng/m^3

4.6.4 WS Trace Metals

Many trace metals are present in leaded and unleaded petrol, diesel oil, anti-wear substances added to lubricants, brake pads and tyres, and are emitted by vehicle exhaust pipes (Caselles et al. 2002). Soluble metals have been implicated in particulate matter-associated respiratory or cardiopulmonary disease in healthy and compromised individuals (Frampton et al. 1999; Chapman et al. 1997). Since man has about 70% body mass as water and given the solubility of WS trace metals in water, WS metals possess an appreciative damage to our health.

The daily mass concentrations WS trace metals found in $PM_{2.5}$ samples at the point block is presented in Table 13. The highest total mass concentration of trace metals occurred at the mid floor of the building. Trace metals accounted for about 3.6% at the low floor, 2.9% at the mid floor and 4.3% at the high floor of the $PM_{2.5}$ mass concentration. Based on the simple comparison of the magnitude, the data

Table 14 Daily mass concentration of WS trace metals at slab block

Metals	Low floor	Mid floor	High floor
Al	702.86 ± 15.14	995.37 ± 20.57	689.29 ± 13.05
Co	4.38 ± 0.45	3.69 ± 0.67	5.69 ± 0.22
Cr	20.60 ± 5.28	26.25 ± 3.88	18.19 ± 3.31
Cu	257.63 ± 30.42	221.84 ± 25.16	164.71 ± 22.29
Fe	265.18 ± 19.33	272.01 ± 20.04	193.15 ± 16.56
Mn	54.72 ± 6.74	44.93 ± 4.20	27.73 ± 5.97
Pb	128.43 ± 15.49	98.37 ± 12.18	56.99 ± 10.52
Cd	5.22 ± 2.15	8.92 ± 0.83	5.03 ± 2.47
Ni	6.50 ± 0.64	6.45 ± 0.81	5.90 ± 1.22
As	6.27 ± 1.36	7.94 ± 1.95	4.88 ± 1.39
Ag	6.01 ± 1.32	5.26 ± 0.77	4.51 ± 1.08
Ti	179.38 ± 16.75	186.24 ± 19.03	194.72 ± 14.57
Zn	13.42 ± 2.84	9.52 ± 1.91	6.75 ± 1.53
V	3.83 ± 0.62	3.65 ± 0.73	2.52 ± 0.46
Total	1654.43	1890.44	1380.06
Total in μg/m^3	1.654	1.890	1.380

All values in ng/m^3

sets can be grouped into three categories: (1) <1–0 ng/m^3: Co, Cd, Mn, Ni, As, Ag, Zn and V; (2) <10–100 ng/m^3: Cr and Mn; and (3) >100 ng/m^3: Al, Cu, Fe, Pb, Ti. Al followed Fe dominated all floors of the building. Cu and Ti are generally present in bulk amount at all the floors.

For the slab block, the daily mass concentrations WS trace metals found in PM$_{2.5}$ samples is presented in Table 14. The highest total mass concentration of trace metals occurred at the mid floor. Trace metals account for about 3.0% at the lower floor, 2.7% at the mid floor and 3.2% at the upper floor of the PM$_{2.5}$ mass concentration. Based on the simple comparison of the magnitude, the data sets can be grouped into three categories: (1) <1–10 ng/m^3: Co, Cd, Ni, As, Ag and V; (2) <10–100 ng/m^3: Cr, Zn and Mn; and (3) >100 ng/m^3: Al, Cu, Fe, Pb, Ti. Al, Cu and Fe dominated all floors of the building. Ti is generally present in bulk amount at all the floors.

In a study done in Singapore by Balasubramanian and Qian (2003), it was reported that Al, Fe and Ti is attributed to construction activities and road dust. Ag, Cd, Cr and Mn appeared to be related to metallurgical industry and motor vehicles while Cu, Pb and Zn are from combustion sources such as biomass burning and vehicular emissions. Zn has been known to be emitted by from motor vehicles. V, Ni and Co were fuel–oil combustion-related pollutants and the sources were related to diesel-driven vehicles and industrial sources involving fossil fuel combustion. Other studies have shown high correlations among the crustal elements Al, Ca, Fe, Mg and Ti in a study in Hong Kong (Ho et al. 2003). Crustal elements originates from soil and road dust. In a study in Sicily, it was found traffic appeared to be responsible for the high levels of Ba, Cu, Cr, Mo, Pb, Sb and Zn (Manno et al. 2006).

5 Reconstruction of Chemical Composition of Traffic-Generated Particles

The chemical composition of the samples was reconstructed from the observed elemental composition using the reconstruction procedure used in the USA IMPROVE study (Eldred et al. 1988). The reconstructed chemical composition was based on the mean mass concentrations of $PM_{2.5}$ at the various floors of the blocks as shown in Figs. 6 and 7.

The results in the point block showed that the seven major components accounted for about 88% of $PM_{2.5}$ mass for the low floor, 95% for the mid floor and 80% for the high floor of the block. The major components of the site were organic matter (29–38%), elemental carbon (12–23%) and sulfate (9–14%).

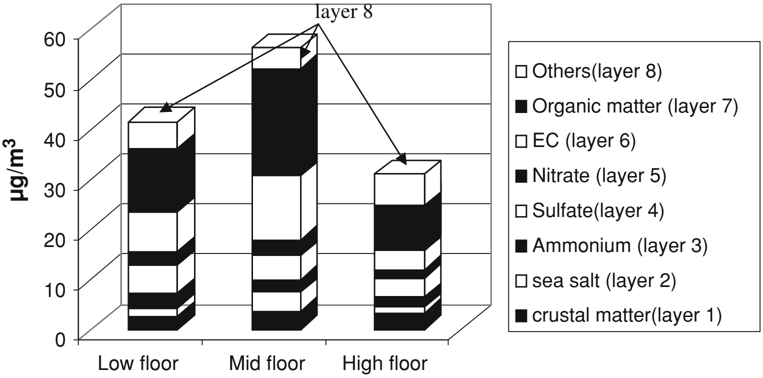


Fig. 6 Mass balance of PM2.5 at point block

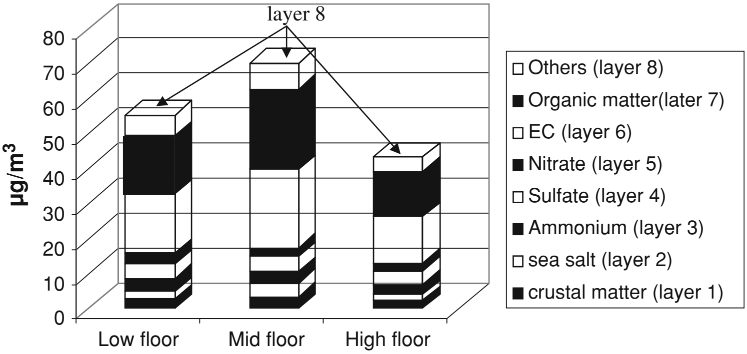


Fig. 7 Mass balance of $PM_{2.5}$ at slab block

Carbonaceous species alone accounted for about 50% of $PM_{2.5}$ mass for the low floor, 61% for the mid floor and 41% for the high floor of the block.

For the slab block, the seven major components of the reconstructed $PM_{2.5}$ mass accounted for about 89% of $PM_{2.5}$ mass for the low floor, 89% for the mid floor and 90% for the high floor of the block. The major components of the site were organic matter (32–36%), elemental carbon (32–37%) and sulfate (7–12%). Carbonaceous species alone accounted for about 68% of $PM_{2.5}$ mass for the low floor, 70% for the mid floor and 69% for the high floor of the block. The reconstructed carbonaceous species were similar to a study by Yu (2002) who reported the total OC and EC mass accounted for about 58–68% of $PM_{2.5}$ mass concentration in a sampling site close to a roadside in Hong Kong. From the reconstructed chemical composition of $PM_{2.5}$ mass, it can be seen that traffic-generated particles contribute to a large extent to the toxicity of outdoor aerosols.

6 Conclusion

6.1 Vertical Distribution Profile of Traffic-Generated Particulate Matter

For both the buildings, experimental results explicitly showed that the daily mean $PM_{2.5}$ mass concentration was highest at the mid floor of the building when compared to those measured at the low and high floors of the building for a typical day regardless of the building configuration. Although the low floors were closest to traffic emissions, the mean particle mass concentration was lower there than that at the mid floors, which could presumably be due to the interception of $PM_{2.5}$ particles by tree leaves or the inflow of clean and drier air from higher altitude with lower aerosol burden mixing with the traffic-polluted air at the lower levels or both. The high floors had the least fine particulate matter mass concentration due to dilution following pronounced mixing of traffic-polluted air with ambient air. The only difference between point block and slab block is that at corresponding floors, the mass concentration levels for slab block are much higher than those of point block under similar meteorological and traffic conditions. The results further support the hypothesis that PM concentrations decrease with increasing height of building is not correct at least in the context of Singapore. The reason could be that in this study, the green belt, which is a unique feature for the naturally ventilated high-rise residential buildings that are in close proximity to expressways, could have had an influence on the vertical distribution profile of the traffic-generated fine particulate matter in these buildings. In other studies, there was no green belt present between the road and building.

6.2 Health Impacts of Traffic-Generated Particulate Matter

6.2.1 Physical Characteristics

For both the buildings, the daily mean mass concentration levels of traffic-generated $PM_{2.5}$ at the various floors of the buildings either exceeded the $PM_{2.5}$ NAAQS annual average value of 15 μg/m^3 or the 24 h value of 35 μg/m^3. The study also showed about 94% of the particles fall below the size range of 0.65 μm while the rest 6% of the particles were in the size range of 0.65–1.6 μm. The size distribution show that majority of the traffic-generated particles has a very high chance of penetrating deeper into the lungs. Toxicological studies have implicated fine and ultra fine particles have considerably enhanced toxicity per unit mass and their toxicity increased as particle size decrease. Residents living close to the expressway have a high chance of developing cancer or respiratory disease. This was supported by the health risk models used in the study.

6.2.2 Chemical Characteristics

For both the buildings, Na^+, NH_4^+, Ca^{2+}, K^+, Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} were detected. Although studies have shown inorganic compounds can cause small adverse health effects to people, they may also facilitate the toxicity of other compounds. For example, sulfate does not act as a direct toxicant, but facilitates the toxicity of reactive metal constituents, e.g., it may play a role in the generation of ROS by functioning as a ligand for particle associated iron. WS trace metals such as Cr, Ni, Cd, Co and Pb were detected in all the samples of both the blocks. IARC has classified Cr together with Ni, Cd and arsenic as known human carcinogens and two others, Pb and cobolt, as probable human carcinogens. Since WS trace metal compounds are present in the fine fraction, they can penetrate deep into the lungs and may cause serious pollution-related respiratory health problems. The dominant particulate PAHs measured at the buildings are Nap, Acy, BbF, Phe, Flt and BPe. Many studies have reported the mutagenic or carcinogenic effects of PAHs. IARC has identified BaA, BaP, DBA, BkF, Ind, BbF and Nap to be carcinogenic compounds. Chemical analysis of the traffic-generated particles shows the toxicity of these particles.

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Semi-volatile Organic Pollutants in the Gaseous and Particulate Phases in Urban Air

Hua Wei and An Li

1 Introduction

There is no clear and widely accepted definition of semi-volatile organic compounds (SVOCs) or simply semivolatiles. Because volatile organic compounds (VOCs) are often considered as compounds with boiling point temperature below 150 °C and vapor pressure greater than 0.1 mmHg (USEPA 2009a), semivolatiles should be those with higher boiling point temperature and lower vapor pressure than VOCs, but still substantially partition into air once released to the environment. In practice, VOCs and SVOCs are often operationally defined based on sampling and laboratory analytical procedures.

The atmosphere has been widely recognized as an important route for SVOCs to disperse in the environment on local, regional and global scales. After being released to the atmosphere, SVOCs are present in both gas and particle phases in the air. SVOCs can be transported with wind, transformed by direct and indirect photolysis during the transport, and removed from the atmosphere by wet and dry deposition. However, gaseous and particle-bound SVOCs may behave differently in the atmosphere. In general, gaseous SVOCs would be more mobile and liable to photolysis compared to those particle-bound. As such, the partitioning between the gas and particle phases is a key factor that significantly affects all the processes in the atmosphere, and the overall environmental fate of SVOCs.

The gas-particle partitioning refers to the propensity for a "typical" molecule of the chemical to exist between the two phases, and is characterized by the partition coefficient K_p. The value of K_p is dependent of not only the physicochemical properties of the chemical such as vapor pressure (P°) and octanol-air partition coefficient (K_{oa}), but also the concentration, size distribution, and chemical

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_16,

composition of the airborne particles as well as the meteorological conditions. Theories have been established to describe and predict the distribution of organic compounds between the gas and particle phases. The most well known are the Junge–Pankow adsorption model and Pankow absorption model using subcooled liquid vapor pressure (Pankow and Bidleman 1992; Pankow 1994), and absorption model using K_{oa} of SVOCs (Harner and Bidleman 1998).

2 Ubiquitous SVOCs in Urban Air

Among the major ubiquitous SVOC pollutants in the urban air worldwide are polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs). Their chemical structures are presented in Figs. 1, 2. Theoretically, there are 57 individual PAHs which contain 2–6 fused six-member benzenoid rings only (Harvey 1997). There are 209 individual PCB congeners and 209 individual PBDE congeners, varying in the number and positions of the substitutions by chlorine and bromine, respectively.

2.1 Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons are a group of chemicals that consist of fused aromatic rings without heteroatoms or substituents. PAHs are usually found in natural crude oil, coal deposits and asphalt. They are also formed from the biosynthesis of phytoplankton and bacteria (Laflamme and Hites 1978). However, the major sources of PAHs found in ambient air are the incomplete combustion of carbon-containing fuels such as wood, coal, diesel, fat, tobacco, or garbage or other organic substances (ATSDR 1995). As a result, anthropogenic emissions outweigh natural ones as the major sources of PAHs in the atmosphere (Masclet et al. 1986; Harrison et al. 1996; Lee et al. 2001). Sixteen PAHs are classified by the United States Environmental Protection Agency (USEPA) as priority pollutants (ATSDR 2005). USEPA has determined that benz[a]anthracene, benzo[a]-pyrene, benzo[b]fluoranthene, benzo[k]fluoranthene, chrysene, dibenz[a,h]anthracene, and indeno[1,2,3-c,d]pyrene are probable human carcinogens (National Toxicology Program 2005).

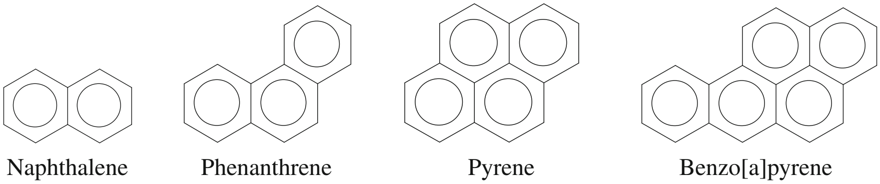
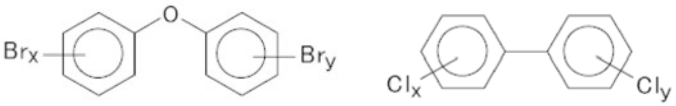


Fig. 1 Structures of selected PAHs



PBDEs (x+y = 1~10) PCBs (x+y = 1~10)

Fig. 2 General structures of PBDEs and PCBs

The relative abundance among the 16 PAHs in urban air strongly depends on the type of emission sources. Naphthalene dominates in both indoor and outdoor air in most cases. Numerous studies also found low molecular weight PAHs are relatively abundant in the atmosphere compared with high molecular weight ones (Chuang et al. 1991; Naumova et al. 2002; Ohura et al. 2004). A study conducted in Chicago found that PAHs with less than four rings behave differently than those of more rings, with the former having higher concentration in the indoor air than in the outdoor air, while the opposite was found for the latter (Li et al. 2005).

2.2 *Polychlorinated Biphenyls*

Polychlorinated biphenyls were commercially produced for over 50 years from 1929 to the 1980s worldwide (Breivik et al. 2002). Commercial PCBs were widely used in a variety of equipment and consumer products, including dielectric fluids in electrical transformers and capacitors, fluids in hydraulic and heat transfer systems, lubricating and cutting oil, paints, plastics, sealants and adhesives (Erickson 1997). Although banned more than two decades ago, PCBs are still found in all environmental compartments including surface seawater (Sobek et al. 2004), soils (Meijer et al. 2003), ambient air (Motelay-Massei et al. 2005) and sediment (Li et al. 2009). PCBs have been found in marine plants, fish, mammals, birds, bird eggs and humans (Erickson 1997). PCBs have been demonstrated to cause a variety of adverse health effects on the immune system, reproductive system, nervous system, and endocrine system; USEPA categorized PCBs as probable human carcinogens (USEPA 2009b).

In general, PCB concentrations are decreasing slowly in the environment in the recent decades (Panshin and Hites 1994; Hillery et al. 1997; Haugen et al. 1999; Hung et al. 2001). However, a limited number of recent studies (Hu et al. 2008; Rodenburg et al. 2009) have found that PCB11 (3,3′- dichlorobiphenyl), a congener that was present at only 0.6% in the PCB products, is widespread and accounts for significant portions of the total PCBs currently found in the environment. This finding suggested continuous emissions of this congener, likely as a byproduct of pigment and paint productions. Studies reported that individual PCB congeners in ambient air were dominated by low-chlorinated congeners, including di-, tri- and tetra-chlorinated biphenyls (Mandalakis and Stephanou 2007).

2.3 Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers are a group of brominated flame retardants massively produced and extensively used around the world in a wide array of products, including building materials, electronics, furnishings, vehicles, airplanes, plastics, polyurethane foams, and textiles. PBDE production started from the 1960s and the global market sales reached 67,000 metric tons by 2001 (BSEF 2003). The market demand for PBDEs has been dominated by three commercial mixtures, penta-, octa- and deca-BDEs, which are manufactured with tetra- to deca-BDE congeners at various proportions (van Esch 1994). Due to their extensive use, PBDEs have contaminated both indoor and outdoor environment. They were found in environmental and human samples literally everywhere (Hale et al. 2003; Hites 2004; Schecter et al. 2005; Dye et al. 2007). Many studies have reported the levels of PBDEs in the atmosphere (Ohta et al. 2002; Agrell et al. 2004; Farrar et al. 2004; Hayakawa et al. 2004; Jaward et al. 2004; Lee et al. 2004; Pozo et al. 2004; Harner et al. 2006) and in work environments (Bergman et al. 1999; Sjödin et al. 2000; Harrad et al. 2004; Pettersson-Julander et al. 2004), however, only a few have systematically investigated the distribution of PBDEs between the gas and particle phases (Strandberg et al. 2001; Shoeib et al. 2004; Hoh and Hites 2005; Chen et al. 2006; Cetin and Odabasi 2008; Mandalakis et al. 2009).

Because PBDEs are mainly used in the indoor environment, their concentrations are usually orders of magnitude higher in indoor air than outdoor air, which will be discussed in the next section. Shoeib et al. (2004) reported an average PBDE concentration of 1,518 pg/m^3 for four house air samples. Allen et al. (2007) reported geometric mean of 69 pg/m^3 for non-209 BDEs and 174 pg/m^3 of BDE209 in the air of 20 residential houses in Boston, MA. Harrad et al. (2006) reported average air concentration of 273 pg/m^3 for total PBDEs in indoor environments in Midlands, UK.

On the basis of individual congeners, PBDEs in ambient air was dominated by BDEs 47, 99 and 100. The higher amount of these congeners in the ambient air is indicative of the source emission of penta commercial products treated materials (Mandalakis et al. 2009). While with heavier congener included, numerous studies found BDE209 was generally dominant. Wei et al. (2009) observed the dominance of heavier PBDE congeners in Chicago ambient particles, including BDEs 209, 206 and 207; BDE209 was the most abundant; the concentration levels of BDE206 and 207 were similar to BDE47 and 99, respectively. Cetin and Odabasi (2008) also reported the dominance of BDE209 followed by BDEs 99 and 47 in the four sampling sites of Izmir, Turkey. Chen et al. (2006) reported that BDE209 was the dominant (>48%) in China. In southern Ontario, Gouin et al. (2006) reported BDE-209 concentration one order of magnitude higher than BDE 47 and 99. BDE209 was also detected at relatively high concentrations compared to other PBDE congeners in most samples from Japan (Hayakawa et al. 2004).

2.4 Concentration Levels of SVOC in the Atmosphere

Numerous studies have reported the concentrations of SVOCs in the atmosphere around the world. Presented in Table 1 are some published data. The concentrations for each group of SVOCs varied significantly among different cities or even within a city. Generally speaking, the levels of PBDEs and PCBs in urban atmosphere in recent years were comparable, while PAH concentration level was orders of magnitude higher than PCBs and PBDEs.

3 Airborne Particles

There are various solid or liquid particles suspended in air, which are often collectively called particulate matter (PM). These particles are usually individually invisible to the naked eyes, yet together they form a "phase" of the atmosphere although the volume of this phase is very small compared with the gas phase under normal conditions.

3.1 Particle Size

The size of airborne particles varies over a range roughly from a few nanometers to hundred micrometers. In particular, PM10 and PM2.5 are used to refer to the PM with the diameter of individual particles smaller than 10 and 2.5 μm, respectively. The concentration of total suspended particles (TSP) was used as one of the air quality criteria set by the US EPA until 1986. Currently, the concentrations of both PM10 and PM2.5 are used to indicate particle pollution of the ambient air in the USA.

Adverse health effects can arise from the inhalation of suspended particles in urban areas. Smaller particles are more likely to stay airborne longer or be re-suspended from surfaces upon disturbing, increasing the likelihood of inhalation and associated health risk. Moreover, smaller particles can penetrate deeper into the respiratory system and accumulate in the lower parts of the lungs, posing a greater risk to human health.

Because of the larger specific surface area of finer particles, chemicals with strong surface affinity tend to be enriched in fine fractions of particulate samples if surface adsorption is the controlling mechanism (Wei et al. 2009). In addition, particle size is the major factor determining the atmospheric behavior of particle-bound SVOCs, including the removal from the air, residence time, transport potential, and photolytic transformation. Fine-particle-bound SVOCs, like those in the gas phase, are susceptible to long-range transport via the air flow thus are able to disperse to remote areas such as the north and south poles. So far, studies have

Table 1 Reported SVOC atmospheric concentration levels around the world

Location	Sampling year	n[a]	Chemical	Gaseous pg/m^3	Particle bound pg/m^3	N[b]	Refs.
Heraklion, Greece	2006	6	PBDEs	3–40 (ave 13)	1–4 (ave 2)	12	Mandalakis et al. (2009)
Athens, Greece	2006	2	PBDEs	6–7 (ave 7)	15–23 (ave 19)	12	Mandalakis et al. (2009)
Birmingham, UK	2002–2003	6	PBDEs	10–33 (ave 21)		5	Harrad et al. (2004)
Malmö, Sweden	2001–2002	36	PBDEs	0–193 (ave 37)		9	Agrell et al. (2004)
Izmir, Turkey (Summer)	2004–2005	4	PBDEs	11–149 (ave 64)		7	Cetin and Odabasi (2008)
Izmir, Turkey (Winter)	2004–2005	4	PBDEs	6–81 (ave 39)		7	Cetin and Odabasi (2008)
Toronto, Canada	2000	23	PBDEs	5–30		15	Harner et al. (2006)
Chicago, USA	1997–1999	12	PBDEs	33–77 (ave 50)		7	Strandberg et al. (2001)
Chicago, USA	2002–2003		PBDEs	ave 100 ± 35		26	Hoh and Hites (2005)
Kyoto, Japan	2000–2001	5	PBDEs	1.5–58 (ave 17)		10	Hayakawa et al. (2004)
Toronto, Canada	2001	2	PBDEs	39–48		10	Shoeib et al. (2004)
Guangzhou, China	2004	32	PBDEs	180–11,634 (ave 2,447)		11	Chen et al. (2006)
Eastern Germany	2001	14	PCBs	36–374 (ave 110)		54	Mandalakis and Stephanou (2007)
Chicago, USA	1994–1995	31	PCBs	270–14,200 (ave 2,251)	DL-590 (ave 116)	87	Simcik et al. (1997)
Chicago, USA	2007	37	PCBs	75–5,500 (ave 835)		209	Hu et al. (2008)
Chicago, USA	1997–1999	12	PCBs	2,900–4,100 (ave 3,100)		105	Strandberg et al. (2001)
Chicago, USA	1988	11	PCBs	300–9,900 (ave 2,100)		34	Cotham and Bidleman (1995)
Toronto, Canada	2000–2001	21	PCBs	66–1,350		13	Motelay-Massei et al. (2005)
Manchester, Clapham, Austwick, UK	1998	12	PCBs	51–720		14	Lohmann et al. (2000)

Table 1 (continued)

Location	Sampling year	n[a]	Chemical	Gaseous pg/m^3	Particle bound pg/m^3	N[b]	Refs.
Athens, Greece	2000	4	PCBs	345 ± 152	3.7 ± 0.4	38	Mandalakis et al. (2002)
Tianjin, China	2004	6	PAHs		144–308 ng/m^3	16	Wu et al. (2006)
Korea	2000	4	PAHs		22.9–410 ng/m^3 (ave 139)	15	Bae et al. (2002)
Chicago, USA	1988	11	PAHs	75–1,410 ng/m^3 (ave 507)		13	Cotham and Bidleman (1995)
Chicago, USA	1994–1995	30	PAHs	27–430 ng/m^3 (ave 122)	3.2–460 ng/m^3 (ave 46)	19	Simcik et al. (1997)
Chicago, USA	2000	108	PAHs		4–180 ng/m^3 (ave 42)	16	Li et al. (2005)
Los Angeles, USA	2000		PAHs	4.2–64 ng/m^3		30	Naumova et al. (2002)
Houston, USA	2000		PAHs	10–160 ng/m^3		30	Naumova et al. (2002)
Elizabeth, NJ, USA	2000		PAHs	12–110 ng/m^3		30	Naumova et al. (2002)
Fuji and Shimizu, Japan	1999–2000		PAHs	72–1,775 ng/m^3		39	Ohura et al. (2004)
Ontario, Canada	2001–2002	67	PAHs	1.3–70 ng/m^3 (ave 11)	0.011–15 ng/m^3 (ave 1.8)	12	Su et al. (2006)
Heraklion, Greece	2000–2002	16	PAHs	31.4–84.7 ng/m^3 (ave 61.9)	3.2–44.9 ng/m^3 (ave 17.4)	24	Tsapakis and Stephanou (2005)
Toronto, Canada	2000–2001	21	PAHs	3.5–61.4 ng/m^3 (ave 61.9)		17	Motelay-Massei et al. (2005)

Ave average of reported concentrations

[a] Number of samples analyzed

[b] Number of chemicals included

found that particle-bound PAHs are mainly associated with fine particles (Aceves and Grimalt 1993; Kaupp and McLachlan 1998; Kiss et al. 1998; Guo et al. 2003); and higher molecule weight PAHs are more associated with finer particle than lower molecule weight ones (Allen et al. 1996; Offenberg and Baker 1999; Kaupp and McLachlan 2000; Wu et al. 2006). A limited number of studies have focused on the size distribution of particle bound PBDEs (Mandalakis et al. 2009) and PCBs (Lee et al. 1996). They were found to be primarily associated with the fine particles, especially the heavy congeners (Mandalakis et al. 2009). However, in the studies on the urban sites of India and Taiwan, PAHs and PCBs were found to be mostly in the coarse particles or to be bimodal (Chen et al. 1996; Lee et al. 1996; Venkataraman et al. 1999).

3.2 Composition of Airborne Particles

The airborne particles differ significantly not only in size but also in chemical composition, depending primarily on the sources of the particles. Desert and other bare lands are sources of dust particles which are primarily made of mineral oxides. Sea salt originated from sea spray consists mainly of sodium chloride. Soil tillage in agriculture produces dust particles characterizing the land surface. In contrast, urban dust is often rich in cement powder, tire scraps, car exhaust particulate. Soot particles generated from various combustion processes are essentially elemental carbon. Combustion also produces fly ash which is rich in oxides and contains toxic metals.

Particularly relevant to the gas-particle partitioning of SVOCs is the carbonaceous fraction of the particles, including organic matter (OM) as well as the elemental carbon (black carbon or soot). The weight fraction of OM, f_{OM}, is an important independent variable in the prediction of K_p for SVOCs. Soot particles are highly porous with large nonpolar surface areas, which render them high affinity for SVOCs, particularly those with planar molecular structures such as PAHs.

4 SVOC Physicochemical Properties Related to Gas-particle Partitioning

4.1 Vapor Pressure

Vapor pressure, P°, is the partial pressure of a chemical in air when at equilibrium with its pure phase, either solid or liquid. P° is 1.0 atm for all gases and less than 1.0 atm for liquid and solid chemicals under normal environmental conditions at sea level.

Vapor pressure can be viewed as coefficients of partitioning between air and the pure chemical, or the equilibrium constant of the evaporation process for liquids. It is related to the free energy of the process, $\Delta_{\mathrm{vap}}G^\circ$:

$$\Delta_{\mathrm{vap}}G^\circ = -RT \ln P^\circ \tag{1}$$

where R is the universal gas constant and T is the temperature in Kelvin.

If the chemical of interest is a solid, it sublimates to pose its vapor pressure. The sublimation process can be viewed as the sum of processes of a hypothetical fusion (melting) to liquid and vaporization from liquid to gas at given temperature and pressure. Such liquid, of course, is hypothetical because it may not exist at the given condition. The vapor pressure of this hypothetical liquid, P_L°, rather than the true vapor pressure of the solid, P_S°, is often generated by various vapor pressure estimation models. P_S° can be converted to liquid vapor pressure P_L° using the fugacity ratio F:

$$P_S^\circ = F \times P_L^\circ \tag{2}$$

$$F = f_S/f_L \approx \exp[(-\Delta_{\mathrm{fus}}S/R) \times (T_m/T - 1)] \tag{3}$$

where f_S and f_L are the fugacity for solid and its hypothetical liquid, respectively; T_m and T are the melting point temperature and the temperature of interest, respectively, in Kelvin; and $\Delta_{\mathrm{fus}}S$ is the entropy of fusion, which reflects the increases in randomness when solids melt. For organic chemicals which are considered as “rigid”, $\Delta_{\mathrm{fus}}S$ value is approximately 56 J/K/mol. This value may be applied to PAHs, PCBs, PBDEs, and many others, to generate order of magnitude estimate for their fugacity ratio and vapor pressure. For flexible molecules such as those with long aliphatic chains, corrections must be made.

4.2 Octanol–air Partition Coefficient

The octanol/air partition coefficient, K_{oa}, is the ratio of the solute concentration in *n*-octanol to that in air when the octanol-air system is at equilibrium. It is a key descriptor of the absorptive partitioning of SVOCs between the atmosphere and organic phases found in soil, in vegetation, and on aerosols. The application of K_{oa} is based on the assumption that the interaction between the SVOCs and the environmental organic phases sufficiently resembles the interaction between the SVOCs and *n*-octanol.

K_{oa} and P° are related. If the K_{oa} is defined for an infinitely dilute solution of the chemical in octanol, the relationship of two parameters is expressed through the following equation (Goss and Schwarzenbach 1998):

$$K_{oa} = RT\big/\left(V_{\mathrm{oct},\infty}\gamma_{\mathrm{oct},\infty}P^\circ\right) \tag{4}$$

where R, T, $V_{oct,\infty}$ and $\gamma_{oct,\infty}$ are the ideal gas constant, temperature, the molar volume of octanol and the activity coefficient of the chemical in octanol at infinite dilution, respectively. The expression $1/(V_{oct,\infty}\ \gamma_{oct,\infty})$ is the solubility of the chemical in octanol if it were to have the same activity coefficient and molar volume as it does at infinite dilution. At dilute concentrations V_{oct} is the same for all chemicals (0.000158 $m^3\ mol^{-1}$), and the above equation can be transformed to the one below (Xiao and Wania 2003). The γ_{oct} can thus serve as a quantitative expression of the difference between the two partitioning properties P° and K_{oa}.

$$\mathrm{Log}\,K_{oa} = -\log P^{\circ} - \log \gamma_{oct} + \mathrm{constant} \tag{5}$$

5 Partition Coefficient between Gas and Particulate Phases

5.1 Definition of K_p

The distribution of SVOCs between the gas and particle phases in air at equilibrium is commonly described by the particle-gas partition coefficient K_p (Pankow 1994):

$$K_P = F/(A \times TSP) \tag{6}$$

where K_p is in $m^3/\mu g$, F is the concentration of the SVOC associated with particles in ng/m^3 particles, A is the gas phase concentration of the SVOC in ng/m^3, and TSP is the concentration of TSP in $\mu g/m^3$.

K_p is temperature dependent and log K_p has a linear relationship with the reciprocal of temperature: $\log K_p = A/T - B$, where A and B are constants that are specific to individual SVOCs (Yamasaki et al. 1982). Relative humidity also affects the particle-gas partitioning. Jang and Kamens concluded that humidity effect on partitioning was the most significant for hydrophobic compounds, such as PAHs, in polar particles (Jang and Kamens 1998). Pankow et al. found a significant negative linear correlation between relative humidity and log K_p for seven PAH compounds (Pankow et al. 1993).

Apparently, the value of K_p is specific to not only the concentration and composition of the airborne particles but also the physicochemical properties of the SVOC. Prediction equations of K_p from P° and K_{oa} have been derived and applied extensively. These are discussed further below. Comparison of the prediction accuracy using these two independent variables suggests negligible differences, due largely to the uncertainty in the measured K_{oa} and its correlation with P° (Xiao and Wania 2003).

5.2 Prediction of K_p Using Vapor Pressure

Usually, organic chemicals are associated with particles through two mechanisms: adsorption onto aerosol surface and absorption into aerosol OM. Both mechanisms drive gas/particle partitioning of SVOCs.

For adsorption onto the aerosol surface,

$$K_P = \frac{N_S \cdot A_{TSP} \cdot T \cdot e^{(Q_l - Q_v)/RT}}{1,600 p_{\mathrm{L}}^{\circ}} \tag{7}$$

where N_S is the surface concentration of sorption sites (sites/cm^2), A_{TSP} is the aerosol surface area (m^2/g), R is the gas constant (8.314 J/mol-K), T is the ambient temperature (K), Q_l and Q_v are enthalpies of desorption and vaporization, respectively (kJ/mol), and P_L° is the subcooled liquid vapor pressure of the SVOC (torr). It was proposed by Junge and critically reviewed by Pankow (Junge 1977; Pankow 1987).

For absorption into the particle OM,

$$K_P = \frac{f_{om} \cdot 760 \cdot RT}{MW_{om} \cdot \gamma_{om} \cdot p_{\mathrm{L}}^{\circ} \cdot 10^6} \tag{8}$$

where f_{om} is the fraction of OM in the TSP, MW_{om} is the average molecular weight of absorbing OM, γ_{om} is the activity coefficient of adsorbate in OM. The model was development by Pankow (1994).

The combination of both adsorption and absorption gives the particle/gas partition coefficient (Pankow 1994).

$$K_p = \frac{F}{A \cdot TSP} - \frac{1}{P_{\mathrm{L}}^{\circ}} \left[\frac{N_s \cdot A_{TSP} \cdot T \cdot e^{(Q_1 - Q_v)/RT}}{1,600} + \frac{f_{om} \cdot 760 \cdot RT}{MW_{om} \cdot \gamma_{om} \cdot 10^6} \right] \tag{9}$$

Both mechanisms and their combination have a similar linear relationship between log K_P and the logarithm of subcooled liquid vapor pressure P_L° (Pankow and Bidleman 1992; Pankow 1994), i.e.,

$$\log K_p = m \log P_L^{\circ} + b \tag{10}$$

Equation 10 is derived by taking the logarithm of the Eqs. 7–9: the intercept

$$b = \log \frac{N_s \cdot A_{TSP} \cdot T \cdot e^{(Q_1 - Q_v)/RT}}{1600}$$

for adsorption;

$$b = \log \frac{f_{om} \cdot 760 \cdot RT}{MW_{om} \cdot \gamma_{om} \cdot 10^6}$$

for absorption; and

$$b = \log\left(\frac{N_s \cdot A_{TSP} \cdot T \cdot e^{(Q_1 - Q_v)/RT}}{1600} + \frac{f_{om} \cdot 760 \cdot RT}{MW_{om} \cdot \gamma_{om} \cdot 10^6}\right)$$

for the combination. Therefore, the value of b mainly depends on the particle properties and temperature.

The relative importance of adsorptive and absorptive partitioning in a given situation will depend on the b values calculated above. Apparently, higher A_{tsp} and $(Q_1 - Q_v)$ will favor adsorption, while higher f_{om}, lower MW_{om}, and γ_{om} will favor absorption. Theoretically, $m = -1$ at equilibrium, assuming that N_s does not vary within a compound class and that $Q_1 - Q_v$ does not vary within a SVOC class for adsorption mechanism (Pankow and Bidleman 1992), or that γ_{om} does not vary within a compound class for absorption mechanism (Pankow 1994). Collectively, regardless of the dominance of adsorption or absorption, a slope of near -1 is expected when plotting log K_p values against log P_L°. In reality, although m values close to -1 were observed for some SVOCs measured with different samplers (Volckens and Leith 2003a), a variety of *m* values have been reported for SVOCs, which are summarized in Table 2. The variability of *m* values may be attributed to difference in sorbent effects (Goss and Schwarzenbach 1998), although nonequilibrium conditions and sampling artifacts cannot be ruled out (Pankow and Bidleman 1992; Cotham and Bidleman 1995; Falconer et al. 1995; Volckens and Leith 2003b).

5.3 Prediction of K_p Using K_{oa}

Studies suggest that activity coefficient γ_{om} in Pankow absorption model may vary substantially among different compounds (Liang and Pankow 1996; Jang et al. 1997). Based on logarithmic transformation of Pankow absorption model, octanol-air partition coefficient, K_{oa}, is suggested as an alternative to vapor pressure for describing absorption of SVOCs to particles (Harner and Mackay 1995; Finizio et al. 1997; Harner and Bidleman 1998). The relationship of K_{oa} and K_p was established accordingly (Finizio et al. 1997):

$$K_p = 10^{-9}\ K_{oa} f_{om} (\gamma_{oct}/\gamma_{om})/(MW_{oct}/MW_{om})/\rho_{oct} \quad (11)$$

where K_{oa} is the octanol–air partition coefficient of SVOCs, γ_{oct} and γ_{om} are the activity coefficients of the absorbing compound in octanol and aerosol OM, MW_{oct} and MW_{om} are the molecular weights of octanol (130 g/mol) and the OM, and ρ_{oct} is the density of octanol (820 kg/m^3).

With the assumptions that $\gamma_{oct}/\gamma_{om} \approx 1$ and $MW_{oct}/MW_{om} \approx 1$ and all of the OM is available to absorb gaseous SVOCs, K_{oa} absorption model can be expressed as the following (Harner and Bidleman 1998):

$$\text{Log}\,K_p = \log K_{oa} + \log f_{om} - 11.91 \quad (12)$$

Table 2 Coefficient of determination, slope and intercept of linearity of log K_p and P_L

Location	Air type	Chemical	Slope (m_r)	Intercept (b_r)	R^2	Refs.
Denver, USA	Urban	PCBs	−0.95	−5.86		Foreman and Bidleman (1990)
Chicago, USA	Urban	PCBs	−0.46	−4.04		Simcik et al. (1998)
Chicago, USA	Urban	PCBs	−0.73	−5.18		Cotham and Bidleman (1995)
Chicago, USA	Urban	PCBs	−0.72	−5.14		Harner and Bidleman (1998)
Manchester, UK	Urban	PCBs	−0.80 to −0.35	−5.5 to −3.8	0.57–0.98	Lohmann et al. (2000)
Clapham, UK	Rural	PCBs	−0.59 to −0.22	−4.5 to −3.1	0.64–0.75	Lohmann et al. (2000)
Austwick, UK	Rural	PCBs	−0.87 to −0.26	−5.9 to −3.6	0.65–0.84	Lohmann et al. (2000)
Augsburg, Germany	Urban	PCBs	−0.60	−5.17		Kaupp and McLachlan (1999)
Chicago, USA	Urban	PCBs	−0.97	−5.68	0.969	Falconer and Harner (2000)
Yokohama, Japan	Urban	PCBs	−0.74	−5.42		Kim and Masunaga (2005)
Melpitz, Germany	Rural	PCBs	−0.16 to −0.59 (ave −0.40)	−4.59 to −2.36 (ave −3.60)	0.32–0.90	Mandalakis and Stephanou (2007)
Athens, Greece	Urban	PCBs	−0.49 to −0.24	−4.81 to −4.16	0.50–0.79	Mandalakis et al. (2002)
Izmir, Turkey	Urban	PBDEs	−0.33 to −0.22	−4.5 to −3.2	0.84–0.92	Cetin and Odabasi (2008)
Izmir, Turkey	Suburb	PBDEs	−0.20	−2.47	0.97	Cetin and Odabasi (2008)
Izmir, Turkey	Industrial	PBDEs	−0.21	−2.83	0.95	Cetin and Odabasi (2008)
Guangzhou, China		PBDEs	−0.762 to −0.607		0.632–0.905	Chen et al. (2006)

(continued)

Table 2 (continued)

Location	Air type	Chemical	Slope (m_r)	Intercept (b_r)	R^2	Refs.
Chicago, USA	Urban	PAHs	−1.04 to −0.38 (ave −0.69)	−6.09 to −2.98 (ave −4.61)		Cotham and Bidleman (1995)
Chicago, USA	Urban	PAHs	−0.64	−3.47		Simcik et al. (1998)
Manchester, UK	Urban	PAHs	−0.77 to −0.62	−5.4 to −4.8	0.77–0.96	Lohmann et al. (2000)
Clapham, UK	Rural	PAHs	−0.81 to −0.58	−5.6 to −4.4	0.73–0.93	Lohmann et al. (2000)
Austwick, UK	Rural	PAHs	−0.87 to −0.71	−5.4 to −4.9	0.87–0.98	Lohmann et al. (2000)
Athens, Greece	Urban	PAHs	−0.69 to −0.47	−5.67 to −4.52	0.74–0.89	Mandalakis et al. (2002)
Los Angeles, USA	Urban	PAHs	−1.06 to −0.753 (ave −0.91)	−5.73 to −4.30 (ave −4.80)		Naumova et al. (2003)
Houston, USA	Urban	PAHs	−1.17 to −0.445 (ave −0.85)	−5.34 to −3.76 (ave −4.82)		Naumova et al. (2003)
Elizabeth, USA	Urban	PAHs	−1.19 to −0.664 (ave −0.98)	−6.22 to −3.38 (ave −4.89)		Naumova et al. (2003)

Table 3 Coefficient of determination, slope and intercept of linearity of log K_p and K_{oa}

Location	Air type	Chemical	Slope (m_r)	Intercept (b_r)	R^2	Refs.
Izmir, Turkey	Urban	PBDEs	0.31–0.50	−8.79 to −5.63	0.88–0.94	Cetin and Odabasi (2008)
Izmir, Turkey	Suburb	PBDEs	0.28	−4.65	0.99	Cetin and Odabasi (2008)
Izmir, Turkey	Industrial	PBDEs	0.28	−5.03	0.97	Cetin and Odabasi (2008)
Chicago, USA	Urban	PCBs	−0.735	−9.947	0.918	Falconer and Harner (2000)
Manchester, UK	Urban	PCBs	0.32–0.65	−9.0 to −5.7	0.62–0.95	Lohmann et al. (2000)
Clapham, UK	Rural	PCBs	0.19–0.57	−8.1 to −4.2	0.61–0.85	Lohmann et al. (2000)
Austwick, UK	Rural	PCBs	0.20–0.74	−10 to −4.7	0.52–0.94	Lohmann et al. (2000)
Manchester, UK	Urban	PAHs	0.58–0.81	−11 to −8.8	0.79–0.97	Lohmann et al. (2000)
Clapham, UK	Rural	PAHs	0.56–0.89	−12 to −7.8	0.62–0.96	Lohmann et al. (2000)
Austwick, UK	Rural	PAHs	0.71–0.90	−11 to −9.4	0.75–0.97	Lohmann et al. (2000)

K_{oa} and f_{om} are easier to measure than the parameters used in Pankow absorption model (Harner and Bidleman 1998; Falconer and Harner 2000). The slope is equal to 1 when plotting log K_p values against log K_{oa}. However, various slope values have been reported in many studies (Table 3).

5.4 *Comparison of Junge–Pankow Adsorption and K_{oa}-based Absorption Models*

Junge–Pankow model and K_{oa} absorption model were found to simulate the data better than each other in different studies indicated by the coefficient of determination in Tables 2 and 3. In a Chicago study, Junge–Pankow model was found to fit the experimental PAH data better than K_{oa}-based absorption model, while K_{oa}-based absorption model better predicted the sorption of PCBs and PCDD/Fs, resolving the difference between multi-ortho and non-ortho PCBs (Harner and Bidleman 1998). In a German study, Junge–Pankow model was found to be better than K_{oa}-based absorption model for PCBs (Mandalakis and Stephanou 2007), although both models tend to underestimate the lower chlorinated PCBs. Another study by Lohmann et al. (2000) who examined partitioning of PCBs in the atmosphere of Manchester also drew the similar conclusion. On the contrary, Harner and Bidleman (1998) concluded that the K_{oa}-based model is more suitable for PCBs compared to the Junge–Pankow model. Chen et al. found that K_{oa} absorption model predicted better for most of PBDE congeners while Junge–Pankow model tended to overestimate the fractions of PBDEs in particle phase in a Chinese study (Chen et al. 2006). The prediction results may vary significantly with the assumption of different OM content and total surface area of particles (Shoeib et al. 2004; Chen et al. 2006; Cetin and Odabasi 2008).

Even though strong correlations were observed between log K_p and log P_L, and between log K_P and log K_{oa}, the slopes may deviate significantly from -1 and 1, respectively. This variability may be attributed to different sorbent effects, nonequilibrium conditions and sampling artifacts (Pankow and Bidleman 1992; Goss and Schwarzenbach 1998; Cotham and Bidleman 1995; Falconer et al. 1995; Volckens and Leith 2003b; Su et al. 2006).

6 Fractionation of SVOCs between Gaseous and Particulate Phases

The most widely used fractionation model (Eq. 13) is based on above mentioned adsorption mechanism. It was proposed by Junge (1977) and evaluated by Pankow (Pankow 1987; Bidleman 1988).

$$\varphi = c\theta/(P_L^{\circ} + c\theta) \tag{13}$$

where φ is the fraction of SVOCs adsorbed onto particles. $c = 17.2$ Pa/cm is typically used, although it might vary with the class of compounds and the particle surface properties (Pankow 1987; Bidleman 1988). θ is the particle surface area (cm^2 of particles/cm^3 of air) often assumed to be 1.1×10^{-5} cm^2/cm^3 for urban air and $4.2–35 \times 10^{-7}$ cm^2/cm^3 for rural air (Bidleman 1988).

Based on the K_{oa} absorption model, K_p can be predicted from the knowledge of K_{oa} of SVOCs and organic fraction of particles f_{om}. Fraction of SVOCs can thus be estimated via the following equation:

$$\varphi = K_p\mathrm{TSP}/\left(1 + K_p\,\mathrm{TSP}\right) \tag{14}$$

The predictability of two methods can be verified with the experimentally measured value by $\varphi = F/(F + A)$.

Hoh and Hites observed that in the east-central US atmosphere lighter congeners of PBDEs with three to six bromines were detected in both particle and gas phases while heavier ones (hepta- through deca-BDEs) were mostly detected in the particle phase, particularly BDE209 accounting for 37–100% of the atmospheric concentration (Hoh and Hites 2005). Strandberg et al. also found that heavier PBDE congeners were more associated with particles; in particular, BDE209 was exclusively in the particle phase around the Great Lakes (Strandberg et al. 2001). Mandalakis et al. observed that particle-bound PBDEs was 71–76% of the total in the city of Athens, Greece (Mandalakis et al. 2009). Farrar et al. reported that particle-bound PBDEs was 33–100% (mean 77%) of the total in the city of Lancaster, England (Farrar et al. 2004).

Contrary to PBDEs, PCBs are primarily present in the vapor phase, whereas a small portion is associated with the particulate phase. The predominance of gaseous PCBs in the atmosphere has been well documented in many studies. Mandalakis and Stephanou (2007) reported particle bound PCBs accounted for only 5% of the total amount of PCBs in the atmosphere of eastern Germany. Reports showed that gas-phase PCBs accounted for 95, 97 and >90% of the total PCBs in Chicago by Tasdemir et al. (2004), Murphy and Rzeszutko (1977) and Simcik et al. (1997). Strandberg et al. (2001) reported 90–98% of PCBs in the gas phase of the Great Lake air. The less-chlorinated PCB homologues, usually with higher vapor pressures, have a greater PCB mass fraction in the gas phase (Lee et al. 1996; Simcik et al. 1997). Falconer et al. found that mono- and non-ortho-PCBs are more associated with particles in air than multi-ortho-PCBs, thereby increasing their likelihood of removal by wet and dry deposition (Falconer et al. 1995).

PAHs are mainly generated by combustion sources and emitted in the gas phase or associated with fine particles (Hildemann et al. 1991; Rogge et al. 1993). PAH can become associated with coarse particles either by the growth of fine particles or by condensation onto coarse particles (Allen et al. 1996). Simcik et al. observed that gas phase PAHs in Chicago accounted for 90% of total atmospheric concentration and were dominated by phenanthrene and fluorene while the particulate phase was dominated by benzofluoranthenes, chrysene, fluoranthene, and pyrene (Simcik et al. 1997). Terzi and Samara found in samples from Greek atmosphere that the three- and four-ringed PAHs were primarily in the gas phase while the five- and six-ring PAHs in the particle phase (Terzi and Samara 2004). Ohura et al. found that two- to three-ring and five- to seven-ring PAHs were detected predominantly in the vapor and particulate phases, respectively, while four-ring PAHs were found to be in both vapor and particulate phases. Gas phase concentrations of PAHs with two- to three-rings (particularly naphthalene) could be orders of magnitude higher than those of particulate phase PAHs (Ohura et al. 2004).

7 Significance of Gas-particle Partitioning

Gas-particle partitioning of SVOCs is an important process which influences their mobility and environmental fate. The knowledge of the gas-particle partitioning can help explain observed mobility, photolytic transformation, and removal from the atmosphere by dry and wet deposition. A great deal is yet to be learned, however, in order to quantitatively define the link of physicochemical properties to the overall environmental transport and fate.

All the three groups of SVOCs concerned in this paper, namely PCBs, PBDEs and PAHs, are persistent and semi-volatile and subject to atmospheric transport to remote locations, through a series of deposition/volatilization hops, known as the "grasshopper" effect. As a result, these compounds have been detected in the Arctic and Antarctic samples in numerous studies. The major factors determining the long-range transport potential (LRTP) are the volatility and the degradation rate, or half life of the SVOCs in the atmosphere.

Comparison among different PBDE congeners reveals that di-, tri-, and tetra-BDEs tend to have higher LRTPs (Gouin and Harner 2003; Wania and Dugani 2003). Wania and Dugani (2003) attribute the relatively low LRTPs of mono-BDEs and heavy BDEs to their high atmospheric degradation rate and low volatility, respectively. Atmospheric half lives are shorter for lighter congeners due to their higher degradation potential in the air. This reduces the distance they are able to travel. On the other hand, congeners with five or more bromines have a high affinity to the airborne particles which settle down through dry deposition process mainly by gravitation, impaction or diffusion, or through wet deposition by coagulation with water droplets. Photodegradation of PBDEs tends to be faster for congeners with more bromines in the molecule. The PBDE debromination was found to be stepwise, with one bromine dropped off in each step (Söderström et al. 2004). BDE209 were found to be photolytic unstable and its half time was reported to be less than 1 h in the solvent (Söderström et al. 2004). However, it still dominates in the atmospheric samples collected from the most studies. It appears that particles have shielded the insides of the particles from light penetration. Surface structure and chemical composition of the matrix are thought to be important factors affecting the photolysis rate (Kajiwara et al. 2008). Hua et al. (2003) demonstrated that the presence of humic acid slows down the photodegradation rate of sand-bound BDE209, indicating that OM may block or attenuate the light intensity. Using silica gel, sand, soil, and sediment, Söderström et al. (2004) found that the photolytic debromination of PBDEs on nonporous surfaces are rapid, while those on porous soil matrix are slow, due to the shielding provided by the pores and the possible binding of PBDEs to the OM of the matrices.

Most PCB congeners do not strongly absorb wavelength above 300 nm (Hawari et al. 1992). The overall degradation rate under natural sunlight is low due to the low intensity of solar radiation with short wavelengths in the troposphere. Photochemical transformation studies were mostly carried out in solvent solutions with sensitizer (Lin et al. 1995). Studies found that dechlorination occurred mostly on the more substituted ring of odd numbered-substituted congeners and ortho-chlorines are preferentially removed (Lepine and Masse 1990; Lepine et al. 1991).

Photochemical transformation has generally been considered to be the most important mode of atmospheric decomposition of PAHs. The dominant transformation process for gas phase PAHs in the atmosphere is photooxidation involving the hydroxyl radical (Finlayson-Pitts and Pitts 1986; Simcik et al. 1997). PAHs can react readily with O_3 and NO_x in the atmosphere. The reaction rate of particle-bound PAHs is strongly influenced by the nature of the substrate (Behymer and

Hites 1988). PAH appear to be more stable when adsorbed on porous particles such as soot or fly-ash than when present in pure form (Korfmacher et al. 1980).

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Secondary Particle Production in Urban Areas

Boris Bonn

1 Introduction

Suspended particles in air and their corresponding mass can originate from three different types of sources. One is primary, expressing the release into the atmosphere as a particle straight away. This includes mineral dust, sea salt, soot, heavy metals, clay and biological material (pollen, bacteria, etc.). Those are usually located at larger diameters above half a micron. The second type originates from atmospheric trace gases (precursors), which react in the gas phase to form products of different volatility and reactivity. Some of them will either form new particles in number or produce new aerosol mass by partitioning between the gas and the aerosol phase. The third source type refers to the cloud phase and is essentially a mixture of both other types. Gases are absorbed in the cloud water, subsequently processed chemically and either stick primary aerosols included in the cloud water as well or form new aggregates. When the cloud starts evaporating as nine of ten clouds do, re-entering the atmosphere either as gases or as particulate matter. The primary particles dissolved in the cloud phase and interacting with the processed chemicals consist mainly of dissolved salts and water-soluble compounds, organic as well as inorganic.

This chapter is focussed on the second type of particle formation, which extends in general to the entire size range of atmospheric aerosols but especially the smallest ones and occurs in every urban area once any significant activity is present (Kulmala et al. 2004).

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_17,

2 Secondary Particle Formation: Precursors

As the reader possibly can imagine, there are hundreds of different trace gases abundant in the urban air, partially from anthropogenic and less from biogenic sources. These include nitrogen containing compounds such as nitric acid and various types of organic nitrates. Sulphur compounds are present as well ranging from sulphur dioxide via sulphuric acid to organic sulphur species. However the largest pool of aerosol precursors is organic in nature. The release of volatile organic compounds (VOCs) by industrial sources, traffic and heating covers various types of fossil fuel compounds from toluene and benzene to less reactive ones ethane and propane. According to Jimenez et al. (2009) a minimum contribution of about 35% of organic compounds is present at all urban sites analysed, which can increase up to 60% depending on the different pollution strengths and industries present as well as the time of the year. Sulphate varies from ca. 15% (Tokyo, Japan and Zurich, Switzerland) to ca. 60% (Okinawa, Japan) with high contribution in oil related industries. This drops towards the urban edges. Nitrate contributes between 3–5% (Pittsburgh, USA) and 30% (Manchester, UK and Zurich, Switzerland) and ammonia between 5% (Mexico City, Mexico) and about 20% (Bejing, China, Tokyo, Japan, Manchester, UK, Pittsburgh, USA and others). Thus, the secondary mass is likely to be dominated by organic compounds. These are generally highly oxidised compounds with a tendency to react further on either in the gas- or in the liquid aerosol phase.

3 Secondary Particle Production: The Phase Transfer

The exact process depends very much on the circumstances such as chemical conditions, temperature and aerosol loadings present. A high pre-existing aerosol load as for instance PM_{10} suppresses new particle number formation but allows secondary mass to be formed on the aerosol surfaces present. The particle size range of secondary aerosol mass is wide spread. Newly formed particles have a diameter close to the molecular size range with a spherical diameter below one nm to around 100 nm. Secondary mass however can be contained by the medium sized and coarse particles up to the lower micrometer size range in particle diameter, making it a challenge to separate different source types and to measure the whole range of sizes.

This following summary of the current state-of-knowledge will start with the formation of new particles in Sect. 3.1 before describing the subsequent processes such as condensation and partitioning of trace gases in Sect. 3.2.

3.1 New Particle Formation

New particle formation is one of the most discussed atmospheric processes, which is caused by two effects.

(A) First of all this is caused by the very tiny mass of such a new aerosol between let us say one and about five nm in spherical diameter. The corresponding amount of gases of a single particle cannot be detected and analyzed in such small concentrations and the required trace gases concentrations for new particle formation are extremely low.

(B) Once these particles have grown beyond about 50 nm in particle diameter they will affect radiation budgets due to direct scattering of solar radiation as well as due to changing cloud properties (indirect effects).

New particle formation in urban areas has been linked to two chemical compound classes, (1) sulphuric acid and (2) anthropogenic organic compounds emitted by for instance fossil fuel consumption. It is believed that sulphuric acid starts the nucleation process and forms a nucleation core, onto which the organic compounds condense to cause the subsequent growth. This is based on particle size distribution and number concentration measurements accompanied with sulphuric acid data, which provide good correlations for the first stage of new particle formation (see Fig. 1 of Riipinen et al. 2007).

Please note that there is a need for a temporal shift between the maximum in sulphuric acid and particle number concentration, proposed to be originating from the growing time between one and three nanometres, which was the starting size for detection at the time of study. However the same is true for measurements besides motorways and the car frequency (Hussein 2005). This causes VOCs to reach their maximum concentration. But the compounds emitted are too volatile to

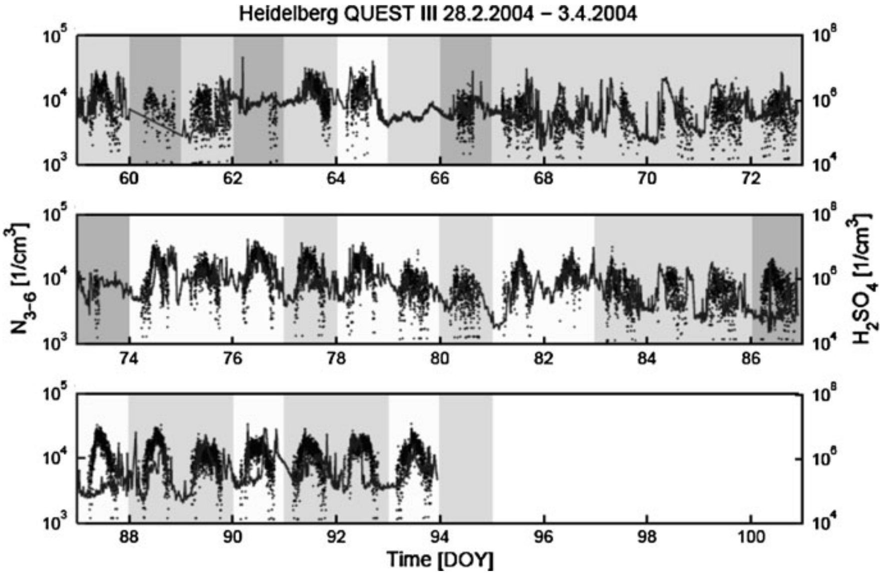

Fig. 1 Particle number concentration between 3 and 6 nm (*solid grey line*, left axis) and sulphuric acid concentration (*dotted points*, right axis) during the QUEST III campaign in Heidelberg (D). Shown is a 2 week period as day of the year (Riipinen et al. 2007)

condense or to nucleate. There are again two possibilities: Either the drop in temperature and thus saturation vapour pressure in the car exhaust establishes a short time of supersaturation, or the subsequent oxidation of the VOCs mainly by OH provides reactive products and radicals that will interact with nucleation inducing molecules (NIMs) resulting in a larger intermediate product. In this context an important handicap for molecules to stick to the smallest nuclei is caused by the surface curvature, which requires a much larger supersaturation than a nearly flat particle (Kelvin effect; Seinfeld and Pandis 2006). On the contrary urban air contains a lot of preformed aerosol particles per cm^3 with a much flatter surface than the nuclei. These will take up the saturated gases and prevent the necessary supersaturation.

In order to solve this problem, nucleation can be formulated as a three step process. In stage one a nucleation inducing core molecule, which is quite large in size and probably reactive, is formed (NIM). Its origin remains speculative, but most likely sulphuric acid is involved. In stage two reactive compounds interact and form larger intermediates with even less saturation vapour pressures and a larger size until in stage three the curvature effect of the products is reduced and further low and semi-volatile substances can stick to the intermediates and cause a further growth. These low and semi-volatile compounds are mainly of organic origin but other substances such as nitrates will contribute too (Fig. 2).

Within these first stages the transformation from a gaseous molecule to particulate matter has to occur. Therefore a new surface as a boundary between the gas phase and the particulate phase has to develop. This particulate phase can be either liquid, solid or some intermediate state, which is commonly be described as amorphous (Pankow 1991). Once a surface has developed the product is called aerosol particle or particulate matter. Beforehand it is named cluster as an arrangement of 10–100 of atoms and molecules. The transfer between molecule, cluster and particle occurs at different sizes. Which size however depends on

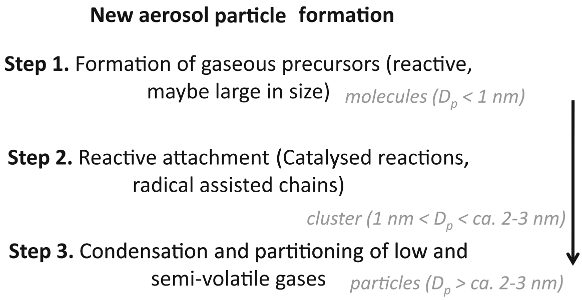

Fig. 2 Steps of atmospheric new particle formation. The formation of a nuclei core molecule or nucleus cluster seems to be followed by reactive attachment of further substances in order to activate the nucleus from a diameter below 1 nm across the cluster range to form a particle at around 2–3 nm in particle diameter. In the third step this can be followed by condensation or partitioning of individual compounds to cause the growth to larger particle sizes

molecular and mixture properties and might range from 10 to 200 molecules (Vehkamäki et al. 2007). The corresponding initial size of a particle corresponds to a range between 1.5 and 3 nm approximately.

Because the detection of these particles is based on the condensation of a liquid, usually either water or butanol, surface effects come into play. The condensation process is the transfer of excess material in one of both phases gas or aerosol and is driven by evaporation/sublimation and condensation, which take place in parallel. Is the surface of an aerosol particle curved molecules can enter the gas phase more easily and the interaction between absorbed molecules is less in strength (Seinfeld and Pandis 2006). Therefore the saturation above a curved, i.e. smaller particle is larger and particles tend to evaporate. This effect is called Kelvin effect after Lord Kelvin, who figured out and explained the effect about 150 years ago. The second effect of relevance is the solution effect. Two different compounds with the potential to get dissolved in each other as for instance a salt in water, will stick to each other even at subsaturation because the evaporation/sublimation is drastically reduced (Raoult effect) (Friedlander 2000).

This effect causes the smallest particles not be grown be condensing vapours, but to either attach reactive species or to dissolve other compounds, because a molecule would tend to stick to a larger particle with a smaller Kelvin effect than vice versa. Some potential processes are polymerization and oligomerization but also acid-catalysed reactions with for instance sulphuric acid as a catalyst (Zhang et al. 2004).

Concluding for new particle formation it can be stated that new particles form gaseous precursors are expected to be formed by the interaction of sulphuric acid and anthropogenic VOCs in urban areas. Solar radiation and OH production are important too, in order to initiate a strong oxidation and precursor formation for aerosol production.

3.2 Secondary Mass Production: Organics

When studying ambient aerosol masses and atmospheric gas phase concentrations of different organic trace gases, there is one fact, which becomes apparent immediately. The organic compounds are never in saturation but always subsaturated. How come they can be found in the aerosol phase? Pankow (1994a, b) explained this by a very strong effect, the absorption and dissolution of ambient organic molecules in the organic aerosol phase. This occurs in a similar way as water molecules in a salt solution droplet. Every absorbed organic molecule provides new organic aerosol mass for other molecules to get absorbed and to stick to. The only two requirements for organic uptake are: The presence of (a) amorphous organic aerosol mass and (b) of organics in the gas phase. Then the concentration in the particle phase can be described by:

$$[\text{compound}](\text{aerosol}) = K_p(\text{compound}) \cdot \text{TSP} \cdot [\text{compound}](\text{gas})$$

$$K_p(\text{compound}) = \frac{f_{om} \cdot RT}{M_w(\text{org.}) \cdot \zeta \cdot 10^6 \cdot p_{sat}(\text{compound})}$$

[compound] of aerosol and gas phase are the concentration of a compound in both phase. TSP is the Total aerosol mass in $\mu g/m^3$, K_p is the partitioning coefficient, which is described in the second line. It depends on the fraction of organic matter in the aerosol phase f_{om}, the ideal gas constant R, the temperature T in Kelvin, the mean organic molar mass of all organic compounds mass weighted M_w(org.), the activity coefficient ζ_i and the saturation vapour pressure p_{sat}(compound). From the equations it is clear that a low saturation vapour pressure enhances the uptake, while a high saturation vapour pressure shifts the compound towards the gas phase. The activity coefficient mentioned above is not well known and can range between one and five. However, it is usually assumed to be unity because of the lack of a better knowledge.

Important is a very first adsorption or attachment of organic matter to allow the partitioning to occur. As described in the previous section this may work by reactive attachment, either of radicals or via for instance catalysed reactions. This was postulated to happen by accretion reactions, i.e. reactive attachment of different types of organic compounds. However, Barsanti and Pankow (2004) found only a minor effect for accretion reactions of rather stable oxidation products. Therefore, these contributions are of minor importance.

The aerosol yield Y of a specific compound i, that is the fraction of the total mass within the aerosol phase, can be derived by restructuration of the first equation:

$$Y = \frac{K_p(\text{compound}) \cdot \text{TSP}}{1 + K_p(\text{compound}) \cdot \text{TSP}}.$$

Odum et al. (1996) formulated an easy approach to calculate the aerosol yield of various precursor compounds with unknown oxidation products by smog chamber experiments. He defined two virtual products a non-volatile and a semivolatile product and fitted a curve through various smog chamber experiments to obtain the fraction of the product α_i and its partitioning coefficient $K_{p,i}$.

$$\begin{aligned} Y(\text{Odum}) &= \frac{\alpha_1 K_{p,1}(\text{compound}) \cdot \text{TSP}}{1 + K_{p,1}(\text{compound}) \cdot \text{TSP}} + \frac{\alpha_2 K_{p,2}(\text{compound}) \cdot \text{TSP}}{1 + K_{p,2}(\text{compound}) \cdot \text{TSP}} \\ &= TSP \cdot \sum_{i=1-2} \frac{\alpha_i K_{p,i}(\text{compound})}{1 + K_{p,i}(\text{compound}) \cdot \text{TSP}}. \end{aligned}$$

This works in smog chamber experiments for instance for toluene, benzene and xylene oxidation, but includes some disadvantages. The disadvantages are: No information about the chemical properties of the aerosol, the observed effect of radicals is not included in this approach and it seems to underpredict the monitored concentrations. These fields of HO_x and RO_x chemistry are currently the uncertain fields of organic aerosol chemistry and hard to cover by the current detection methods. Nevertheless, these areas are very important for health and climate aspects (Hallquist et al. 2009).

As a summary we can conclude with the estimated lower estimate of anthropogenic VOC contribution to global secondary aerosol of 0.3–1.1 Tg per year (Tsigaridis and Kanakidou 2003), which is about a factor of a hundred or more less than the global contribution of biogenic VOC oxidation products (Goldstein and Galbally 2007). However, the production is very concentrated on some areas and therefore highly important.

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The Effect of Asian Dust on Urban Airborne PM in Japan

Chang-Jin Ma

1 Introduction

Sand and dust storms are widespread natural phenomena in the world. Springtime weather in Asia causes intense windstorm events that can pass over the Gobi Desert along the northern China/Mongolia border and other desert regions in China. These winds are capable of generating the huge yellow clouds of suspended dust that is based on the direction of the prevailing wind can be sent out to sea. In addition to the natural dust storm, human activities act as the potential sources for dust emission (e.g. through the process known as desertification: Zhang et al. 2003).

Desertification is an important ecological problem in the world today. Desertification is a process of environmental degradation under fragile ecological conditions and intensive human activities.

Although ADS can cause many disasters, it is said that ADS makes a contribution to the neutralization of acid rain caused by consumption of a large amount of fossil fuels. By use of a simplified reaction model between SO_2 and NO_2 in the ambient air and various oxides in ADS particles, Kim et al. (1997) predicted that K_2O, Na_2O and CaO in a 9 μm ADS particle are consumed as much as 51.3, 30 and 9.8%, respectively, by reacting with SO_2 and NO_2 in the atmosphere during the long-range transport through East Asia.

This ADS finally dissipates when the particles are removed from the atmosphere by dry and wet removal processes. Gravitational settling of large particles (>10 μm) occurs near the source within the first day of transport. Wet removal occurs sporadically throughout the 5–10 days lifetime of the remaining smaller size dust particles.

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*, Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_18,

Until now, numerous studies aided by the field and model simulations have been carried out to determine the characteristics of ADS particles (Duce et al. 1980; Braaten and Cahill 1986; Wang and Guanghua 1996; Zhang et al. 2003; Kim et al. 2003). However, there were only a few studies which focused on the assessment of the wet scavenging of ADS storm particles. The results of such studies are expected to provide a better knowledge concerning the removal characteristics of ADS particles (Ma et al. 2004b; Wang et al. 2002).

In the present study, in order to fully understand the nature of ADS particles, the size-resolved ADS particles were measured in urban receptor areas, Japan. Also, for the study of those wet scavenging properties, both bulk rainwater and individual raindrops were collected during the ADS storm period.

2 Material and Methods

2.1 *Sampling and Monitoring of Dust Particles*

Aerosol sampling and monitoring were performed simultaneously from a ground-based site in Fukuoka, Japan during both a non-ADS and ADS periods in April 2005. Kyushu is Japan's third largest island, located southwest of the main island, Honshu. The city of Fukuoka located in the northwest part of Fukuoka Prefecture is Kyushu's largest city and one of Japan's ten most populated cities. Because of its closeness to the Asian mainland, this area can be directly exposed to the outflow of air masses from the Asian continent during springtime (see Fig. 1). Therefore, this area is one of the well suited sites to monitor the occurrences of ADS in Japan. A ground-based sampling station (with a height of 15 m above ground) is located at the Fukuoka Women's University building (33.40° N; 130.26° E) and is marked as an empty square in Fig. 1.

For the sampling of aerosols as a function of their size, a low pressure Andersen impactor (LPAI) sampler (Tokyo Dylec Co.) was operated with 25 L per minute

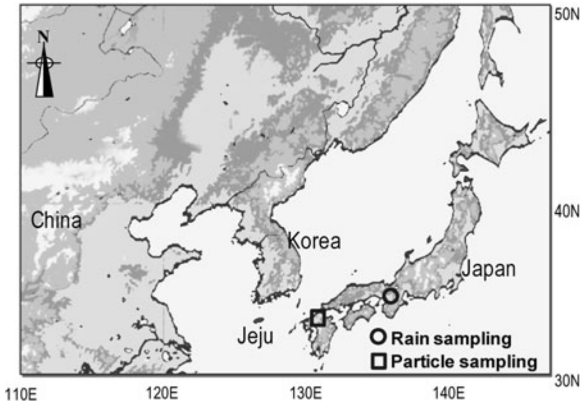


Fig. 1 A map showing sampling points for aerosol and rain

flow rate during both a non-ADS (from Apr. 7 to Apr. 10) and ADS (from Apr. 19 to Apr. 22) periods.

As one of the multi-stage particle sampling instruments (a 13-stage classification between 0.01 and 10.85 μm), the LPAI with multi-orifice was designed to measure the size distribution and mass concentration levels of particulate matter. Particles were sampled directly on a substrate material (80 mm diameter Nuclepore® filter) arranged behind the jet-nozzles of each stage. The detailed cut-off particle diameter of each stage for the LPAI has already been described elsewhere (Kasahara et al. 1996b; Ma et al. 2001b). Before and after sample collection, all filters were conditioned in a desiccator with constant temperature (20 ± 0.5 °C) and relative humidity (30%) to remove the unwanted moisture. And then, for the gravimetric analysis of sample mass, all filters were pre- and post-weighed on a microbalance.

The number-size distribution of ambient particles was monitored by an optical particle counter (OPC) (RION, KC-01D). Information concerning the accuracy of the OPC's size determination was checked by the manufacturer (RION). The four-step known size monodisperse polystyrene type latex (PSL) spheres (0.294, 0.505, 1.001, and 2.106 μm) were employed. The OPC sizing accuracy check was conducted by sampling of these PSL particles. In the field measurement, OPC was operated at intervals of every 30 min. The flow rate for the OPC was 3×10^{-2} m^3 h^{-1}. During the sampling period, the ranges of temperature and relative humidity (RH) were 12.8–28.4 °C and 30–79%, respectively.

2.2 Sampling and Handling of Rainwater and Individual Raindrops

Yellow rainfall episode occurred in the Kyoto region of Japan (see Fig. 1) on Apr. 7, 2001. This yellow coloration of rain was induced by soil particles originating from the desert and loess areas in China. Using a polyethylene funnel and flask, bulk rainwater samples were collected as a function of the rainfall amount. The first 2 mm of rainfall was assumed as the initial rainfall. The rain fallen after initial rainfall was considered as the subsequent rainfall. These initial and subsequent rainfalls were sequentially divided into soluble and insoluble fractions. For the fractionation of rainwater into soluble and insoluble fractions, a 10 mL rainwater sample was filtered through a 0.2 μm pore-size polycarbonate Nuclepore® filter (Whatman). Then, 40 μL of filtrate was mounted on a non-whole Nuclepore® filter and evaporated by an infrared lamp. The residues of filtrate on a non-whole Nuclepore® filter and the deposited particles on a 0.2 μm pore-size Nuclepore® filter were considered to be soluble and insoluble fractions, respectively.

In order to collect raindrop individually, the collodion film replication method was applied (Ma et al. 2001a, 2004a). A 200 μL of viscous collodion solution (3 %) was mounted onto the Mylar ($C_{10}H_8O_4$) film with a 10 μm thickness just before sampling. When raindrops fell onto the thin layer of collodion film (130 ± 10 μm), they gently settled. By allowing the alcohol and ether to evaporate, a thin film containing the replication of individual raindrops was left on the Mylar film. The detailed process of replica formation for the individual droplets has been described elsewhere (Ma et al. 2004a). This replication technique enables us not only to keep a whole raindrop on the film surface but also to analyze residual materials. However, this collodion film method did not allow to sample of raindrops larger than a 2.1 mm diameter because a breakup of raindrops can occur due to their collision with collodion film surface (Ma et al. 2001a, 2004a). Thus, the sampling of individual rain droplets was carried out during the initial rainfall.

2.3 Chemical Analysis

2.3.1 Bulk Particle Analysis

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (HewPackard Co. HP 2500 Series300) was applied to the elemental analysis of bulk particulate matters. ICP-MS is one of the powerful analytical techniques which allow detection of trace elements (often at the part per trillion level) contained in a wide variety of samples (Olesik 1996). The closed vessel microwave acid digestion system was applied to sample digestion. This microwave was equipped with a fiber-optic thermometer and pressure sensor; it works at a maximum pressure of 800 psi. A solution of HNO_3 mixed with HCl was employed in digesting of samples in microwave digestion system. Digested liquid samples are introduced into the carrier gas (argon) by a nebulizer. The analyte ions are transported by the argon and focused by a series of ion lenses into a quadrupole mass analyzer; the ions are then separated as a function of their mass/charge ratio. Four main processes of elemental analysis with ICP-MS are as follows: (1) sample introduction and aerosol generation, (2) ionization by an argon plasma source, (3) mass discrimination, and (4) the detection system.

2.3.2 Determination of Chemical Components in Bulk Rainwater

The absolute quantities of elements contained in both the soluble and insoluble fractions were determined by particle induced X-ray emission (PIXE) analytical method. PIXE analysis was performed with a proton beam of a 6 mm diameter and a 2.0 MeV energy from a Tandem Cockcroft accelerator installed at the Quantum Science and Engineering Center of Kyoto University. Beam intensities from 10 to 60 nA were employed, and the total dose was about 20 μC. An X-ray with an energy of up to 14.8 keV emitted from the target was detected by a Si (Li) detector with a resolution of 152 eV at 5.9 keV. The calibration method of PIXE was similar to that described elsewhere (Kasahara et al. 1993) and is described here briefly. The relationship of an X-ray yield and the mass thickness was measured first using the 18 single element standard samples prepared by a vacuum deposition method (Kasahara et al. 1993). The sensitivity for all objective elements, defined as (PIXE yield per unit dose)/(mass thickness), was determined experimentally and theoretically.

2.3.3 Analysis of Individual Ambient and Raindrop Residual Particles

Microbeam Particle Induced X-ray Emission (PIXE), often called micro-PIXE, was used for single particle analysis. The greatest advantage of this system is excellent detection limits in the order of 10^{-15}–10^{-16} g. It also has the merit of a multielement non-destructive technique with a wide range of elements for various samples.

This micro-PIXE analytical measurement was carried out with the facilities of the Takasaki Ion Accelerators for Advanced Radiation Application. Micro-PIXE measurements were performed with a scanning 2.6 MeV H+ micro beam accelerated by a 3 MeV single-ended accelerator. Beam diameter and beam current were supplied as 1–2 μm and <100 pA, respectively. The target scanning portion was allocated by Scanning Transmission Ion Microscope (STIM) method. By making a beam spot size smaller than a few micrometers and by scanning this micro beam through individual raindrop samples, it is possible to describe spatial distribution patterns of trace elements in a single raindrop. Beam collection time for each sample was about 5–10 min. More detailed information concerning analytical procedures and experimental set-ups used for PIXE and micro-PIXE analyses were described elsewhere (Kasahara et al. 1993; Sakai et al. 1998).

3 Results and Discussion

3.1 Temporal Variation of Particle Number Concentration

Figure 2 shows the time dependent variation of particle number concentration at ground-based site of Fukuoka, Japan during non-ADS period (from April 7 to April 9) and ADS period (from April 19 to April 22). The number concentration of particles raging from 2.0 to 5.0 μm increased during ADS period reparative to that observed in non-ADS period. The particles larger than 5 μm showed a remarkable increase during ADS period. These gigantic particles (e.g. larger than 5 μm) was measured to be 10 times higher in ADS period than in non-ADS period.

3.2 Size-resolved Bulk Particles

The mass concentrations of the size segregated gravimetric particle were measured by weighing each filter before and after sampling in two measurement periods.

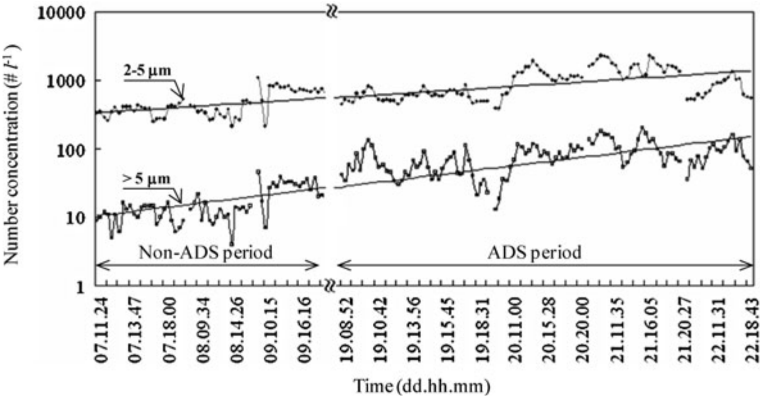
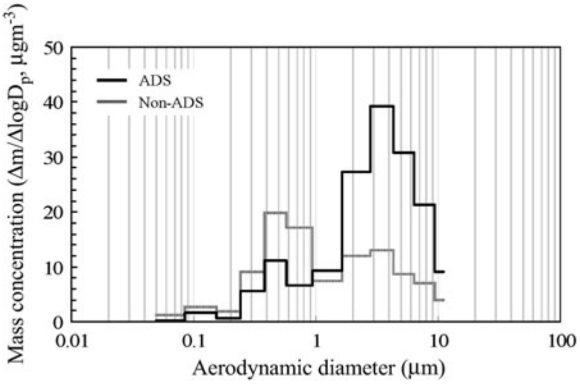


Fig. 2 Time series variation of particle number concentration at Fukuoka during non-ADS period and ADS period in April 2005

The particle mass concentration on ADS event showing the bimodal distribution is enriched in the coarse fraction ($D_p > 2.1$ µm), while that of non-ADS period shows the major peak in the fine fraction around 0.5 µm (Fig. 3). Especially, there is a marked increase of mass concentration in the range of 3.5–7.7 µm in ADS event. This result thus indirectly indicates that those transported dust particles were predominately in the size range between 3.5 and 7.7 µm. The enrichment of mass concentrations in this particle size range is in fact in a good agreement with the result of OPC measurement.

Figure 4 shows the size resolved soil fraction, sea-salt fraction, and particle mass concentration in the two measurement periods. The fractions of soil and sea-salt were estimated by 11.63x[Al] and by 3.27x[Na] (Ohta and Okita 1990), respectively. The soil fractions of coarse particles increased in ADS period. They can also account for a relatively large portion of particle mass concentration. In ADS event, soil fraction consisted of 57.9–70.1% of particle mass concentration in

Fig. 3 Size-resolved mass concentration during non-ADS period and ADS period in April, 2005



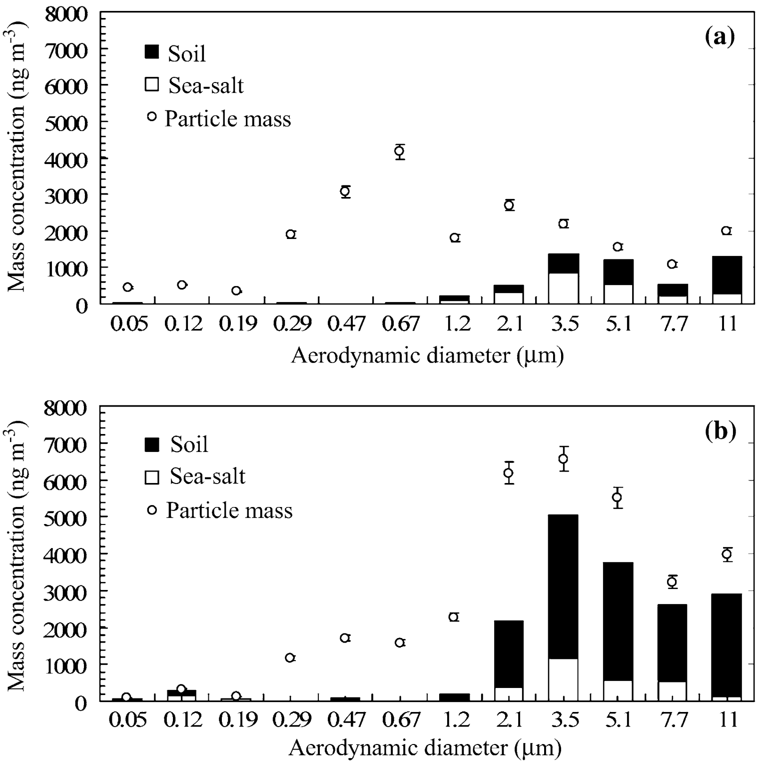


Fig. 4 Size-resolved soil and sea-salt fractions during non-ADS (**a**) period and ADS (**b**) period in April, 2005

coarse particles larger than 3.5 μm. On the other hand, soil fraction corresponded to a relatively small portion (between 23.8 and 51.2%) of the mass loading in non-ADS period. In the case of sea-salt, there were no remarkable differences in ambient loading levels between non-ADS and ADS periods.

3.3 Single Particles

An example of micro-PIXE elemental maps shown in Fig. 5 was drawn on a 25 μm × 25 μm scanning area including a single large dust particle. In Fig. 5, "row" and "col" are pixels corresponding beam scan area. In addition, the scale bar shows the intensity of characteristics X-ray count. Each elemental map can be drawn on the 128 × 128 pixels by scanning of about 1 μm micro beam on the surface of the individual particles. Several elements in and/or on a single particle (D_p: 7.7 μm) were detected successfully. Soil components (such as Ca, Fe, and K)

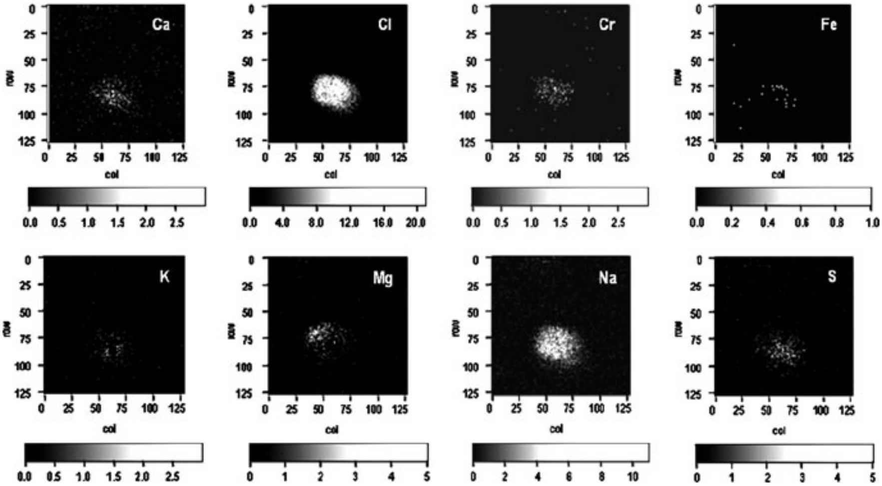


Fig. 5 An example of micro-PIXE elemental maps taken on individual ADS particles collected on the stage-1 (50% cut-off size: 7.7 μm) of LPAI sampler. Scanning area is 25 × 25 μm^2

are reproduced as elemental maps. Both marine (Cl, Mg, and Na) and artificial components (Cr and S) are also distributed at the same portion. Therefore, undoubtedly it could be addressed that the micro-PIXE technique enables us not only to identify chemical compositions of individual particles but also to understand the chemical mixing state of individual particles.

On the basis of the reconstructed elemental distribution by micro-PIXE analysis, we made an attempt to classify individual coarse particles into several types. A total of 200 individual particles chosen indiscriminately (collected in ADS event) for each three-stage (3.5, 5.1, 7.7 μm) were irradiated by microbeam. Figure 6 shows the occupation rate of each type of size-resolved particles. The percentage values were calculated from the fraction of each particle type to the total particles (200) based on particle size. This result thus indicates that the chemical mixing states in and/or on individual particles have the strong particle size dependence. Relatively non-aged sea-salt and mineral particles were dissociated, and they can account for about one-third of total analyzed particles. Mixed particles (with crustal plus sea-salt; crustal plus artificial; and the combination of crustal, sea-salt and artificial) were found to be the dominant type in overall particle fractions. The mixed particles can account for 60.6, 69.2, and 77.2% of the particle size with 3.5, 5.1, and 7.7 μm, respectively. It is suggested that relatively small particles were mixed less efficiently than large ones. The fraction of non-aged (not chemically transformed) mineral particles tends to decrease with increasing particle size. A slight decrease of sea-salt particle was also observed with increasing particle size.

Figure 7 exhibits the presumed aging processes of the ADS particles in accordance with their transport to east. To explain the chemical mixing processes

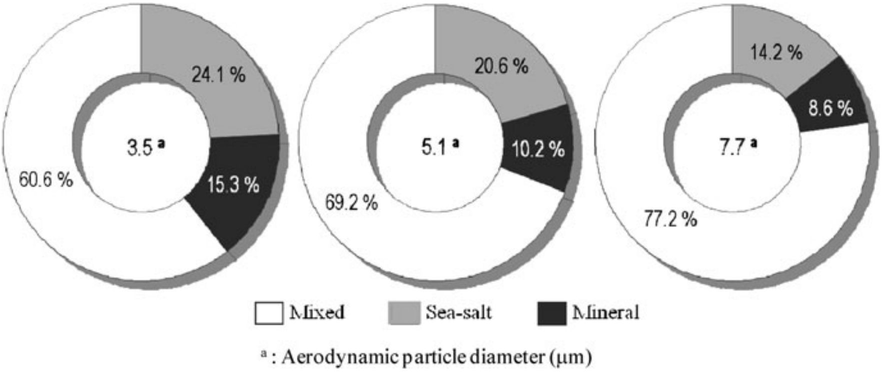


Fig. 6 Relative fraction of three-type of the size-classified individual particles collected in ADS event

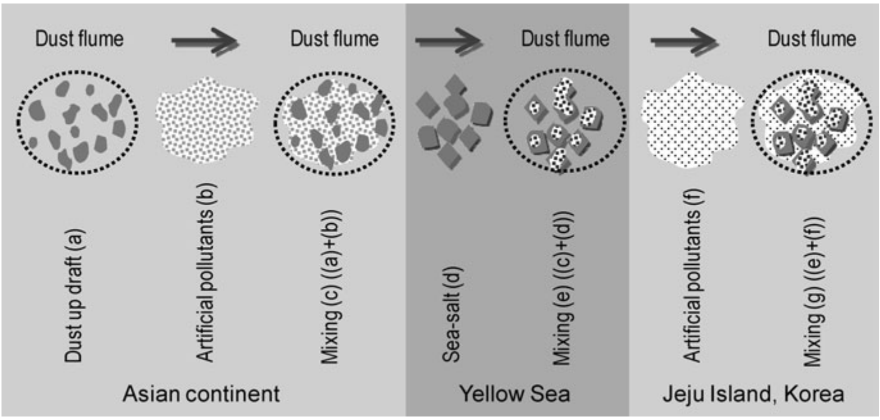


Fig. 7 A conceptual view to explain the aging processes of the Asian dust particles

of dust storm particles with sea-salt and artificial particles, it is essential to fully understand how dust storm particles age and how anthropogenic pollutants are incorporated into this dust and marine particles. It is expected that the following several mechanisms are responsible for the internal mixing of ADS particles with sea salts: (1) Brownian coagulation; (2) impaction by differential sedimentation; (3) coalescence of cloud droplets containing minerals with those containing sea salts. However, as stated by Andreae et al. (1986), Brownian coagulation and impaction by differential sedimentation cannot explain internal mixture in particles (with diameter of 2–4 μm) during long-range transport. Therefore, the internal mixture of crustal with marine components in the particles (ranging 3.5 μm) occurred probably by the cloud condensation nuclei (CCN) in an atmosphere with low supersaturation. Cloud droplets should be formed individually on the ADS particles and sea salt particles in the marine boundary layer. Then the internal mixing of dust particles with marine particles should occur on evaporation of the cloud droplets (Friedlander 1977; Song and Carmichael 1999).

In the case of mixing process between crustal and anthropogenic components, it is suggested that the incorporation of anthropogenic components into dust storm particles may occur at the industrial areas in China, Jeju Island in Korea, and at the receptor area in Japan. The coalescence of two cloud droplets which are containing different particles (e.g. dust and man-made particles) is also considered as other aging mechanisms of dust particles with man-made components.

3.4 Bulk Rainwater

Table 1 summarizes the elemental concentration in the initial and subsequent rainwater as a function of water solubility during yellow rainfall episode and non-ADS period (Kasahara et al. 1996a). The scavenging rates at initial rainfall for two kinds of rainfall events were determined. As it is expected, major components in yellow rain, especially in insoluble fraction, were mainly of soil origin. These soil-derived components can contribute to 92% of total elemental concentration in insoluble fractions at initial rainfall. The concentration ratio of soluble to insoluble fraction indicates that S and Cl are present predominantly at soluble fraction, regardless of rainfall event and rainfall amount. The mass concentration of every element drops considerably to low level at subsequent rainfall. Especially, most of S and Cl in insoluble fraction were scavenged at the initial rainfall. Although there was the low scavenging rate at initial rainfall for insoluble Fe and soluble Si at non-yellow rainfall, most pollutants were found to be scavenged during the early stage of rainfall in our sampling period. There is a good agreement in the results between the present and previous studies (Kasahara et al. 1996a). Generally speaking, every element in insoluble fraction shows higher scavenging rate at the initial rainfall stage than those in soluble fraction at both yellowish and the general rainfalls. According to the study of Tenberken et al. (1995), the influence of giant particles (>1 μm) on the raindrop size-dependence of elemental concentration is reduced with increasing time. They generally show very high scavenging efficiencies, as they are scavenged efficiently at the beginning stage of a rain event. In the case of insoluble fraction in the initial rainfall, the concentration ratios of Si, K, Ca, and Fe in yellow rain to those in non-yellow rain are 104, 194, 97, and 106, respectively. They also show the overwhelmingly high ratios at soluble fraction. In addition to this, we cannot make an account of the fact that several anthropogenic components also show relatively high mass loading in yellow rain relative to those in non-yellow rain. There is a growing demand to better understand how the ADS particles age and how anthropogenic pollutants are mixed with this dust. Song and Carmichael (1999) suggested that the prevailing westerly and the longitudinal mixing can

Table 1 Elemental concentration of rainwater samples in the initial and subsequent collection stages as a function of water solubility during a yellow rainfall episode and non-ADS period

	Insoluble fraction (mg L^{-1})						Soluble fraction (mg L^{-1})						Scavenging rate at initial rainfall (%)[a]			
	Initial rainfall			Subsequent rainfall			Initial rainfall			Subsequent rainfall			Insoluble		Soluble	
	Yellow rain	Rain[b]	Y/R[c]	Yellow rain	Rain	Y/R	Yellow rain	Rain	Y/R	Yellow rain	Rain	Y/R	Yellow rain	Rain	Yellow rain	Rain
Si	61.5	5.9E-01	104	36.8	3.3E-01	112	59.3	5.8E-01	102	23.6	3.0E-01	79	62.6	64.1	71.5	65.9
s	4.2E-02	N.D[d]	–	3.2E-05	N.D.	–	2.6	2.6E-01	10	1.7	5.OE-02	34	99.9	–	60.0	83.9
CI	1.7E-02	N.D.	–	1.2E-05	N.D.	–	4.2	1.8E + 00	2	2.2	9.6E-02	23	99.9	–	66.0	94.9
K	8.1	4.2E-02	194	2.6	9.0E-03	293	9.2	1.1E-01	84	5.4	6.OE-02	91	75.5	82.4	63.0	64.7
Ca	3.6	3.7E-02	97	1.1	1 .OE-02	106	17.5	3.1E-01	56	8.8	5.2E-02	169	77.2	78.7	66.5	85.6
Ti	1.5	1.9E-02	78	0.4	4.8E-03	81	N.D.	3.4E-02	–	N.D.	3.2E-02	–	79.1	79.8	–	51.5
V	1.1	2.0E-02	55	0.1	–	–	0.5	5.2E-03	96	0.2	2.5E-03	96	88.6	–	67.4	67.5
Cr	0.5	5.0E-02	10	0.1	3.0E-04	171	0.1	7.2E-03	19	N.D.	9.9E-04	–	91.0	99.4	–	87.9
Mn	1.0	3.9E-02	25	0.2	6.0E-03	33	0.7	1.1E-02	62	0.3	3.1E-03	91	83.2	86.7	71.0	78.0
Fe	19.9	2.4E-01	106	6.0	1.9E-01	25	15.3	6.1E-02	251	9.1	1.8E-02	508	76.7	55.8	62.6	77.2
Cu	2.0	1.9E-01	10	0.1	4.0E-03	25	N.D.	7.5E-03	–	N.D.	7.2E-03	–	95.1	97.9	–	51.0
Zn	0.9	5.0E-02	17	0.1	1.7E-03	46	0.3	2.3E-02	12	0.2	1.2E-02	14	91.7	96.7	62.5	65.7
Br	0.8	1.5E-02	55	0.1	9.0E-04	89	N.D.	7.1E-03	–	N.D.	1.6E-03	–	91.2	94.3	–	81.6
Pb	1.5	1.3E-01	12	0.1	N.D.	–	N.D.	6.4E-03	–	N.D.	2.9E-03	–	95.1	–	–	68.8

[a] Initial/(Initial + Subsequence) × 100

[b] Rainfall in non-Asian dust storm period reported by Kasahara et al. (1996a)

[c] The ratio of yellow rainfall to general rainfall

[d] Not detected

facilitate the mixing processes among dust particles, sea-salt, and anthropogenic aerosol precursors.

3.5 Single Raindrop

As mentioned above, it is possible to maintain insoluble particles, which were scavenged by raindrop, on individual raindrop replicas by collodion film technique. These insoluble particles are the target of micro-PIXE analysis. An example of the elemental map for Si, S, Cl, K, Ca, and Fe is drawn in Fig. 8. Each elemental map was drawn on the 128 × 128 pixels by scanning of about 1 μm micro beam on the sample surface. Because the residual particles were retained on a raindrop replica as several clusters, we could not radiate the microbeam to individual residual particles. However, the visualized elemental maps of six element types in several particle clusters enable us to estimate the chemical mixing state of raindrop residual particles. In addition, it is also presumed that the chemical transformation of dust particles is made by wet scavenging processes.

According to the mapping results of micro-PIXE, nearly all the solid particles incorporated into the raindrop exist in a mixed elemental state consisting of crustal (Si, K, Ca, Fe), sea-salt (Cl), and sulfur. As already pointed by other researchers (Wang and Guanghua 1996), this result suggests that the ADS particles were absorbed or coalesced with particles containing marine and artificial components during the long-range transport. Figure 9 illustrates the scavenging of ADS particles by rainout and washout mechanisms and their transformation within the

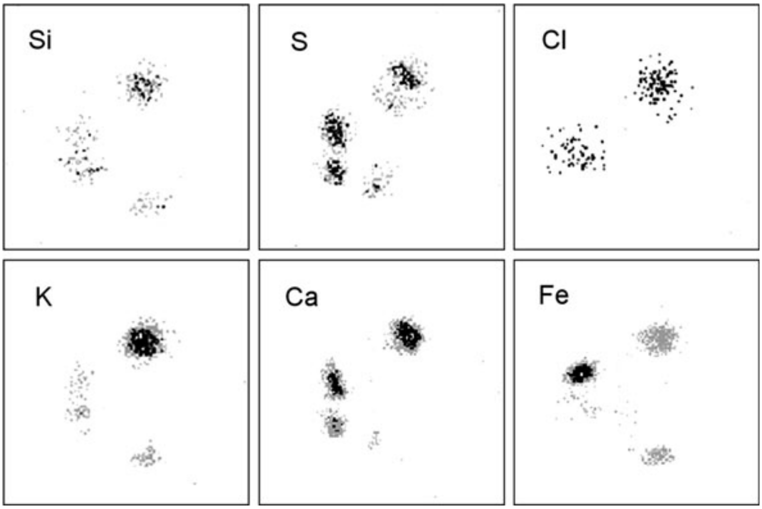


Fig. 8 Micro-PIXE elemental maps (scanning area: 760 × 760 μm^2) on a whole single raindrop (0.5 mm diameter) fallen in a yellow rainfall event

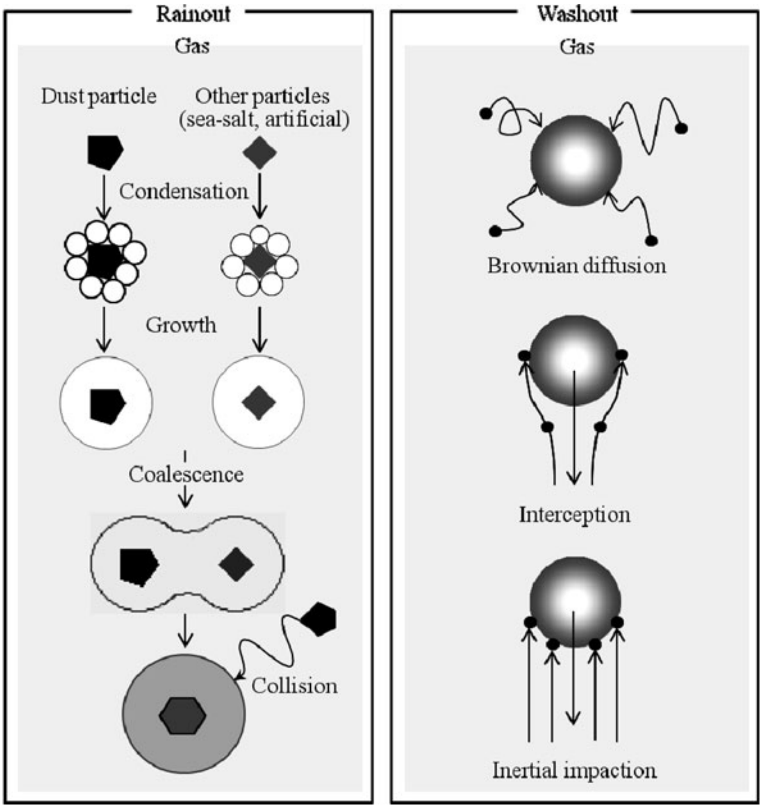


Fig. 9 An illustration depicting the scavenging mechanism of ADS particles by rainout and washout mechanisms

droplet. It is known that fresh mineral particles are mostly hydrophobic. However, if the ambient water droplets spread on them as a horizontal film, their surface can be said to be perfectly wettable (hydrophilic). This enables the transfer of mineral particles into cloud droplets via nucleation scavenging. If mineral particles do not take up any water (i.e. they cannot be dissolved in cloud droplet by itself), they can be scavenged by droplet (i.e. through collision). Furthermore, it should be addressed that ADS particles can also be scavenged by falling raindrops. This washout process generally comprises Brownian diffusion, interception, and inertial impaction.

4 Conclusions

In the present study, in order to fully understand the nature of ADS particles and their wet precipitation at urban receptor area, Japan, a combination of bulk and single sample analyses for particulate matter and raindrop was carried out. In the particles larger than 5 μm, a remarkable increase of number concentration was seen during ADS period event. In the dust storm period, soil fraction accounted for a marked portion of the total particle mass loading. The chemically mixed particles constituted the most abundant ADS particles, while pure dust particle amounted to a small proportion of total particle in the ADS event. The micro-PIXE technique enabled us not only to identify chemical compositions of individual dust particles but also to understand the degree of their chemical mixing. The elemental maps obtained by the micro-PIXE technique indicate that the chemical mixing states of individual ADS particles are strongly dependent on particle size. The visualized elemental maps of individual ADS particles, which cannot be obtained by bulk sample analysis, suggest that relatively large ADS particles are mixed more efficiently than small ones. Major components in rainwater were of soil-origin. It was possible to analyze the insoluble particles retained in individual raindrops by micro-PIXE. Nearly all the solid particles in raindrops were found to exist as a mixed elemental state with crustal, sea-salt, and sulfur. In view of the results achieved in the present study, a study on the combination of bulk rainwater and individual raindrops is found to be helpful to understand the precipitation scavenging. The application of PIXE and micro-PIXE analytical techniques to the determination of elemental compositions in rain samples newly makes certain of the truth that the wet removal processes is one of final dissipation mechanisms of ADS particles.

Acknowledgments The authors express sincere thanks to M.-S. Park who is a Ph. D. student in the Division of Earth & Environmental Engineering, Dong-A University and S. Yoshitake who is an alumna of the Department of Environmental Science, Fukuoka Women's University for their sampling and analyzing support.

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The Assessment of SO_2 Emitted into Atmosphere by the Pyrometallurgical Complex of Ghazaouet (NW, Algeria)

B. Dahmani, F. Hadji and L. Benaabidate

1 Introduction

Anthropogenic activities remain the main sources of hazardous chemicals elements. Those elements may cause adverse effects on human health and environment and thus on the economy. Air pollution has both acute and chronic effects on human health, affecting a number of different systems and organs.

According to recent epidemiological studies, the majority of cancer cases derive from environmental causes, whose factors are attributed to either the indoor environment or outdoor air pollution and soil contamination (Doll and Peto 1981). In deed, the relative risk of lung cancer mortality increases by some 8–27% in heavily polluted areas (Beeson et al. 1998). Ghazaouet city homes the complex of non-ferrous metals (En-Metanof) which uses the pyrometallurgical process. It uses 100000–115000 t/year of raw material for polymetallic sulphide (El Abed blend), and produces 30000–40000 t/year of Zn, 100–150 t/year of Cd and 50000–80000 t/year of H_2SO_4.

In 1970, the implementation of En-Metanof complex was subject to several significant criteria such as the utilization of mineral resources (blends) of El-Abed,

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_19,

creation of an industry for exportable products, unemployment reduction, thus, the emigration to abroad or the release of human potential to the big cities, the use of port and railways facilities already in place and the sea water for cooling the complex installations. These criteria were economically important but they have some disadvantages to the environment of Ghazaouet region such the emission of SO_X gases and aerosols causing the air pollution and liquid and solid wastes that pollute the Mediterranean Sea (Dahmani 1988, 1997).

The population of Ghazaouet city and its vicinity worried about air pollution since 1985/1986. Indeed there was an urgent problem dealing with pollution, especially in 1986, before its stopping for maintenance, the plant operation was unstable because of substantial leakage of gas and liquids from production equipment (furnace, boiler, heat exchangers, chillers etc…) and significant releases of SO_2 in the stack due to the low yield of the catalytic conversion of SO_2 into SO_3.

2 Plant Site and Process Descriptions

The ore of El-Abed which is highly concentrated in sulphides, especially ZnS (57%), is oxidized in a furnace turbulence (grid) producing about 300 t/day of grilled (ZnO). The characteristics of gases are the outlet temperature of the roaster (960 °C), the dust content in gases (310 g/Nm^3), the gas flow rate of (28,500 Nm^3/h) and, therefore, a dust rate of 8.84 t/h. This amount represents approximately 70% of the production, 3.50 t/h (approximately 40%) is recovered by the boiler, 4.85 t/h (55%) by cyclones and electrostatic precipitators, 0.45 t/h (5%) is eliminated by the purification tower. The concentration of sulphur dioxide (SO_2) is about 6–10%. Other gaseous trace compounds are also present. The content of the dust out roasting workshop is 0.120 g/Nm^3 and the outlet temperature roasting workshop is 290 °C.

In 1974, in order to ovoid atmospheric pollution, a purification process had been installed which concerns the conversion of SO_2 into SO_3 (by catalysis with vanadium pentoxide) allowing a production of sulphuric acid. After this step, the flow of emissions from the chimney of the plant (100 m) were 37,000 Nm^3/h, concentration of SO_2 of 0.156%, temperature of 71 °C (Dahmani 1988).

3 Materials and Methods

From the diffusion theories of pollutants in the atmosphere and computer simulations (Viswanadham and Santosh 1990; Anghel and Ozunu 2006; Calder 2007) conducted at the National Office of Meteorology (ONM) of Oran, it was able to make the choice of the sampling sites and the methods of analysis and its sensitivity (Perrino et al. 2009). These sampling stations were distributed according to a Gaussian model in the wind sector dominating the Northwest (Fig. 1).

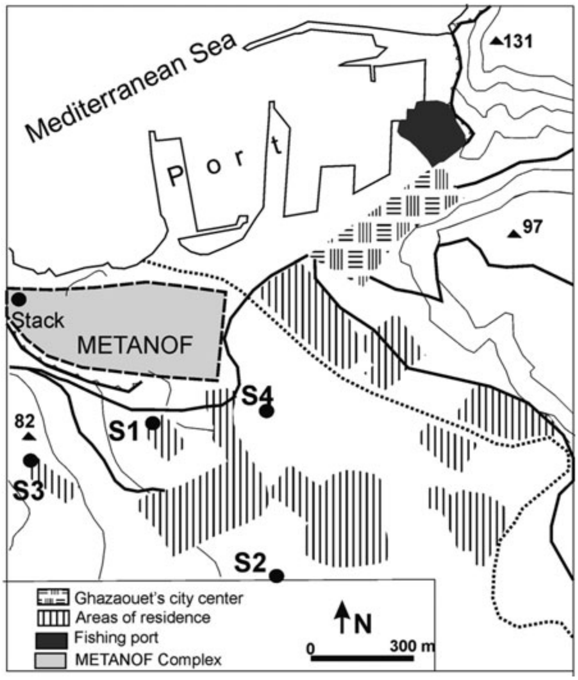

Fig. 1 Sampling stations according to the Gaussian model and depending on the main stack

The assessment of meteorological parameters used in gases diffusion formulas is very important since, according to some authors; the arbitrary determination of these parameters could vary, from 1 to 10, the values finally obtained.

The method for measuring pollution from sulphur dioxide must be both specific for this gas and allows its concentration measure. Its specificity depends on the presence of a physical property or a chemical reaction that detects sulphur dioxide without interference with other atmospheric constituents. The concentration measurement involves the determination of SO_2 in a given volume of air, and therefore the use of an adequate instrument comprising a sampling tube, an absorption device, a meter air and a pump. In order to track pollution changes, it is desirable that each step (measure) is carried out over a short period. However a period of 24 h is the maximum allowable.

The method of tetrachloromercurate sodium is perfectly specific. It requires the use of a molecular absorption spectrometer UV–Visible as well as frequent and regular inspections of the calibration curve and it is effective in terms of sampling and precisely because it can measure the quantities of sulphur dioxide to very low absolute value, less than 100 $\mu g/m^3$, with very short periods of sampling: 5 min to 6 h.

This method relies on the absorption of sulphur dioxide by a flow of air into a solution of tetrachloromercurate sodium where it forms a stable bisulfitomercurate. The assessment of sulphur dioxide amount is done from the obtained colour by adding to the solution a dye fuchsine (hydrochloride para-rosaline). The colour change is estimated by reading the indication given by the spectrometer for which a calibration curve has been carried out in advance (Dahmani 1988, 1997).

4 Results and Interpretation

The effects of kinetic and thermal energies are causes to plume elevation (ΔH), leading to an effective chimney height defined by the following relationship: $H = Hg + \Delta H$, where; H is the geometric height and ΔH the plume height when its axis is more or less horizontal (±10° according to Sutton).

The knowledge of the effective height (H) is a value particularly important in problems of pollution. Calculation of ΔH is therefore essential, but extremely delicate to determine (Young and Jung 1985; Dulal and Sinha 1992; Magnuz 2001). The maximum effective height (H) reached by the emissions plume from the main stack of En-Metanof of Ghazaouet depending on wind speeds and the following conditions (Table 1) will be determined theoretically with $Hg = 100$ m (Tables 2, 3) (Doury 1972).

By observation, we found that the average height of the emissions plume from the main stack of En-Menatof was about 25 m for an average wind speed of 4.25 m/s, so the actual maximum height used for calculations of concentrations on ground is that deducted from the Bosanquet formula ($H = 124.33$ m).

The simulation of air pollution by sulphur dioxide at the site of Ghazaouet was conducted by taking into account 16 directions in relation to the source represented by the main stack of the plant and taking also into account the altitude of the site on a radius of 13,000 m. Table 4 lists the conditions of this simulation (Larsen et al. 1967).

Table 1 Conditions for maximum effective height calculations

Parameters	Symbols	Values
Temperature of atmosphere	T_a	286 °K
Measured volume flow	Q	10.3 m^3/s
Temperature of the gas flow	T_s	344 °K
Density of gas	r	1.1 kg/m^3
Temperature at which the density of gas is equal to that of the atmosphere	T_1	262 °K
Temperature excess	$\Delta T = T_s - T_1$	82 °K
Chimney height	Hg	100 m
Exit diameter of the chimney	d	1.5 m
Speed of gas flow	V_s	5.82 m/s
Vertical gradient of potential temperature	G	0.003 °K/m
Input (calorific flow)	$q_h = Q_m$ (kg/s) * 240 * $(T_s - T_a)$	157,714 cal/s
Wind speeds	U (m/s): 1.00; 2.75; 4.25; 6.50; 9.25; 12.50	

Table 2 Plume elevation (ΔH) depending on wind speeds

	ū (m/s)					
Formula	1.00	2.75	4.25	6.50	9.25	12.50
Bosanquet	430.30	63.83	24.33	10.29	4.97	2.71
Holland	19.60	7.10	4.60	3.00	2.11	1.60
Concawe	48.60	23.95	17.66	13.10	10.25	8.30
Lucas	478.30	173.90	112.50	73.30	51.70	38.26

Table 3 Effective height maximum for a wind speed ū = 4.25 m/s

Formula	ΔH (m)	H (m)
Bosanquet	24.33	124.33
Holland	4.60	212.50
Concawe	17.66	104.60
Lucas	112.50	117.66

Table 4 Simulation conditions

Parameters	Values
Effective height of the chimney	124 m
Temperature of atmospheric air	286 °K
Temperature output of polluting gases	344 °K
Diameter of the chimney at the exit	1.5 m
Speed output of polluting gases	5.8 m/s
SO_2 mass flow at the exit	10.3 g/s
Atmospheric stability (state most conducive to pollution)	Class F (très stable)
Wind speed	1 m/s

Table 5 Theoretical maximum concentration on ground

Wind direction	ψ_o (μg/m^3)	X_o (m)
N	25 to 57	630 to 13300
NW	8 to 57.5	3800 to 13300
NE	19 to 59	1900 to 13300

Simulation of gaseous emissions of the plant was conducted, depending on wind direction, in three different sectors (N, NW and NE). Orders of magnitude of maximum ground concentration of SO_2 (ψ_o) from this simulation and its position relative to the chimney are located in the following intervals (Larsen 1969) (Table 5).

The terms of distribution used to determine the maximum concentration on ground are recorded in Table 6. The calculations have given results that are noted in Table 7. Based on these calculations it can be concluded that the magnitude of the maximum ground concentration of SO_2 (ψ_{om}) and its position relative to the main stack is located in the following intervals; 53 μg/m^3 $< \psi_{om} <$ 65 μg/m^3 and 1240 m $< X_{om} <$ 3430 m. Figure 2 corroborates the theoretical domains obtained above after simulation.

Table 6 Diffusion terms of distribution used to determine the maximal concentration on ground

Parameters	Symbols	Values
Height of the chimney	H	124 m
Flow of gaseous pollutants	Q	10.3 m^3/s
Density of gas	r	1.1 kg/m^3
Temperature of the atmosphere	T_a	286 °K
Average wind speed	$\bar{u}$	4.25 m/s
Bosanquet parameters	P	0.05
	q	0.05
Sutton parameters	Cy	0.10
	Cz	0.10
	n	0.25
Mass flow	–	11.33 kg/s
SO_2 content	–	0.16%

Table 7 Maximum concentration of SO_2 on ground (ψ_{om}) at an optimal distance relative to the main stack

Formulae	ψ_{om} ($\mu g/m^3$)	X_{om} (m)
Bosanquet–Pearson	52.90	1240
Sutton	64.96	3430

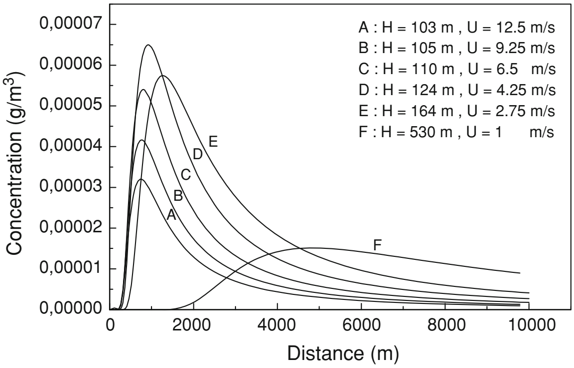

Fig. 2 Theoretical concentrations on ground of sulphur dioxide depending on effective height of the chimney and wind speed

Table 8 Characteristics of sampling stations

Station	Situation	Distance X (m)	Altitude Z (m)
S1	Maison de la culture	700	25
S2	CFPA	1900	100
S3	CEM Ouled Ziri	650	85
S4	SNCFA station	900	4,5

Depending on the availability of equipment and the simulation made, we have sampled atmospheric air in four stations (Fig. 1; Table 8).

Obtained results are recorded in Table 9.

Table 9 Concentrations of sulphur dioxide at the selected sampling stations

Step	S1		S2		S3		S4	
	Duration	ψ_{om} (μg/m^3)	Duration	ψ_{om} (μg/m^3)	Duration	ψ_{om} (μg/m^3)	Duration	ψ_{om} (μg/m^3)
1	6 h 13 min	92.31	23 h 21 min	27.29	06 h 00 min	32.83	05 h 14 min	41.08
2	3 h 51 min	185.86	09 h 39 min	1.20	14 h 42 min	4.69	4 h 25 min	45.23
3	16 h 07 min	81.65	10 h 41 min	0.97	10 h 14 min	11.80	10 h 20 min	11.47
4	5 h 49 min	4.94	08 h 05 min	2.65	14 h 42 min	4.69	7 h 54 min	16.14
5	10 h 20 min	77.07	03 h 43 min	2.58	24 h 08 min	2.97	16 h 54 min	6.24
6	14 h 42 min	4.50	15 h 32 min	0.62	10 h 08 min	7.94	08 h 32 min	11.61
7	7 h 51 min	6.52	4 h 53 min	7.27	3 h 42 min	10.37	13 h 44 min	7.43
8	16 h 57 min	3.20	–	–	10 h 42 min	2.62	10 h 14 min	6.68
9	8 h 24 min	128.50	–	–	4 h 54 min	13.59	4 h 51 min	15.65
10	16 h 09 min	2.82	–	–	10 h 05 min	11.77	15 h 14 min	2.65
11	03 h 51 min	7.26	–	–	–	–	4 h 58 min	27.47
12	15 h 17 min	2.65	–	–	–	–	10 h 18 min	4.84
13	4 h 58 min	25.44	–	–	–	–	–	–

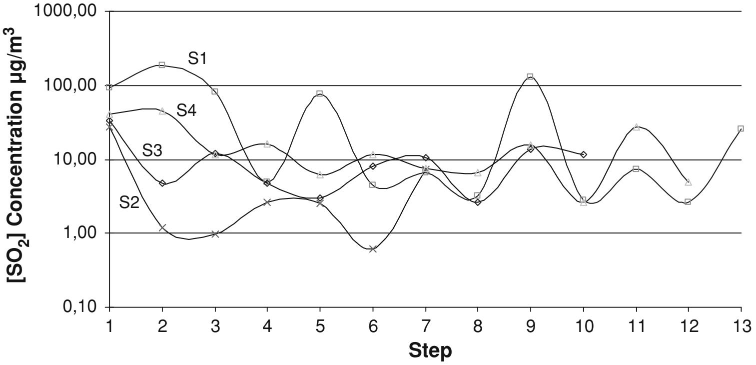

Fig. 3 Concentrations of SO_2 µg/m^3 in air measured in stations according to the periods in Table 9 of data measurements for each station

Among the 120 measures of maximum ground concentrations of SO_2, five of them are higher than the EU standards. The maximum concentration of 185 mg/m^3 for a sampling time of 3 h 51 min was recorded at station S_1. Other concentrations, derived from simulations (Fig. 2) and measurements realized in the same period (Table 9) are below the standards and they are between 100 and 150 mg/m^3 in 24 h and between 40 and 60 mg/m^3 for 1 year (Fig. 3).

To minimize the SO_2 emissions, the roasting and catalysis workshop of the pyrometallurgical complex must be periodically maintained and should operate under optimal conditions for a maximum efficiency of the catalytic tower (i.e., for a maximal transformation of SO_2 and SO_3 into H_2SO_4) (Zimmer and Larsen 1965) The content of SO_2 released to atmosphere from the main stack must be minimal and less than 0.156% to avoid a negative influence on public health and Ghazaouet's environment (Fig. 4).

5 Conclusion

At the station S1, significant levels of about 185 mg/m^3 have been detected for a sampling time of 3 h 51 min. This station appears to be the most affected by SO_2 emissions. Ghazaouet city has the disadvantage of being in the path of prevailing winds (between NW and NE). This requires a stable supply of metallurgical complex so that pollution should be minimized and remains below international standards regardless of weather.

Stops and starts of the roasting workshop must be uncommon because in these cases, momentary pollution is higher compared to the international standards. Proper operation and regular maintenance of production facilities of the complex would prevent fluctuations in gaseous (gaseous wastes). Several research topics on environmental protection of Ghazaouet's city could be conducted in collaboration

Fig. 4 Influence of SO_2 emission on trees located at 700 m from the main stack (Station S_1)

with industry, researchers of University Hospital Center to improve the quality of life.

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Part IV
Bioavailability and Toxicology of Airborne Particulate Matter

Clare L. S. Wiseman and Fathi Zereini

As discussed previously, there is strong evidence for an association between ambient PM exposures in urban populations and patterns which have been observed in cardiopulmonary mortality and morbidity. Fine PM exposures have been particularly identified as posing a risk, especially in the elderly, those with a compromised health status and children with their developing respiratory systems. Less is known regarding the chemical constituents of PM and their bioavailability and the toxicological mechanisms through which they exert a negative health effect; crucial issues in the development of air quality policy and emissions regulations which are protective of human health. Part IV contains three sections which discuss important aspects of the bioavailability of PM exposures and the toxicological mechanisms involved in the induction of negative health outcomes.

In the first chapter, Leopold and Schuster discuss a method for the preparation and use of a standardized material to investigate the chemical behavior and bioavailability of palladium (Pd) emitted from traffic, a metal which has been found in increasingly greater amounts in the environment due to its popular use as a catalyst in automotive catalytic converters. In presenting the results of a study they conducted on barley plants, they provide an empirical example as to how the environmental bioavailability and impacts of PM constituents can be assessed. The final two sections address issues related to the toxicological mechanisms through which airborne PM and its chemical constituents may exert an effect in humans and their assessment. Specifically, Valavanidis et al. discuss the primary mechanisms involved in the generation of reactive oxygen species (ROS) in their research using traffic-related PM and exhaust soot from diesel and gasoline powered vehicles in the second chapter. As part of this, they detail the role of stable free radicals, polyaromatic hydrocarbons (PAHs) and transition metals and their interactions in contributing to the cytotoxic and carcinogenic potential of PM. In the third chapter, Akhtar et al. provide a comprehensive overview of the results and methods used to assess the toxicology of PM both in vivo and in vitro. As they discuss, in vivo and in vitro toxicology studies have significantly contributed to our understanding of the pathophysiological mechanisms underlying PM-induced health effects. In particular, they have revealed the importance of oxidative stress-initiated inflammation as being a major pathway of PM-induced respiratory and cardiovascular disease. They conclude, however, that knowledge gaps remain; most notably those that pertain to the mechanisms responsible for the induction of human health effects at low dose PM exposures.

Pd Particles as Standardized Test Material for Bioavailability Studies of Traffic Related Pd Emissions to Barley Plants

Kerstin Leopold and Michael Schuster

1 Introduction

Since the early 1980s of the last century air pollutant emissions from individual traffic were reduced by the introduction of automotive exhaust catalysts. Several noble metals, like platinum, rhodium, and palladium (platinum group metals, PGMs), catalyze the conversion of carbon monoxide, nitrogen oxides, and hydrocarbons into non-hazardous gases. On the other hand, thermal and mechanical stresses during operation of the catalyst material lead to PGM emissions into the environment. About 90% of these emissions are particulate matter varying in size from >10.2 μm to <5 nm. The coarse particles consist of alumina particles that carry dispersed PGM particles with diameters of a few nanometers (Abthoff et al. 1994; Artelt et al. 1999a, b; Herz and Shinouskis 1985). The fine particles of a few nm in diameter are mainly elemental PGM (Inacker and Malessa 1996). The amount of PGM emitted from exhaust converters is dependent on several parameters, such as the age of the exhaust converter, the driving speed and the type of converter and ranges in the order of several 10 to 100 s ng/km (Ek et al. 2004; Ravindra et al. 2004). Several authors studied the size distribution of platinum containing particles and showed that about a third of the total Pt emission can be found as particles <5 nm (Inacker and Malessa 1996), 43–74% is in the particle fraction >10.2 μm, 11–27% in the 3.14–10.2 μm fraction, and 11–36% in the particle fraction <3.14 μm (Artelt et al. 1999a, b). In urban environments with high traffic densities these emissions can contribute considerably to airborne particulate matter. Newer automotive catalysts use palladium as the main or only

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_20,

catalytic element and due to its toxicological and allergenic potential, traffic caused palladium emissions were studied by a number of scientists in the last decades (Leopold et al. 2008a, b; Whiteley 2005; Fang et al. 2005; Lesniewska et al. 2004; Palacios et al. 2000). A high solubility of Pd from these particles could be shown in artificial rain by Jarvis et al. 2001. (Zereini et al. 2007) found palladium even in a depth of about 12–16 cm in the ground near a German highway. Furthermore, the uptake of Pd in plants and animals in the environment was studied by several groups and high uptake factors were reported (Sures et al. 2002; Schäfer et al. 1998). Numerous laboratory exposure studies have also been published, some of them are summarized in (Zereini and Alt 2006). However, in these studies either original road dust (e.g., Zimmerman et al. 2002; Sures et al. 2001) or dissolved palladium species ($Pd^{(II)}$) (Sures and Zimmermann 2007) were used for exposure experiments. The use of original road dust guarantees an exposure of environmentally relevant Pd species, but the biological effects arising with this kind of exposure overlap with other traffic-emitted heavy metals such as Pb, Zn, Cd, Sb and Cu, which may also affect the biological reaction of plants and animals (Schäfer et al. 1998). Exposure experiments with soluble Pd species, on the other hand, do not reflect the conditions actually occurring in the environment and the chemical form of bioavailable Pd might not only be dissolved Pd. (Speranza et al. 2009) who studied the growth of Kiwi pollen exposed to either soluble $Pd^{(II)}$ or Pd nanoparticles found significant differences in their vitality depending on the Pd exposure species. Consequently, drawing conclusions on the bioactivity of traffic related Pd emission can not be made by experiments based on the application of water soluble $Pd^{(II)}$ compounds only. Another approach, the application of grinded car catalyst material for Pd bioavailability/uptake studies suffers from the problem, that only the surface of the ceramic monolith material used in typical car exhaust catalysts contains the catalytically active Pd particles, whereas the bulk material mainly consists of oxides of aluminium, silicon, magnesium, and cerium (Martin et al. 2003), which at best shows a (bio) chemically neutral behaviour. In the case of used catalysts, the grinded material also may contain toxic compounds resulting from the combustion process (oil residues, additives etc.,) or engine abrasion material, which may interfere Pd related biological studies. New catalysts on the other hand undergo rapid chemical and physical changes (Martin et al. 2003) which make them less suitable for biological or chemical investigations.

Therefore preparation of non-contaminated and well defined particulate material, which resemble Pd particles emitted from automobile catalysts into the environment and which are available in higher standardized quantities, is very reasonable. A comparable approach for platinum was made by Ruehle et al. (1997) focussing on traffic related platinum emissions, but for palladium appropriate material was not yet available. Synthesis of the Pd particles was performed by chemical reduction of Pd^{II} to Pd^{0} in aqueous solutions similar to a method first described by Mucalo et al. (1991). Optimization of this method yielded in a simple, fast and very reproducible preparation method for appropriate Pd nanoparticles with a narrow size distribution. Three types of Pd particles—Pd nanoparticles dispersed on micrometer silica support particles (Pd/SiO_2), Pd nanoparticles (Pd-NPs) and Pd micrometer particles (Pd-MPs)—were prepared and characterized in detail by transmission electron microscopy (TEM), high resolution (HR) TEM, selective area diffraction (SAD), laser granulometry and graphite furnace atomic absorption spectrometry (GFAAS). Silica was chosen as a support material instead of alumina because of its higher chemical resistance and lower impact on plant health. However, these particles resemble very well those emitted from catalytic converters in size distribution. Applying those particles in exposure studies with plants guaranties that observed affects can be ascribed to Pd solely. Thereby, basic information can be provided establishing a first step towards general knowledge on the uptake of Pd from particles, like, e.g., draw a deduction of the up-taken Pd species and ratios.

The three types of different particulate Pd material were then applied to study the uptake of Pd in barley plants. Seeds were exposed to nutrient solutions spiked with Pd at different concentrations as suspended Pd particles. The raised sprouts were harvested after 2 weeks and Pd was determined in the leaves, seeds and roots. The plant growth was assessed and the uptake of potassium (K) and calcium (Ca) in the plants as representatives of macronutrients was investigated.

2 Materials and Methods

All chemicals were purchased in the highest available purity from Merck (Darmstadt, Germany). Ultra pure water (at least 18.2 MΩ) was obtained from a Milli-Q-Gradient-System (Millipore GmbH, Schwalbach, Germany) and used for the preparation of all solutions and suspensions.

2.1 Preparation and Characterization of Pd Nano and Micrometer Particles

Pd nanoparticles (Pd-NPs) colloidal solution and Pd micrometer particles (Pd-MPs) suspension with a concentration of 1.1–10.6 mg Pd L^{-1} were prepared by chemical reduction of $Pd^{(II)}$ to $Pd^{(0)}$ in aqueous solution following the protocol described in (Leopold et al. 2008a, b). For this purpose an adequate amount of a $Pd(NO_3)_2$ standard solution was diluted in ultra pure water and a freshly prepared sodium borohydride solution was added for reduction. Depending on the addition rate of reductant and reaction temperature the formed particles diameter varies. At a temperature of 0–5 °C Pd-NPs with a size distribution from 5 to 10 nm (Fig. 1a) are formed, whereas at room temperature larger, agglomerated particles with a diameter of 0.5–5 μm are obtained (Fig. 1d). Immediately after preparation the solution/suspension was either used for characterisation of the particles or mixed with nutrient salts for exposure studies. For HRTEM and SAD

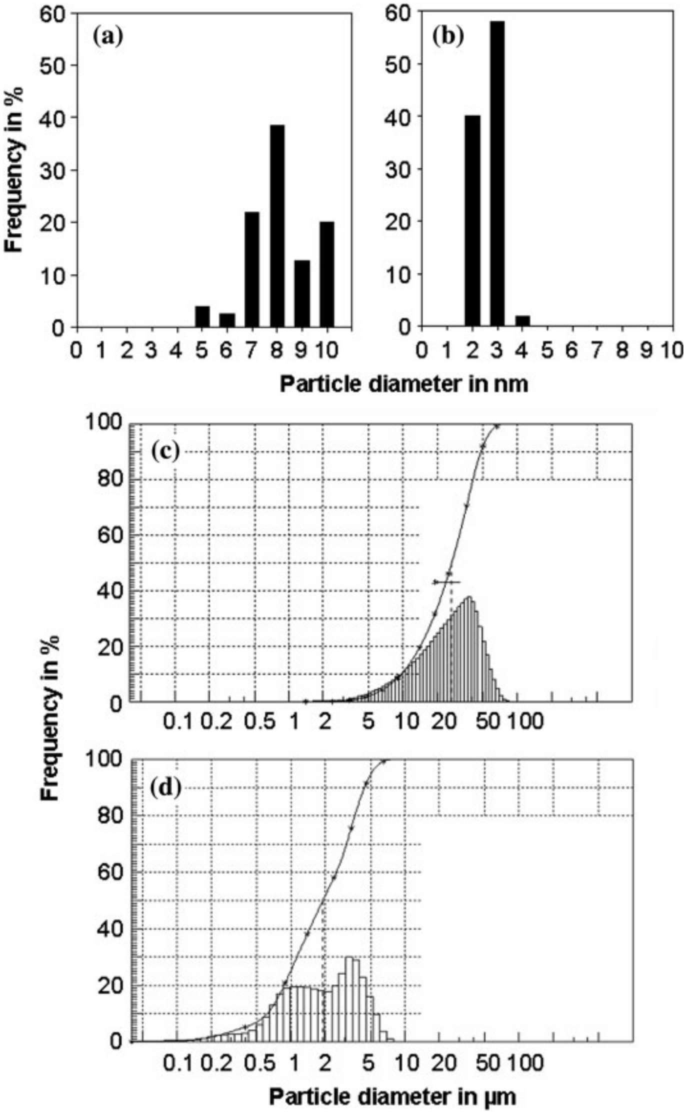

Fig. 1 Particle size distribution of **a** Pd nanoparticles, **b** Pd particles on silica support (Pd/SiO$_2$), **c** silica support particles, **d** Pd micrometer particles. Data obtained by evaluation of different series of TEM images (**a**, **b**; n = 100; particles were obtained from three independent syntheses) or measured by laser granulometry (**c**, **d**)

measurement a JEM 100CX transmission electron microscope (Joel, Tokyo, Japan) equipped with a tungsten cathode (operated at 120 kV) was used for visualisation of Pd nanoparticles and for selective area diffraction measurement. Samples of the suspensions were treated with ultra sound for 5 min and then 5 µL of the particle containing liquid were swabbed on a double holy-carbon grid. Particle size distribution of Pd-MPs was measured with a laser granulometer 1064 (CILAS, Orléans, France).

2.2 *Pd Nanoparticles Dispersed on Silica Support*

Similarly to the Pd-NPs preparation Pd nanoparticles on silica support particles (particle size 5–80 μm, Fig. 1c) were also obtained by chemical reduction of $Pd^{(II)}$ to Pd^0 in the presence of silica powder suspended in ultra pure water. The resulting Pd/SiO_2 suspension was centrifuged and subsequent the supernatant was decanted. For the removal of adherent chemicals the Pd/SiO_2 particles were re-suspended in ultra pure water and again isolated by centrifugation and decanting. This procedure was repeated twice before the particles were oven dried at 100 °C for at least 12 h. The particle size of the Pd on the silica surface was investigated by TEM and is given in Fig. 1b. A selective area diffraction (SAD) measurement confirmed the oxidation state of $Pd^{(0)}$ as the only Pd present. Measurement of Pd content of Pd/SiO_2 particles revealed 480 ± 3 μg Pd g^{-1} SiO_2, i.e., 0.5 wt%.

2.3 *Experimental Set-up for Pd Exposure of Barley*

Barley seeds were raised at the German Research Center for Environmental Heath (Institute of Biochemical Plant Pathology, Neuherberg, Germany) for 2 weeks according to a procedure described by Battke et al. (2008) in a modified Hoagland's E medium (Arnon and Hoagland 1940) spiked with Pd-NPs, Pd-MPs, or Pd/SiO_2 particles at different Pd concentrations. For this purpose the nutrient salts were dissolved in Pd particle suspensions in ultra pure water resulting in a final

Table 1 Composition of the nutrient medium for Pd exposure studies of barley plants

Nutrient salts	Concentrations in nutrient medium (mg L^{-1})
$MgSO_4 \cdot 7H_2O$	12.3
$Ca(NO_3)_2 \cdot 4H_2O$	27.14
KH_2PO_4	3.4
KNO_3	12.625
H_3BO_3	0.7125
$MnCl_2 \cdot 4H_2O$	0.0455
$ZnSO_4 \cdot 7H_2O$	0.0055
$Na_2MoO_4 \cdot 2H_2O$	0.00225
$CuSO_4 \cdot 5H_2O$	0.00225
$FeCl_3 \cdot 6H_20$	0.484
EDTA	1.25

Table 2 Parameters for Pd exposure studies of barley plants

Plant species	Nutrient medium	Pd species in nutrient medium (respectively)	Pd concentrations in nutrient medium (mg L^{-1})	Exposure duration (days)
Barley *Hordeum vulgare* L. cv. Barke (seeds)	5% Hoag-land's E medium	Pd-NPs Pd-MPs Pd/SiO_2 particles	0 (control) 1.1 2.7 5.3 8.0 10.6	14

nutrient salts concentration of 5% of the normal Hoagland's E medium. The final composition of the nutrient medium is given in Table 1.

For each Pd concentration and control two identical beakers were prepared, sealed with Parafilm and put in a controlled cabin with 14 h light (T = 22 °C) and 10 h dark (T = 18 °C) per day. The exposure parameter for barley plants are summarized in Table 2.

After 2 weeks the plants were harvested and the roots were rinsed with ultra pure water to remove traces of Pd and other elements from the nutrient solution. The plants were fractioned into different tissues by cutting the leaves and roots from the seed. Then the leaf length was measured and the tissues were dried and grinded for the determination of Pd concentrations in leaves, seeds and roots.

2.4 Experimental Set-up for Pd, K and Ca Measurement

Determination of Pd, potassium (K) and calcium (Ca) in the plant material was performed after total digestion of the homogenized and dried material. For this purpose a microwave-assisted oxidative digestion was performed with a mixture of concentrated nitric acid and hydrogen peroxide reaching a maximum pressure of 30 bar and a maximum temperature of 220 °C (Battke et al. 2008). The resulting digests were transferred quantitatively into volumetric glass flasks and filled up with ultra pure water to a defined volume.

Pd concentration in the digests was measured by GFAAS with a SIMAA 6000 instrument (Perkin Elmer, Überlingen, Germany). Standard instrumentation parameters were applied according to the recommendations of Perkin Elmer for Pd analysis (wavelength 247.6 nm, slit width 0.7 nm). In a Pd concentration range of 15–500 μg L^{-1} the instrument calibration was performed by measuring aqueous solutions of $Pd^{(II)}$, prepared by dilution of adequate aliquots of stock standard $Pd(NO_3)_2$ solution in 0.5 M HNO_3 and 1,000 mg Pd L^{-1} (Merck) in 0.25 M HNO_3. The Pd blank value for the sample preparation procedure resulted in a GFAAS signal intensity of 0.0009 ± 0.0001 A-s, which is more than five-times lower than the detection limit for this method (13.2 μg Pd L^{-1}).

Samples with Pd concentrations below 1 μg L^{-1} were measured after selective pre-concentration of Pd on a micro column using a modified FIAS-400 flow injection analysis system equipped with an autosampler AS-90 (Perkin Elmer) which was directly coupled to the GFAAS instrument. Calibration was performed by measuring aqueous solutions of $Pd^{(II)}$, in a concentration range of 25–1,000 ng Pd L^{-1} achieving a detection limit of 16 ng Pd L^{-1} (sample volume of 2.7 mL). A detailed description of the pre-concentration procedure can be found in Leopold et al. (2008a, b).

The K and Ca contents of barley leaf digests were determined using total reflection X-ray fluorescence (TXRF) analysis with an Atomika 8010 instrument (Oberschleissheim, Germany). For internal calibration, Vanadium (V) was chosen in a concentration range of 1–10 mg L^{-1}. For this purpose, an adequate volume of a V standard solution (NH_4VO_3 in 0.5 M HNO_3 and 1000 mg V L^{-1}) was added to a defined volume of the sample digestion solution. After thorough mixing, 1 μL of the sample solution was pipetted onto a silicon wafer, desiccated by water evaporation on a heated plate and measured by TXRF. Blank values resulting from contaminations in the digestion reagents were considered by correcting the measured sample values with this reagent blank. The detection limit for this method was 10 mg L^{-1}.

Three replicates of each standard and digestion solution were measured.

3 Results and Discussion

3.1 Pd Uptake in Barley

Pd content in roots, seeds and leaves of barley plants raised for 2 weeks in a nutrient solution spiked with Pd as either Pd-NPs, Pd-MPs, or Pd/SiO_2 particles in concentrations up to 10.6 mg Pd L^{-1} was determined. Negligible Pd concentrations were detected in barley plants raised without Pd spikes in the nutrient

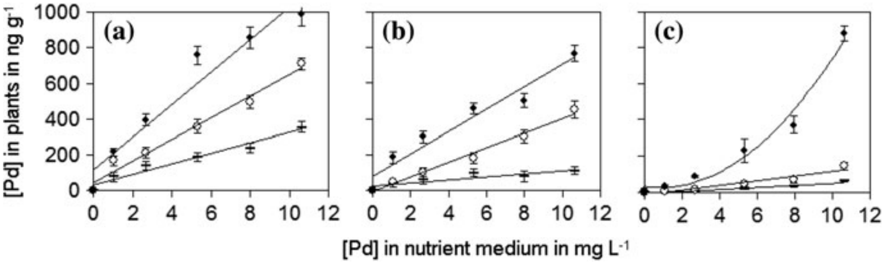

Fig. 2 Pd content in **a** roots, **b** seeds, and **c** leaves of barley plants raised for 2 weeks in a nutrient solution spiked with Pd as either (*filled circle*) Pd-NPs; (*empty circle*) Pd-MPs; or (*dash*) Pd/SiO_2 particles at different Pd concentrations ([Pd] = 0, 1.1, 2.7, 5.3, 8.0, 10.6 mg L^{-1}; n = 3; *error bars* represent ± one standard deviation, regression coefficients R^2 for linear regression in **a** (*dash*) 0.96, (*empty circle*) 0.98, (*filled circle*) 0.94; **b** (*dash*) 0.79, (*empty circle*) 0.99, (*filled circle*) 0.95; and polynomial regression in **c** (*dash*) 0.98, (*empty circle*) 0.98, (*filled circle*) 0.98)

solutions (controls). Furthermore, results showed that barley Pd content increased with increasing Pd concentration in the nutrient medium (Fig. 2). Linear correlation between Pd exposure concentration and Pd content in roots and seeds was observed (Fig. 2a, b), whereas Pd uptake in the leaves follows polynomial increase (Fig. 2c). Highest Pd contents were observed in the plants exposed to Pd-NPs and lowest contents occurred in plants exposed to Pd/SiO_2 particles.

There are two reasonable explanations for the higher Pd uptake from Pd-NPs spiked medium compared to the uptake from Pd-MPs and Pd/SiO_2 spiked medium:

1. Better solubility of Pd-NPs in the nutrient medium, i.e., transformation of particulate $Pd^{(0)}$ to soluble $Pd^{(II)}$; or
2. Direct uptake of Pd-NPs by the plants roots. In order to clarify this question, a few microliter of the sap of a barley sprout exposed to Pd-NPs were investigated by TEM and indeed Pd-NPs were observed (Fig. 3). This finding is in good agreement with recently reported uptake of metal oxide and fluoride nanoparticles by the roots of different plant species (Hirschmoeller et al. 2009; Lin and Xing 2008; Zhu et al. 2008). Whereas ZnO-NPs were adhered onto the roots surface and observed in apoplast and protoplast of the root endodermis and stele of ryegrass (Lin and Xing 2008), Fe_2O_3-NPs were observed in all fractions of pumpkin plant tissues (roots, stem and leaves) (Zhu et al. 2008).

Pd-MPs and Pd/SiO_2 particles are both too large for direct uptake by the roots and therefore here only soluble $Pd^{(II)}$ is expected to enter the plants. However, Pd solubility from the Pd/SiO_2 particles might be expected higher than that from the Pd-MPs due to the larger active surface of the nanometer scaled Pd particles on the silica surface. But, on the other hand silica offers a large surface for re-adsorption of formed $Pd^{(II)}$ and this effect seems to be preponderate in the nutrient solutions. Hence, higher Pd values occurred in the plants exposed to the Pd-MPs.

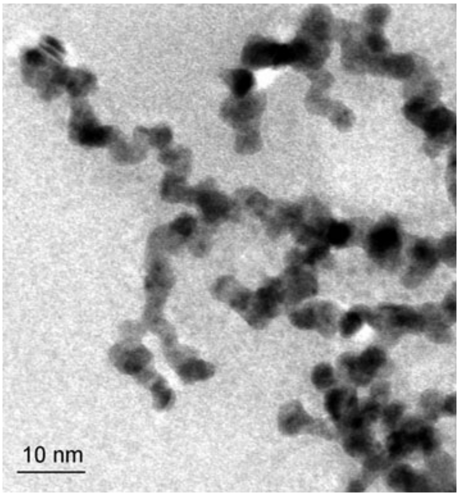

Fig. 3 Transmission electron microscopic image of the sap of a barley sprout exposed to a nutrient solution spiked with Pd-NPs

3.2 Effects of Pd Uptake in Barley Plants

Plant growth for Pd exposed barley plants and control was evaluated by measuring the leaf length after 2 weeks exposure. At higher Pd exposure concentration lower leaf lengths were observed (Fig. 4a). Linear regression analysis demonstrated a dose–effect relationship for Pd-NPs and Pd-MPs exposure (Pearson correlation coefficient $p < 0.0001$), whereas for Pd/SiO$_2$ exposure no significant correlation was observed. Furthermore, correlation analysis of leaf length and Pd leaf levels showed linear decreases for the different types of Pd particles ($p < 0.0001$; Fig. 4b). Similar slopes where obtained for Pd-MPs (−0.195) and Pd/SiO$_2$ (−0.193) exposure whereas a lower decrease was observed for Pd-NP exposure (slope −0.0913, when omitting the highest found Pd value of 879 ng g^{-1}).

Similar affects on biomass production are reported by Lin and Xing 2008 in the above mentioned study of ryegrass exposed to ZnO nanoparticles and the observed effects could not exclusively be ascribed to the dissolved Zn^{2+} ion concentration in the nutrient solution. Conversely, no effects occurred after uptake and distribution of Fe_2O_3 nanoparticles in pumpkin plants (Zhu et al. 2008). Hence, the chemical composition of the nanoparticle and/or the plant species plays an important role in this context.

The contents of the macronutrients potassium (K) and calcium (Ca) in the barley leaves decrease with higher Pd content following a logarithmic decrease (Fig. 5). Again, the effect is stronger in case of Pd/SiO$_2$ (slope −4.3 Ln) and Pd-MPs (slope −3.7 Ln) exposure compared to Pd-NPs exposure (slope −2.9 Ln). Nevertheless, the K and Ca decrease is significant in all experiments (p: Pd-NPs, K 0.003, Ca 0.0006; Pd-MPs, K < 0.0001, Ca 0.0001; Pd/SiO$_2$, K 0.0003, Ca 0.0008). This finding is in agreement to the observations made by Speranza et al. 2009 who studied the vitality and growth of Kiwi pollen exposed to either soluble

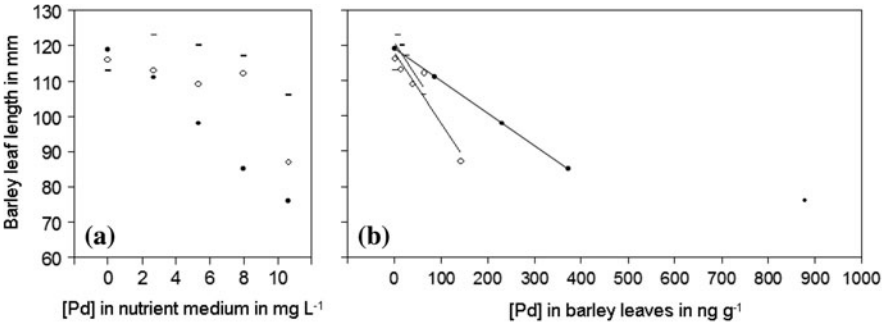

Fig. 4. Effects of Pd exposure on the average leaves length of barley plants raised for 2 weeks in a nutrient solution spiked with Pd as either (*filled circle*) Pd-NPs; (*empty circle*) Pd-MPs; or (*dash*) Pd/SiO$_2$ particles dependent on **a** Pd concentrations in the nutrient medium ([Pd] = 0, 1.1, 2.7, 5.3, 8.0, 10.6 mg L^{-1}; n = 30; SD = 10 mm); **b** Pd content found in the barley leaves ($n_x = 3$; $n_y = 30$; linear regression coefficient R^2 for (*dash*) 0.51, (*empty circle*) 0.89, (*filled circle*) 0.99)

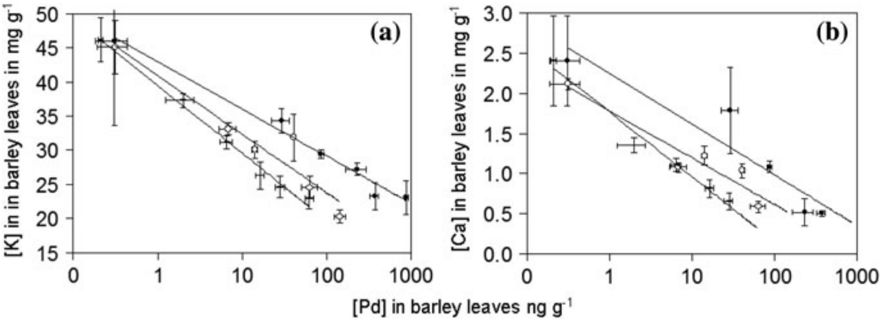

Fig. 5 Effects of Pd exposure on **a** potassium and **b** calcium concentration in barley leaves dependent on the Pd concentration found in the leaves of plants raised for 2 weeks in a nutrient solution spiked with Pd as either (*filled circle*) Pd-NPs; (*empty circle*) Pd-MPs; or (*dash*) Pd/SiO_2 particles at different Pd concentrations ([Pd] = 0, 1.1, 2.7, 5.3, 8.0, 10.6 mg L^{-1}; $n = 3$; *error bars* represent ± one standard deviation; regression coefficient R^2 for **a** (*dash*) 0.92, *empty circle* 0.98, *filled circle* 0.99; **b** *dash* 0.98, (*empty circle*) 0.89, (*filled circle*) 0.91

$Pd^{(II)}$ or Pd-NPs. Here, a decrease in Ca uptake of Kiwi pollen similarly to the correlation found in this study has been reported.

However, from the experiments performed it is not possible to decide whether the decrease in K and Ca levels results from a depletion caused by membrane damages due to Pd uptake [as reported for Kiwi pollen (Speranza et al. 2009)] or if Pd cations simply replace other cations in the plants. Probably both mechanisms occur. Similar trends were observed for sulphur and manganese, but their concentrations in the plant tissues were comparably low and therefore no significant correlation was found.

4 Conclusions and Outlook

The synthesized Pd particles are well characterized and suitable for exposure studies with plants showing reasonable and reproducible results. As shown Pd uptake by barley plants is dependent on the Pd species in the nutrient medium. In case of Pd-MPs and Pd/SiO_2 exposure presumably only soluble $Pd^{(II)}$ was taken up whereas Pd-NPs can enter the plants directly, at least into the sap. Therefore, highest Pd concentrations where found in the plants exposed to Pd-NPs. However, strongest affects on plant growth and macronutrient uptake were caused by Pd uptake from Pd-MPs and Pd/SiO_2. Obviously, Pd-NPs can enter the plant leaves to a high amount, but do not affect leaf growth or nutrient uptake as strong as soluble Pd species. However, in this study plants were grown for only 2 weeks and dissolution of Pd-NPs in the plants seems likely, i.e., the high amounts of Pd taken up by the plants might show delayed affects. Therefore, longer period exposure studies and solubility test in, e.g., sap are planned with the model particles.

Furthermore, Pd solubility from the particles in other media than nutrient solution will be investigated, since soil or road dust constituents might improve the Pd solubility and/or dissolved Pd species might (re-)adsorb on soil or dust particles.

Acknowledgments The authors are very grateful to Dr. Florian Battke (German Research Center for Environmental Heath, Institute of Biochemical Plant Pathology, Neuherberg, Germany) for raising the barley plants.

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The Role of Stable Free Radicals, Metals and PAHs of Airborne Particulate Matter in Mechanisms of Oxidative Stress and Carcinogenicity

Athanasios Valavanidis, Konstantinos Fiotakis and Thomie Vlachogianni

1 Introduction

Epidemiological investigations have established an association between exposure to particulate matter (PM) from various air pollution sources and increased human morbidity and mortality (Yang and Omaye 2009; Valavanidis et al. 2008). Acute and chronic exposure to ambient inhaled particles is associated with pulmonary, cardiovascular diseases and cancer (Brunkreef and Holgate 2002; Chen et al. 2008; Puett et al. 2008; Samoli et al. 2008).

Although exposure to airborne PM has been correlated with increased rates of respiratory and cardiovascular morbidity and mortality, there is still a fundamental lack of understanding of the underlying biological mechanisms. Airborne particles in urban air pollution episodes have been proved to be potent oxidizing agents towards important biological molecules, either through direct attack in the cellular compartments or indirectly through the activation of intracellular pathways (Shinyashiki et al. 2009; Ying et al. 2009). Experimental observations in vivo and in vitro showed that particulate air pollutants cause pulmonary toxicity by retention and direct interaction in airways and alveoli, interference with either mucociliary or phagocytic clearance, transport of toxic chemicals adsorbed onto the surface of the particle and generation of oxygen free radicals which produce inflammatory responses (Martin et al. 1997; Bai et al. 2001). Furthermore, inhaled PM, either directly or through uptake into epithelial cells and macrophages, activate oxidant pathways releasing more cytotoxic reactive oxygen species (ROS) thus increasing oxidative stress (Fujii et al. 2001; Li et al. 2000; Lundborg et al. 2001; Mo et al. 2009; Renwick et al. 2001).

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_21,

The aerodynamic diameter (a.d.) plays an important role for the penetration into the lungs' alveoli increasing the PM cytotoxicity. The PM_{10}, "thoracic" particles (a.d. < 10 μm, penetrating into the lower respiratory system), the $PM_{2.5}$ ("respirable" particles, a.d. < 2.5 μm, penetrating into the gas-exchange region of the lungs), and the ultrafine particles (a.d. < 0.1 μm, very large surface area but negligible particle mass) are the most important from the cytotoxicity perspective PM. It has been recognized that ultrafine particles, with a mass median diameter of <0.1 μm, are more toxic when inhaled than PM_{10}, because of their ability to be absorbed into tissues and ultimately to enter blood circulation. The greatly increased surface area of ultrafine particles is an important factor in their cardiopulmonary toxicity (Brown et al. 2001; Ferin et al. 1992; Liu et al. 2009).

During a pollution episode, each human lung acinus can receive on average 30 million particles and each alveolus about 1,500 particles every 24 h, of which 50% are being deposited in the lungs (Seaton et al. 1995). The lung airways retain mostly $PM_{2.5}$ rather than PM_{10}, a finding supported by observation. Analytical electron microscopy measurements in never-smoking, long-term residents of urban areas showed that 96% of the effectively retained particles in the lung parenchyma were $PM_{2.5}$ and 5% were ultrafine particles (Churg and Brauer 1997, 2000).

Heavy metals and their complexes associated with PM surfaces were found to cause acute lung injury in rats (Dreher et al. 1996). Bioavailable metals in the surface of PM are found experimentally to have a causative role in the lung tissue damage, through generation of oxygen free radicals (Ghio et al. 1992). Iron released from airborne PM or metals with redox potential, play a catalytic role in the generation of reactive oxygen species (ROS), especially hydroxyl radicals ($HO^{\bullet}$) causing extensive damage to cellular biological molecules (Donaldson et al. 1997; Pritchard et al. 1996; Valavanidis et al. 2000; Van Maaren et al. 1999).

Combustion of fuels produces particulates which are chain-aggregated masses of fine carbonaceous spheres, containing persistent organic free radicals, metals and PAHs. Generation of ROS from PM can be considered very important, because it can be linked to inflammatory reaction in the lungs as well as to pulmonary and cardiovascular injury. Electron Paramagnetic Resonance (EPR) spectra of PM show a single broad unstructured signal corresponding to a family of quinone-semiquinone radicals (Dellinger et al. 2001; Squadrito et al. 2001). These radicals are found at high concentrations, are remarkably persistent and have the ability to generate ROS (including $HO^{\bullet}$) by quinoid redox cycling. The redox cycling of semiquinones has been proposed as a mechanism of toxicological importance in the lungs for PM. Researchers have established that the carcinogenicity of quinones results from the formation of ROS, through redox cycling reactions (shuffling electron enzymatically or nonenzymatically among their reduced and oxidized forms and/or their semiquinone radicals) and with the involvement of metal ions and NADH (Balakrishna et al. 2009).

Polycyclic aromatic hydrocarbons (PAH) are mainly products of incomplete combustion and can be found at high concentrations in PM. PAHs require metabolic activation to electrophiles, catalyzed by various enzymes through free radical mechanisms, to exert their carcinogenic effects. Research found that there are three principal pathways of metabolic activation of PAHs: (a) generation of diol epoxides, catalyzed by several cytochrome P450s, leading to DNA adduct formation which are considered essential to PAH carcinogenesis, (b) formation of radical cations, catalyzed by P450 peroxidases, and (c) formation of redox active *o*-quinones, catalyzed by dihydrodiol dehydrogenases, which can contribute to PAH carcinogenesis because they can act as tumor promoters (Bolton et al. 2000; Gelboin 1980; Penning et al. 1999; Qui and Cadenas 1997).

The aim of this study was to experiment with various airborne PM samples and explore possible redox mechanisms, interactions and parameters influencing the formation of ROS of toxicological and carcinogenic interest. We collected a series of PM samples from various traffic-related pollution sources including Total Suspended Particulates (TSP), PM_{10}, $PM_{2.5}$ and $PM_{0.7}$ from a commercial area with heavy vehicle traffic in the center of Athens, Greece. Also, we collected fresh soot produced from the ex-haust pipes of diesel and gasoline vehicles. Our investigation focused on: (a) the presence of quinoid stable free radicals (studied by EPR) and their spectroscopic features, (b) the formation of superoxide anion ($O_2^{\bullet -}$) and hydroxyl radicals ($HO^{\bullet}$) in physiological pH, through the involvement of the transition metals, and (c) the formation of the mutagenic adduct 8-hydroxy-2′-deoxyguanosine (8-OHdG) by hydroxyl radicals, which was produced from suspensions of PM in aqueous buffer solutions in the presence of 2′-deoxyguanosine.

2 Materials and Methods

Spin-traps DMPO (5,5-dimethyl-1- pyrroline-N-oxide), MNP (2-methyl-2-nitroso-propane, dimer), dG (2′-deoxyguanosine monophosphate), 8-HOdG standard (8-hydroxy-2′-deoxyguanosine) and deferoxamine mesylate were purchased from Sigma; phosphate buffer (pH 7.4), hydrogen peroxide (H_2O_2) (30%), were purchased from Merck. All other chemicals used were of analytical quality.

2.1 Samples of Airborne Suspended Particulates

TSP samples were collected using high volume pumps (80 m^3/h) on pre-weighed glass microfibre filters (Whatman GF/A 20.3 × 25.4 cm) with a 99% collection efficiency for particles with 0.3 mm diameter. The sampling site was in a central street of Athens influenced by local traffic (Division of Atmospheric Pollution and Noise Control, Ministry of Environment, Regional Planning and Public Works). $PM_{10,}$ $PM_{2.5}$ and $PM_{0.7}$ were collected in the same site with a high volume sampling system equipped with a six-stage slit cascade impactor (Andersen) with back-up filter. PM were separated into seven fractions, with the following cut-off diameters at 50% efficiency: >10.2, 10.2–4.2, 4.2–2.5, 2.5–1.4, 1.4–0.73, 0.73–0.41, <0.41 μm. Unloaded and loaded filters were kept in a darkened desiccator for 48 h before weighing. Loaded filters were wrapped in solvent-rinsed aluminium foils and kept refrigerated (−20°C) until extraction.

Samples from diesel vehicles (Diesel Exhaust Particles, DEP) were collected on annealed glass–fibre filters (Ø 5 cm), using a low volume air sampler, at a distance of 0.5 m from the exhaust pipe of a diesel car. Sampling lasted for about 30 min. Vehicle exhaust emissions sampling represent warm-engine operation at 800 (idle mode) and 2,500 rpm (simulating urban driving conditions). Gasoline Exhaust Particles (GEP) were collected on annealed glass–fibre filters (Ø 5 cm) in a similar way. Vehicle exhaust emissions sampling lasted 1 h and was used as "fresh" soot.

Also, we examined a limited number of PM samples, DEP and GEP for their fractal morphology and size. Samples of soot aggregates were examined by TEM (Transmission Electron Microscopy) and light scattering (Hitachi, H-600).

2.2 EPR Characterization of PM Samples

Some EPR spectra of solid PM were measured using a Bruker ESP-300 EPR equipped with X-band Klystron and 100 kHz modulator. Hyperfine splitting and g values were determined directly from the spectrometer's field scan. g factors were measured by comparison with aqueous solution of Fremy's salt ($g = 2.0055$). The majority of EPR spectra were measured using a Varian E-4 EPR spectrometer. Typical parameters: 100 kHz, X-band; microwave frequency 9.4 GHz; attenuation power 20 mW; modulation amplitude 1–2 G; scan time 8 min; receiver gain 2.5×10^2–5×10^3. The g values of EPR spectra were calculated from the g value of 2.0036 of the stable free radical of 2,2-diphenyl-1-picrylhydrazyl (DPPH).

Solid pre-weighed samples of TSP, PM_{10}, $PM_{2.5}$, $PM_{0.7}$, DEP and GEP were inserted in quartz EPR tubes and their spectra were recorded at room temperature. Also, solid PM samples (100 mg) were washed with 20 ml Methanol, dried under dry nitrogen and kept in a desiccator for 48 h under reduced pressure. Their EPR spectra were recorded again to investigate changes in the features of the EPR broad signal, structure, g value and intensity.

2.3 Extraction of PM from Filters

Filters were cut into smaller pieces and added to a conical flask with 50 ml of deionised water. PM were extracted, first by vigorous shaking (20 min) and subsequently by sonication in a water bath at 20°C for another 20 min. A blank filter was treated the same way and was used as a control in all experiments. The suspensions were centrifuged for 20 min and the precipitates were dried with a speed vacuum-dryer and kept in a desiccator for 48 h under reduced pressure and in the presence of calcium chloride.

2.4 Spin Trapping Measurement of Superoxide Anion and Hydroxyl Radicals

Pre-weighed samples of soot (approximately 50–100 mg) were placed in a conical flask with 50 ml phosphate buffer (pH 7.4) and aqueous extraction was performed under sonication for 30 min. Extracts were centrifuged at 25,000 rpm for 5 min and the supernatant solution was used for EPR experiments. The first set of experiments focused on the generation of superoxide anion ($O_2^{\bullet -}$) spin-trapped by DMPO. The mixture consisted of 1 ml of soot extract, 2 ml of buffer and 2 ml of DMPO (50 mM) agitated gently by a mechanical shaker for 3 min and transferred to an EPR quartz flat-cell for measurements. The spin-trapped species DMPO-OOH have to be measured within 7–8 min because of their unstability. The positive standard for $O_2^{\bullet -}$ is based on the spin-trapping of DMPO-OOH generated by KO_2 in DMSO with the addition of 18-crown-6 ether (Arudi et al. 1981). The basic reactions involve the reduction of oxygen by the semiquinone radical ($QH^{\bullet}$) to superoxide anion, which leads to the formation of H_2O_2. Measurements of the EPR spectra was performed with a flat-type quartz cell in a Varian E- 4 spectrometer operating with 1 G (0.1 mT) modulation amplitude, 20 mW microwave power, 3×10^3–1.25×10^4 receiver gain, 100 G scan range, 1 s time constant and 4 min scan time.

2.5 Spin Trapping and Measurement of $O_2^{\bullet -}$ and $HO^{\bullet}$ Generated in Aqueous Buffer Solution of Supernatant Fractions and Total Suspension of PM

Filters were cut into small pieces and immersed in 30 ml aqueous buffer solution and shaken for 10 min with subsequent sonication for 10 min in a water bath to release a suspension of PM. The suspension contains soluble and insoluble carbon particles, metal ions, inorganic salts, polycyclic aromatic hydrocarbons (PAHs) and quinoid compounds. The final particle concentration of PM preparations was estimated by comparative turbidometry at 405 nm using carbon black as a standard to ensure use of equal concentrations of particles by the method of Knaapen et al. (2002). The first set of experiments concerned the generation of $O_2^{\bullet -}$ spin-trapped by DMPO, without addition of hydrogen peroxide in the final volume of the mixture. The mixture consisted of soot suspended in a total of 5 ml of buffer solution, containing 50 mM DMPO. The suspension was not degassed, and was agitated gently on a mechanical shaker for 2 min and transferred quickly to a quartz flat-cell for EPR measurements, because of the instability of the spin-trapped species DMPO-OOH. Measurements of the EPR spectra were performed with a flat-type quartz cell in a Varian E-4 spectrometer operating with 1 G (0.1 mT) modulation amplitude, 20 mW microwave power, 3×10^3–1.25×10^4 receiver gain, 100 G scan range, 1 s time constant and 4 min scan time. The original spin-trapped radical DMPO-OOH was converted in 8–10 min to the

DMPO-OH radical (1:2:2:1 quartet pattern). Complimentary experiments were carried out with the supernatant solution after centrifugation (20 min) and filtration (0.1 μm filter), containing soluble metal salts and other inorganic salts, in order to test the production of radicals without H_2O_2. The supernatant solution did not generate spin-trapped radical signals, but in the presence of H_2O_2 the DMPO-OH (1:2:2:1 quartet) EPR spectra were recorded, as expected (results not shown). In experiments with the whole suspension (after extraction of PM without centrifugation), the addition of 0.1 M H_2O_2 increased substantially the DMPO-OH signal; however, the DMPO-OOH adduct was not observed.

2.6 *Spin-Trapping Measurements of Hydroxyl Radical Oxidative Damage to 2′-Guanosine-5′-Phosphate*

Samples of PM from various pollution sources were extracted by dichloromethane then evaporated to dryness and resuspended in phosphate buffer (pH 7.4). These samples were tested for their ability to produce oxidative damage to the nucleobase, 5′-guanosine monophosphate, sodium salt (G-5′-P) through the production of hydroxyl radicals. As a standard method, a solution of Fe^{2+}/EDTA(sodium salt)-H_2O_2 coupled in phosphate buffer (pH 7.4) was used and the produced radical of the nucleobase was spin-trapped by the MNP (2-methyl-2-nitroso-propane, dimmer, $Me_3C{-}N{=}O$). The MNP solution contained 10–15% acetonitrile (having been left to stir for 2–5 h to bring about the dissolution of the spin-trap). The EPR spectra support the formation of a mixture of C_5 and C_4-hydroxyl adducts. To test the effect of chelators on the radical generating activity of PM samples, we used EDTA-Na_2 and desferrioxamine. Ferrous ions (Fe^{2+}) form complexes with EDTA which increase the ability to produce hydroxyl radicals by lowering the redox potential of iron via chelation. Desferrioxamine blocks all available valences of iron thus reducing substantially its redox potential. Concentrations of the reactants in the final sample were typically 15–30 mg cm^{-3} (substrate, nucleobase), MNP 10^{-2} mol dm^{-3}, 25–50 mg cm^{-3} sample of particulate matter, hydrogen peroxide, H_2O_2, 1×10^{-2} mol dm^{-3}, phosphate buffer (pH 7.4). Before and during mixing, solutions for EPR experiments were purged with dry nitrogen for 2 min to expel oxygen and then transferred in a EPR flat-type quartz cell.

3 Results and Discussion

3.1 *Size and Morphology of PM and Theories of Oxidative Mechanisms*

The morphology and size of PM from combustion sources has been investigated extensively and there are numerous publications on the subject (Harrison and van Grieken 1999; Donaldson and Borm 2006). Combustion carbonaceous aerosols are observed as chain-like or grape-bunch-like aggregations of spherical particles, consisting of a small number, through to many thousands of spheres. The spectrum of spherical particles is controlled by various factors including the fuel:oxygen combustion ratios. The soot formation involves an initial particle nucleation from fuel pyrolysis forming PAHs, addition to the nucleus by gas molecules, coagulation by particle–particle collision and structural rearrangements of the condensed materials. The central part of the soot particle-sphere, which has an approximate diameter of 10 nm, is composed of concentrically-piled carbon networks. Some individual networks have poor organization, creating large intranetwork spaces (pores) which have the potential to absorb materials such as VOCs, sulphur and transition metals. The outer part of the soot particle-sphere is ordered in a more stable and composed microcrystallite of oriented carbon sheets (of a backbone of graphite structure, associated with C–O functions and hydrocarbon segments). Obviously, the chemical components of the soot spheres that are adsorbed on the surface area or are incorporated into the body of the sphere are of great interest to respiratory toxicologists due to its toxic potential. A more detailed analysis, composition, Transmission Electron Microscopy (TEM) (Xi and Zhong 2006) photos and structural features of airborne PM from combustion sources can be found in the bibliography (Mansurov 2005; Siegla and Smith 1981; Bockhorn 1994).

A schematic presentation of soot formation, soot aggregates, microstructure arrangements and micrographs of diesel soot with their polymerized "honeycombs" of PAHs are presented in Fig. 1.

There are several theories to explain the cellular toxicity of airborne PM from combustion processes, especially their oxidative damage to macromolecules (lipid peroxidation) and carcinogenic mechanisms involving oxidative damage or mutagenic adducts to cellular DNA. One theory suggests that PM toxicity results from the accumulation of solid particles in the epithelial lining of the lungs and that oxidative effects are associated with certain size fractions (especially ultrafine particles). Another theory suggests that certain chemical constituents (transition metals, PAHs, nitropyrenes, etc.) are involved in the formation of ROS, which play an important role in oxidative stress and carcinogenic mechanisms. A third theory assumes that injury results also from the activation of lung macrophages by water soluble oxidants (H_2O_2, organic peroxides) which generate more ROS and cause extensive oxidative damage to biological macromolecules (Salma et al. 2002; Salvi et al. 1999; Sun et al. 2001; Van Eeden et al. 2001). It is obvious from the experimental results, in vitro and in vivo, that airborne particles of fine and ultrafine size that are retained in the lung parenchyma and in the alveoli releasing their toxic substances initiating inflammatory responses which ultimately lead to cell injury.

3.2 Toxicological Role of Persistent Quinoid Radicals in PM

All solid PM samples showed EPR spectra with a single broad unstructured signal with g value in the range of 2.0035–2.0040, corresponding to a signal from the semiquinone ($QH^\bullet$) radical.

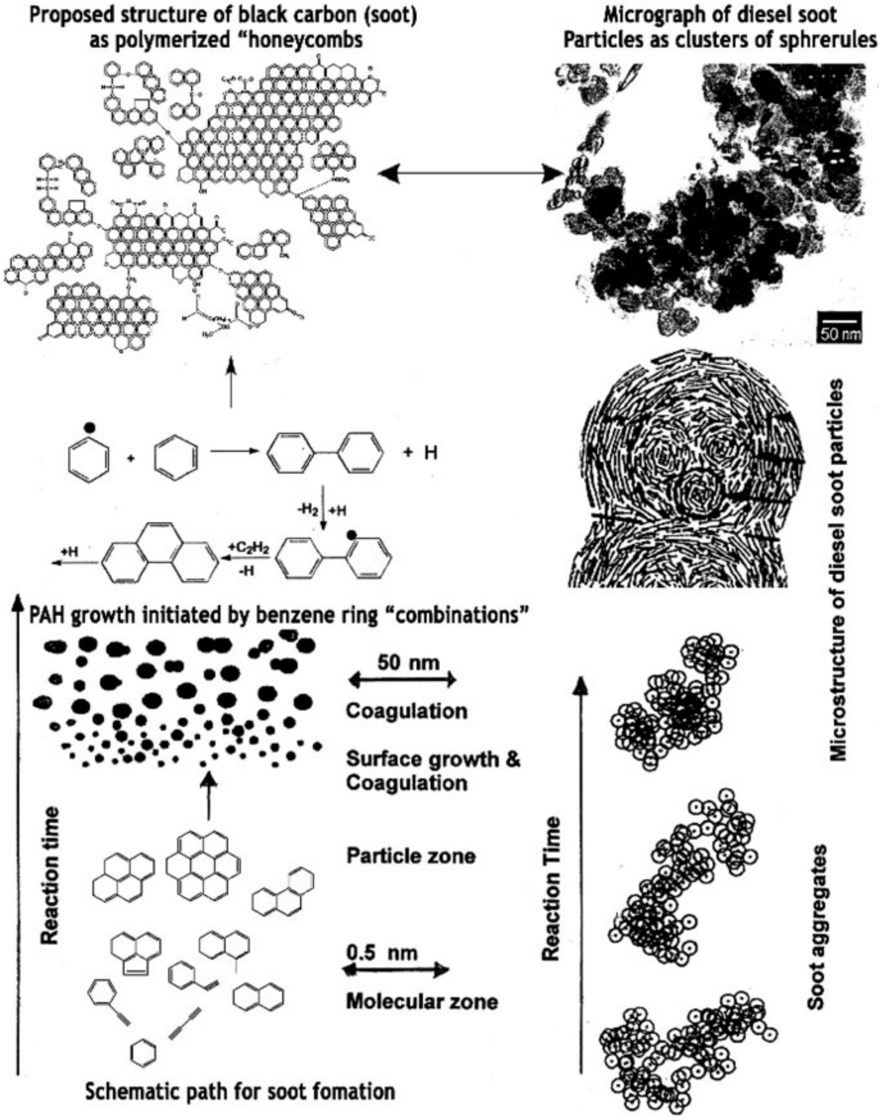


Fig. 1 Schematic presentation of soot aggregates, coagulation of particles, formation of particle clusters and how PAHs combine to form polymerized "honeycomb" structures. Various VOCs, transition metals and other toxic substances can be adsorbed on the surface of the spheres

The broadness ($\Delta Hp\text{-}p = 9.5\text{–}10$ G) of the EPR signal indicates that it is the result of a group of semiquinone, but it may also be due to the inhomogeneity of the samples and various interactions of the semiquinones with metal ions [28, 29]. The EPR signal of PM samples showed a broad and featureless feature indicating the presence of multiple radicals or strong matrix interactions [46].

The radicals are persistent and are observed in stored samples for several months. As in the case of EPR spectra of solid cigarette tar, these semiquinone radicals are considered as a dynamic mixture of hydroquinone (QH_2), semiquinone ($QH^\bullet$) and quinone (Q). The quantitative measurements (with standard the stable free radical DPPH) showed that the free radical concentrations were in the range of 10^{15}–10^{17} spins/g. This range of spins/g is comparable to the solid tar of cigarette smoke, collected on a Cambridge filter, extracted with benzene and dried under reduced pressure) (Squadrito et al. 2001; Valavanidis et al. 2005a, b).

Active quinoid substances are chemisorbed to the surface of the particles and may not be easily leached, but others which are adsorbed on the particles may be held with weaker forces and can be leached out into the aqueous phase of the alveoli.

Various mechanisms have been proposed for the generation of superoxide anion by the dynamic mixture $QH_2/QH^\bullet/Q$ of quinoids in cigarette tar and, similarly, PM. Superoxide anion can be transformed easily into H_2O_2 and the biologically damaging hydroxyl radical in a metal-dependent reaction. Also, hydroxyl radicals can be produced by the reaction of $O_2^{\bullet-}$ and H_2O_2, as shown in the following reactions (Dellinger et al. 2001; Squadrito et al. 2001) (Fig. 2).

$$QH^\bullet + O_2 \rightarrow Q + O_2^{\bullet-} + H^+ \tag{1}$$

$$O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \tag{2}$$

$$Q + e^- + H^+ \rightarrow QH^\bullet \tag{3}$$

$$OH^\bullet + e^- + H^+ \rightarrow QH_2 \tag{4}$$

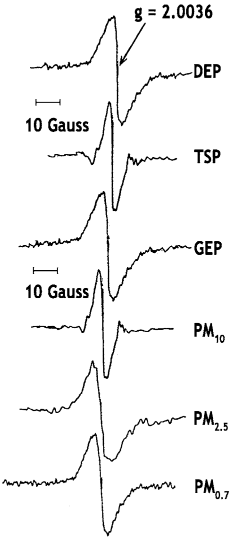


Fig. 2 EPR spectra for solid PM samples from air pollution and vehicular exhaust. Diesel exhaust particles (DEP), Total suspended particles (TSP), Gasoline exhaust particles (GEP), PM_{10}, $PM_{2.5}$ and $PM_{0.7}$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + HO^{-} \quad (5)$$

$$H_2O_2 + O_2^{\bullet -} \rightarrow HO^{\bullet} + HO^{-} + O_2 \quad (6)$$

These reactions establish a redox cycle, where the dynamic quinoid mixture in the presence of oxygen produces cytotoxic hydroxyl radicals which are well known to induce damage to proteins, lipids and DNA. Transition metals play also an important role, such as in the Fenton-like reaction (5) in the generation of $HO^{\bullet}$. Reaction (6) can take place after the formation of hydrogen peroxide (reaction 2) (Dellinger et al. 2007; Roginsky et al. 1999; Sagai et al. 2000). Also, H_2O_2 can be synthesized endogenously by certain cell types as a response to activation by specific cytokines or growth factors, and exists physiologically at low concentrations in the lung tissues. It has been reported that $O_2^{\bullet -}$ was produced during the metabolism of benzo[a]pyrene and 1-nitropyrene (both substances contained in PM in appreciable amounts) in the presence of lung microsomes (Sullivan 1985; Nachtman 1986).

3.3 Superoxide Anion Radicals from PM Extracts

The production of superoxide anion ($O_2^{\bullet -}$) from PM extracts is considered an important step in the initial generation of H_2O_2 which, in turn, results in the damaging by-product $HO^{\bullet}$. Experiments with whole suspension of PM (both soluble and insoluble parts) in DMSO with the spin trap DMPO (110 mM) showed the production of $O_2^{\bullet -}$ after 10 min and was stable up to 20 min. Fresh diesel exhaust particles (DEP) was the most active compared to other PM samples. These results were similar to in vitro experiments by Sagai and co-workers (Bai et al. 2001; Sagai et al. 1993). Production of $O_2^{\bullet -}$ was proven to be the result of quinoids in the PM particles. When PM and DEP were washed with Methanol (removing most of the adsorbed organic substances) the remaining solid soot under similar experimental conditions did not produce superoxide. The supernatant solution and the whole suspension of PM were (incubated in the presence of DMPO), after 2 min mixing showed the presence of $O_2^{\bullet -}$ (spin-trapped as DPMO-OOH) But the EPR signal was replaced very quickly (9–10 min) by hydroxyl radical adducts [DMPO-OH] due to the spontaneous thermal decay (Figs. 3, 4).

3.4 EPR Measurements of $HO^{\bullet}$ from PM with the Addition of H_2O_2

The previous investigation showed that $HO^{\bullet}$ can be generated in suspensions of PM without H_2O_2 through the redox cycling of quinoids and subsequent reactions, but the addition of hydrogen peroxide (0.02–0.1 M) in the PM suspension enhanced

Fig. 3 Representative EPR measurements of $O_2^{\bullet-}$ and $HO^{\bullet}$ generated from PM samples (suspensions) in phosphate buffer (pH 7.4). **a** and **b** are for DEP, **c** and **d** for GEP, **e** for $PM_{2.5}$, **f** washed DEP with methanol, **g** is a simulation of the spin-trapped radicals, **h** is the simulation for DMPO-OOH

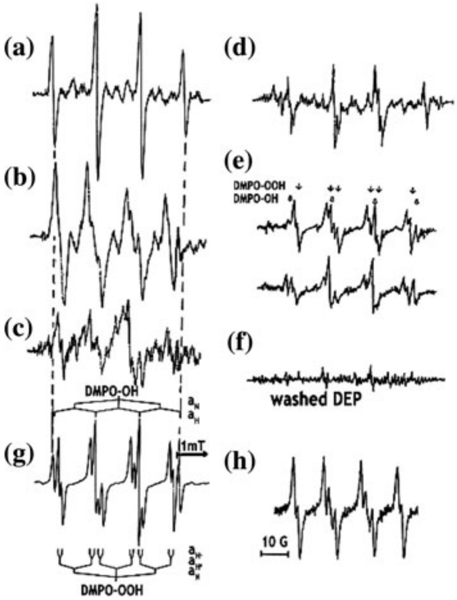
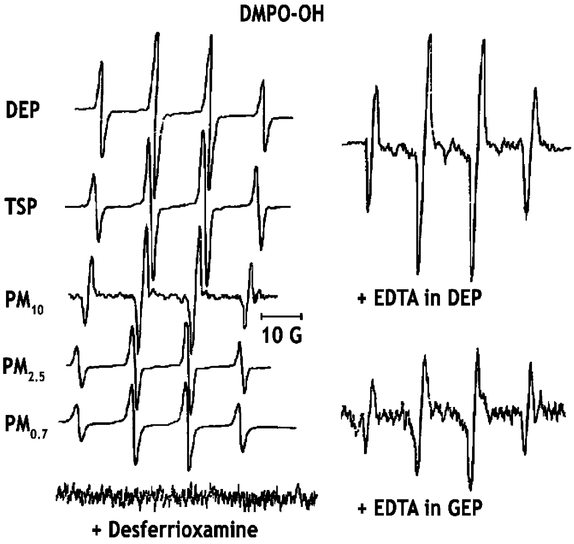


Fig. 4 EPR spectra of DMPO-OH. Production of $HO^{\bullet}$ radicals by various PM samples with the addition of H_2O_2. Addition of EDTA increased the generation of $HO^{\bullet}$, whereas desferrioxamine reduced the EPR signal completely by blocking all valences of iron



the production of $HO^{\bullet}$. Ferrous ions have been found in fresh diesel and gasoline particles, as well as in TSP samples from urban areas (Donaldson et al. 1997; Pritchard et al. 1996; Valavanidis et al. 2000). Also, soluble ferric ions (but not Fe_2O_3) are more abundant in airborne PM in urban areas and were observed in TSP. Another important step in the mechanism of $HO^{\bullet}$ generation is the reduction of soluble ferric ions to ferrous ions by the production of superoxide anion.

$$Fe^{3+} + O_2^{\bullet -} \rightarrow Fe^{2+} + O_2.$$

Iron is the most prominent transition metal present in airborne PM related to traffic air pollution. Iron chelators such as EDTA and desferrioxamine can be used to assess its role in ROS production. Addition of EDTA-Na_2 in the mixture with PM increased the hydroxyl radical production, whereas the addition of desferrioxamine inhibited $HO^\bullet$ formation totally by blocking all available valences of iron.

3.5 EPR Spectra of Hydroxy Adducts to Guanosine Nucleobase

Spin-trapping experiments confirm that hydroxyl radicals produced by various samples of PM in the presence of H_2O_2 induce damage in the form of hydroxy-adducts to guanosine 5′-monophosphate nucleobase in phosphate buffer solutions (pH 7.4). The EPR spectra observed are similar to the ones observed with the Fe^{2+}-EDTA/H_2O_2 couple, producing hydroxyl radicals. The hyperfine splittings: $\alpha(\alpha\text{-N}) = 1.54$ mT (or 15.4 G) is the dominant signal triplet of triplets (1:1:1), and $\alpha(\text{b-N}) = 0.3$ mT is assigned to with the spin trapping of the C_4–OH radical (Davies et al. 1995). A weaker splitting is from the other two radical adducts C_5–OH or C_8–OH.

The quantitative measurements of 8-hydroxy-2′deoxyguanosine (8-OHdG) adduct, from the nucleoside 2′-deoxyguanosine by various PM samples and exhaust particles (DEP and GEP) in aqueous buffered solutions, was performed by HPLC analysis. These quantitative measurements were published in a recent paper by our research group (Valavanidis et al. 2005a, b). The results showed that the fractions with smaller size particles (such as PM_{10}, $PM_{2.5}$ and DEP) were more active in the formation of the 8-OHdG adduct, compared to higher fractions and TSP. Transition metal concentrations and their redox potential in PM were an important factor for the samples. The mutagenic lesion 8-OHdG is considered an important biomarker of carcinogenesis and its measurement in vitro and in vivo is considered very interesting quantitative indicator of future development of malignant neoplasms (Valavanidis et al. 2009) (Fig. 5).

4 Conclusions

Suspended PM is considered an important atmospheric pollutant for adverse health effects through the production of ROS and advancing oxidative stress in biological systems (Shinyashiki et al. 2009). Through these experiments, oxidative stress has been demonstrated to be the pivotal mechanism for the toxic effects of PM in the lungs. Experimental results showed that redox-cycling quinoids, redox-active transition metals and PAHs contained in fractions of PM and DEP act synergistically in the production of ROS, especially hydroxyl radicals (Alessandrini et al.

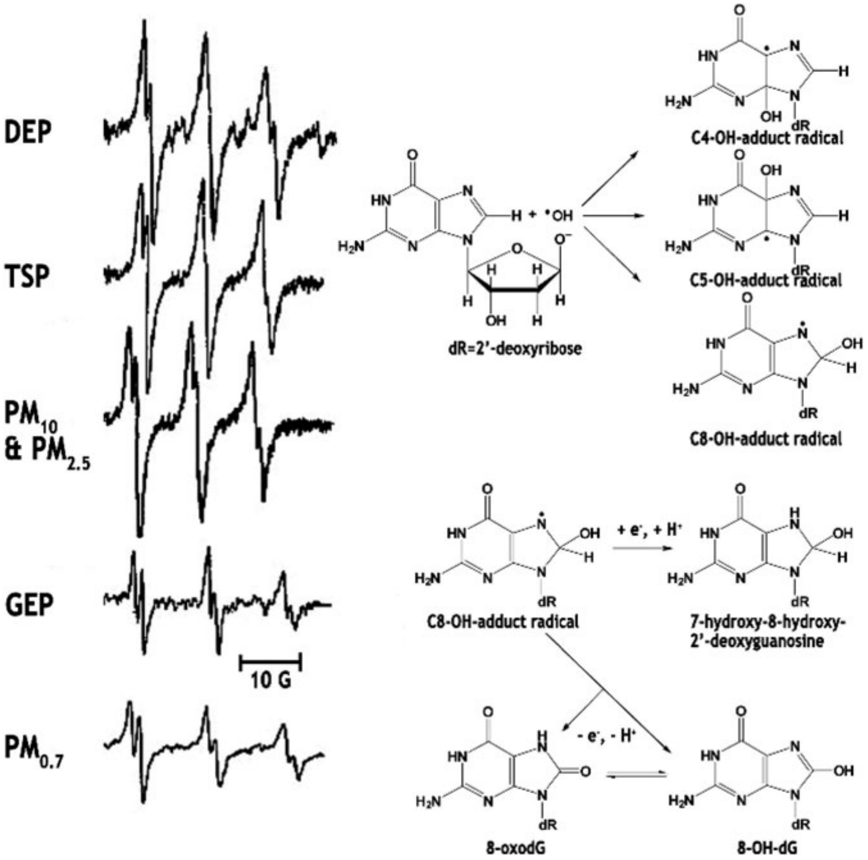


Fig. 5 EPR spectra obtained from the reaction of $HO^{\bullet}$ with 2′-deoxyguanosine at pH 7.4. Samples of PM: DEP, TSP, PM_{10} and $PM_{2.5}$, GEP and $PM_{0.7}$

2009; Ohyama et al. 2007; Xia et al. 2004). Exposure to ambient PM has been associated to mechanisms of carcinogenesis through the formation of mutagenic adducts, strand breaks and inhibition of DNA repair mechanisms. The role of ROS, generated by PM as mediators of genotoxicity is emphasized in all these studies (Healey et al. 2006; Mehta et al. 2008; Sanchez-Perez et al. 2009).

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In vivo and In vitro Assessment of Particulate Matter Toxicology

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1 Introduction

Air pollution is a major threat to human health worldwide. According to a World Health Organization report (WHO 2006), more than two million premature deaths can be attributed each year to air pollution. In Canada, premature deaths associated with chronic exposure to air pollution are expected to rise 83% between 2008 and 2031, and estimated economic costs of air pollution will be over $ 250 billion by 2031 (CMA 2008). Adverse health effects associated with air pollution may be caused by both gaseous (nitrogen oxides, sulfur oxides, ozone, etc.) and particulate pollutants. Epidemiological studies have found consistent correlations between all-cause or cause-specific (respiratory and cardiovascular) mortality and inhalation of particulate matter (PM), even at low and moderate ambient PM concentrations (Brook et al. 2003; Katsouyanni et al. 2003; Schwartz 1994). These correlations suggest that PM air pollution is responsible for about 0.8 million premature deaths and 6.4 million years of life lost globally (Cohen et al. 2005). Though emission of gaseous pollutants has decreased significantly over the last few decades because of the implementation of stringent regulations and better emission control technologies, PM concentrations have decreased at a slower rate. This is due to the simultaneous increase in combustion-based energy use, such as the increase in motor vehicles

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_22,

worldwide, specifically in urban areas (Valavanidis et al. 2008). The physicochemical properties of PM, specifically size-distribution and composition, have also changed with time (Valavanidis et al. 2008). In recent years, PM air pollution has been the subject of a multitude of epidemiological and toxicological studies because of its intense effects on human health and economy.

Ambient PM is a complex mixture of gaseous, solid, and liquid substances with variations in size, composition, and origin (Mazzarella et al. 2007; Sioutas et al. 2005; Brook et al. 2003). PM is generally classified by size as this determines the transport and removal rate of PM in the air. In terms of health effects, PM size determines the deposition site of PM within the respiratory tract (USEPA 2004). Particles with an aerodynamic diameter (AD) less than 10 μm are considered as the respirable fraction; those larger than 10 μm are removed in the nasal passages (Squadrito et al. 2001). For measurement and regulatory purposes, PM less than 10 μm AD are divided into three major fractions: PM_{10} ($AD < 10$ μm), $PM_{2.5}$ ($AD < 2.5$ μm) and ultrafine (UF) ($AD < 0.1$ μm) (USEPA 2004). PM10 are further divided as coarse (AD 2.5–10 μm) and fine ($AD < 2.5$ μm) PM. The physicochemical properties of PM, such as size-distribution and composition, largely depend on the source. While fine and UF particles are predominantly produced by combustion processes, coarse particles are generated mainly by mechanical processes. Fine and UF particles consist primarily of inorganic ions, hydrocarbons, and metals, whereas coarse particles consist of crustal materials, such as sea salt, abrasion products, and bioaerosol (Kok et al. 2006; Squadrito et al. 2001).

Numerous epidemiological studies have found significant associations between PM exposure and adverse health effects, specifically in respiratory and cardiovascular systems. Associations ranged from increased hospital admissions and emergency department visits for treatment of respiratory and cardiovascular diseases to increased lung cancer and cardiovascular diseases mortality as mentioned in Chapter “Health Risks of Urban Airborne Particles, Andreas D. Kappos”. These effects were quite severe in the elderly and in populations with pre-existing cardiopulmonary diseases (Zanobetti and Schwartz 2005; Goldberg et al. 2000). Variable levels of significance of PM-associated health effects have been reported in different studies. The main reason for such variation among the studies is the difference in geographic location. Thus, it is important to recognize the regional variability of PM sources, composition, population exposure, and potential susceptible populations (USEPA 2004).

Several epidemiological studies have examined the health effects of size-fractionated PM (PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$). These studies suggested that, of the different size fractions, $PM_{2.5}$ was most significantly associated with mortality (Brook et al. 2003; Fairley 1999). While chronic exposure has been associated with increased atherosclerosis (Kunzli et al. 2005), short-term exposure to $PM_{2.5}$, for as little as two hours, may elevate the risk of acute cardiovascular events (Peters et al. 2001). Although only a few epidemiological studies on UF particles have been published to date, there is emerging evidence that they also contribute significantly to adverse health effects (Sioutas et al. 2005; Peters et al. 1997). It has been postulated that UF particles may actually underlying the morbidity and mortality that have been associated with $PM_{2.5}$ (Delfino et al. 2005). Preliminary results have found a positive correlation between UF particles and increased mortality and morbidity for respiratory and cardiovascular effects in susceptible populations (Politis et al. 2008). However, considerable further investigation of UF-particle exposure-related health effects is required. While standards for PM_{10} and $PM_{2.5}$ have already been established in North America, an ambient standard for UF particles has yet to be established. In recent years, epidemiological studies have focused more toward investigating the health impacts of different size-fractionated PM, including UF particles.

As increased rates of mortality and morbidity have been observed for both short- and long-term exposures to PM at ambient levels, the general consensus is that PM concentrations should be decreased as much as is reasonably achievable. In a study of the reductions in $PM_{2.5}$ concentrations in 51 US cities over the last two decades, Pope et al. (2009) found that a decrease of 10 $\mu g/m^3$ in the fine PM concentration was associated with an increased average life expectancy of seven months. However, these observations have primarily been through epidemiological associations. A parallel knowledge of PM toxicity is essential in order to develop scientifically established standards and health policies regarding ambient PM concentration. Considerable progress has been made toward understanding the pathophysiological mechanisms of PM-induced adverse health effects over the last decade. This chapter describes our current understanding of PM-induced respiratory and cardiovascular diseases with the different methodologies used to evaluate PM toxicity.

2 Importance of Physiochemical Properties of PM

The physical and chemical characteristics of inhaled particles can have a profound effect on the nature and degree of the toxic effects of PM. As described in Chapter "Health Risks of Urban Airborne Particles, Andreas D. Kappos", particle size is one of the most important factors determining the deposition site and consequent clearance in the respiratory tract—the smaller the particles, the deeper the deposition site in the respiratory tract, the slower the clearance rate, and the higher the probability of particle–cell interactions. Of all the PM fractions, deposition of UF particles is of great interest as these particles could remain in the pulmonary tissue, and their retention may cause lung damage (Politis et al. 2008). UF particles may also cross the lung epithelium barrier and translocate into the systematic circulation (Brook 2008). This translocation may contribute to acute manifestation of cardiovascular diseases (Nemmar et al. 2004), as well as neurological alterations (Calderon-Garciduenas et al. 2004). Nemmar et al. (2002) also demonstrated that inhaled UF carbon particles can pass rapidly into the systemic circulation. Studies have observed translocation of inhaled UF particles to the brain in rats (Oberdörster et al. 2004); however, no studies have confirmed translocation of ambient UF particles to extra pulmonary organs (i.e., the liver and brain) in the human body (Möller et al. 2008). Experimental studies have observed higher pulmonary responses, such as indications of inflammation, for UF particles compared to fine particles of the same material (Li et al. 2003; Oberdörster 2001). Findings from recent studies suggest that, along with size other physical properties of UF particles (i.e., higher total surface area and number concentration per unit mass) may also contribute significantly toward the observed response (Wittmaack 2007; Oberdörster 2001).

In addition to the physical characteristics, accumulating evidence suggests that particle composition is also responsible for particle-associated adverse health effects. While ambient particles may be composed of thousands of chemicals and constituents, including inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds (Hetland et al. 2004; USEPA 2004), the components responsible for the observed toxic effects remain largely unknown. The effects on human health could be related to a single PM component or to a possible synergistic interaction of multiple components. Based on experimental studies, it has been proposed that transition metals and organic compounds are primarily responsible for inducing oxidative stress within lung cells. Oxidative stress was positively correlated with high organic carbon and polycyclic aromatic hydrocarbons (PAHs) content of PM (Li et al. 2000, 2002, 2003). Oxidative stress-mediated cytokine production could be metal-dependent, as transition metals (e.g. iron, vanadium, nickel, lead) may catalyze free radical production in the lung cells (Carter et al. 1997). Several studies have also revealed that the presence of endotoxins on particle surfaces may initiate inflammatory response in the cells (Hetland et al. 2004; Becker et al. 2003). Therefore, different physicochemical PM properties, including size, surface area, number, and composition, can play a significant role in initiating PM induced health effects. Nonetheless, no single physical or chemical characteristic has been identified that could explain most of the health effects observed.

3 Toxicological Investigations of Particulate Matter

Although epidemiological studies provide extensive evidence of PM-associated health effects, there are some limitations. Primarily, it is difficult to demonstrate causality and to also eliminate the confounding effects of other pollutants through epidemiology alone (Devlin et al. 2005). Thus, toxicology studies are essential to complement epidemiological findings and can provide insight into the pathophysiological mechanism(s) underlying the adverse health effects that are observed in epidemiological studies. Evidence of toxicity from toxicology studies is also essential for establishing guidelines (WHO 2006). Two approaches are most commonly used to study of PM toxicity: in vivo-controlled human and animal exposure studies, and in vitro-exposure of cells to PM. Although both of these approaches have well defined strengths and limitations, each approach provides a needed contribution to understanding the impact of PM on human health. Recent in vivo and in vitro studies have mainly focused on determining the pathophysiological mechanisms of PM-induced health effects, the PM characteristics (i.e., size, surface area, chemical composition, etc.) responsible for the observed effects, and the susceptible subgroups that are at increased risk of adverse health effects due to PM exposure.

3.1 In vivo Studies

3.1.1 Human Exposure Studies

Controlled human exposure studies are essential to establish the health consequences of PM exposures. These studies are typically designed to study inhalation of size-defined PM under highly controlled conditions that will allow the characterization of exposure-response relationships. Since humans are exposed to the pollutant of interest, specifically size-fractionated PM, causality can be established easily and the confounding effects of other pollutants can be minimized (Devlin et al. 2005). Another advantage of such clinical studies is the ability to select subjects with a known clinical status (i.e., healthy vs. a specific disease, typically cardiovascular or pulmonary disease) and observe the pathophysiological responses of interest. However, controlled human exposures have some limitations (Utell and Frampton 2000). For both practical and ethical reasons, clinical studies are restricted to exposure concentrations and durations that will only elicit transient responses in human subjects. These studies involve a small number of sample subjects, which excludes susceptible populations at higher risk. Chronic exposure or high PM concentration related health effects are not attainable by the clinical studies. These experiments are also very costly to perform.

3.1.2 Subjects

For PM exposure studies, subjects are typically classified by age, gender, smoking habit, residence locations, and physical conditions such as lung function and cardiovascular status, etc. Healthy subjects are non-smokers who have no history of chronic respiratory and cardiovascular diseases, and are further characterized by the absence of allergies, chronic medical conditions or chronic medications, and airways that are not hyper-responsive, as assessed by inhalation challenge tests (Brook et al. 2009; Dubowsky et al. 2006; Beckett et al. 2005; Gong et al. 2005). Susceptible individuals are more vulnerable to PM than healthy subjects, thus clinical studies of susceptible groups along with healthy subjects are of great interest to policy makers developing national ambient standards. These standards are usually designed to protect susceptible groups (Utell and Frampton 2000). The choice of susceptible population depends on the outcomes of the research interests. Generally, elderly persons, individuals with previous history of asthma, chronic obstructive pulmonary diseases (COPD), and cardiovascular disease are considered as susceptible populations for PM exposure studies (Mills et al. 2008; Dubowsky et al. 2006; Gong et al.

2003). Depending upon the design of the study, comparisons of health-outcomes can be made with healthy controls, or subjects can act as their own controls when exposed to PM and filtered air over multiple sessions (Urch et al. 2005).

3.1.3 Exposure Conditions

Clinical PM exposure studies are typically conducted in environmentally controlled chambers up to 20 m^3 (e.g., 4.5 × 2.5 × 1.5 m in LWH) in volume. These studies employ different exposure methods, such as full-body, mouth-only, nose-only, and mouth-nose inhalation exposures (USEPA 2004). Full-body exposure is the most realistic approach as it mimics the typical environmental exposure conditions that are experienced daily. For ethical reasons, exposure protocols are designed to elicit transient, clinically insignificant (i.e., safe) effects with minimally invasive measurement techniques to assess outcomes (Utell and Frampton 2000). Subjects are exposed to higher PM concentrations than would not typically be observed for ambient concentrations in most regions. The major consideration for using high concentration is that in real life human are exposed to ambient PM chronically (i.e., years); however, the clinical studies are conducted acutely (i.e., hours). Thus, a high concentration exposure may induce effects similar to chronic exposure. It is also assumed that exposure of healthy subjects to relatively high concentrations may reconcile for the compromised tissue/organ functions of susceptible individuals contributing to the observed health effects in epidemiological studies (USEPA 2004). Exposure concentrations can also be selected based on findings from animal exposure studies (Beckett et al. 2005). Most exposures are conducted over a two-hour duration period, which may include intermittent or continuous exercise to induce oral breathing and increase ventilation. From the exposure perspective, the augmented oral breathing and ventilation reduces the fraction of PM loss in the nasopharyngeal region and consequently enhance the PM dose that reaches the lower respiratory tract (WHO 2006; Utell and Frampton 2000). Some studies allow the subjects to perform tasks while monitoring and characterizing the ambient PM concentrations. These tasks can include: outdoor running (Rundell et al. 2007) or going for a day trip (Dubowsky et al. 2006). These exposures better match conditions that may be encountered on a daily basis, but also include many confounding factors.

Concentrated ambient particle system (CAPS) is a new technology that has been developed to allow ambient particles to be concentrated in real time by factors of 25 or more (Sioutas et al. 1995). CAPS chambers are typically smaller in size (3–5 m^3 in volume) and mimic the ambient conditions in a particular geographical area. Variations in particulate composition between cities can affect the impact of the findings (Mills et al. 2008). Furthermore, exposure concentrations can vary from day to day depending on ambient levels of PM from which the air is taken, as well as the concentrating factor of the instrument used. Exposure concentrations in CAPS can range from relatively low levels to concentrations much higher (23–311 μg/m^3) than those commonly found in polluted cities (USEPA 2004).

In the CAPS, PM can be separated from other atmospheric gaseous pollutants that facilitate the study of PM-induced effects individually, among others. Current technology allows exposure to all PM size-fractions including coarse, fine, and UF particles (Graff et al. 2009; Mills et al. 2008; Gong et al. 2005). CAPS for human exposure studies are still rare with two facilities in the US and one in Canada at the Southern Ontario Centre for Atmospheric Aerosol Research (SOCAAR) located at the Gage Occupational and Environmental Health Unit, within the University of Toronto's Faculty of Medicine (SOCAAR 2007). Several clinical studies have used diesel engine exhaust and smoking machines as model anthropogenic pollutants (Peretz et al. 2008; Weiss et al. 1999). Model particles with specific physical and chemical characteristics are used in some exposure studies which allow the investigation of the appropriate dose metrics (i.e., size, surface area, composition, etc.) responsible for the observed effects (Beckett et al. 2005).

3.1.4 Endpoints

As would be expected from the above description of the human exposure studies, the respiratory and cardiovascular outcomes assessed in human clinical studies are determined based on scientific and practical considerations. Results from epidemiologic studies and/or animal exposure studies work as guidelines for selecting outcome measures. In most of the respiratory response studies, a symptom questionnaire is prepared and results are recorded as a score with a standardized grading system. The most commonly used pulmonary function test (PFT) is the spirometry test, which measures the breathing pattern. Typically evaluated breathing parameters in spirometry are the forced vital capacity (FVC), forced expiratory volume in 1 s (FEV_1), maximal mid-expiratory flow (MMEF), and peak expiratory flow (PEF) (Gong et al. 2003, 2005; Ghio et al. 2000; Utell and Frampton 2000). These outcomes are easy to perform and are generally reproducible within subjects. Arterial oxygen saturation (SpO_2), an indication of the amount of oxygen bound to hemoglobin, can be measured continually by pulse oximetry (Gong et al. 2003, 2005). To collect cells and epithelial lining fluid of the lower respiratory tract in humans, sputum induction is often used (Gong et al. 2003, 2005; Beckett et al. 2005). Fiberoptic bronchoscopy is another analytical method that allows more invasive collection of samples from the respiratory tract for further analysis (Utell and Frampton 2000). A number of techniques have been developed based on fiberoptic bronchoscopy, which allows sampling of fluids and cells from the lower respiratory tract. Bronchoalveolar lavage (BAL) samples the epithelial lining fluid and cells of the distant airways. Other techniques developed using fiberoptic bronchoscopy are bronchial brushing (to collect airway epithelial cells and tissue), and endobronchial (to collect bronchial epithelium cells) or transbronchial (to collect alveolar tissue and distal bronchial epithelium) biopsy. Fiberoptic bronchoscopy has also been used for the intrabronchial instillation of PM in human subjects at definite locations in the lung (Ghio and Devlin 2001). Analysis of the collected cells and fluid can provide a useful measure of airway inflammation. Measurement of nitric oxide in exhaled air is another useful tool to detect lung inflammation (Delfino et al. 2006; Adamkiewicz et al. 2004).

Vascular function is measured in a variety of ways. The most basic tests that can be performed non-invasively during exposures are: blood pressure (BP), heart rate (HR), and heart rate variability (HRV) (Brook et al. 2009; Urch et al. 2005; Beckett et al. 2005; Gong et al. 2003). Furthermore, brachial artery diameter (BAD), flow-mediated dilatation (FMD), nitroglycerin-mediated dilatation (NMD), and arterial compliance can also be measured in subjects (Brook et al. 2009; Rundell et al. 2007; Brook et al. 2002). To examine the effect of PM on vasomotor function, vasodilatation can be induced using intravascular infusions of bradykinin, acetylcholine, sodium nitroprusside, and verapamil, and measuring the forearm blood flow (Mills et al. 2007; Törnqvist et al. 2007). Electrocardiograms can also be used to determine any increases in ischemic burden (Brook et al. 2009; Mills et al. 2007). Finally, blood tests can be used to determine fibrinolytic function as an indicator of blood viscosity (Mills et al. 2007; Törnqvist et al. 2007). Blood, sputum, cells and fluids of the respiratory tract are collected after exposure and are analyzed for complete blood cell count (Brook et al. 2009), different markers of oxidative stress and systemic inflammation, such as leukocytes, polymorphonuclear neutrophils (PMN), cytokines, and platelets (Graff et al. 2009; Mills et al. 2008; Ghio et al. 2000), serum C-reactive protein (Brook et al. 2009; Mills et al. 2008; Dubowsky et al. 2006), and alterations in gene expression (Törnqvist et al. 2007; Dubowsky et al. 2006).

3.1.5 Animal Exposure Studies

To compensate for the limitations described previously, animal exposure studies are commonly used to assess causality and potential biological mechanisms at higher PM concentrations and under chronic exposure conditions (Devlin et al. 2005). Animal exposure studies are relatively inexpensive to perform when compared to clinical studies; however, one major limitation of animal exposure studies is that they require the appropriate extrapolation of doses and biological responses from animals to humans. Thus, the similarities and differences between laboratory animal species and humans in regards to the anatomy of the respiratory tracts and cardiovascular system, life span, diet, exercise, genetic variability, and biological and physiological response must be recognized before extrapolation of these findings can be made possible (Valentine and Kennedy 2008; McClellan 2000).

3.1.6 Subjects

The most commonly used animals in PM exposure studies are rodents, including rats, mice, guinea pigs, and hamsters. Rodents have been used extensively in inhalation toxicology studies, and hence a large amount of information is available on the physiological responses of rodents (Valentine and Kennedy 2008). These animals are generally used as inbred strains, thus reducing the genetic heterogeneity compared with human subjects; and whole litters can be treated similarly, allowing siblings to act as controls for exposures. Therefore, there is a lesser degree of variability in the responses in animal models. Rodents are most commonly used for studying chronic toxicity and carcinogenesis effects as they have a relatively short lifespan as compared to humans (Valentine and Kennedy 2008). As more adverse responses have been observed in populations with a pre-existing history of respiratory and cardiovascular disease, specific animal models can be used to study the effects of PM that are observed in susceptible populations, including acute and chronic airways inflammation, representative of obstructive and restrictive lung disease, surgically-induced ischemic heart disease or myocardial infarction, or mice that are genetically predisposed toward hyperlipidemia (Maier et al. 2008; Saldiva et al. 2002; Suwa et al. 2002). PM exposure studies have also been conducted on dogs and on dogs with an induced coronary artery occlusion to investigate exacerbation of myocardial ischemia during coronary artery occlusion due to PM exposure (Bartoli et al. 2009; Wellenius et al. 2003).

3.1.7 Exposure Condition

Animals are exposed to PM using the same exposure routes (i.e., full-body, nose-only, and/or mouth-only) as the clinical studies described above. In the nose-only exposure system, animals are restrained in a small chamber and allowed to inhale though an exposure hole. While restraint can induce stress, thus affecting the heart rate (Narciso et al. 2003), blood pressure (Vincent et al. 2001), and gene expression in the lung (Thomson et al. 2009) in the exposed animals, this approach allows for increased certainty in terms of the actual exposures delivered. In contrast, a full-body exposure chamber provides a more realistic approach of PM inhalation, but can be complicated if the animals are allowed to roam (i.e., free-range). Exposure durations in full-body chambers may last from five to six hours for animals (Araujo et al. 2008; Saldiva et al. 2002; Dormans et al. 1999) compared with only one to two hours for humans. Daily exposures can be allowed to continue for several weeks to develop subchronic (Carter et al. 2006) and chronic (Mauad et al. 2008) exposure models. Along with inhalation experiments, intrapharyngeal or intratracheal instillation of collected PM, via the nose or trachea, have also been applied to animal exposure models. Instillation studies allow delivery of a higher dose directly to the lung (USEPA 2004; Suwa et al. 2002; Ulrich et al. 2002), and also allow exposure to known concentrations of well-characterized PM suspended in an aqueous medium (Suwa et al. 2002).

3.1.8 Endpoints

Many of the endpoints examined for animals are the same as those for humans. These include clinical signs of pulmonary function and responsiveness to contractile agonists (i.e., methacholine or histamine); vascular function tests such as HRV, ST-segment elevation, and frequency of arrhythmias before and after exposure; and, BAL analysis (Carter et al. 2006; Wellenius et al. 2003; Saldiva et al. 2002; Ulrich et al. 2002). PM concentration relative to body weight or organ weight (post-exposure) can also be measured to determine PM deposition in the organ (Dormans et al. 1999). Furthermore, because experimental animals are often euthanized at the end of the experiment, the end-points can be more invasive and allow for a greater dissection of tissue-specific mechanisms. Histopathological changes of the lung, heart, and other organs (i.e., liver, kidney, spleen, etc.) can also be assessed following PM exposures (Araujo et al. 2008; Saldiva et al. 2002; Suwa et al. 2002). Blood samples can also be collected to assess the effect of PM on different hematological parameters, such as hemoglobin, differential white blood cell count (WBC), clinical chemistry (i.e., pH, total protein, albumin, etc.) (Dormans et al. 1999). In dog models, a hydraulic balloon occluder is implanted in dogs around a coronary artery to facilitate particulate exposure. Factors such as myocardial blood flow, arrhythmia incidence or acute myocardial ischemia are measured during forced occlusions that usually occur after PM exposure (Bartoli et al. 2009; Wellenius et al. 2003).

3.2 *In vitro Studies*

As the next logical step in the reductionist approach, in vitro studies have the potential to describe the underlying cellular and molecular mechanisms, while in vivo studies can provide interpretation of the underlying pathophysiological mechanisms (Devlin et al. 2005). In vitro studies allow interactions between specific cell lines of interest and PM in ways that are not feasible with in vivo studies. A major advantage of in vitro models is that cellular and subcellular functions (i.e., cell growth and cell-to-cell interactions) and the molecular pathways can be studied in a more detailed manner (Rothen-Rutishauser et al. 2008). Another advantage of in vitro studies using human cells over animal models is that uncertainty regarding extrapolation from animal to human models can be minimized. Human cells cultured by following standardized cell culture practices are considered to yield high reproducible results (Rothen-Rutishauser et al. 2008). However, one drawback of in vitro studies is that the cells may not respond as they would when they are in the body, particularly in regards to immortalized cell lines. These cells do not interact with the multiple cell types in the tissues and are not supported by endogenous nutrients or other paracrine factors (Maier et al. 2008). Nonetheless, results obtained from in vitro studies exposing PM to human cell lines generally concur with the findings obtained in the human clinical studies (Devlin et al. 2005). Thus, in vitro models of human cells with appropriate growth and exposure techniques can advance the research while reducing the use of animal models for PM toxicity studies (Bakand et al. 2006).

3.2.1 Exposure Techniques

In vitro exposure of cells to PM requires special exposure apparatus that allows close contact between the cells and the test compounds for significant exposure durations (Aufderheide 2005). A number of methods have been developed to date—the simplest, least expensive, and most widely used of these methods is to collect PM on filters. Once collected, the PM is resuspended in a liquid medium and the suspension is added to the cells. The cellular responses can then be investigated in detail (Mazzarella et al. 2007; Hetland et al. 2004; Becker et al. 2003). However, there are major limitations with this method, including changes in PM size fractions and chemical characteristics during the sample collection, extraction, and resuspension. For example, the composition of collected PM may change due to loss of volatile organic compounds and the size distribution of PM can also be altered by agglomeration of small particles (Bruijne et al. 2008). Thus, particles are added to the cells as a suspension in culture medium which differs substantially from the actual deposition of airborne particles onto cells. The quantity (i.e., mass or number) of particles that actually interacts with the cells cannot be determined (Maier et al. 2008). Alternatively, impingers have also been used to collect PM directly in a liquid medium (Li et al. 2002); however, the composition and surface characteristics of PM are changed whenever it is transferred into a liquid media (Bruijne et al. 2008).

Compared to the above-mentioned methods, exposure of cells at the air-liquid interface (ALI) is the most realistic method. Using the ALI system, the apical surface of the epithelial cell monolayer is exposed to PM while the basolateral surface of the cells is fed with the medium through the porous membrane (Aufderheide 2005) (Fig. 1). In this process, the PM characteristics remain unchanged prior to deposition. The Navicyte Horizontal Diffusion Chamber (Harvard Apparatus, USA) is one such system. It is designed to expose cells to the atmosphere while media is supplied through a porous membrane. The exposure chamber is mounted on a heated block at 37 °C (Bakand et al. 2006). Aufderheide

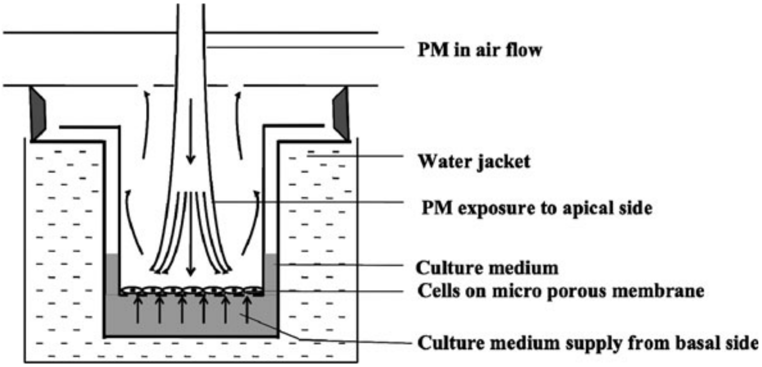


Fig. 1 Air–liquid interface (ALI) cell exposure system

(2005) developed a new in vitro exposure system—the Cultex® (Hanover, Germany), based on the ALI cell culture approach. This system has been used successfully for in vitro investigations of gaseous compounds (Ritter et al. 2001), cigarette smoke (Fukano et al. 2006), and automobile exhaust (Knebel et al. 2002); however, it has not been used for ambient PM. A recent advance in the field of in vitro study of PM exposure is the use of the electrostatic precipitator (ESP). Electrostatic precipitation is usually used in PM collection and monitoring, and has recently been adapted for direct exposure of airway epithelial cells to PM (Bruijne et al. 2008). With this method, PM carried in the sample flow is charged and then subjected to a convergent electrostatic field. PM drifts across the flow and deposits on a collection plate at the bottom of the instrument (Bruijne et al. 2008). In the case of in vitro investigations of cell exposure to PM, the PM collection plate is replaced with a cell containing well/plate. This method overcomes the modification of PM characteristics caused by collection in media and provides higher collection efficiency.

Cells are typically exposed to ambient PM (PM_{10}, $PM_{2.5}$, UF), diesel exhaust particles (DEP), or cigarette smoke using these exposure systems (Mazzarella et al. 2007; Fukano et al. 2006; Hetland et al. 2004; Li et al. 2002). Some studies have used well-characterized standard reference materials (SRMs) from the National Institutes of Standards and Technology (NIST 2009) and engineered nanoparticles, such as zinc oxide, titanium dioxide, in liquid medium (Li et al. 2003; Oberdörster 2001; Boland et al. 1999). Although standard or engineered materials are not true ambient PM, the materials are representative of ambient PM. These materials also elicit similar responses in cells to the ambient PM. The majority of the in vitro studies use doses in the range of 10–1000 μg/mL (PM mass/volume of the suspension solutions) with exposure durations of 2–72 h (Mitschik et al. 2008).

3.2.2 Cell Lines

In vitro studies have been conducted using a range of human and animal cells to examine the effects of PM exposure. In this chapter, attention has been focused on human derived cells only. The cells may be collected from freshly isolated tissues (primary cells) or may be generated from a continuous cell line (secondary cells) (Rothen-Rutishauser et al. 2008). The application of primary cells has some limitations, including the lack of availability from healthy persons, limited numbers of cells from each isolation, and inter-donor variation. In contrast, secondary cells are homogenous and more stable, and thus allow reproducibility. However, these cells are not supported by endogenous nutrients or other paracrine factors and exhibit little phenotypic differentiation (Rothen-Rutishauser et al. 2008). The most studied secondary cell lines are: airway epithelial cell lines—Calu-3, 16HEB14o-, BEAS-2B, alveolar epithelial cell line—A549, and a macrophage cell line—THP-1 (Mitschik et al. 2008; Rothen-Rutishauser et al. 2008). Most in vitro studies using PM investigate the effect on the lung cells, as it represents the first line of defense to the outside environment and has the greatest surface area for exposures. However, certain studies have examined the exposure effects of PM on the circulatory system, focusing primarily on pulmonary artery endothelial cells (Bai et al. 2001; Karoly et al. 2007). A triple co-culture in vitro model of the human airway barrier has been developed by growing human blood monocytes derived macrophages and dendritic cells on the apical and the basal sides of A549 cells to study the interaction of particles with a complex cell culture system (Rothen-Rutishauser et al. 2005). Translocation of particles (AD 1 μm) was observed between the cells, although the dendritic cells were not exposed directly to the particles. This complex model is more realistic and better characterizes particle uptake and translocation, and allows cell-to-cell communication upon particle exposure. Though, more investigation is required in order to recognize the pathway(s) of interplay between different cell types.

3.2.3 Endpoints

Several endpoints can be studied in vitro, including PM translocation into the cells, cytotoxicity, induction of oxidative stress, inflammation, DNA damage, and apoptosis, specifically in human pulmonary epithelial cells and pulmonary artery endothelial cells (Mazzarella et al. 2007; Karoly et al. 2007; Li et al. 2000, 2002, 2003; Bai et al. 2001). Table 1 summarizes findings from several in vitro studies focusing mainly on oxidative stress, inflammation, and the cytotoxic effects of PM. Upregulation of antioxidant enzymes and proinflammatory cytokines are considered as markers of oxidative stress and the inflammatory response in human cells. Among the antioxidant enzymes, glutathione (GSH), superoxide dismutases (SOD), and heme oxygenase (HMOX-1) have been measured in several studies (Li et al. 2000, 2002, 2003). The decrease in GSH/glutathione disulfide (GSSG) ratio was measured by glutathione assay as an indicator of oxidative stress. Inflammation can be investigated by determining upregulation of proinflammatory cytokines, such as interleukins (IL-6, IL-8), tumor necrosis factor (TNF-α), macrophage inflammatory protein (MIP); and chemokines, such as monocyte chemotactic protein (MCP)-1, granulocyte colony-stimulating factor (GCSF), and granulocyte macrophage colony stimulating factor (GM-CSF). Expression profiling of genes responsive to oxidative stress and inflammation can be analyzed based on mRNA or protein synthesis, using reverse-transcription polymerase chain reaction (RT-PCR)/RNase Protection Assay (RPA), and western blotting/enzyme-linked immunosorbent assays (ELISAs), respectively (Mazzarella et al. 2007; Hetland et al. 2004; Li et al. 2002). Cell viability is generally determined using colorimetric assays, such as the MTT (Watterson et al. 2007) and WST assays (Bai et al. 2001), and/or staining test, such as trypan blue exclusion (Fujii et al. 2001; Boland et al. 1999) and propidium iodide (PI) test (Hetland et al. 2004). In the colorimetric assays, the tetrazolium salts MTT and WST are reduced to formazan only by metabolically active cells, which can be quantified by spectrophotometric means. In the staining tests, viable cells with an intact membrane exclude certain dyes, such as trypan blue and PI, whereas dead cells take up the

Table 1 Summary of selected in vitro studies using different human cell models

References	Cell type	PM type	Exposure cond.	Endpoints	Findings
Di Pietro et al. (2009)	A549	Oil fly ash (collected from power plant)	Serial dilution of original sample 1, 2, 4, 6, 8, 14, and 24 h	Cell viability, intracellular ROS production, DNA damage, lipid peroxidation assessment, and determination of the cellular compartments responsible for ROS production and lipid peroxidation	A dose and time-dependent relation found between metal content, and both ROS generation and lipid peroxidation. ROS generation significantly correlated with DNA damage. In the absence of the morphological damage, cytoplasmic compartment generated ROS
Mazzarella et al. (2007)	A549	Diesel exhaust $PM_{1.0}$	100, 200, 400 µg/ml 24, 48, 72 h	Immunocytochemistry, intracytoplasmic cytokines assessment, and ELISA for IL-6 and -8	Cell wall alternation, PM internalization, cytoplasmic vacuolization and dose dependent increase in IL-6 and -8 observed
Karoly et al. (2007)	HPAEC	UF or vehicle exhaust particles	100 µg/ml UF or vehicle particles, 4 h with Affymetrix HG U133 Plus 2.0 chips	Quantitative-PCR for selected genes, western blotting for tissue factor (F3) regulation	Coagulation marker up-regulation, expression of HMOX-1, IL-6 and -8 with UF exposure
Fukano et al. (2006)	A549	Whole cigarette smoke	About 50–500 µg/vessel	Cell viability and RT-PCR for HMOX-1	No significant change in cell viability and dose dependant HMOX-1 expression observed
Hetland et al. (2004)	A549	Ambient coarse, fine, UF	0, 200, 400, 600, 800, 1000 µg/ml 40 h	Cell viability, ELISA for IL-6 and -8, apoptosis	Dose dependant increase in IL-6 and -8 observed, but decreased at higher conc. due to toxicity. Cytokine induction potency same for all size

Table 1 (continued)

References	Cell type	PM type	Exposure cond.	Endpoints	Findings
Becker et al. (2003)	Primary alveolar macrophage	Coarse, fine, UF	50 µg/ml 18–20 h	ELISAs for IL-6, TNFα, MCP-1, and MIP-1α, and phagocytosis	Cytokine induction order: coarse > fine > UF. Microbial products on coarse caused higher cytokine induction
Li et al. (2002)	THP-1	DEP	10, 25, 50, 100, 200 µg/ml, 16, 18 h	Western blotting for HMOX-1, manganese-SOD, and c-Jun N-terminal kinase cascade (JNK), apoptosis, GSH/GSSG ratio	HMOX-1 expression at low oxidative stress, proceeds to JNK activation and IL-8 secretion at intermediary level, and cellular toxicity observed at higher level
Bai et al. (2001)	HPAEC	DEP	15 µg/ml for 1.5 or 24 h30 µg/ml for 2 or 24 h	Cell viability of confluent and subconfluent cells using WST-8 assay	Decrease in cell viability with 15 µg/ml in subconfluent, 30 µg/ml subconfluent and some confluent
Fujii et al. (2001)	Primary HBEC	PM_{10}	10, 100, 500 µg/ml 2, 8, 24 h	Rnase and ELISA for leukemia inhibitory factor (LIF), GM-CSF, IL-1 and -8	mRNA levels of LIF, GM-CSF, IL-1 and -8 increased in a dose-dependent manner
Boland et al. (1999)	16HBE-14o-	SRM 1650 DEP	0-20 µg/cm^2 6, 12, 24 h	Cytotoxicity, phagocytosis, ELISA for IL-8, GM-CSF, and IL-1 β	DEP underwent phagocytosis by epithelial cells and translocated through the cells. A time-dependent increase in IL-8, GM-CSF, and IL-1β observed

dye. The numbers of viable cells can then be counted using a microscope or a flow cytometer for trypan blue or PI tests, respectively.

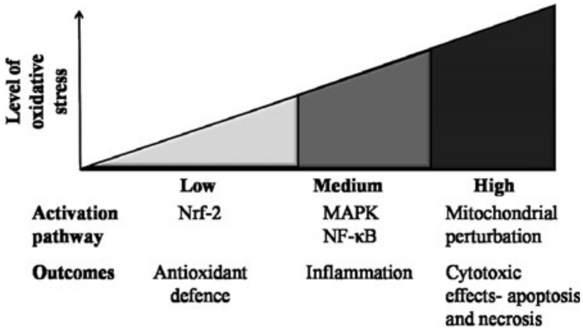
4 Biological Mechanisms of Toxicity

Several pathophysiological mechanism pathways have been proposed to explain PM induced adverse health effects. Oxidative stress is the most investigated mechanism relating to PM exposure and incidence of different cardiopulmonary diseases (Li et al. 2008; Valavanidis et al. 2008). PM mediated oxidative stress may arise from a number of sources; the largest of which is reactive oxygen species (ROS) such as H_2O_2, $O_2^{\bullet\bullet-}$, $OH^{\bullet}$, etc. These species are either present on the PM surface, generated by components within the PM, or generated through the biological response. Squadrito et al. (2001) showed that fine PM may contain large quantities of free radicals (10^{16} to 10^{17} unpaired spins/g). The presence of soluble transition metals, such as iron, copper, chromium, and vanadium, or organic compounds, such as quinones, on PM surfaces can induce ROS generation in biological systems (Squadrito et al. 2001). Furthermore, ROS can also be generated from activated immune cells during particle-elicited inflammation (Schins and Hei 2007). It is not yet known to what degree each mechanism contributes to overall PM-induced generation of ROS. Excessive generation of ROS may overwhelm the antioxidant defence system of the human body resulting in oxidative stress. This leads to the activation of a number of redox-sensitive signaling cascades that can be injurious to the cell, tissue, organ, and ultimately, to the organism as a whole (Li et al. 2003).

4.1 Respiratory System

Li et al. (2008) proposed a three phase hierarchical cellular oxidative stress model that provides a mechanistic platform to understand how PM elicits adverse health effects in the respiratory system (Fig. 2). Initially, at low levels of oxidative stress, protective effects are induced by transcription factors, such as nuclear factor erythroid-2 (Nrf2), to reduce biological damage as it activates more than 200 protective antioxidant and detoxification enzymes. Collectively, these enzymes are known as phase 2 enzymes which act in a coordinated manner to protect the lungs from oxidant damage. For example, while SOD catalyzes $O_2^{\bullet\bullet-}$ dismutation to H_2O_2, catalase (CAT) and glutathione peroxidase (GPx) prevent formation of the hydroxyl radical ($O\dot{H}$) from H_2O_2 and detoxify H_2O_2 to non-toxic products (oxygen and water) (Quinlan et al. 1994). If this protective antioxidant response fails to provide protection against ROS generation, increasing ROS production can generate a proinflammatory response. Oxidative stress activates the mitogen-activated protein kinase (MAPK) and nuclear factor kappa beta (NF-κB) signaling

Fig. 2 Hierarchical cellular oxidative stress model (adapted from Li et al. 2008)



cascades. MAPK controls the synthesis of activator protein (AP)-1, regulating gene expression related to inflammation, and other important functions, including cell proliferation or death. These signaling cascades are responsible for the expression of cytokines, chemokines, and adhesion molecules, which cause inflammation in the lungs. Finally, at toxic levels of oxidative stress, apoptosis and necrosis can occur. Perturbation of mitochondrial permeability transition pores can release proapoptotic factors such as cytochrome c and induce apoptosis of the lung cells. Continuous exposure to PM can result in chronic pulmonary inflammation and eventually cause and/or aggravate impairment of lung development and lung diseases, including COPD, cystic fibrosis, and asthma (Kok et al. 2006). Chronic inflammation can ultimately cause lung fibrosis and epithelial cell hyperplasia, potentially resulting in lung tumors and cancer (Oberdörster 1996).

4.2 Cardiovascular System

Although it is clear that PM has a profound effect on cardiovascular health, the mechanisms underlying this process are still unclear. Three mechanisms have been proposed linking PM and CV effects: (1) irritation of the pulmonary system leading to systemic release of pro-inflammatory or pro-oxidative mediators; (2) autonomic imbalance leading to sympathetic nervous system activation or parasympathetic nervous system withdrawal; and (3) direct transfer of nanoparticles to the circulatory system through the alveoli (Brook 2008; Nemmar et al. 2002). The cardiovascular consequences of PM exposures are likely caused by more than one pathway occurring simultaneously. The first pathway- release of pro-inflammatory and pro-oxidative mediators is supported by the results of human exposures. Several studies have observed increases in leukocytes, platelets, PMN, and cytokines (i.e., IL-6 and TNF-α) in peripheral blood (Mills et al. 2008; Törnqvist et al. 2007; Dubowsky et al. 2006) with exposure to dilute diesel PM. Similarly, increased levels of 8-isoprostane in exhaled breath when exposed to CAP suggest oxidation of tissue phospholipids (Mills et al. 2008). The second pathway- autonomic imbalance is also supported by current research. HRV, a marker of autonomic tone, has been shown to be affected by PM (Fakhri et al. 2009; Brook et al. 2004; Gold et al. 2000). Short-term reduced low-frequency HRV has been associated with sudden death in patients with chronic heart failure (La Rovere et al. 2003). Furthermore, the deposition of PM on pulmonary nerve endings may cause an imbalance in autonomic control of the heart, leading to decreased HRV. The decreased HRV, in turn, raises the possibility of sudden death in sufferers of chronic heart failure (Karoly et al. 2007). The third proposed pathway remains controversial. Attempts to prove translocation of (^{99m}Tc)–labelled carbon nanoparticles ("Technegas") from the lungs to the circulatory system have had mixed results (Nemmar et al. 2002). Despite the controversy, the implications of translocation of nanoparticles would be incalculable, given that UF particles have the highest number concentration of all PM. Chan and his group (University of Toronto, Canada) are currently working on quantifying nanoparticles such as carbon and gold nanoparticles in excised organs, after in vivo dosing for many innovative applications in diagnostics (Fischer et al. 2007). It is hypothesized that low-to-moderate grade inflammation induced by chronic PM exposure may initiate and accelerate atherosclerosis. Acute exposure to high concentrations of PM may cause vasoconstriction leading to myocardial infarction (Peters et al. 2001) or other ischemic events (Dominici et al. 2006).

5 Conclusion

Knowledge generated through epidemiological, in vivo and in vitro studies has allowed substantial progress in recent years in our understanding of the pathophysiological mechanisms underlying PM-induced adverse health effects. There is a mounting body of evidence indicating that human exposure to ambient PM at concentrations typical of urban areas can cause serious health problems. The respiratory and cardiovascular systems have been identified as the primary targets of inhaled PM. Both in vivo and in vitro toxicology studies have identified oxidative stress-initiated inflammation as one of the major pathways of PM-induced respiratory and cardiovascular diseases. Although the assessment of PM toxicity has been studied extensively, knowledge gaps still remain. Most of the in vivo and in vitro studies have observed biological responses at very high PM concentrations; however, epidemiological studies have found increased mortality even at relatively low ambient PM concentrations. The mechanisms responsible for the increased health risks associated with these low PM concentrations have not yet been identified in toxicological investigations. There is also no clear consensus on a unique physicochemical characteristic of PM that could explain the observed biological responses. More rigorous animal exposure studies which investigate the pathophysiological consequences of well-characterized PM exposures are required to identify the effects of both acute and chronic PM exposure in both healthy and diseased models. Further investigation is also required to develop an optimal in vitro exposure system to determine which properties of PM may be causing the biological effects and to define the mechanisms underlying these biological effects observed in vivo. New findings obtained from both in vivo and in vitro studies will allow regulatory agencies to develop better air quality standards in order to reduce health risks to both in the general public and susceptible individuals.

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Part V
Airborne Particulate Matter Exposures and Health Risks

Clare L. S. Wiseman and Fathi Zereini

Various methods have been developed and applied over the years to document human exposures to particulate matter (PM) in both indoor and outdoor environments for the assessment of risk. Generally, there are several ways through which exposure routes and levels and related health impacts can be determined. This includes the direct measurement of ambient PM levels using stationary or mobile sampling equipment, equipping human subjects with personal air quality monitors to more thoroughly assess exposures as a consequence of time-activity patterns in various microenvironments, using environmental indicators such as plants to measure and monitor air quality and collecting human biological materials such as urine and blood to measure chemical constituents or the metabolic by-products of PM exposures. This information, combined with epidemiological, occupational and clinical investigations, is critical in furthering our ability to fully assess the human and environmental health risks associated with airborne PM. This part contains six contributions that discuss exposures to PM and its constituents in both humans and environmental media and their health risks. These are described as follows.

In the first chapter, Walker discusses the use of snow, soil and lichens to monitor contaminant levels in airborne PM in North-Eastern European Russia. As part of this, Walker provides evidence for the particle-bound transport of metals via the deposition of coal fly-ash from power generating stations, an important source of airborne emissions in this region. The use of biomonitoring to assess exposures of toxic constituents in ambient PM in urban and industrialized areas is discussed by Klumpp and Ro-Poulsen in the second chapter. Specifically, they present two widely applied biomonitoring procedures in Europe: the standardised ryegrass exposure method for monitoring trace metals and the standardised exposure of curly kale for monitoring polycyclic aromatic hydrocarbons (PAHs). In presenting the results of a Europe-wide biomonitoring study undertaken in eleven cities using these two procedures, they highlight the value of biomonitoring to assess trace metal and PAH pollution in urban areas. The third chapter, authored by Sabaliauskas and Evans address the outdoor and indoor exposures to ultrafine PM in cities, which have a diameter of less than

100 nm. Although they contribute little to the overall PM mass found in urban air, they are the most prevalent in terms of particle number and may pose the greatest health risk due to their size. Sabaliauskas and Evans discuss the various sources and processes which influence ultrafine concentrations and the important factors to be considered in the design of human exposure studies in urbanized areas. In the fourth chapter, Iavicoli et al. provide a comprehensive overview of current knowledge regarding the environmental monitoring of subjects occupationally exposed to urban PM such as traffic police and taxi and bus drivers. As they discuss, studies have provided clear evidence for an association between occupational exposures to urban PM, especially that derived from traffic, and adverse health effects. Among other things, their discussion emphasizes the need to directly monitor exposures among those occupationally exposed, as air quality data derived fixed monitoring stations are not likely reflective of the actual exposures which occur in roadside environments. Kappos provides an overview of the results of epidemiological and clinical investigations which have linked ambient PM exposures to a variety of negative human health outcomes in the fifth chapter. Effects which are particularly relevant to public health policy are the focus of discussion, including the body of evidence linking short-term exposures to cardiovascular and respiratory morbidity and mortality and that relating long-term exposures to respiratory health in children and the development of cancer. Finally, Wiseman and Zereini review current knowledge regarding platinum group element (PGE) levels measured in airborne PM of biological concern and discuss their possible health effects in humans. As they argue, recent studies on PGE in biologically relevant media such as airborne fine and ultrafine PM suggest that exposures to these metals are indeed a human health concern due to their mobility and solubility in the environment, their potential to be transformed into more toxic species upon uptake by humans and by the very fact that the contribute to a suite of metals found in fine PM that have been associated with various negative health effects.

The Use of Snow, Soil and Lichens as Biomonitors of Contaminants in Airborne Particulate Matter in North-Eastern European Russia

Tony R. Walker

1 Introduction

Fossil fuel combustion, particularly coal, has been the principal fuel source for electrical power generation in Russia (Hill 1997). The continuing exploitation of non-renewable resources in Russia has created some large Arctic towns (Ziegler 1987), which increases the risk of localised urban environmental pollution (Pryde 1991). The Pechora Basin in north-eastern European Russia has been subject to a range of industrial impacts such as densely populated areas of industrialization including oil and gas fields, coal and ore mining. Coal combustion (associated with power generation) has historically been the principal source of particulate emissions, SO_2 and heavy metal pollution in the Pechora Basin (Vinogradova 2000; Solovieva et al. 2002; Walker et al. 2003a, b). Other sources include gas and oil extraction, cement production, pulp and paper production, construction and oil refineries (State of the Environment of the Komi Republic 1998). Exploitation of Pechora Basin coal is in decline due to its poor quality and associated high transportation costs (Lausala and Valkonen 1999). Recently, however, the oil and gas industries have boomed and are expected to expand further, bringing about significant risks of environmental pollution from gas flaring (Vilcheck and Tishkov 1997; Walker et al. 2005).

Recent overwhelming scientific evidence compiled by the Intergovernmental Panel on Climate Change (IPCC 2007) have highlighted linkages between climate change, environmental pollution, anthropogenic green house gas emissions (GHG)

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_23,

and reduced air quality from coal fly-ash fall out in urban centre's. Russia is rapidly emerging as a global energy supplier particularly with intermediate energy sources in recent years, such as, liquefied natural gas (LNG) (Mahalingam 2004), but despite Russia's shift to greener energy (compared to coal) coal combustion remains the principal source of urban particulate emissions in the Pechora Basin (Walker et al. 2005).

Impacts of particulate emissions from coal fly-ash pollution have been seen close to emission sources in and around the cities of Vorkuta and Inta where there are examples of environmental damage due to acidification, reduced air quality and eutrophication (Getsen et al. 1994; Virtanen et al. 2002; Walker et al. 2003b). However, it should be emphasised that vast areas of the Russian Arctic appear close to pristine condition (Rovinsky et al. 1995).

The objective of this paper aims to present recent studies on the ecological and human health impacts resulting from the deposition of coal fly-ash particulates from emissions due to fossil fuel combustion within the Pechora Basin. Problems exist when monitoring airborne particulate deposition around urban centers, as air and precipitation chemistries show high temporal and spatial variation (e.g. Reimann et al. 1999). Elemental concentrations are usually low and sample contamination is a significant problem. Approaches include the analysis of ecological materials that accumulate contaminants (e.g. snow, soils and lichens) which become modified by exposure to pollution from airborne particulate deposition.

The analysis of the chemistry of snow provides useful information on the distribution patterns of anthropogenic substances emitted into the atmosphere (Shaw et al. 1993). Concentrations of metal elements in snow can be used to estimate deposition during winter and the analysis of the underlying soil can also be used to evaluate long term accumulation of airborne pollutants (Reimann et al. 2000). Analysis of soil samples allows for assessment of aerial deposition by comparison of concentrations per unit area, provided sampling is carried out to sufficient depth to audit all the analytes of interest. Numerous investigations have used variation in soil chemistry to map pollution deposition, particularly in the case of heavy metals (e.g. Reimann et al. 2000). In highly polluted areas near industrial centers, physical and chemical properties of top-soils can become radically modified. Soil contamination due to alkaline emissions from coal combustion has been widely reported (Larssen and Carmichael 2000; Walker et al. 2003a). The high tolerance of lichens to most metal contaminants and their slow growth are among the main factors that make them effective accumulators (Nash 1989). Accordingly, spatial variation in the chemical composition of lichens has been frequently used to map atmospheric deposits (Nimis et al. 1990; Riget et al. 2000).

The data presented here provides evidence of particle-bound metal transport via the deposition of coal fly-ash from power generating stations in Vorkuta and Inta through the collection and subsequent chemical analysis of snow, lichens and top-soil (Walker et al. 2003 a, b, 2006a, b; Walker 2005, 2008).

2 Materials and Methods

2.1 Site Locations

Transects through point sources were undertaken to assess the distribution of pollutants from coal mining and burning in the principal towns of Inta (66°03′N, 60°10′E) and Vorkuta (67°30′N, 64°05′E) and from oil and gas extraction and use in Usinsk (66°01′N, 57°30′E) (Table 1; Fig. 1). These sampling locations and transects have been illustrated and described in greater detail elsewhere (see Walker et al. 2003a, b). Sampling locations were selected along each transect at roughly logarithmically increasing distances from each town. At each location, three sub-sites were selected, approximately 1 km apart, and at each site 6 replicate samples of snow, soil and lichens were collected >10 m apart in open areas subject to minimal tree canopy effects (Reimann et al. 1999). Powder-free Low Density Polyethylene (LDPE) gloves

Table 1 Summary of main sampling sites along four transects within the Pechora Basin study area

Site no.	Name of site	Co-ordinates	Distance from nearest town
Transect 1			
1.1	Lake Padvaty	67°27′N 63°05′E	45 km W of Vorkuta
1.2	Malen’kiy arvozh	67°30′N 63°30′E	30 km SW of Vorkuta
1.3	Vorkuta	67°34′N 64°09′E	2 km NE of Vorkuta
1.4	Lake Ngayats’yakha	67°35′N 64°15′E	12 km NE of Vorkuta
1.5	Lake Mutnoye	67°44′N 64°52′E	40 km NE of Vorkuta
1.6	Lake Protochnoye	67°47′N 65°37′E	70 km NE of Vorkuta
Transect 2			
2.1	Khosedayu River	67°15′N 59°37′E	130 km N of Inta
2.2	Lake Tumbulovaty	67°07′N 59°34′E	110 km N of Inta
2.3	Two Lakes near Adak	66°35′N 59°45′E	62 km N of Inta
2.4	Lake Lyz’vad	66°16′N 60°13′E	20 km N of Inta
2.5	Lake Swan (Lebedinoye)	66°06′N 60°15′E	7 km N of Inta
Transect 3			
3.1	Vangyr river	64°59′N 59°12′E	110 km SW of Inta
3.2	Mezhgornyye lakes	65°15′N 59°40′E	90 km SSW of Inta
3.3	Lake Van’kavad	65°59′N 59°27′E	32 km SSW of Inta
3.4	‘Fox Lake’	65°59′N 60°01′E	7 km SSW of Inta
3.5	Inta	66°03′N 60°10′E	2 km SSW of Inta
Transect 4			
4.1	Lake Bosmanvad	65°48′N 57°03′E	30 km SW of Usinsk
4.2	Lake Chakty	65°58′N 57°16′E	15 km W of Usinsk
4.3	Usinsk	65°59′N 57°35′E	2 km E of Usinsk
4.4	Lake Kankur’ya	65°57′N 57°42′E	10 km NE of Usinsk
4.5	Isaak-Ty/Shar’yu	66°07′N 58°18′E	35 km NE of Usinsk
4.6	Adz’vavom	66°33′N 59°16′E	100 km NE of Usinsk

Fig. 1 Map showing transects through the towns of Vorkuta (W–NE), Inta (N–S) and Usinsk (SW–NE) in the Pechora Basin, North-eastern European Russia. The *grey dashed line* indicates the approximate position of the tree line and *grey shading* indicates land above 500 m. Adapted from Walker et al. (2009)

were worn when handling ecological materials in the field and laboratory to minimise contamination.

2.2 Historical Particulate Contamination in Lake Sediments

In separate collaborative studies surface sediment samples were taken by Solovieva et al. (2002) to assess the spatial distribution of historical pollution as measured by the concentration of spheroidal carbonaceous particles (SCPs) which are an unequivocal signal of fossil fuel combustion. Short sediment cores representing the last *c*. 200 years were also collected and dated radiometrically. An historical pollution signal was established by the stratigraphic record of the SCPs. Further methodological details are given in Solovieva et al. (2002). Lakes were sampled as close to transects in this study as possible.

2.3 Snowpack and Filter Residues

Snowpack was sampled between March and April, prior to the onset of the spring thaw. At each sub-site along transects, six replicate snow pits were excavated in open areas. Snow collections and analysis were made according to Walker et al. (2003a). Cellulose acetate membrane filters were used to filter the snow-melt and the retained suspended solids were determined gravimetrically and subsequently photographed. Six cellulose acetate membrane filters from each sub-site were digested together in 10 mL of concentrated HNO_3 and elemental analysis of trace metals was undertaken by graphite furnace or flame atomic absorption spectrophotometry (GF-AAS and F-AAS); concentrations were recalculated in relation to the volume of filtered meltwater to allow direct comparison with the solution data (Reimann et al. 1996).

2.4 Top-Soil

Soil samples were collected between July and August from the same sub-sites as snow samples; details of sampling and analysis are given in greater detail in Walker et al. (2003a). Collection involved excavating organic and mineral top-soil to a standard depth of 5 cm from a 20 cm^2 plastic quadrat with a stainless steel hand trowel, which was cleaned between samples to avoid cross contamination. Soil samples were passed through a 4 mm stainless steel sieve in the field, double-wrapped in polythene bags and were stored at −20 °C prior to analysis. The thickness of the surface organic layer was recorded for all quadrats. Frozen soil samples were allowed to thaw overnight at room temperature and a representative sub-sample (5–10 g) was oven dried at 105 °C. Samples were ashed in a furnace at 450 °C overnight, allowed to cool in a dessicator and weighed for loss on ignition (LOI). A sub-sample (1 g) of soil ash was digested in 10 mL of concentrated HNO_3. The digest residue ($\sim$1 mL) was diluted and filtered through Whatman No. 42 ashless filters then made up to 100 mL using ultra-pure water to give a final matrix of 1% HNO_3. Analysis of soil trace metals was undertaken using GF-AAS and F-AAS.

2.5 Lichens

At each sub-site along the Vorkuta transect, six replicate samples of the terricolous mat-forming lichen *Cladonia arbuscula* were collected at distances 10–20 m apart in open tundra to provide biomarkers for atmospheric deposition. Lichen samples were air-dried in the field, sealed in LDPE containers and stored at 4 °C until analysis. Lichens were rehydrated overnight by exposure to water-saturated air (over water in a dessicator) at 4 °C, then fully saturated by spraying lightly with deionised water and cleaned of extraneous debris using forceps. Samples were dried overnight at 80 °C and then weighed, where *c.* 100 mg of apical (5 mm) tissue was digested to dryness in 1 mL of concentrated HNO_3 at 175 °C. The residue was dissolved in 10 mL 1 M HNO_3 and appropriate quantities of ionisation suppressant and releasing agent ($CsC1_2$, $LaC1_2$) added. Zinc was selected because it was one of several trace metals found to contaminate snow and soils locally in the survey region (see Walker et al. 2003a; Walker 2005) and was measured by F-AAS; concentrations were recalculated in relation to the mass of dried apical lichen tissue to allow direct comparison with the solution data (see Walker et al. 2003b).

3 Results and Discussion

3.1 Historical Particulate Contamination in Lake Sediments

Coal production in Vorkuta and Inta peaked between the 1980's and 1990's (Fig. 2). This was also reflected by substantial particulate emissions from coal combustion in Inta and Vorkuta over the same period. The amount of solids emitted in the Vorkuta area from 1992 to 1998 were between 5 and 8 times greater than for Inta, which in turn was approximately 3 times greater than for Usinsk (State of the environment of the Komi Republic 1998). The mean value of solids emitted from Vorkuta from 1992 to 1998 was 84,000 t year^{-1} with the greater part of these emissions comprising of hydrocarbons followed by solid particles of fly-ash originating from coal combustion and a cement factory (State of the environment of the Komi Republic 1998).

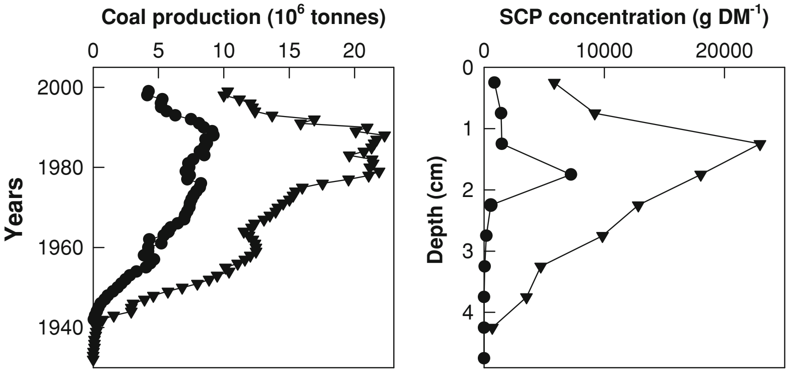


Fig. 2 Mean annual coal production in Inta (*filled circle*) and Vorkuta (*filled inverted triangle*); profiles of SCP's from lakes along the Inta (site 2.5) and Vorkuta (site 1.6) transects. Adapted from Walker et al. (2006b)

The concentrations of SCPs in surface sediments clearly increased in the vicinity of Inta and Vorkuta during the same period corresponding to the high volumes of coal combustion and production (Fig. 2). According to Solovieva et al. (2002) the higher concentrations of SCPs and high sulphur deposition in Vorkuta reflect the legacy of industrial activity. The historical perspective obtained from the analysis of lake sediment stratigraphy shows that present day concentrations of SCPs in surface sediments of lakes near Inta and Vorkuta are lower than they were in the past and that past peaks in SCP deposition correspond to peaks in coal production (Fig. 2). This suggests that although air pollution is still apparent today it is of a lower magnitude than in the past.

3.2 Snowpack and Filter Residues

The majority of snow pits excavated at sites around Inta and Vorkuta were typified by horizontal layers of coal fly-ash particles (Fig. 3). Subsequent filtration of these snowmelt samples revealed residues collected on dried cellulose acetate filters. The spatial extent of the sphere of influence of coal fly-ash emissions from Vorkuta compared with the Usinsk transect (where there are no coal fired power generating plants) are illustrated in Fig. 4. Only those sites at the extremes of the Vorkuta transect are apparently unaffected by these localised urban particulate emissions. The darker filters close to Vorkuta are a result of the ash fallout from coal combustion which is also reflected in Fig. 5, which shows the concentration of suspended solids collected on cellulose acetate filters following filtration of thawed snow. The trend along each transect strongly suggests a substantial contribution from coal combustion in Inta and Vorkuta. The amount of solids emitted in the Vorkuta area from 1992 to 1998 were much greater than for Inta, which in turn was approximately 3 times greater than for Usinsk (State of the environment

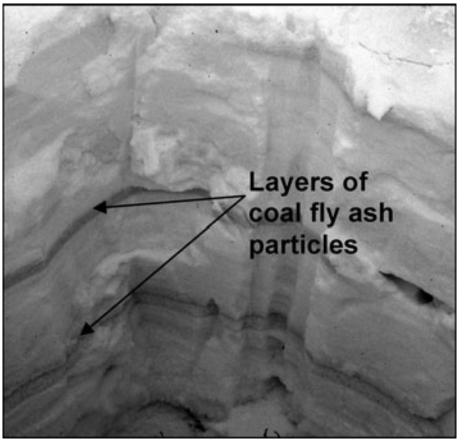


Fig. 3 Layers of coal fly-ash particles within snowpack (*Photo*: T.R. Walker)

Fig. 4 Dried filters showing particulates collected from snow samples taken along transects through the industrial towns of Vorkuta (**a**) and Usinsk (**b**). Adapted from Walker (2005)

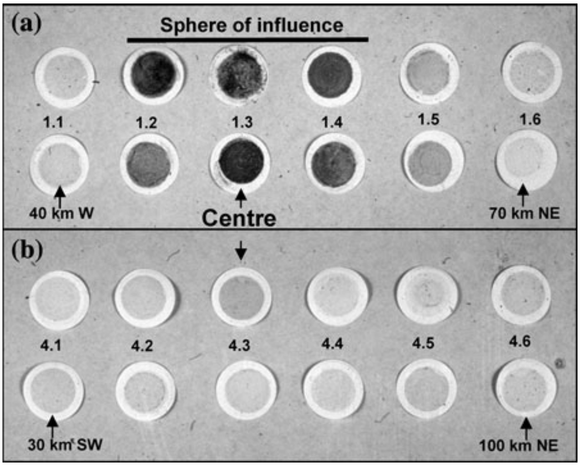
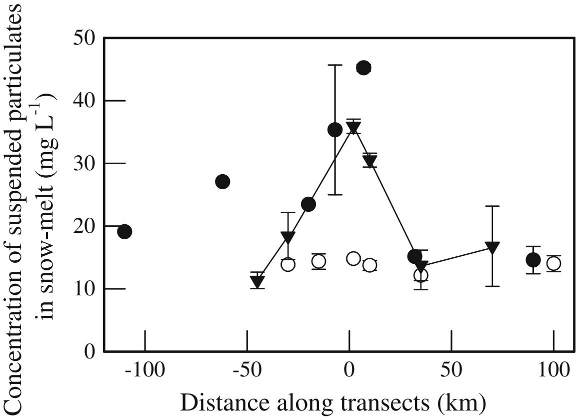


Fig. 5 Plot showing the concentration of suspended solids in filtered snow-melt samples taken along transects through Inta (*filled circle*), Vorkuta (*filled inverted triangle*) and Usinsk (*open circle*), during spring 1998 and 1999. Plotted values are means ± SE ($n = 3$). Adapted from Walker et al. (2003a)



of the Komi Republic 1998). The greater part of emissions from Vorkuta and Inta were comprised of hydrocarbons followed by solid particles of coal fly-ash originating from coal mining. In contrast the majority of emissions from Usinsk were CO_2 from the oil and gas industry based there.

In the immediate vicinity of Vorkuta and Inta there were elevated concentrations in suspended solids in snow-melt of the major combustion ash constituents: Al and Sr (Fig. 6). Urban plumes for Pb are evident from analysis of snow-melt particulates around Vorkuta and Inta. In addition, elevated concentrations of Ba, Ca and K in snow were found around Vorkuta, which may suggest that combustion ash was the source (Reimann et al. 1996). The entire transect through Usinsk generally reflected background concentrations in suspended solids in snow-melt similar to those observed in pristine areas at both ends of the Inta and Vorkuta transects.

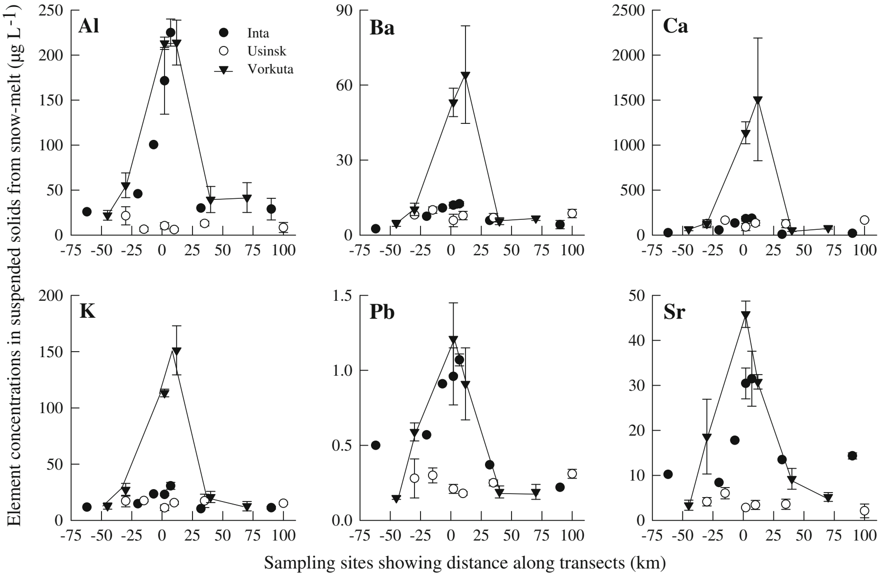


Fig. 6 Concentrations of metal elements within filter residue digest samples taken along transects through Vorkuta (*filled inverted triangle*), Inta (*filled circle*), and Usinsk (*open circle*), during spring 1998 and 1999. Plotted values are means ± SE ($n = 3$). Adapted from Walker et al. (2003a)

Along transects through Vorkuta and Inta filtered snow-melt collected at sites closest to the towns also contained elevated concentrations of Ba and Sr. Arsenic concentrations were greatest at the urban sites around Vorkuta and lower, respectively, in Inta and Usinsk and concentrations of the trace metals Cd, Cu, Ni, Pb and Zn were uniformly low at all sites. However, the absence of a pronounced urban peak in solution concentration may have been a result of adsorption onto alkaline ash (data not shown; Walker et al. 2003a). The slope of correlations between element concentrations in suspended solids and filtered snow provide evidence that the majority of the major constituents of combustion ash were in particulate form (data not shown; see Walker et al. 2003a). Mean solid : solution ratios for the total quantities of Ca, Ba and Sr were 12, 17 and 10 respectively. This confirms that estimates of deposition from filtered snow-melt only, can seriously underestimate deposition rates by up to 90% for certain elements where there is significant particulate pollution (Reimann et al. 1996).

3.3 Top-Soil

The depth of the surface organic layer in top-soil from each quadrat varied between 0.5 and >5 cm. For the less common soil constituents found in combustion ash e.g. Ba and Sr (Fig. 7) there was clear evidence of increased loading close to Vorkuta. There may also be soil enrichment of Zn around Vorkuta. The spatial extent of the local alkalisation of top-soil at sites around Vorkuta corresponds with vegetation changes evident in satellite images which have been confirmed by ground plot field observations (Virtanen et al. 2002). The distribution of the pH (data not shown) within top-soil provide evidence of the effects of the emission sources of Vorkuta and Inta; the most acidic samples were collected at remote sites. The higher soil pH values around Vorkuta correlate well with the Ca concentrations in snow and suspended solids. This indicates an important role for ash input from coal combustion and cement dust from the nearby cement factory in regulating snow and soil pH.

Walker (2005) found that the high soil metal loadings found locally around Vorkuta could not be explained by current deposition rates. This discrepancy between measured element concentration within soil and the amount of time required to accumulate this from current deposition rates may have arisen for a number of reasons. Firstly, there has been a substantial decline in coal mining in Vorkuta, since the peak of activity in the 1960s and 1970s. Within the last decade, the thirteen coal mines operating in 1990 were reduced to just seven by 1999 and coal production at the largest mine, has fallen by half between 1991 and 1999, from nearly 21 × 10^6 tonnes to 13 × 10^6 tonnes (State of the environment of the Komi Republic 1998). This trend is consistent with data on spherical carbonaceous particles (SCPs) found in lake sediment profiles showing that a peak in SCPs is found at 1.5 cm below the sediment surface and suggesting that SCP deposition rate has since been in sharp decline (Solovieva et al. 2002) and changes in tundra vegetation (Virtanen et al. 2002). Secondly, Vorkuta has a total population of around 200,000 inhabitants and urban development on this scale within the tundra ecosystem requires a great deal of construction activity, which would import considerable quantities of cement dust and other particles, resulting in elevated deposition of alkali-earth elements (Jalkanen et al. 2000). It is therefore likely that elemental concentrations in soils within 20–30 km of Vorkuta do not reflect current deposition rates but are a historical legacy of greater construction and industrial activity in the recent past.

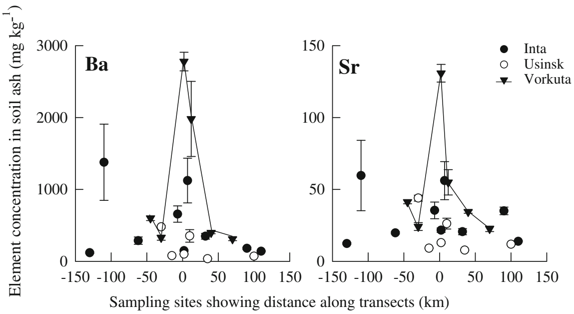


Fig. 7 Concentrations of Ba and Sr in soil ash along transects through Inta (*filled circle*), Vorkuta (*filled inverted triangle*) and Usinsk (*open circle*). Plotted values are means ± SE ($n = 18$). Adapted from Walker et al. (2006)

3.4 Lichens

There was significant localized higher Zn concentrations in the apices of *C. arbuscula* in the vicinity of Vorkuta ($P < 0.001$). For example, the highest concentration of apical Zn in *C. arbuscula* was found at the two sites closest to the town (see Fig. 8). Variation in Zn concentration in the apices of *C. arbuscula* around Vorkuta correlates well with other pollution signals from earlier work relating to concentrations of SO_4, Ca, K, pH in snow; metal contamination in soil and N concentration in the apices of lichens ($r = 0.90$, $P < 0.01$, $n = 6$) (Walker et al. 2003a, b).

3.5 Boarder Context of Local Contamination of Airborne Particulate Matter

Social studies by Karjalainen and Habeck (2004) about environmental pollution in Vorkuta revealed that air pollution was perceived to be the primary environmental threat, the principal sources being coal combustion from power and heating plants, coal mines and a cement factory. Here, local inhabitants evaluated air pollution by direct observations and personal experiences, such as contamination of washed clothes left out to dry, discolouration of snow, and respiratory problems.

Satellite imagery revealed profound changes the vegetation revealed around Vorkuta (Virtanen et al. 2002). Two principal impact zones were could be resolved. The first was designated a 'Pollution Zone' (150–200 km^2) in which there were dramatic changes in plant species composition, most notably an increase in abundance of willows and a reduction of lichens. The second was designated a 'Slight Pollution or Disturbance Zone' (600–900 km^2), in which, similar vegetation changes are observed, but to a lesser degree than in the first zone together with an increased abundance of herbs and grasses compared to unpolluted areas. The causal agents for these pollution zones were attributed to fertilization

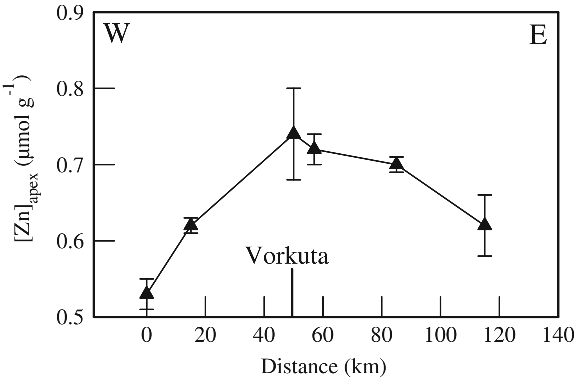


Fig. 8 Variation in apical Zn concentration in *Cladonia arbuscula* (*filled triangle*) along the transect passing through Vorkuta. Plotted values are means ± SE ($n = 18$). Adapted from Walker (2008)

effects due to emissions from the local power plant and dust cover from the cement factory and combustion ash (Virtanen et al. 2002). As well as being clearly demarcated in the satellite images, these zones were also easily recognized in the field although less dramatic than the near total destruction of vegetation that has occurred in the most polluted areas of the Kola Peninsula and around Norilsk (Mikkola 1996; Toutoubalina and Rees 1999).

Measurements of spheroidal carbonaceous particles made by Solovieva et al. (2002) in surface sediments of lakes on the same transects as those studied here corroborate a wider extent of particulate fallout around Vorkuta. This class of particle, which is an emission product of coal combustion, was present at sites 1.1 and 1.6 at higher concentrations than at any of the other remote sites examined in the study area (e.g. sites 3.2 and 2.2).

Therefore, measurements across a series of indicators systematically point to a more severe and regionally extended impact of air pollution around Vorkuta than around Usinsk, such as changes in vegetation communities and elevated contaminant levels in lakes (e.g. levels of SCP's and alkalization), snow, soil and lichen samples (e.g. elevated levels of metal elements associated with coal combustion and cement dust) (Solovieva et al. 2002; Walker et al. 2003a, b, 2006b; Virtanen et al. 2002). Karjalainen and Habeck (2004) found that air pollution was of greater concern in Vorkuta and Inta than in Usinsk.

4 Conclusions

In conclusion, results show considerable local contamination of airborne particulate matter in the top-soil, snow-pack and lichens around Vorkuta; in the vicinity of Inta local contamination of airborne particulate matter was only apparent in snow-pack. Deposition of coal ash around both towns is mainly responsible, with possible contributions from a cement factory located in Vorkuta. Near pristine areas located more than 30 km from Vorkuta and Inta appear to be unaffected by ash deposition, and are characterised by near background concentrations in both snow-pack and top-soils. Sites along the entire transect through the town of Usinsk, which is supplied by a gas-fired power station, were near pristine. There were elevated concentrations of Al, Ba, Ca, K and Sr in suspended solids and snow-pack around Vorkuta and Inta. Most of the deposition of elements commonly associated with combustion ash, occurred in particulate form. There was evidence that trace element concentrations of Pb, Cu and Zn in snow-pack were reduced around Vorkuta, due to adsorption onto alkaline ash particles. Extremely high elemental concentrations of Ba and Sr in top-soils around Vorkuta could not be explained by current deposition rates. This discrepancy may be the result of greater coal mining and construction activity in previous decades.

Acknowledgments This paper is dedicated to our late colleague and talented scientist, Dr. Galina Mazhitova. Special thanks to Dr. P.D. Crittenden and Dr. S.D. Young for help with this study. Dr. H. Zhang for processing ICP-MS samples. Help with logistics was provided by colleagues at the Institute of Biology Komi Science Centre (IB-KSC), Syktyvkar, especially Dr. V.I. Ponomarev. Dr. P. Kuhry, for co-ordinating the TUNDRA project, which was supported by the Environment and Climate Programme of the EC (contract number: ENV4-CT97-0522).

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Biomonitoring of Toxic Compounds of Airborne Particulate Matter in Urban and Industrial Areas

Andreas Klumpp and Helge Ro-Poulsen

1 Introduction

In recent years, the atmospheric concentrations of particulate matter in urban areas have gained special attention by policy-makers, various stakeholders and the public in general. This is due to the fact that deposition of airborne particulate matter, besides causing direct and indirect effects on plants, animals, and whole ecosystems, is known to strongly affect human health. Particularly the respiratory and the cardio-vascular system are obviously compromised by elevated levels of particulate matter, especially the smaller PM_{10} and $PM_{2.5}$ fractions, resulting in increased morbidity and mortality rates in urban areas as has been proven by many epidemiological studies worldwide. Several studies have also documented the relationship between ambient particle levels and the occurrence of genotoxic effects in standardised bioassays, indicating the potential contribution of PM pollution to mutations and carcinogenesis (Bofetta 2006; Carreras et al. 2006). Finally, accumulation of toxic components of particulate matter in the environment and their biomagnification in food webs may contribute to indirect effects via contamination of foodstuffs, animal feed, and drinking water.

The direct and indirect toxicity and genotoxicity of particulate matter after its ingestion or inhalation by humans is determined by its physical features such as size, number and surface area of particles, but also by their chemical composition. Elemental carbon and inorganic anions like sulphate and nitrate seem to be the

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_24,

main constituents of PM_{10} and $PM_{2.5}$ (Putaud et al. 2004), but trace metals and persistent organic compounds like polycyclic aromatic hydrocarbons (PAHs) may also play a major role concerning toxicity and ecotoxicity of dust particles and their adverse health effects (Götschi et al. 2005; Valavanidis et al. 2006). This importance can be explained by the observation that many of these PM components have a high affinity to the very fine and ultrafine, i.e., inhalable, aerosol fractions (Moreno et al. 2006).

Sampling and analytical methods for the collection and measurement of different size classes of PM as well as of particle-bound metals, organic compounds, and other substances are a major issue of the present book. Routine air monitoring networks based on physico-chemical measurements provide continuously data on ambient PM_{10} and $PM_{2.5}$ concentrations, but in most cases do not inform about the chemical composition of the dust load. If trace compounds of PM are monitored at all, such measurements are restricted to few components. Hence, knowledge about the chemical composition of PM, the local and regional distribution of airborne particle-bound substances and their toxic, genotoxic and ecotoxic potential is still very limited. Moreover, data on atmospheric pollutant concentrations do not permit to draw conclusions on possible adverse effects on human beings and ecosystems as their sensitivity to air pollution is influenced by many abiotic and biotic factors.

As a consequence of limited data availability and restricted knowledge about relationships between pollutant concentrations and effects, biomonitoring of ambient pollution using bioindicator plants is suggested and has been widely applied. Even the European "Directive relating to arsenic, cadmium, mercury, nickel and PAHs in ambient air" (EU 2004) recommends that, in addition to mandatory measurements of atmospheric pollutant concentrations, "the use of bioindicators may be considered where regional patterns of the impact on ecosystems are to be assessed." Atmospheric concentrations of trace metals and of PAH are generally too low to cause easily detectable, visible injury symptoms as, e.g., ambient concentrations of ozone or hydrogen fluoride do. Hence, accumulative bioindicator plants are to be used when biomonitoring of particle-bound air pollutants is performed. Exposure of accumulative bioindicator plants in urban and industrial areas and subsequent determination of a wide range of substances accumulated in plant material can provide a more detailed information about the spatial and temporal distribution of air pollution and about the chemical composition of PM, but can also give hints on the potential direct and indirect health risks imposed by PM pollution.

In Germany, cultures of Italian ryegrass (*Lolium multiflorum* Lam. ssp. *italicum* cv. Lema) have been used as accumulative bioindicator plants of trace elements, sulphur, fluoride, and organic pollutants since the early 1970s. This species presents a high capacity for the accumulation of toxic substances, as well as a high tolerance against most air pollutants, without showing any visible injury due to ambient pollution levels. Being a commonly grown fodder plant, the accumulation of toxic substances in ryegrass may serve for estimating the potential biomagnification of contaminants along the food chain and the potential health risk for humans and livestock. Based on a standardised procedure elaborated and published by the Association of German Engineers (VDI 1978), this procedure has been used extensively in Germany to assess the accumulation of toxic substances like lead, copper, chromium, fluoride, etc., but also “novel” environmental contaminants such as antimony, platinum and palladium in regional and local surveys, along major roads and around industrial plants (Dietl et al. 1996, 1997; Franzaring et al. 2007; Nobel et al. 2004; among others). Similar methods have been applied in biomonitoring studies in several European countries (Öhlinger and Döberl 1992; Stabentheiner et al. 2004; De Temmerman and Baeten 1988; De Temmerman et al. 2007; Caggiano et al. 2001; Rey-Asensio and Carballeira 2007; Klumpp et al. 2009), and even in South America (Domingos et al. 1998; Klumpp et al. 1994).

Biomonitoring of PAH and other persistent organic chemicals such as PCB or dioxins are frequently performed by the standardised exposure of curly kale. The special suitability of curly kale is based on the large surface area of the strongly crimpled leaves and the prominent wax layer on the leaf surface that favours the accumulation of lipophilic substances. Besides, as curly kale is a vegetable grown for human diet, the accumulation of toxic compounds in its leaves may be used to conclude on potential health risks as well. This method has also been described by a national German guideline (VDI Verein Deutscher Ingenieure 2008). Results from curly kale biomonitoring in German networks were reported, e.g., by Nobel et al. (1992, 2004), Radermacher and Krause (2002), and Wäber et al. (1996), and from other European countries by Klumpp et al. (2002, 2004), Franzaring and van der Eerden (2000), and Tonneijck et al. (2002).

In the following, standardised procedures for ryegrass and curly kale biomonitoring are presented, and the suitability of both methods illustrated by giving examples from own monitoring networks established in urban areas and around industrial emission sources in the vicinity of residential areas. Pros and cons of these methods will be discussed, and the need for further standardisation of such procedures as a pre-requisite for their extensive use in air quality monitoring networks in Europe and elsewhere will be outlined.

2 Methodology

Design and size of biomonitoring networks depend primarily on the aims and goals of the monitoring study, but also on kind, strength and spatial distribution of emission sources, building density and traffic infrastructure of urban areas, climatic features such as prevailing wind directions and air exchange corridors, as well as on technical and financial constraints. Basic recommendations for the establishment of biomonitoring grids have been made by various authors and have also been addressed in technical guidelines (e.g., VDI Verein Deutscher Ingenieure 1999). In Chap. 5.2.3, results from a European effort to apply standardised biomonitoring procedures over a wide geographical range will be presented. In this project (‘European Network for the Assessment of Air Quality by the Use of Bioindicator Plants’—EuroBionet), local biomonitoring networks of 8–10 sites per city were established and run in 11 urban agglomerations in eight European countries. The study aimed at testing bioindication methods in regions characterized by different climatic conditions and pollution situations. Local monitoring networks aimed at covering pollution conditions over the whole municipal area including urban and suburban as well as traffic, industrial and reference sites.

The standardised grass exposure method has been extensively described by (VDI Verein Deutscher Ingenieure (2003) and summarized by Klumpp et al. (2009). Grass cultures of *Lolium multiflorum* var. Lema are grown from seeds using commercial unfertilised standard substrate, plastic pots and a watering system made of glass fibre wicks inserted in the substrate and connected to a water basin. Vigorous grass cultures are cut back to a stubble height of 4 cm and exposed to ambient air for consecutive periods of 28 days each using specific exposure devices which consist of a supporting rod and a water reservoir fixed to the rod at a height of 1.5 m above ground. After 4 weeks of field exposure, the grass cultures are again cut back to 4 cm and replaced by new cultures. Trace element concentrations in dried samples are then determined by common analytical procedures such as AAS or ICP–MS using certified reference material for quality control.

The standardised exposure of curly kale (*Brassica oleracea* var. *acephala*) has been described by VDI Verein Deutscher Ingenieure (2008) and summarized by Klumpp et al. (2004). Curly kale plants of commercial cultivars characterized by low height growth are cultivated in commercial fertilised potting soil using plastic pots and the watering system described above. Plants with about ten fully developed leaves are then exposed to ambient air making use of specific exposure devices which consist of a metal rack and water basins. Exposure is usually done for a period of 8 weeks during autumn or winter time at about 1 m above ground. After field exposure, eight pre-determined leaves of each plant are sampled avoiding any contamination due to the sampling procedure. The samples are then packed in glass or metal vessels or aluminium foil, and transported to the lab in cooled or shock-frozen conditions. Twenty PAH components including the so-called 16 priority pollutants according to US-EPA are determined by GC–MS.

According to the technical guidelines applied, neither ryegrass nor curly kale leaves are washed prior to chemical analysis because both species are used as indicators of the total air pollution impact on vegetation and/or fodder plants under the actual weather conditions during the field exposure period. However, in specific investigations it might be recommendable to wash the leaf material or part of it before further processing, e.g., if curly kale is used as an indicator for potential health risks or if there is a need to distinguish between externally deposited pollutants and those which were incorporated into the leaves.

The EuroBionet project placed special emphasis on the standardisation of all procedural steps, including plant cultivation and exposure at the monitoring sites, sampling of plant material, analytical methods, data acquisition and processing (see also previous sections). This strict harmonisation was designed to eliminate potential external factors that could influence plant response and to reduce methodological error. More details on the quality assurance and control measures were given by Klumpp et al. (2006b).

3 Results and Discussion

3.1 *Biomonitoring of Traffic-Related Trace Metals in Urban Monitoring Networks*

In the Europe-wide biomonitoring study EuroBionet, conducted in eight European countries from Scotland and Denmark in the North across Central Europe to Spain and Greece in the South, the standardised grass culture method proved to be a useful and reliable tool to monitor and to assess environmental levels of potentially toxic compounds of particulate matter. Klumpp et al. (2009) recently published a comparison of biomonitoring results among 11 municipal networks which revealed a clear differentiation of trace element pollution among cities and regions. Spanish cities, e.g., featured much higher pollution loads by trace elements deriving from vehicular emission sources. The report also pointed at clear differences in trace metal accumulation in grass cultures exposed at urban, suburban, traffic-exposed and rural sites within the local monitoring networks. A more detailed view on such differences is being presented in the following taking the monitoring grids of Copenhagen (Denmark), Düsseldorf (Germany), and Klagenfurt (Austria) as examples.

In large cities such as Düsseldorf and Copenhagen with significant contribution of vehicular traffic to the total PM load, clear differences in trace element concentrations in ryegrass cultures among the different monitoring sites and large ranges between maximum and minimum values of element accumulation was registered. This was especially true for the trace elements copper (Cu), chromium (Cr), iron (Fe), lead (Pb), and antimony (Sb) which were presumed to be mainly emitted by car traffic according to previously performed rank correlation analyses (Klumpp et al. 2009). In Düsseldorf, for example, the monitoring sites 4 and 6 which were located close to a major road in the city centre and to a big road crossing in the north of the city featured significantly higher concentrations of Cu, Pb, and Sb (Fig. 1a, b) but also of Fe and Cr (data not shown) than other sites classified as urban, suburban, or reference locations. Antimony seemed to characterise traffic-related pollution better than Pb or other elements. This can be demonstrated on the example of site 8 which is classified as an industrial site with low to moderate influence by traffic. Here, Sb values were not different from suburban or even reference sites whereas lead levels were significantly higher than at most other locations indicating some local emission source, possibly of industrial origin.

In Copenhagen, another major city of the whole network, street sites (sites 3b and 3c) were also characterized by significantly higher trace element concentrations in grass cultures than most other sites in the municipal area (Fig. 1c, d). Urban sites such as sites 1 and 4 also showed somewhat higher elements levels than suburban and reference locations. On the example of sites 3b and 3c in Copenhagen, also the small-scale spatial differentiation of biomonitoring results can be demonstrated. Both these sites were installed at a major square in the city

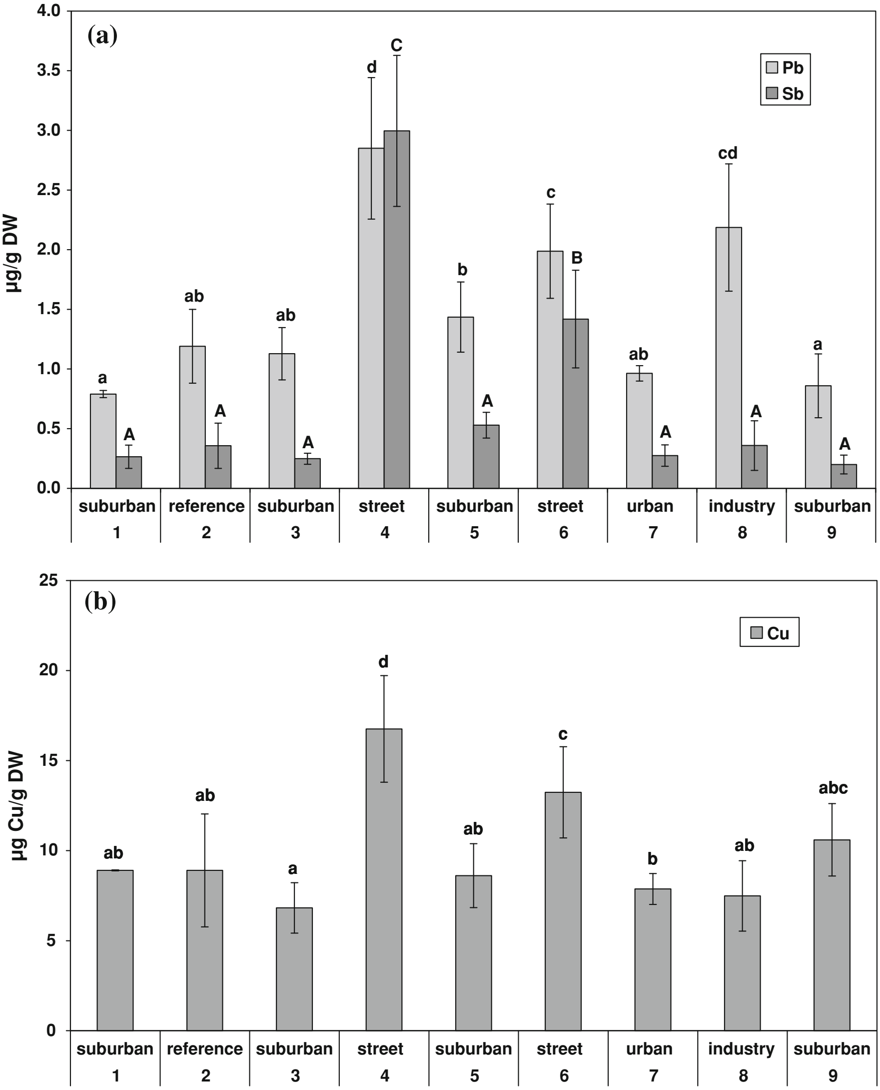

Fig. 1 Trace metal concentrations (µg/g DW) in ryegrass cultures exposed in the local biomonitoring networks of Düsseldorf/Germany (Fig. 1a, b) and Copenhagen/Denmark (Fig. 1c, d) in 2001 (mean values ± standard deviation; n = 5). Sites with significant ($p < 0.05$, LSD test) differences to others are marked by different *lowercase* or *capital letters*, respectively. Trace metal concentrations (µg/g DW) in ryegrass cultures exposed in the local biomonitoring networks of Düsseldorf/Germany (Fig. 1a, b) and Copenhagen/Denmark (Fig. 1c, d) in 2001 (mean values ± standard deviation; n = 5). Sites with significant ($p < 0.05$, LSD test) differences to others are marked by different *lowercase* or *capital letters*, respectively

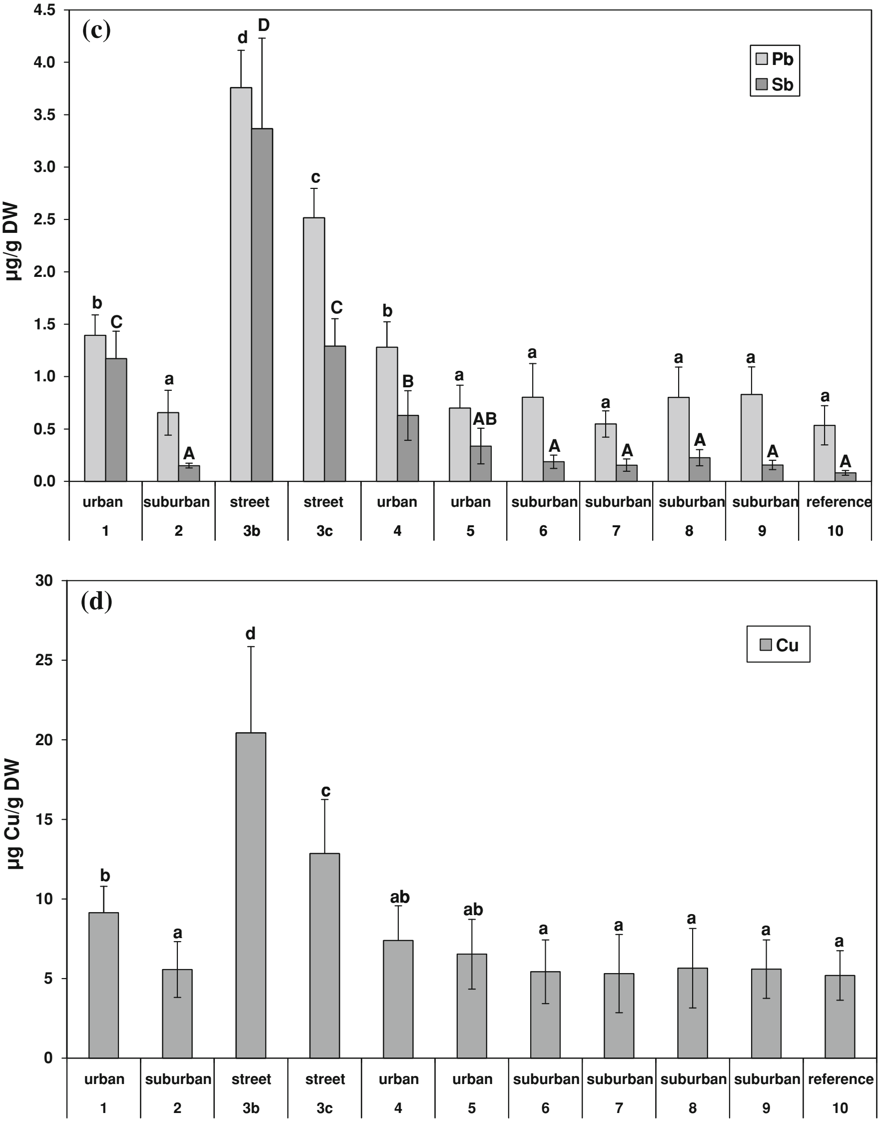

Fig. 1 (continued)

centre with intense car traffic, but site 3b was located close to the edge of the road whereas site 3c was on the pavement in a distance of about 8.5 m from site 3b. Both sites reflect the strong influence of car emissions with clearly elevated Cu, Pb and Sb levels, but also show a clear decline with increasing distance from the emission source, i.e., the edge of the road. Trace element emissions from car traffic generally originate not only from fuel combustion itself, but also from other

Table 1 Cr, Cu, Pb, and Sb concentrations (µg/g DW) in ryegrass cultures exposed at eight biomonitoring sites in Klagenfurt (Austria) in 2001 (mean values ± standard deviation; n = 4)

Site No.	Type of site	Cr	Cu	Pb	Sb
1	Industry	1.03 ± 0.45a	4.75 ± 0.50ab	0.62 ± 0.15a	0.135 ± 0.029ab
2	Suburban	1.40 ± 0.64a	4.49 ± 0.43ab	0.36 ± 0.10a	0.099 ± 0.021ab
3	Urban	1.06 ± 0.58a	4.68 ± 1.13ab	0.52 ± 0.26a	0.199 ± 0.054b
4	Reference	0.76 ± 0.65a	4.96 ± 1.08ab	0.47 ± 0.22a	0.084 ± 0.005a
5	Reference	0.94 ± 0.24a	3.80 ± 1.46a	0.6 ± 0.30a	0.067 ± 0.015a
6	Suburban	1.10 ± 0.70a	4.09 ± 0.79ab	0.45 ± 0.17a	0.116 ± 0.032ab
7	Suburban	0.94 ± 0.28a	4.11 ± 1.54ab	0.41 ± 0.25a	0.091 ± 0.037ab
8	Street	1.01 ± 0.41a	5.31 ± 0.42b	0.63 ± 0.26a	0.460 ± 0.203c

Sites with significant ($p < 0.05$, LSD test) differences to others are marked by different letters

sources such as drip losses and abrasion of brake linings, tyres and pavement. The latter seems to have contributed to the high metal levels at sites 3b/3c, as shredded electrical wastes were obviously used as filling material in the asphalt paving (personal communication K. Kemp, National Environmental Research Institute, DK).

A completely different pattern was found with smaller cities such as Klagenfurt in Austria (Table 1). There were also some differences between street and urban sites on the one hand and suburban and rural sites on the other hand. But significant differences were only found for Cu at one street site and for Sb for two sites compared to the other sites of the network, whereas Pb and Cr levels exhibited some variability, however, without any significant differences between the sites.

3.2 Detection of a Strong Heavy Metal Emission Source in an Urban Area

Exposure of standardised ryegrass cultures within the EuroBionet programme gave in some cases striking results not expected by the local environmental authorities. Grass cultures exposed on a school yard located close to a major highway and near to an industrial estate in the city of Sheffield (UK) featured high heavy metal concentrations. Especially Cr concentrations were extremely elevated in comparison to all other sites of the entire network, but also Ni values were strongly increased. In 2000, the average Cr contents of grass cultures at this site amounted to about 50 times the normal background levels of Sheffield (Table 2). This extreme Cr accumulation excluded the possibility that vehicular traffic on the highly frequented highway was the only emission source for this pollutant. Dust emissions from a nearby steelworks or even re-suspension of contaminated soil particles were considered as possible reasons for the observed contamination of grass cultures. Chemical analyses of randomly taken samples from natural vegetation (pasture grass, tree leaves) confirmed the high Cr pollution at this site. This result also reinforced the hypothesis of the steelworks as main emission source as metal concentrations in plant samples decreased with increasing distance from this

Table 2 Cr concentrations (μg/g DW) in ryegrass cultures exposed at eight biomonitoring sites in Sheffield (UK) in 2000 and 2001 (mean values ± standard deviation; n = 4 in 2000 and n = 5 in 2001)

Site No.	Type of site	2000	2001
1	Suburban	1.32 ± 0.33a	1.45 ± 0.97a
2	Suburban	1.39 ± 0.28a	0.85 ± 0.15a
3	Suburban	2.70 ± 0.69a	1.89 ± 0.76a
4	Suburban	2.21 ± 0.56a	1.79 ± 0.69a
5	Suburban	2.40 ± 0.48a	2.66 ± 1.43a
6	Industry	118.68 ± 65.97b	42.02 ± 9.79b
7	Urban	3.19 ± 1.17a	3.35 ± 0.78a
8	Urban	2.46 ± 1.24a	2.26 ± 0.47a

Sites with significant ($p < 0.05$, LSD test) differences to others within one exposure year are marked by different letters

potential emitter although the steel plant was not located in the main wind direction. After first remedial measures at the steelworks imposed by local authorities, average Cr accumulation in grass cultures decreased during exposure experiments in 2001 compared to 2000, but the Cr levels at this site still remained 20 times the local background (Table 2). Due to the limited duration of this project, biomonitoring studies were not continued after 2001. A recent publication by Schelle et al. (2008) on heavy metal concentrations in tree bark sampled at various sites in Sheffield during 1998–2002, confirmed the pollution problems in that part of the municipal area.

3.3 Biomonitoring of PAH Compounds in Urban Areas

Exposure of curly kale plants in the EuroBionet network during the winter months 2000/2001 and 2001/2002 clearly showed a differentiation in PAH pollution load depending on the size (in terms of population number) of the participating cities and on the site characteristics of the various urban monitoring grids. A strong differentiation between urban and traffic sites on one hand and suburban and reference sites on the other hand was found in the major cities of the network, whereas differences between different sites were smaller in smaller cities (Klumpp et al. 2004). Like with most heavy metal elements, PAH compounds were especially accumulated in kale plants exposed at sites with strong car traffic influence. In Düsseldorf, for example, the two traffic sites which featured the highest trace metal accumulation in ryegrass cultures were also characterized by highest levels of PAH compounds in curly kale plants (Fig. 2). The same was true for the traffic-exposed sites in Copenhagen (data not shown).

When going into detail, it was stated that the toxicologically important carcinogenic PAH compounds with more than four aromatic rings occurred in higher proportions at the strongly polluted traffic sites than at the reference or rural

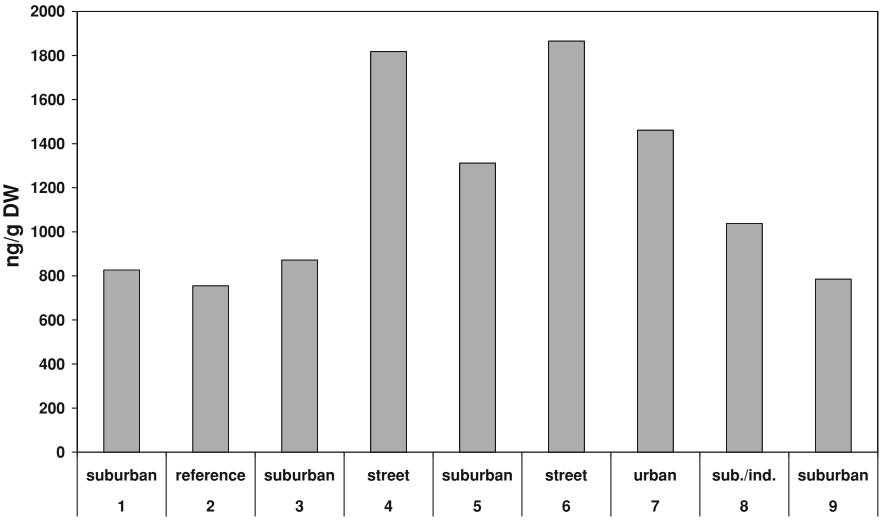

Fig. 2 Sum values (ng PAH/g DW) of the 12 less volatile PAH compounds in curly kale plants exposed in the Düsseldorf monitoring network for 8 weeks during winter 2001/2002

stations. This can be attributed to the fact that components with higher molecular weight are almost exclusively particle-bound and are therefore deposited in shorter distance from the emission source, whereas compounds with three and four aromatic rings occur both in the gas and particle phases and can therefore spread out much further.

Among the PAH compounds occurring in ambient air, benzo(a)pyrene (BaP) is of special concern because of its high mutagenicity and carcinogenicity, and is therefore generally used as a tracer substance for the whole PAH mixtures. In this biomonitoring programme, highest BaP values were detected in the cities of Düsseldorf, Copenhagen, and Sheffield (Fig. 3). Within the individual municipal networks, high BaP concentrations in kale leaves indeed correlated significantly with high total PAH sums. Although BaP emissions are frequently associated with coal burning, a clear relationship between BaP accumulation in plants and traffic intensity could be observed as well.

Even though the limited number of data in the present study did not allow for assigning PAH or BaP pollution to specific emission sources, the occurrence of maximum PAH sum values and especially the increased proportion of substances with high molecular weight at streets with strong traffic pollution in the inner city areas indicates that, aside from domestic heating during winter months in Central and North European cities, motor vehicle traffic and in particular the emissions from diesel engines is one of the main PAH sources at such locations. This was also confirmed by Nielsen (1996) in previous emission studies which showed that at a street with heavy traffic pollution in Copenhagen (corresponding to the biomonitoring site with highest PAH accumulation in our study) 80% of PAH

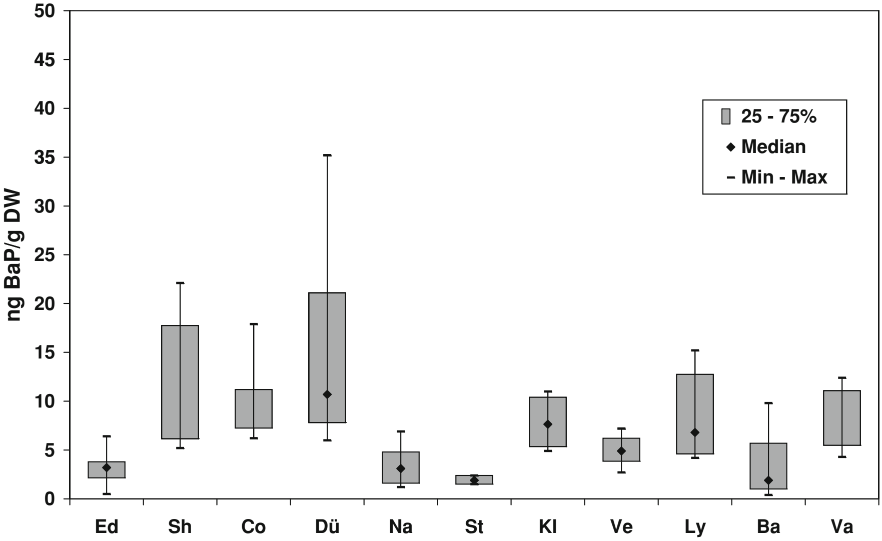

Fig. 3 Box-Whisker-Plot of benzo(a)pyrene concentrations (ng BaP/g DW) in curly kale plants exposed in the local city monitoring networks for 8 weeks during winter 2001/2002 (25–75% box: range including 50% of the values in the individual cities). *Ed* Edinburgh, *Sh* Sheffield, *Co* Copenhagen, *Dü* Düsseldorf, *Na* Nancy, *St* Stuttgart, *Kl* Klagenfurt, *Ve* Verona, *Ly* Lyon, *Ba* Barcelona, *Va* Valencia

pollution during winter was due to vehicle traffic, while in a nearby park traffic only contributed to 40% of ambient PAH pollution levels.

4 Conclusions and Outlook

Based on the results of the European biomonitoring programme EuroBionet presented here as well as in other publications, and on many other studies on local and regional scales, the following conclusions on the applicability of bioindicators in air quality control and on next steps towards broader implementation in routine environmental monitoring programmes and environmental legislation can be drawn:

- The exposure of standardised ryegrass cultures according to the VDI guideline proved to be a simple and reliable tool for assessing and monitoring trace elements in urban and/or industrial areas throughout Europe. This highly standardised methodology worked well under varying climatic conditions and provided valuable data on distribution and accumulation of airborne trace elements within local networks and among different regions in Europe. Biomonitoring of a range of toxicologically relevant organic pollutants (PAH) by exposing curly kale plants under standardised conditions was successfully applied Europe-wide and is particularly recommended for monitoring of air pollution during winter months under moderate and cool climatic conditions. Another biomonitoring method not described in the present paper, the Tradescantia micronucleus test (Klumpp et al. 2006a), is widely applied to provide data on the genotoxic potential of urban air pollution. Hence, a range of well established biomonitoring procedures is now available that allow for monitoring the toxic, ecotoxic and genotoxic effects of major constituents in urban and industrial particulate matter thus meeting the recommendations of the EU Directive (EU 2004).

- Exposure of bioindicator plants may serve as a proxy for the pollution load or deposition in a given area, but biomonitoring does not (pretend to) substitute technical air monitoring by physico-chemical methods as abiotic factors (e.g., weather conditions during exposure, co-occurrence of other pollutants) and biotic factors (growth rate, physiological status, leaf surface characteristics) influence pollutant accumulation. This is not considered a drawback of the methodology, but rather an advantage as only by these methods pollution-induced effects including the accumulation of potentially toxic substances can be assessed and evaluated. Moreover, exposure of common fodder plants like ryegrass and of vegetables like curly kale renders it possible to draw conclusions on the potential entry of contaminants into the food chain and on the potential risk posed to human and animal health.
- As a consequence of the above statements, we recommend to apply standardised biomonitoring procedures much more extensively as additional methods of routine environmental monitoring programmes in urban areas and around industrial emission sources. This will allow for co-monitoring airborne pollutant concentrations and environmental effects/accumulation simultaneously and at the same monitoring sites. Due to their cost-effectiveness, biomonitoring networks may even be denser than technical monitoring networks thus providing information on a smaller scale. Chemical analysis of a wide range of organic and inorganic substances in exposed bioindicator plants may additionally enable to detect "novel" air pollutants earlier than happened in the past (Wiseman and Zereini 2009). The rapidly increasing ambient levels of platinum-group elements and antimony due to emissions from traffic sources, e.g., were only detected by environmental monitoring methods including exposure of bioindicator plants. The major obstacle for a wide application of biomonitoring procedures in routine monitoring networks and the implementation of its use in environmental legislation has been the low level of standardisation of applied methods which complicated the comparison of results obtained in different monitoring networks and countries. However, standardised methods have meanwhile been established and published in Germany, France, and other countries. They now serve for the Europe-wide standardisation in the frame of the recently established CEN (European Committee for Standardization) working group on "Biomonitoring Methods with Flowering Plants".

Acknowledgments This study was supported by the LIFE Environment Programme of the European Commission, DG Environment, under the grant LIFE/99/ENV/D/000453. We thank the following local and regional authorities and their respective project leaders and co-workers for their valuable support: Landes-hauptstadt Düsseldorf, Umweltamt (H.-W. Hentze, M. Wiese), Communauté urbaine de Lyon, Ecologie urbaine (O. Laurent), Comune di Verona, Servizio Ecologia (T. Basso, N. Belluzzo, S. Oliboni, S. Pisani, R. Tardiani), The City of Edinburgh Council, Air Quality Section (T. Stirling), Sheffield City Council, Environment & Regulatory Services (G. McGrogan, N. Chaplin), Landeshauptstadt Klagenfurt, Abt. Umweltschutz (H.-J. Gutsche), City of Copenhagen, EPA (J. Dahl Madsen), Generalitat de Catalunya, Dept. Medi Ambient, Barcelona (X. Guinart), Communauté Urbaine du Grand Nancy (F. Perrollaz), City of Glyfada (G. Kolovou), and Ayuntamiento de Valencia, Oficina Tècnica de la Devesa-Albufera (A. Vizcaino, A. Quintana) as well as the municipalities of Ditzingen, Plochingen, Deizisau and Altbach (Germany). We thank J. Breuer (State Institute of Agricultural Chemistry, University of Hohenheim) and A. Trenkle (Agricultural Research Institute LTZ Augustenberg, Germany) for performing analyses of antimony concentrations in ryegrass and PAH concentrations in curly kale, respectively. The donation of ryegrass seeds by Nordddeutsche Pflanzenzucht is gratefully acknowledged. Gratitude is also expressed to the staff of all institutions involved in the present studies.

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Exposure to Ultrafine Particles in Urban Centres

Kelly Sabaliauskas and Greg Evans

1 Introduction

Ambient particulate matter (PM) is often classified based on particle size due in part to the size dependence of particle deposition within the respiratory system. Ultrafine particles (UFP) are the smallest particles, with diameters less than 100 nm. They can originate from anthropogenic sources such as fossil fuel combustion, or naturally through nucleation of biogenic sulphuric acid, water, and ammonia molecules. The mass of PM per cubic meter is the most commonly used metric to describe airborne particles. Despite being few in number, the largest particles contribute the majority of the PM mass. In contrast, the majority of all atmospheric particles are found in the ultrafine size range. Although numerous, UFP contribute little to the overall mass of PM in the atmosphere.

From a health and policy perspective, a mass metric does not adequately describe exposure to UFP. The number or surface area of particles per unit volume may be a better metric. However, at this time, only limited exposure data based on number concentration exists and no number concentration based ambient standards have been established. Further, there is no consensus yet as to whether size, chemical composition, or some combination thereof provides the best measure of UFP toxicity.

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Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_25,

UFP has been shown to vary spatially over small distances in relation to traffic patterns on nearby roadways. Significant sources of UFP also exist within homes. Consequently, there may be substantial exposure variability across an urban population.

This paper will examine sources of both outdoor and indoor exposure to UFP in cities. Sources and processes influencing UFP concentrations are also discussed along with their spatiotemporal variability. Approaches for assessing exposure are introduced along with considerations for the design of urban exposure studies.

2 Exposure and Dose

The differentiation between exposure and dose is important. Exposure, according to the National Academy of Sciences (NAS), is defined as *an event that occurs when there is contact at a boundary between a human and the environment with a contaminant of specific concentration for an interval of time* (NAS 1991). The NAS defines 'dose' as *the amount of contaminant that is absorbed or deposited in the body of an exposed individual*. For the purposes of this discussion, the contaminant of interest is UFP and the 'boundary of contact' is limited to external features on the human body such as the eyes, mouth, nostrils, and skin. Dose is assumed to be proportional to time integrated exposure without further consideration of the proportion of the UFP that deposits at sites of interest in the human body such as the lungs or other organs.

2.1 Contaminant Concentration Assessment

Air quality monitoring networks have been established in many jurisdictions in order to determine if a given region meets ambient air quality standards or objectives. Since these air quality monitoring networks were designed for compliance purposes, rather than health studies, the data that is provided is more likely to reflect an ambient background concentration to which the population is exposed when outdoors. The data is not predisposed to reflect the typical likely concentration that an individual may encounter in his or her daily life. According to the European Guidelines for exposure assessment (EU 1999), measurements of a given pollutant should:

1. Provide data on the areas where the highest concentrations occur to which the population is likely to be exposed, and
2. Provide data on levels in other areas, which are representative of the exposure of the general population (background sites).

2.2 Quantifying Exposure

Most epidemiological studies of PM health effects have relied primarily on outdoor ambient samples to assess population exposure (Pope et al. 2002; Dockery et al. 1993; Katsouyanni et al. 1997). Relying on outdoor measurements at central sites may not be the best approach for assessing a population's exposure to air pollutants. Studies comparing outdoor ambient measurements and those collected alongside an individual or indoors have observed large differences that are attributable to both lifestyle choices and socioeconomic status.

The 'Total Exposure Assessment Methodology' study by Wallace et al. (1991) demonstrated that the concentration of hazardous air pollutants can be higher when measured alongside an individual compared to concentrations that are based on an ambient measurement. Furthermore the 'Relationship of Indoor, Outdoor and Personal Air' study conducted by Weisel et al. (2005) demonstrated that indoor sources can have a greater effect on personal exposure to hazardous air pollutants than those of outdoor origins. Additionally the 'National Human Exposure Assessment Survey' study demonstrated that socioeconomic factors influence exposure to PM and volatile organic compounds (Pellizzari et al. 1999). It can be argued, then, that relying on outdoor measurements at central sites is not the best approach to assessing a population's exposure to air pollutants.

Exposure assessment using personal monitoring seeks to measure the range of potential concentrations that an individual encounters while performing common tasks in his or her home, workplace, or vehicle. Personal exposure monitoring studies can be described as either being direct or indirect. The direct method, also known as the point-of-contact method, measures the concentration of the pollutant of interest alongside a study participant by using small unobtrusive exposure sampling devices. This method requires that the study participant carry or wear the instrumentation for the entirety of the study. The indirect method, also referred to as the scenario approach, instead assesses exposure by measuring the concentration of a pollutant of interest in microenvironments where individuals spend their time. Three types of microenvironments are typically studied: outdoors, indoors non-industrial, and in-transit. It should be noted that a 'microenvironment' is a concept used by researchers to categorize exposure locations into groups. Each group can then be represented within a model by a specific concentration distribution or set of average concentrations (Ott 1982; Duan 1982).

In the indirect method to estimate personal exposure two parameters are required: the concentration of the pollutant of interest in each microenvironment and the time individuals spend in a given microenvironment. Weighted average concentrations can then be calculated based on the relative amounts of time spent in each microenvironment.

Time-activity databases have been widely used to provide estimates of the time individuals within a specific population spend in different microenvironments. Surveys or diaries are used in time-activity studies to examine where people spend their time, what they do in these locations and for how long. In order to identify behaviour differences within the population of interest time-activity studies also categorize people in terms of age, gender, and socioeconomic status. In the United States, Canada, and several European countries time-activity studies have established that individuals spend up to 90% of their time indoors.

Time-activity patterns studied in the United States, for example, suggest that individuals spend 87% of their time indoors with 6% of their time enclosed in vehicles and the remaining time outdoors (Kleipeis et al. 2001). Graham and McCurdy (2004) suggest that an individual's lifestyle and life-stage (e.g., the role in a family as it changes over time) are strong predictors of the amount of time spent indoors. Gender, education, work status, employment status, having children, living alone, and the time of year are also strong predictors of the amount of time an individual typically spends indoors (Schweizer et al. 2007).

There are a variety of variables that affect study results. The design of an exposure study has profound implications for the conclusions that can be drawn on a population's exposure to air pollutants. As well, the type of data that is used to assign time-activity patterns to the study population greatly influences the results. The accuracy of the time-activity information becomes increasingly important for pollutants that exhibit high spatiotemporal variability, such as UFP. For example, some epidemiological studies have relied on PM exposure interpolated from census information and hospitalization data to assess the associated risk. The associations that have been observed are true of the aggregate data. However, these associations may not be applicable to sub-populations or individuals within the aggregate of individuals. Studies with this design are referred to as ecologic studies. An ecological fallacy occurs when one concludes that an association between variable x and y at the aggregate level also applies to the individual level. Traditionally ecologic studies are considered useful only in generating hypotheses to be tested at the individual level (Young 1998).

2.3 Processes Governing Ultrafine Particle Characteristics

UFP can be emitted directly from anthropogenic sources such as vehicles, furnaces or other technologies involving the combustion of fossil fuels. They can also form through a series of secondary chemical reactions in the atmosphere. There are five main processes that govern the formation, transformation and removal of UFP: nucleation, condensation or evaporation of semi-volatile species, coagulation, deposition, and dilution. The effect of each of these processes on the total number of particles in the atmosphere and their size is summarized in Table 1. Each process affects the number and size of UFP and operates over vastly different characteristic times. Further, these processes have varying importance for different sized particles.

The dominant formation processes of UFP are binary nucleation from interactions between sulphuric acid and water as well as ternary nucleation between sulphuric acid, ammonia, and water. Once formed, the particles 'age' by accumulating layers

Table 1 Effect of each formation, transformation and removal process on the size and number of observed UFP

Process impacts on ultrafine particle number and size

Process	Effect on the number of particles	Effect on average particle size
Nucleation	Increase	Decrease
Dilution	Decrease	Preserved
Condensation	Conserved	Increase
Evaporation	Conserved	Decrease
Coagulation	Decreases number of small particles	Increase
Deposition	Decreases number of particles	Variable

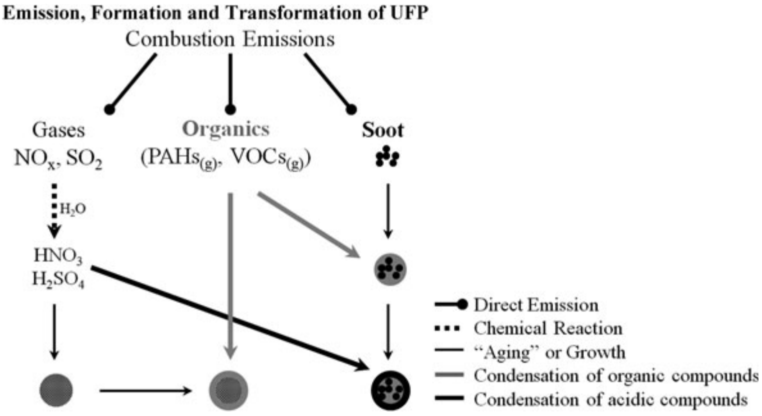

Fig. 1 The dominant formation and transformation processes governing the growth of UFP

of organic and other semi-volatile compounds (see Fig. 1). Particles are further transformed through coagulation whereby growth occurs through collisions between particles of the same or different sizes.

The relative importance of each transformation and removal processes varies by size. For the smallest particles, diffusion to surfaces, evaporation, and coagulation are favoured as transformation and removal processes. As the particle gets smaller (<10 nm) the Kelvin effect becomes more important thus making it easier for molecules to leave the particle's surface by evaporation. It is suggested by Hinds' (1999) research that the Brownian motion for a 10 nm particle is 80 times faster than for particles greater than 100 nm. As a result, the smallest particles are more likely to collide with each other and diffuse to surfaces than their larger counterparts. Conversely, larger particles can be removed through impaction, or wet or dry deposition. Thus loss through deposition tends to be lowest for the intermediate accumulation mode (greater than 90 nm in diameter) particles.

Dilution and evaporation are posited by Zhang and Wexler (2002, 2004) as being the most dominant processes affecting the size distribution of UFP. Evaporation plus coagulation appeared to explain a large portion of the observed evolution in nuclei mode (less than 50 nm in diameter) size distributions as shown by Jacobson et al. (2005). Zhu et al. (2002a) argue that dilution for the largest particles and coagulation for the smallest particles are the most important mechanisms for the transformation of the size distribution. It should be noted that the relative importance of coagulation as a removal process for the smallest particles remains a subject of debate in the literature.

2.4 Sources of Ultrafine Particles in Urban Centres

Assessing urban residents' exposure to UFP is complex due to numerous possible indoor and outdoor sources that can contribute to their exposure. In urban settings, vehicles are the dominant source of UFP observed outdoors. Although regional scale nucleation and growth events can contribute to the particle number concentration, these events are believed to only contribute a small portion of the UFP in urban settings. In indoor microenvironments significant sources of UFP include cooking, second-hand tobacco smoke, candles, and household cleaners in addition to air fresheners.

UFP sources found in different indoor and outdoor microenvironment types are unique in size, chemical composition, and morphology. It remains unclear if size, chemical composition, morphology or some combination thereof is the best predictor of toxicity. As a result, the relative risk associated with different UFP sources remains unknown.

3 Ultrafine Particles Emission from Vehicles

The size, chemistry, and emission rate of UFP from vehicles depends on the vehicle fleet's characteristics, their fuel types, and the fleet operating conditions.

3.1 Vehicle Fleet Characteristics

Fleet characteristics refer to the different classes, ages, control technologies and fuel requirements of vehicles on a given roadway. The vehicles used in the majority of cities are powered using gasoline or diesel fuels. Each of these fuel types requires specific engine technologies and emission control strategies. Gasoline powered vehicles rely on a volatilized fuel and air mixture ignited by a spark plug. Diesel powered engines rely on the heat of compression to ignite and burn the fuel, which is injected into the combustion chamber during the final stage of compression. Since these engines each rely on different processes to ignite the fuel, the resulting emissions are very different.

The differences between these two methods of combustion lead to differing emissions depending on engine load and driving conditions. Zielinska et al. (2004) conclude that diesel vehicles typically emit more UFP mass than spark ignition vehicles. Particles derived from diesel-powered vehicles contain non-volatile and semi-volatile polycyclic aromatic hydrocarbons, elemental carbon or “soot”, and sulphate. In contrast, the UFP emitted from spark ignition vehicles have been shown to contain little sulphate but significantly more ammonium and calcium than diesel-powered vehicles.

The control technology that is applied to the vehicle itself also has consequences to the ultimate emission and formation of UFP. Diesel particulate traps are now commonly used to control the mass emissions of PM. There are new classes of continuously regenerating diesel particulate filters that allow for PM emissions to be controlled. One of the consequences of this technology is an increased formation of small particles (<10 nm) due to the absence of elemental carbon downstream of the trap.

3.2 Fuel and Lubricating Oil Characteristics

Now that many jurisdictions regulate the sulphur and biodiesel content of diesel fuel, significant variability exists in diesel fuel composition and, consequently, UFP emissions. One investigation has demonstrated a 30% decrease in PM emissions with use of 100% biodiesel fuel but the soluble organic fraction increased by 40% (Sharp 1998). The sulphur content in diesel fuel also greatly influences the observed UFP emissions. In jurisdictions that have implemented ultra-low sulphur fuel, significant reductions in ambient UFP have been observed (Wåhlin 2009).

Kittelson et al. (2006) demonstrated that for diesel emissions on roadways, most of the mass (>97%) in the 12–30 nm range was volatile with properties consistent with C24–C32 *n*-alkane compounds typical of lubricating oil. The high molecular weight molecules used in lubricating oil typically have lower volatility than unburned hydrocarbons. As a result, compounds from lubricating oil are more likely to be found in the smallest particles because they are more likely to condense first during cooling.

3.3 Engine Operating Conditions

Traffic density and congestion in cities depends on a balance between the number of vehicles, roadway design, and traffic management. The resulting operating conditions of individual vehicles can be described in terms of idling, cruising, deceleration, and acceleration. An increase in particle number concentration and decrease in particle size with increasing vehicle speed was reported by Kittelson et al. (2004). The composition of UFP also varies due to engine operation. Kubo et al. (2006) concluded that hydrocarbons from oxygenated fuel dominated the UFP composition during idling conditions (>C19) and lubricating oil dominated during deceleration (>C35) while sulphate contributed most to UFP under high engine loads for diesel vehicles.

3.4 Urban Scale Variability in Ultrafine Particle Concentrations

When studying the factors that influence exposure to vehicle generated UFP in cities three spatial scales need to be considered. The first scale is on the order of 1–2 m where UFP is formed near the tailpipe of a vehicle. Scale two considers the dilution and transformation processes that occur within 100 m from the roadway. Third, the urban scale, is on the order of kilometres. The time scales related to the abovementioned spatial scales are on the order of seconds to several hours. Meteorology is also an influence on the extent of mixing and dilution on a regional scale causing day-to-day variability in UFP concentrations. As a result, each component of this transformation cannot be studied independently. Figure 2 summarizes UFP concentration ranges that are found at each of the abovementioned spatial scales based on studies conducted in urban and rural settings throughout the world (Buzorius et al. 1999; Cyrys et al. 2008; Kaur et al. 2006; Ketzel et al. 2004; Mejía et al. 2008; Puustinen et al. 2007; Kim et al. 2002; Westerdahl et al. 2005; Zhu et al. 2002a, b).

From an exposure assessment perspective, Fig. 2 also demonstrates that, depending on an individual's location within a city, the outdoor UFP number

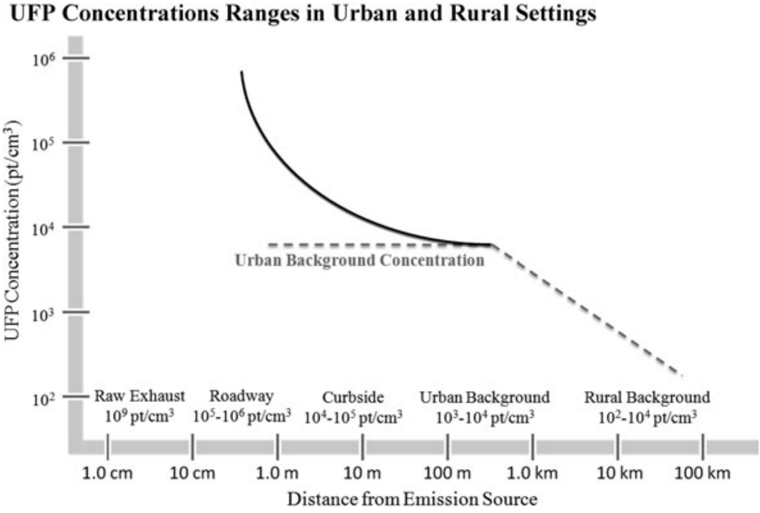

Fig. 2 The range of UFP concentrations reported in the literature for each spatial scale is shown

concentration can vary by as much as three orders of magnitude. Furthermore, it should be noted that the size distribution, and presumably the chemistry of UFP, at each spatial scale also differs. Near roadways, there are many small particles (<30 nm) that are derived from traffic sources. As distance from the roadway increases (100–300 m from the road), the number of small particles decreases due to evaporation and growth processes and the UFP size distribution is dominated by larger particles (>60 nm). One of the implications for these observations is that UFP not only exhibits spatial heterogeneity in terms of the total number of particles but also exhibits significant variability in size in relation to proximity to traffic.

3.5 Factors Influencing UFP Exposure Near Roadways

While individuals may only spend 7% of their time outdoors (Kleipis et al. 2001), they often spend that time outdoors near traffic sources such as when they walk along high traffic roads, wait at intersections, sit in vehicles with the windows open, or when working in buildings near traffic. This time spent near roadways results in exposure to elevated total UFP number concentrations and to smaller particles than is typically observed further away from roadways. There are, therefore, profound implications for individuals living near major arterial roadways because vehicle-generated UFP will also increase their indoor exposure.

Several studies have reported large spatial gradients in UFP concentrations beside major arterial roads and highways. However, the mechanisms underlying the associated evolution in particle size distribution are still under investigation. On major arterial roads, particles with diameters less than 50 nm (nuclei particles) are dominant. Both Zhu et al. (2002b) and Kittelson et al. (2004) observed no nuclei-sized particles at distances greater than 90 m away from the roadway. Fushimi et al. (2008), in turn, observed a particle size distribution with a modal diameter of 20 nm that was present at a roadside site but absent at a background site.

UFP exposure near roadways in cities also varies temporally over very short time scales. When an individual walks along a major arterial roadway, he or she is exposed to a combination of an urban background concentration as well as a vehicle signal that consists of many spikes caused by passing diesel vehicles. The lifetime of these UFP concentration spikes is on the order of 1–2 min. Therefore, these UFP concentration spikes are most consequential for individuals sitting in vehicles with the windows open, and when walking or cycling along major arterial roadways. The intensity and frequency of these spikes relates directly to the nearby vehicle characteristics and operating conditions.

Illustrated in Fig. 3 is a transition from a roadway with 25,000 vehicles per day to one with less than 2000 vehicles per day. On the high traffic road there are frequent spikes that correspond to passing diesel vehicles. On the low traffic road the frequency of these UFP concentration spikes decreases due to fewer

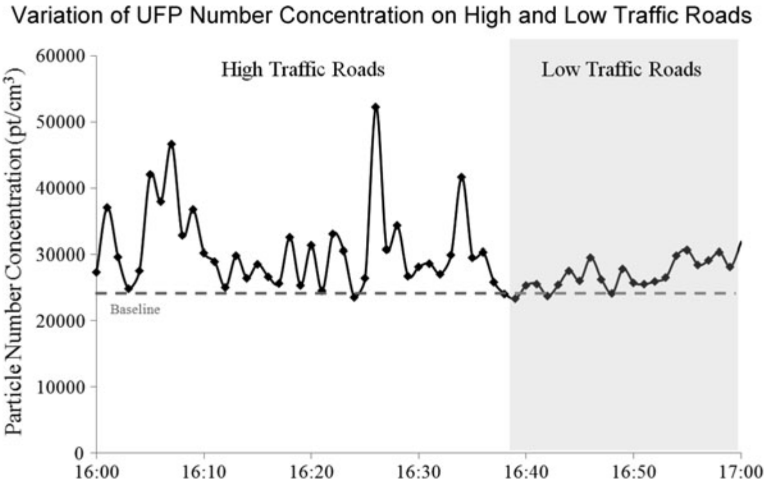

Fig. 3 The variation of UFP number concentration while walking along high and low traffic roads in Toronto, Canada

diesel-powered vehicles. Despite moving away from a significant traffic source, a constant UFP baseline or urban background concentration is observed in both locations. Another interesting characteristic of note is that urban background concentration varies both temporally and spatially but over much larger and longer time scales than the spikes. This background is also strongly influenced by the traffic density within a few kilometres as well as by day-to-day changes in meteorology.

3.6 Factors Influencing UFP Exposure Indoors

While vehicles are the major source of UFP within cities, other indoor sources also contribute to UFP within homes. Hoek et al. (2008) studied the particle number concentration in homes in four major European cities. It was observed that UFP number concentrations in the study participants' homes were poorly correlated with central site measurements during the day. This correlation improved slightly at night. The difference between the indoor and outdoor UFP concentrations was attributed to the presence of numerous indoor sources. Koponen et al. (2001) measured the indoor and outdoor size distribution of UFP and demonstrated that accumulation mode particles (>90 nm) are directly related to outdoor sources while nuclei mode particles (<50 nm) originate from indoor sources.

The influence of outdoor sources on indoor UFP concentrations is related to the ventilation characteristics of the building in addition to the outdoor concentration. Three types of air exchange processes are common: mechanical ventilation, natural infiltration, and windows open. In order to differentiate the effects of different air exchange processes, the indoor–outdoor ratio (I/O) is used. This value is obtained from the division of the indoor concentration by the ambient concentration collected simultaneously (or very close to the time the indoor measurement was collected).

With windows open, the concentration of UFP inside a home is directly related to the outdoor concentration with an I/O ratio near 1.0. With windows closed, the concentration of UFP may still be related to the outdoor concentration but I/O ratios may drop as low as 0.3. Zhu et al. (2005) investigated the indoor and outdoor variation of UFP near a highway under three ventilation conditions: natural infiltration, fan on, and windows open. In the case of natural infiltration, the highest I/O ratio was observed for the largest particles. It was hypothesized that since the UFP in the smallest fractions are likely more volatile, their infiltration behaviour is likely very different than that of the older larger non-volatile particles. With windows open, the UFP I/O ratio was near 1.0 for all sizes. In the case of mechanical ventilation (fan on), the I/O ratio was below 1.0 for all sizes and it was hypothesized that some filtration of outdoor air was provided by the ventilation system itself.

Wallace et al. (2004) studied the effect of the mechanical ventilation system on UFP concentration. Their research found that mechanical ventilation system use increased the deposition rate of all particle sizes regardless of whether an in-duct filter was present. The study concluded that a further reduction could be obtained by using an in-duct filter and that home owners could reduce the UFP concentration by properly maintaining the filter. Filters are highly efficient for the largest (>1000 nm) and smallest particles (<50 nm) but are found to be very inefficient for mid-range sized particles. The smallest particles are captured on the fibres through diffusion losses while the largest particles are captured through impaction. Consequently, most in-duct filters have an efficiency curve that approaches 100% for the smallest and largest particles and efficiencies of around 20–30% for 300 nm particles.

4 Indoor Sources

Many studies have been conducted in homes or in constructed chambers that simulate the conditions found in homes. The choice of instrumentation and its configuration can dramatically affect the outcome of the study. For example, the source strength obtained from an instrument with a size cut-off of 6 nm will be significantly higher than that obtained from an instrument with a size cut-off of 20 nm. Furthermore, the placement of the instruments themselves relative to the source also has the capacity to greatly affect the observed source strength. The observed concentrations will depend on both the rates of particle production and removal. Consequently, the ranges of UFP concentrations that are reported in the literature for the same “source” of UFP are often subject to significant inter-study variability.

Frying and broiling have been identified as significant sources of UFP in homes (Wallace and Howard-Reed 2002). The World Health Organization, for example, has identified cooking fumes from high temperature frying as "probably carcinogenic to humans" (Straif et al. 2006). At present it is unclear as to what percentage of these fumes is actually carcinogenic. During frying a small portion of the fatty acid esters that make up edible oils and fat can be oxidized and volatilized. These compounds then form and condense onto pre-existing particles. See et al. (2006) generated a significant amount of ultrafine particles using a gas stove that increased the concentration of UFP between 2 and 24 times over the background level. Up to 90% of all particles produced by deep frying were found to be between 10 and 50 nm.

There are several parameters that influence cooking-related UFP in homes that should be considered. The amount of UFP produced depends on the method of cooking, type of oil used, and type of food. For example, high temperature frying has been shown to greatly increase the UFP concentration in homes. The persistence of high concentrations of UFP depends on the presence and properties of a cooking range's exhaust hood (Evans et al. 2008), as well as the air exchange rate within the house.

4.1 *Other Indoor Sources*

Numerous UFP sources exist within homes in addition to cooking sources. In the homes of non-smokers, other significant sources of UFP include air fresheners, cleaning products, burning candles and incense. Additionally, the self-cleaning oven feature and gas and electric burners found on most residential ovens and stoves have been shown to produce significant amounts of UFP. Table 2 presents maximum concentrations of UFP observed while studying common sources found in homes.

The majority of the processes presented in Table 2 involve combustion (e.g., burning candles) or the heating of a surface (e.g., electric element of a stove). The UFP from air fresheners and cleaners are the result of nucleation due to secondary chemical reactions with ozone. These secondary reactions are most commonly observed with pinene and limonene (and other terpenes) containing compounds found in pine and lemon scented cleaning products (Nazaroff and Weschler 2004).

5 Exposure Assessment

At the beginning of this paper, an indirect exposure assessment method was described that utilizes microenvironment UFP concentrations and time-activity patterns to assess population exposure. Although this approach is known to underestimate the extreme exposures that may exist within a population, it may

Table 2 Comparison of indoor UFP sources

Indoor UFP sources, sizes, and study types

Source	Study Type	Size (nm)	Max UFP (pt/cm^3)
Cigarette smoke	Chamber	>20	213
	Home	>7	26
	Home	>14	36
Air freshener	Chamber	>20	29,900[a]
Pure wax candles	Chamber	>20	241,500[a]
Scented candles	Chamber	>20	69,600[a]
Frying meat	Chamber	>20	150,900[a]
Frying vegetables	Home	>20	20,000–80,000[d]
Cooking oil	Lab Kitchen	>6	110,000–120,000[e]
Electric air heater	Chamber	>20	116,800[a]
	Home	>7	87,100[b]
Electric radiator	Chamber	>20	218,400a
Electric stove	Chamber	>2	111
	Lab kitchen	>6	26400–94
	Home	>7	61
Gas stove	Chamber	>20	79,600[a]
	Lab kitchen	>6	17,000–150,000[e]
Vacuum cleaner	Chamber	>6	21,400[a]
	Home	>7	41,300[b]

[a] Afshari et al. (2005), [b] He et al. (2004), [c] Hussein et al. (2006), [d] Evans et al. (2008), and [e] Buonanno et al. (2009)

still be used as a tool to estimate the "average" UFP exposures for urban residents. This average may be calculated as:

$$E_i = \sum_{j=1}^{n} E_{ij} = \sum_{j=1}^{n} f_{ij} C_{ij}$$

where E_{ij} is the exposure of individual i in microenvironment j, f_{ij} is the fraction of the day individual i spent in microenvironment j and C_{ij} is the average UFP concentration in microenvironment j when individual i was in that microenvironment.

Existing UFP concentration data originates from studies in both indoor and outdoor microenvironments (Diapouli et al. 2007). An important gap in our knowledge is how those measurements compare to the UFP number concentrations collected alongside an individual. To date, limited personal monitoring for UFP has occurred due to the size and operation requirements of the existing instruments. One study that used technicians to measure UFP alongside 16 urban residents during a single "typical day" was reported by Stieb et al. (2008). This study demonstrated that significant UFP exposure variability exists within the population and that this exposure is closely related to lifestyle choices. Exposure assessment to UFP is an evolving area of research. It will likely change rapidly with the development of inexpensive and small instruments that are capable of accurately measuring particles in the ultrafine range.

6 Summary

It has been established that numerous sources and processes govern the characteristics of UFP. As a result, UFP concentrations, size distributions, and presumably chemistry, exhibit large spatiotemporal variability in cities. Vehicles are the dominant source for UFP outside. Roadside concentrations vary over a range of characteristic times and distances. Nearby vehicles can produce short-lived concentration spikes while the concentration away from busy roads is related to neighbourhood traffic density and meteorology. Cooking, along with other sources, contribute to indoor UFP concentration. As a result of this large spatiotemporal variability, UFP exposure assessment is strongly dependent on the reliability of time-activity relationships. Finally, both lifestyle and life-stage has an effect on an individuals' exposure.

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Occupational Exposure to Urban Airborne Particulate Matter: A Review on Environmental Monitoring and Health Effects

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1 Introduction

Airborne particulate matter (PM) is a complex chemical mixture of extremely small solid particles and liquid droplets that can derive from both natural and anthropogenic sources (USEPA 2008; Vedal and Sullivan 2007).

PM differs in size and composition. The size is subdivided into different groups depending on their aerodynamic diameter. If the particle diameter is less than 10 µm, it is called PM_{10}. PM_{10} includes "inhalable coarse particles" with diameters larger than 2.5 µm and smaller than 10 µm, "fine particles" with diameters that are 2.5 µm or smaller ($PM_{2.5}$) and "ultrafine particles" that are smaller than 0.1 µm (UFPs) (Polichetti et al. 2009). PM is classified as primary or secondary, according to particle origin. The primary particles are emitted directly from the source, while the secondary particles are formed within the atmosphere by complicated chemical reactions between precursor gases or between these gases and primary particles (volatile organic compounds (VOCs), SO_2, NO_x and NH_3) (Lükewille et al. 2001). Secondary particles are mainly concentrated in the fine particle size fraction (<2.5 µm diameter), while primary particles tend to be concentrated in the coarse particle fraction (>2.5 µm) (QUARG 1993).

The particle composition of PM is extremely changeable since it depends on many factors such as climate variations, emission sources, and geographical position. Its main components are transition metals, ions, organic compounds, quinoid stable radicals of carbonaceous material, minerals, reactive gases and biomaterials (Valavanidis et al. 2008).

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*, Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_26,

In urban areas, PM concentrations tend to be higher and many people are exposed. The presence of PM is correlated to road traffic which is the most important source of emission in metropolitan areas where exhaust emissions, tyre and brake wear, and re-suspension of dust contribute considerably to the mass of particles (Almeida et al. 2007). The traffic on main roads and principal routes cause an appreciable rise in $PM_{2.5}$ concentrations above the urban background level (Barrowcliffe et al. 2002). Consequently urban PM is currently of great interest for public health since it is believed to play a crucial role in the gradual deterioration of air quality afflicting many large cities. Furthermore, the adverse impact of PM on human health is an important issue. In fact, many epidemiological studies report significant associations between PM concentration in the air and adverse health effects (USEPA 1997; Vedal 1997).

In this chapter we have reviewed and summarized current knowledge regarding the environmental monitoring of subjects occupationally exposed to urban PM and have indicated the most important adverse health effects correlated to this kind of exposure.

2 Environmental Monitoring

Air quality in urban areas continues to be a growing concern on account of its health and environmental impact. Many cities across the world are experiencing high levels of air pollution due to emissions resulting mainly from road traffic (Sokhi 2005). Among the numerous pollutants that affect air quality, PM is the most widespread threat to health. For this reason many countries have imposed air quality standards to establish permissible levels. EU standards (EU Directive 1999/30/EC) are based on annual and daily limit values for PM_{10} levels of 40 and 50 $\mu g/m^3$, respectively. However, the EU Directive 2008/50/EC established that a Member State can be exempt from the obligation to apply the limit values until 11 June 2011 when these cannot be achieved because of site-specific dispersion characteristics, adverse climatic conditions or transboundary contributions.

In the United States, the Environmental Protection Agency (EPA) revised the air quality standards for PM in 2006. The Clean Air Act amendments of the same year established a 24-h and an annual standard for $PM_{2.5}$ of 35 and 15.0 $\mu g/m^3$ respectively, and a 24-h standard for PM_{10} of 150 $\mu g/m^3$ (McCarthy 2006).

In recent years, several researchers have focused their attention on the environmental monitoring of PM in categories of subjects occupationally exposed to urban PM in order to determine and evaluate levels of exposure, to ascertain if these comply with the limits set by law and to establish a possible correlation with clinical manifestations.

2.1 PM_{10}

One of the first studies that attempted to evaluate occupational exposure to urban PM in truck drivers was performed in Geneva (Switzerland) (Guillemin et al. 1992). Workers ($n = 9$) were employed in the transportation of materials between different building sites in the city. All samples were collected inside the truck cabs during a workday of about 8–9 h, both by a direct-reading instrument and by sampling. The sampling of inhalable dust resulted in an average concentration of 261 μg/m^3 (range 150–450 μg/m^3), whilst the average PM_{10} concentration was 255 μg/m^3.

An interesting study was performed in Scotland to investigate the differences between measurements of personal exposure to PM_{10} and static area measurements in a group of 16 traffic wardens (Watt et al. 1995). Personal air sampling was carried out from 8 am to 4 pm for four consecutive working days over a period of 2 consecutive weeks in November 1994. The results showed that in the first week of sampling, mean PM_{10} concentration was 123 μg/m^3, whereas in the second week it decreased to 41 μg/m^3.

Public bus and tram drivers constitute another category of workers exposed to urban PM. A study performed between February 1993 and October 1996 evaluated the exposure of passengers and drivers of the Munich (Germany) transportation system to PM_{10} (Praml and Schierl 2000). The samples were taken on tramways, circular bus lines and radial bus lines for a total of 201 journeys, each of the duration of approximately 4 h. The use of gravimetric sampling was accompanied by a continuous recording of PM_{10}. Average PM_{10} concentration in the interior of all vehicles was 155 μg/m^3 with a range of 71–279 μg/m^3. Average PM_{10} concentrations in trams and the circular and radial bus lines were 163, 161 and 107 μg/m^3, respectively.

A similar study was conducted 10 years later in 16 air-conditioned buses and 15 non air-conditioned trams in the city of Hong Kong (China) (Jones et al. 2006). The concentration of PM_{10} was measured using an aerosol monitor placed next to the driver's seat. The levels of PM_{10} in air-conditioned buses were 265.4 ± 83.2 μg/m^3 (mean ± standard deviation), while in non air-conditioned trams values were 161.1 ± 103.1 μg/m^3 (mean ± standard deviation). The authors hypothesized that the air filters in the air-conditioned buses were not adequate to filter out larger particles as well as dust and maintain an optimal air-conditioning system within the bus compartment.

The same category of workers (42 bus drivers) was studied alongside two other groups of professional drivers (39 taxi drivers and 40 lorry drivers) in Stockholm (Sweden) between September 1997 and October 1999 (Lewné et al. 2006). PM_{10} samples were collected by personal monitoring during the working hours of the drivers (the average workday for taxi, bus and lorry drivers was approximately 10, 8 and 8 h, respectively) with a logging instrument by nephelometric monitoring. All bus drivers worked in the city and its suburban area, whilst the taxi and lorry drivers spent part of their working time also in the surrounding districts of

Stockholm. Results showed that the lorry drivers were exposed to the highest levels of PM_{10} and the taxi drivers to the lowest. Mean PM_{10} concentrations in taxi, bus and lorry drivers were 26, 44 and 57 $\mu g/m^3$, respectively. For bus drivers in the city and suburban area mean PM_{10} concentrations were 47 and 40 $\mu g/m^3$, respectively, whereas average PM_{10} concentrations in lorry drivers in the city and suburban area were 49 and 62 $\mu g/m^3$, respectively.

The exposure of urban workers to PM was also studied by Chinese researchers who carried out a large sampling survey in six districts of Hong Kong in 3 winter months from November 1998 to February 1999 (Ng and Lam 2001). In each of these districts, 12 roadside magazine and newspaper vendors, situated along busy roads with heavy traffic, were randomly selected for measuring urban PM_{10} concentration so as to provide a good representation of the roadside working environment. Monitoring was undertaken in the daytime from 10 am to 5 pm to include most of the business hours, and average 5-minute concentrations were taken and logged to track real-time variations in PM_{10} levels. Findings indicated that the average 1 h PM_{10} concentration was higher in densely populated commercial areas (325 and 284 $\mu g/m^3$) and lower in residential areas (<200 $\mu g/m^3$).

Maître et al. (2002) performed a study in Grenoble (France) to evaluate exposure to respirable particles in 8 policemen working close to traffic. Sixty-two personal active air samples were collected during the work shifts. Moreover, using the same sampling devices, 17 stationary air samples were monitored in the same area where the policemen operated. Finally, outdoor concentrations of PM_{10} were obtained at a fixed monitoring station located on a busy road in the city centre. All samples were collected in the summer and in the winter. Respirable particle concentration was determined using the gravimetric method. In June, the respirable particle mean concentrations for personal and stationary sampling and daily PM_{10} levels were 58.1, 25 and 43.25 $\mu g/m^3$, respectively, while in January they were 123, 124 and 85 $\mu g/m^3$, respectively.

The same order of magnitude was observed in Seoul (South Korea) when exposure to urban PM_{10} was assessed in 32 shoe stall workers (Bae et al. 2004). The authors measured PM_{10} concentrations simultaneously in indoor and outdoor environments. Indoor samplers were positioned inside the shoe stalls, whereas the outdoor samplers were placed outside the shoe stalls (within 15 m of the road). Average sampling duration was 10 h, depending on working hours. Data from this study yielded an average PM_{10} indoor concentration of 127.7 $\mu g/m^3$, with values ranging from 44.7 to 214.5 $\mu g/m^3$, whilst the average PM_{10} outdoor concentration was 138.7 $\mu g/m^3$ with a minimum value of 25.8 $\mu g/m^3$ and a maximum value of 228.1 $\mu g/m^3$. These results indicated that PM_{10} concentrations in the indoor shoe stalls were significantly correlated with outdoor PM_{10} concentrations (Spearman $r = 0.481$, $P < 0.01$). This correlation might be due to the fact that indoor PM_{10} concentrations could be affected by inflow from the ambient outdoor air.

An interesting study evaluated PM_{10} exposure in 31 indoor shopkeepers and 33 outdoor roadside vendors in the Mongkok district of Hong Kong (Jones et al. 2008). PM_{10} concentration was measured inside and outside air-conditioned shops using an aerosol monitor placed in the subject's working environment next to where the roadside vendors sat or in the centre of the shop. The mean PM_{10} concentration in the roadside shops was 130 μg/m^3, a level significantly lower than the 210 μg/m^3 value measured outside the shops.

In 2000–2001, Violante et al. (2006) studied personal exposure levels to PM_{10} in two different categories of urban workers: 126 traffic policemen and 50 parking wardens. The sampling campaign was carried out during four separate weeks in all seasons of the year. Each subject wore an active sampler and a single PM_{10} personal exposure monitor inlet. PM_{10} concentrations in the traffic policemen and the parking wardens was very similar. In fact, the mean PM_{10} level was 181 μg/m^3 in the first category and 185.3 μg/m^3 in the second. A similar study was performed on traffic policemen in Tianjin (China) during the summer of 2005 (Hu et al. 2007). Personal environmental monitors were fixed on the policemen's collars to collect personal samples from the breathing zone. In this study, the PM_{10} levels measured at the road intersections during the traffic policemen's work shift ranged from 192 to 403 μg/m^3 with an average value of 293.0 μg/m^3. That was considerably higher than concentrations observed in Italy by Violante (2006).

Tables 1 and 2 summarize the mean PM_{10} exposure levels in indoor environments and in outdoor workers.

2.2 $PM_{2.5}$

Fewer studies have evaluated this PM fraction as an indicator of occupational exposure. A study conducted in London in September 1996 measured concentrations of Total Suspended Particulate (TSP) and $PM_{2.5}$ using personal samplers (Pfeifer et al. 1999). Samples were collected over two consecutive 7-day periods in 10 taxi drivers. Mean concentrations of $PM_{2.5}$ and TSP were 33.36 ± 20.73 and 53.90 ± 39.19 μg/m^3, respectively.

Riediker et al. (2003) studied $PM_{2.5}$ exposure in 10 non-smoking North Carolina State Highway Patrol troopers over a total of 25 days in August, September and October 2001. Each trooper was monitored in his personal patrol car on four consecutive workdays during the late shift that lasted from 3 pm to midnight. In this study the sampling strategy consisted of a particle collection on filters with gravimetric analysis ($PM_{2.5\mathrm{Mass}}$) and a real-time particle mass estimation performed by nephelometers ($PM_{2.5\mathrm{Realtime}}$). Data were also collected simultaneously at a site reflecting urban ambient concentrations and from multiple stationary roadside locations near busy roads in Wake County. The results showed that mean concentrations during the analyzed shifts were 24.1 and 23.0 μg/m^3 for $PM_{2.5\mathrm{Realtime}}$ and $PM_{2.5\mathrm{Mass}}$, respectively. These levels were lower than the mean concentrations observed at ambient site ($PM_{2.5\mathrm{Realtime}} = 35.4$ μg/m^3 and $PM_{2.5\mathrm{Mass}} = 31.7$ μg/m^3) and at roadside ($PM_{2.5\mathrm{Realtime}} = 30.9$ μg/m^3 and $PM_{2.5\mathrm{Mass}} = 29.9$ μg/m^3). These findings contrasted with results observed in a study conducted in London by Adams et al. (2001) where average $PM_{2.5}$ concentration inside public transport buses was 39 μg/m^3 and the urban background level was 14 μg/m^3.

Table 1 PM_{10} levels in professional drivers and in indoor environments

Site of sampling	Year of sampling	Methodology of sampling	Duration of sampling (h)	Type of workers (*n*)	Average PM_{10} levels ($\mu g/m^3$)	Notes on sampling and results	References
Geneva	1987–1988	Real time and gravimetric	8–9	Truck drivers (9)	255	Instruments were placed inside the cab of trucks	Guillemin et al. (1992)
Munich	1993–1996	Gravimetric	4	Bus drivers and tram drivers	Total: 155 Trams: 163 Circular lines: 161 Radial lines: 107	Samplings were carried out on tramways, circular and radial bus lines for a total of 201 journeys	Praml and Schierl (2000)
Stockholm	1997–1999	Real time with nephelometric method	10	Taxi drivers (39)	26	Mean PM_{10} levels of bus and lorry drivers in the city area and in suburban area were 47, 49, 40 and 62 $\mu g/m^3$, respectively	Lewné et al. (2006)
			8	Bus drivers (42)	44		
			8	Lorry drivers (40)	57		
Seoul	2001–2002	Gravimetric	10	Polishers and repairmen (32)	127.7	Indoor samplers were placed inside participant's shoe stalls at mid-location at least 1 m off the ground	Bae et al. (2004)
Hong Kong	2003–2004	Real time	0.4	Bus drivers	265.4	Instruments were placed next to the driver's seat in 16 buses and in 15 trams	Jones et al. (2006)
			0.4	Tram drivers	161.1		
Hong Kong	2005	Real time	0.4	Shopkeepers (31)	130	Samplings were carried out in the centre of shops along a busy major road	Jones et al. (2008)

Table 2 PM_{10} levels in outdoor urban workers

Site of sampling	Year of sampling	Methodology of sampling	Duration of sampling (h)	Type of workers (*n*)	Average PM_{10} levels ($\mu g/m^3$)	Notes on sampling and results	References
Aberdeen	1994	Gravimetric	8	Traffic wardens (16)	123 (first week); 41 (second week)	Personal samplings were carried out over two consecutive weeks	Watt et al. (1995)
Hong Kong	1998–1999	Real time with light scattering method	7	Roadside magazine and newspaper vendors (72)	231 (mean value of all samples)	PM_{10} levels were highest in densely populated commercial areas (325 and 284 $\mu g/m^3$) and lower in residential areas (<200 $\mu g/m^3$)	Ng and Lam (2001)
Bologna	2000–2001	Gravimetric	From 3 to 6	Traffic police workers (126)	181	PM_{10} levels of stationary samplings were significantly lower	Violante et al. (2006)
				Parking wardens (50)	185.3		
Seoul	2001–2002	Gravimetric	10	Polishers and repairmen (32)	138.7	Outdoor samplers were placed on the outside of the shoe stalls (within 15 m from roadways)	Bae et al. (2004)
Grenoble	2002 (year of publication)	Gravimetric	7	Policemen (8)	58.1 (June); 123 (January)	PM_{10} levels of stationary samplings were significantly lower	Maître et al. (2002)
Hong Kong	2005	Real time	0.4	Roadside newspaper, food and confectionery vendors (33)	210	Samplings were carried out next to where the roadside vendors sat	Jones et al. (2008)
Tianjin	2005	Gravimetric	6	Traffic police workers (10)	293	The personal environmental monitors were fixed on the policemen's collars and sampling was carried out at the road intersections	Hu et al. (2007)

Several categories of urban workers were enrolled in a study carried out in Trujillo (Peru) in July 2002 to assess exposure to traffic-related pollutants (Han et al. 2005). Among the 58 workers included in the study, 26 were drivers (8 bus drivers, 8 combi drivers and 10 taxi drivers), 8 street vendors, 6 traffic policemen and 18 gas station attendants. A gravimetric analysis was performed to measure $PM_{2.5}$ exposure. Data from this study indicated that bus and combi drivers had the highest full-shift $PM_{2.5}$ exposures: their mean exposure levels were 161 and 114 $\mu g/m^3$, while those of gas station attendants were the lowest (64 $\mu g/m^3$).

Exposure to $PM_{2.5}$ in four bus drivers, six lorry drivers and four taxi drivers was also determined in Stockholm between October 2002 and June 2004 (Lewné et al. 2007). Samples were collected by pump units and the concentration was determined using the gravimetric method. Exposure levels determined in this study were significantly lower than those observed in Peru. In fact, the geometric $PM_{2.5}$ mean in bus and lorry drivers was 15.7 $\mu g/m^3$, while the mean concentration for taxi drivers was 17.3 $\mu g/m^3$. The authors also assessed PM_1 levels (using the same gravimetric method) and conducted a real-time monitoring of particles ranging from 0.1 to 10 μm. Findings indicated PM_1 concentrations of 13.5 $\mu g/m^3$ in bus and lorry drivers, and of 11.3 $\mu g/m^3$ in taxi drivers. Corresponding values for real-time sampling in the two categories of workers were 31.1 and 14.4 $\mu g/m^3$.

A nationwide survey of particulate exposures in the US trucking industry was conducted in 36 different trucking terminals across the United States between 2001 and 2005. In this study, several occupational groups were investigated: dockworkers, hostlers, mechanics, combination workers, clerks and truck drivers (Smith et al. 2006). The latter category included two main types of truck driving operations at each terminal, i.e. local pick-up and delivery (P&D) operations and long haul (LH) during which trailers were transported to and from terminals several hundred miles away. The P&D drivers pick up and deliver freight to local customers. Since our goal is to determine occupational exposure to urban PM, here we report only the data relative to P&D drivers. $PM_{2.5}$ was collected for a 1-week period with a sampling box mounted in the cab. The $PM_{2.5}$ concentration was then determined by gravimetric analysis. The mean level of $PM_{2.5}$ observed in P&D drivers was 27.8 $\mu g/m^3$. According to the smoking status, non-smoker P&D drivers showed a mean $PM_{2.5}$ concentration of 19.1 $\mu g/m^3$, while in smoker P&D drivers the $PM_{2.5}$ level was 50.1 $\mu g/m^3$ (Davis et al. 2007a). The same group of researchers carried out a similar study between 2004 and 2006 to investigate $PM_{2.5}$ levels in city truck drivers in 15 different U.S. cities (Davis et al. 2007b). The sampling strategy was the same as in the previous study. Mean $PM_{2.5}$ concentrations in non-smoker P&D drivers and in smoker P&D drivers were 15.98 and 37.83 $\mu g/m^3$, respectively.

A recent study measured $PM_{2.5}$ concentrations in both old and modern models of buses and trams in Helsinki (Finland) during a 2-week period from mid-June to the beginning of July 2005 (Asmi et al. 2009). Measurements included four sets of 2-day trials. Bus and tram routes were mostly coincident. Sampling time was limited by the vehicle operational shift period. In both bus types and the older trams, the cabin space was open. In the modern trams, a separate driver's compartment was equipped with air conditioning. Mean $PM_{2.5}$ values for the first and second day of measurement were 9 and 12 $\mu g/m^3$ inside the old trams, 14 and 13 $\mu g/m^3$ inside the new trams, 29 and 24 $\mu g/m^3$ inside old buses and 15 and 12 $\mu g/m^3$ inside a new buses, respectively.

Mean $PM_{2.5}$ exposure values in professional drivers are summarized in Table 3.

3 Health Effects

Several epidemiological studies conducted in the past 30 years have demonstrated that elevated PM levels are correlated with several health outcomes and are the cause of a considerable increment in mortality, hospitalization for respiratory and cardiovascular diseases, aggravation of asthma attacks and adverse lung functions (WHO 2003; Brook et al. 2004, 2009; Pope and Dockery 2006; Brook 2008; Valavanidis et al. 2008; Mills et al. 2009; Russell and Brunekreef 2009). Some groups of the general population such as elderly people, children, and individuals with chronic lung and heart diseases are particularly susceptible to the adverse health effects of urban PM [Environmental Protection Department (EPD) 1996]. Most of the studies have focused on the effects of particle mass, either the thoracic fraction, PM_{10}, or the fine fraction, $PM_{2.5}$ (Asmi et al. 2009), while others have shown that health effects are related to particle size or number rather than mass (Ferin et al. 1992; Donaldson et al. 1998; Penttinen et al. 2001). Concerning the particle size, numerous epidemiological studies have been published on the health effects associated with PM_{10} (Health Effects Institute 2003; Peng et al. 2008). Nevertheless, research on the health effects of the “coarse thoracic particles” is limited and findings have been mixed (Brunekreef and Forsberg 2005; Peng et al. 2008). More recent work has focused on $PM_{2.5}$, for which strong evidence of an association with mortality and morbidity has been found (Dominici et al. 2006; Pope and Dockery 2006).

The chemical composition of PM also plays an important role in determining potentially toxic human health effects (Gil et al. 2003). Unlike other pollutants, PM exposure is much more complex since it includes various chemical species in particles that have an ample range of diameters and shapes and widely varying toxicities. Given the complex mixture of urban PM, it is not easy to identify the biological mechanisms that have harmful effects on human health. Moreover, the mechanisms involved in the range of health outcomes associated with exposure to urban PM are probably multiple (Hopke and Rossner 2006).

Nevertheless, these possible negative health effects have become a growing concern also among job categories that are occupationally exposed to urban PM. In fact, policemen, traffic wardens, professional drivers (tram, bus, taxi, lorry and truck drivers), roadside vendors, postal workers, street sweepers and other outdoor urban workers spend most of their work time exposed to urban PM. Although it has been difficult to demonstrate the relative risk of death or illness associated with PM, researchers have reported a number of health effects on workers (Gamble and Lewis 1996). In this section we review the adverse health effects observed in workers exposed to urban PM.

Table 3 $PM_{2.5}$ levels in professional drivers

Site of sampling	Year of sampling	Methodology of sampling	Duration of sampling (h)	Type of workers (*n*)	Average $PM_{2.5}$ levels ($\mu g/m^3$)	Notes on sampling and results	References
London	1996	Gravimetric	–	Taxi drivers (10)	33.36	In this study the sampling of TSP (53.9 $\mu g/m^3$)was also performed	Pfeifer et al. (1999)
Raleigh	2001	Real time and gravimetric	9	Highway patrol troopers (10)	24.1 (realtime); 23 (gravimetric)	Each trooper was monitored in his personal patrol car on 4 consecutive workdays	Riediker et al. (2003)
Trujillo	2002	Gravimetric	From 6 to 14	Bus drivers (8)	161	In this study the exposure of 10 taxi drivers, 8 street vendors and 6 policemen was also evaluated but the Authors did not provide their values	Han et al. (2005)
				Combi drivers (8)	114		
				Gas station attendants (18)	64		
Stockholm	2002–2004	Gravimetric	8	Bus and lorry drivers (10)	15.7	The Authors also performed the environmental monitoring of PM_1 in bus and lorry drivers and in taxi drivers (13.5 and 11.3 $\mu g/m^3$)	Lewné et al. (2007)
				Taxi drivers (4)	17.3		
United States (U.S.)	2001–2005	Gravimetric	From 8 to 12	Pick up and delivery drivers	27.8	The sampling boxes were mounted in the cab of trucks; the smoking status significantly affects the results	Smith et al. (2006)
Helsinki	2005	Real time with light scattering method	From 10 to 16	Bus drivers	Old bus New bus	The sampling devices were mounted in the cab or driver's compartment and samplings were carried out on two different days	Asmi et al. (2009)
				Tram drivers	Old tram New tram		
15 different cities of U.S.	2004–2006	Gravimetric	From 8 to 12	Pick up and delivery drivers	15.98 (non smokers); 37.83 (smokers)	–	Davis et al. (2007a, b)

3.1 Cardiovascular and Haematological Effects

In 2001, Riediker et al. (2004a,b) investigated the sources of $PM_{2.5}$ potentially responsible for cardiovascular and haematological effects in nine highway patrol troopers of Wake County (USA). Members of this police force spent the majority of their working time in or near their cars, and often in heavy traffic. The patrol troopers' $PM_{2.5}$ exposure levels were described above (Riediker et al. 2003). The subjects were studied on four consecutive days during their shift (from 3 pm to midnight) and also the following night. The authors carried out an analysis of the chemical composition of $PM_{2.5}$ and subsequently, using two different source models, identified different source factors (crustal, steel wear, soil and road surfaces, gasoline combustion, speed-changing traffic). Data from this study indicated that most health endpoints were associated with a $PM_{2.5}$ source factor that reflected speed-changing traffic and was dominated by the presence of copper, aldehydes and sulphur. $PM_{2.5}$ originating from speed-changing traffic modulated autonomic control of heart rhythm, increased the frequency of premature supra-ventricular beats and elicited pro-inflammatory and pro-thrombotic responses. In fact, the speed change factor was significantly associated with an increase in the percentage of neutrophil leucocytes, a decrease in the percentage of lymphocytes and with changes in markers of endothelial activation and haemostasis. Moreover, $PM_{2.5}$ particles originating from speed-changing traffic were associated with changes in mean red blood cell volume and with a significant increase in the heart beat interval of mean cycle length, heart rate variability and supra-ventricular ectopic beats. A subsequent reanalysis investigating on $PM_{2.5}$ components potentially contributing to such effects showed that calcium was associated with increased uric acid and von Willebrand factor, and decreased protein C; chromium was related with increased white blood cells and interleukin 6 and copper with increased blood urea nitrogen and mean cycle length of normal R–R interval; Sulfur with increased ventricular ectopic beats (Riediker 2007).

Several studies on animals and humans have suggested a correlation between exposure to xenobiotics (metals and VOCs) contained in PM and alterations in blood pressure (Puri 1999; Schuhmacher et al. 1994; Kotseva and Popov 1998; Gericke et al. 2001). However, little research has been carried out on this association in occupational categories exposed to urban PM. In a study conducted in the period March–April 2001 on 77 Rome (Italy) police officers, an ambulatory 24-h blood pressure monitoring was performed to evaluate the possible correlation between exposure to urban PM and alterations in systolic and diastolic blood pressure (Tomei et al. 2004). The mean monthly values of PM_{10} observed in the city and measured by fixed stations located in districts with different traffic intensity were 60, 45 and 30 $\mu g/m^3$, respectively, in a municipal park. In non-smoker male police officers, ambulatory systolic blood pressure mean values over 24 h (day time and night time) were significantly higher than controls, while ambulatory diastolic blood pressure mean values over 24 h (between 6 am and 11 am and between 10 pm and 6 am), were significantly higher in non-smoker male police officers compared to controls. In non-smoker female police officers, ambulatory systolic and diastolic mean blood pressure levels were not significantly different from controls. These results suggested that occupational exposure to urban PM may influence cardiovascular system activation. The police officers of Rome were also studied to ascertain whether their exposure to urban PM could cause alterations in red blood cells (RBC), haemoglobin (HGB), haematocrit (HCT), mean cell volume (MCV), mean cell haemoglobin (MCH) and mean corpuscular haemoglobin concentration (MCHC) (Tomei et al. 2008). During the period October–December 2000, the Rome Municipality monitored PM_{10} concentrations in fixed stations located in districts with different traffic intensity, registering mean monthly min/max values in a municipal park of 44–76 and 43–76 $\mu g/m^3$, respectively. Results showed that in traffic police of both sexes, mean RBC, HGB and HCT levels were significantly higher compared to controls, whilst no significant differences were found when mean levels of MCV, MCH, and MCHC in male and female traffic police officers were compared to controls. Moreover, in the same group of workers, occupational exposure to urban PM might be able to reduce resistance to physical effort and increase the risk of cardiovascular changes (Volpino et al. 2004). In fact, the results of a study conducted in 2001 on 68 traffic policemen and 62 office workers showed that the first group had a significantly lower workload with lower double product (maximum heart rate × maximum blood pressure), a shorter exercise time at anaerobic threshold and maximal effort and a lower and slower restoration of cardiopulmonary parameters to basic values at recovery time. Moreover, symptoms limiting continuation of the exercise test (elevated blood pressure, arrhythmias and ST deviation) were observed only in the traffic policemen. The mean environmental PM_{10} level obtained from recordings of four municipal monitoring stations in the metropolitan area of Rome during the period 2000–2001 was 53.7 $\mu g/m^3$.

Cardiovascular mortality has been linked to coarse PM exposure only in the general population, and not in subjects occupationally exposed to urban airborne PM (Ostro et al. 2000; Mar et al. 2000, 2003; Villeneuve et al. 2003; Brunekreef and Forsberg 2005; Kan et al. 2007; Wilson et al. 2007; Perez et al. 2009). Some evidence has also indicated that coarse PM had a strong effect on total cardiovascular hospital admissions (Burnett et al. 1997, 1999; Lippmann et al. 2000). However, some other studies did not found the same correlation (Fairley 1999; Anderson et al. 2001; Host et al. 2008; Peng et al. 2008). A few studies have associated coarse PM with inflammatory responses as well as with decreases in heart rate variability among susceptible people (Yeatts et al. 2007; Lipsett et al. 2006).

3.2 Respiratory Effects

A study carried out in Thailand from 1998 to 1999 evaluated pulmonary function and respiratory symptoms in 78 male traffic police officers in Bangkok

(Karita et al. 2001). These workers were employed in activities next to busy roads. Observed PM_{10} levels were continually higher than Thailand's National Air Quality Standard of 120 μg/m^3. Corrected for age, height and smoking index, mean levels of forced expiratory volume in 1 s (FEV_1) and maximal expiratory flow rate in 25% of vital capacity (V25) were significantly lower in policemen than in control subjects. Moreover, the prevalence of cough, phlegm, wheezing and dyspnea symptoms among the urban workers were slightly higher than among policemen working in the rural area. The same group of researchers evaluated chronic, non-specific respiratory symptoms (NSRD) in 1,603 policemen living and working in areas with three different levels of airborne particulates (Tamura et al. 2003). Site selection was based on the distance from inner Bangkok. Distance from the city centre was less than 8 km in the most urban, heavily polluted area (H), between 8 and 15 km in the moderately polluted area (M) and more than 15 km in the least exposed or control area (C). The average annual PM_{10} levels from monitoring stations of the Pollution Control Department was $\geq$80 μg/m^3 in H, between 70 and 60 μg/m^3 in M and <60 μg/m^3 in the C area (Jinsart et al. 2002). The prevalence of NSRD in the heavily polluted, moderately polluted, and suburban areas was 13.0, 10.9, and 9.4%, respectively. In keeping with the results of previous studies, Karita et al. (2004) ascertained whether the increased risk of respiratory impairment due to air pollution was restricted only to traffic policemen or was also likely to affect the general population. They investigated the prevalence of respiratory problems in 530 policemen and their wives in Bangkok in relation to their residential area locations and according to the area division previously described (Tamura et al. 2003). Their residential address was divided into four areas determined by distance from the city centre of Bangkok: less than 8 km in H (heavily polluted area), between 8 and 15 km in M (moderately polluted area), between 16 and 25 km in L (less polluted area) and more than 25 km in R (rural area). The average annual PM_{10} levels from the Pollution Control Department monitoring stations was $\geq$80 μg/m^3 in H, between 70 and 60 μg/m^3 in M and <60 μg/m^3 in the L area (Jinsart et al. 2002). The prevalence of respiratory symptoms such as cough, phlegm and wheezing was higher in police officers than in their wives. In policemen, frequent cough or phlegm symptoms were found to be significantly associated with working in the areas with higher PM_{10} levels.

A similar study was performed on 60 traffic policemen in Jalgaon city (India) (Ingle et al. 2005). These subjects worked for at least 10 h at road crossings where they were exposed to a heavy dose of vehicular pollution. PM_{10} air monitoring was conducted from May 2003 to April 2004 at three sampling locations in the study area. The pulmonary function test of the target groups and controls (60 healthy adults from the same location) was conducted during the winter season. In this period average PM_{10} levels were 239, 213 and 222 μg/m^3 at the three sampling locations of the study area. Spirometric analysis of the traffic policemen showed significant impairment in Peak Expiratory Flow Rate (PEFR), FEV_1 and Forced Vital Capacity (FVC). Furthermore, a significantly greater number of policemen suffered from respiratory symptoms (frequent cough, shortness of breath and irritation in respiratory tract) as compared to controls. The corresponding odd ratio for the symptoms studied were 2.96, 1.22, 7.5, respectively.

Jones et al. (2006) evaluated the lung function and respiratory symptoms of Hong Kong bus and tram drivers exposed to PM_{10} in the period between June 2003 and June 2004. In particular, the authors compared the effect of long-term exposure to PM_{10} on 359 drivers in air-conditioned buses (ACB) to 129 drivers of non air-conditioned buses and trams (NACB). At functional pulmonary tests, NACB drivers exhibited significantly lower FVC, FEV_1 and maximal ventilatory volume (MVV) compared to ACB drivers. These findings were worse than those of a control cohort of academic personnel not occupationally exposed to urban PM_{10}. The authors suggested that the decrease in lung function in the drivers with the lower level of exposure to urban PM was the result of prolonged exposure. The same researchers also evaluated lung function parameters and respiratory symptoms in 33 outdoor roadside vendors and 31 indoor shopkeepers of Hong Kong (Jones et al. 2008). All lung function parameters and the frequency of symptoms were similar in the two groups of exposed workers. However the FVC of shopkeepers and roadside vendors was lower than the FVC of a cohort of controls working in a university environment extracted from a previous study (Jones et al. 2006). Furthermore, both the shopkeepers and roadside vendors had a higher frequency of complaints such as cough, sputum and shortness of breath on mild exertion compared to the university personnel. Exposure levels in the occupational categories evaluated in the previous studies were described above (Jones et al. 2006, 2008).

Laden et al. (2007) studied rates of cause-specific mortality in U.S. trucking industry workers in order to provide insight into mortality patterns associated with job-specific exposures (Laden et al. 2007). Among these workers, P&D drivers, who were the most exposed to urban PM, had an increased standardized mortality ratio for lung cancer and ischemic heart disease (Davis et al. 2006; Smith et al. 2006; Garshick et al. 2008).

Evidence regarding the general population, but not workers exposed to urban airborne PM, indicated that coarse PM had as strong a short-term effect, or stronger, as fine PM on asthma, chronic obstructive pulmonary disease, and respiratory hospital admissions (Yeatts et al. 2007; Brunekreef and Forsberg 2005; Burnett et al. 1997, 1999; Chen et al. 2004, 2005; Sheppard et al. 1999; Lippmann et al. 2000; Lin et al. 2002; Host et al. 2008). However, heterogeneous results are present in literature (Anderson et al. 2001; Peng et al. 2008). With respect to respiratory caused mortality Kan et al. (2007) did not find a significant effect of $PM_{10–2.5}$. This is consistent with most prior studies (Anderson et al. 2001; Fairley 1999; Ostro et al. 2000; Villeneuve et al. 2003).

3.3 Other Effects

The relationship between occupational exposure to urban PM and health effects on the endocrine system has been evaluated in several studies (Tomei et al. 2003, 2009;

De Sio et al. 2005) that have focused in particular on the effects on the hypothalamic-pituitary-adrenal (HPA) axis and related systems in traffic police officers. The data obtained suggested that occupational exposure to PM could affect hormone concentrations. However, it is also well known that traffic policemen are a working population exposed to high levels of stress (Piercecchi-Marti et al. 1999) and psychosocial stressors are able to alter the HPA axis causing alterations to the neuroendocrine system. Moreover, a clear correlation between PM exposure and observed effects on the HPA axis cannot be established since personal PM monitoring of exposed occupational categories has not yet been performed. Consequently, caution should be used when considering the results of these studies.

A series of studies was performed to correlate micronucleus (MN) frequencies in peripheral lymphocytes and levels of DNA bulky adducts detected in outdoor urban workers to levels of PM exposure. Maffei et al. (2005) found a significantly higher mean MN frequency in the traffic police officers of Bologna compared to controls. In this city, during the period of the study, municipal air quality stations recorded total suspended PM levels below 150 $\mu g/m^3$. As regards the DNA adducts, the literature contains contrasting data. Indeed, Palli et al. (2008) found significantly higher levels in workers exposed to traffic (PM_{10} levels ranged from 100 to 27 $\mu g/m^3$) compared to controls, while in a study on 53 policemen exposed to PM_{10} (range 32–55 $\mu g/m^3$) and $PM_{2.5}$ (range 27–38 $\mu g/m^3$) Binkova et al. (2007) failed to find significant differences between the exposed population and the control group.

Regarding the association between coarse PM and total mortality in the general population, data are heterogeneous. According to our knowledge, no data are available on subjects occupationally exposed to urban airborne PM. Several studies found no evidence that coarse PM was associated with all cause mortality (Schwartz et al. 1996, 1999; Klemm et al. 2000; Pope et al. 2002; Dockery and Pope 1993; Anderson et al. 2001; Fairley 1999; Klemm and Mason 2000; Lipfert et al. 2000; Ostro et al. 2000; Lippmann et al. 2000; Burnett et al. 2000, 2003; Villeneuve et al. 2003; Ito 2003; Brunekreef and Forsberg 2005; Kan et al. 2007). On the contrary other studies showed positive correlations (Cifuentes et al. 2000; Castillejos et al. 2000; Mar et al. 2000) and more recently, Zanobetti and Schwartz (2009) demonstrated a significant association between course PM and for all-cause mortality in a multipollutant model, which included both $PM_{2.5}$ and PM coarse. Moreover a recent study showed a significant association between coarse PM and cerebrovascular effects (Perez et al. 2009).

4 Discussion and Conclusions

Despite the air quality standards enacted by Governments around the world, air pollution in urban areas is still a very important concern because of its environmental consequences and its possible adverse effects on human health. In fact, millions of people still live in cities with unacceptable levels of air quality. Air pollution in urban areas is the result of a range of emissions—road traffic being the dominant source. Among the several pollutants that affect urban air quality, PM is the most widespread health threat. In fact, road traffic represents the most important source of PM emission and contributes considerably to the mass of particles in urban air on account of exhaust emissions, tyre and brake wear, and re-suspension of dust (Almeida et al. 2007).

Consequently several research groups have focused their attention on the environmental monitoring of PM in these workers. A comparison of the results reported in different studies is not easy and should be approached with caution since samples may be collected with different sampling devices and over different sampling periods. However, most of the studies on the environmental monitoring of PM_{10} we reviewed reported PM_{10} levels significantly higher than the air quality standards of the European Union (annual PM_{10} standard = 40 μg/m^3, 24-h PM_{10} standard = 50 μg/m^3), the United States of America (24-h PM_{10} standard = 150 μg/m^3) and other countries (e.g. in Hong Kong the 1-year and 24-h air quality objectives are 55 and 180 μg/m^3, respectively). An interesting issue regarding the environmental monitoring of PM_{10} is related to the discrepancies observed between data provided by fixed air monitoring stations in various cities and personal samplings carried out on outdoor urban workers, or the monitoring performed in particular indoor environments such as the driver's cab of buses, trams and trucks. In a study carried out by Watt et al. (1995), personal sampling conducted on traffic wardens gave higher values (about tenfold greater) of particulate exposure than the static levels provided by area sampling. A comparison of average personal PM_{10} exposure levels (185.1 ± 38.5 μg/m^3) recorded on the same workers and on traffic police officers in Bologna together with data on daily atmospheric levels (43.5 ± 24.1 μg/m^3), measured by fixed monitoring stations, yielded similar results (Violante et al. 2006). The same trend was observed by studying the exposure of roadside magazine vendors in Hong Kong (Ng and Lam 2001) where PM_{10} concentrations (the highest 1-h PM_{10} concentrations in Mongkok, Tsuen Wan and Shatin districts were 789, 319 and 422 μg/m^3, respectively) were significantly higher than those recorded by nine fixed air quality monitoring stations of the Environmental Protection Department of the city (the highest 1-h PM_{10} concentrations in the same districts were 380, 280 and 226 μg/m^3, respectively). Finally, in Munich buses and trams, PM_{10} concentrations recorded by fixed sampling stations were 1.7–3.9 times higher than outdoor values (Praml and Schierl 2000). The most likely explanation for these differences is that fixed air monitoring stations are usually located some metres above road level and quite a few metres from the side of the road. For example, in Hong Kong these monitoring stations are installed at a height of 2–25 m above street level, in Munich they are located 3.5 m above road level and in Aberdeen they are positioned about 20 m from and 4 m above the roads. Measurements provided by these fixed sampling stations may therefore give an indication of ambient PM_{10} levels but are not indicative of the roadside exposure to which urban workers are constantly exposed.

Although outdoor PM_{10} concentrations in streets can reach relatively high levels e.g. in roadside magazine vendors (Ng and Lam 2001), PM_{10} levels measured inside vehicles are usually higher (Mucke et al. 1984; Rohbock and Muller 1980). In fact, the average PM_{10} concentration recorded inside the cab of nine truck drivers in Geneva (Switzerland) was 255 μg/m^3 (Guillemin et al. 1992). Measurements carried out in the city of Hong Kong in 16 air-conditioned buses (265.4 μg/m^3) and 15 non air-conditioned trams (161.1 μg/m^3) yielded results of the same order of magnitude (Jones et al. 2006), and the corresponding value observed in Munich buses and trams was 155 μg/m^3 (Praml and Schierl 2000). A 4possible explanation for these findings could be the re-suspension of particulates from the road surface and "vacuum cleaning" in the interior of vehicles. Moreover, the re-suspension of dust from the floor of vehicles due to passengers moving around or taking a seat, has to be taken into account.

Real exposure of the urban population and workers to many airborne pollutants as a result of substances present in the microenvironments where people spend their working time seems to be different from (and often greater than) that measured by fixed monitoring stations. Consequently, it is clear that an appropriate evaluation of urban workers' exposure to PM should be performed by environmental monitoring carried out with personal samplings or with fixed sampling stations located in close proximity to the workplaces of these job categories. As regards different sampling methodologies, the use of gravimetric sampling provides a single value representing the full sampling period, which in the case of low levels may be of quite long duration. The synchronous application of continuous recording may produce helpful information about eventual fluctuations or uniformity of PM exposure. For this reason, continuous recording devices should be used in addition to air samplers in order to reveal and rule out artefact anomalies.

This review of the literature confirms that the use of $PM_{2.5}$ as an indicator of occupational exposure to PM in urban workers is still very limited. Even if epidemiological studies can demonstrate associations between all PM fractions and health endpoints, a WHO Working Group recently stated: "There is strong evidence to conclude that fine particles (<2.5 μm) are more hazardous than larger ones (coarse particles) in terms of mortality and cardiovascular and respiratory endpoints in panel studies" (WHO 2003). Future studies should therefore focus particularly on the assessment of urban $PM_{2.5}$ levels in workers occupationally exposed to this type of particulate. Moreover, to our knowledge, almost all of the studies that have investigated occupational exposure to $PM_{2.5}$ in urban workers have been performed on professional drivers. However, $PM_{2.5}$ exposure in these workers, who spend the majority of their working time in specific microenvironments, may be influenced by a number of variables such as the re-suspension of dust from the vehicle floor or the presence and efficiency of air conditioning systems. Consequently, in future it would be better to assess $PM_{2.5}$ exposure also in the categories of outdoor urban workers such as policemen, traffic and parking wardens, roadside vendors, street sweepers and postal workers who usually work near roadways. In conclusion, to our knowledge there are very few studies that have evaluated UFP exposure in urban workers. Data provided by the WHO indicate that there is also an urgent need to investigate this fraction of PM in exposed workers in order to assess current levels of exposure and eventual correlations with adverse health effects in these job categories.

The biological monitoring of urban PM is rather complicated and very difficult to achieve because PM is a complex chemical mixture and because the general population or urban workers are usually simultaneously exposed to different xenobiotics. Even if numerous occupational studies have carried out the biological monitoring of the chemical components of PM, only a few studies conducted by Iavicoli et al. (2004, 2007, 2008a, b) have provided details of the levels of some metals in PM_{10} or $PM_{2.5}$. This has inevitably limited interpretation of the biological monitoring results and has failed to establish a correlation between the biological levels of these chemicals and occupational exposure to urban PM. In order to assess this essential link, future studies must perform both biological monitoring and measurement of the same xenobiotics in the different PM fractions.

Furthermore, studies on the presence of adverse health effects in these groups of urban workers should follow the same pattern. In fact, during the 1990s PM toxicity was mostly related to size, and variations in composition were considered less important. Nevertheless, recently many publications have indicated that chemical composition plays a very important role in particle toxicity (Alfaro-Moreno et al. 2007). As regards health effects related to PM exposure and observed in urban workers, it should be noted that very few studies correlated health outcomes with personal exposure to PM, whilst most of the studies took into account the ambient PM levels recorded by fixed air monitoring stations in various cities. However, we have already stressed the fact that these data are not indicative of the roadside exposure to which urban workers are constantly exposed. Thus, in order to make a correct assessment of a possible causal link between exposure to PM and adverse health effects in these workers, studies must be carried out to assess the real exposure of these groups through personal samplings.

A correct interpretation of the data relative to the PM exposure health effects, particularly on the cardiovascular system, in urban workers should take carefully in consideration important possible confounders like road traffic noise. Recent published studies support the hypothesis that long-term exposure to road traffic noise could increase the risk for ischaemic heart disease, including myocardial infarction (Babisch 2006, 2008; Selander et al. 2009). With respect to traffic noise and hypertension, data are contrasting (Babisch 2006). However, recent studies showed a positive association between road traffic noise and hypertension even if results were mixed with respect to effect size (Leon Bluhm et al. 2007; Selander et al. 2009), effects among males and females (Barregard et al. 2009; Björk et al. 2006) and with respect to effects across age groups (de Kluizenaar et al. 2007; Bodin et al. 2009). Currently, there is much discussion about how noise can affect human health and well-being (van Kempen et al. 2002). The suggested effect mechanism of noise is based on the general stress concept (Beelen et al. 2009), in fact several studies demonstrated that traffic noise as a stressor could cause discomfort, sleep disorders and can disturb daily-live activities (Evans 2001; Ising and Kruppa 2007; Maschke and Hecht 2007; Griefahn et al. 2008; Michaud et al. 2008; Wagner et al. 2010). From the studies previously reviewed, it emerges clearly that future research, would mostly clarify the real role of the occupational exposure to urban airborne PM in causing cardiovascular effects.

In conclusion, the literature help us to identify the categories of workers most heavily exposed to urban PM, but epidemiological studies should be performed to assess the frequency and incidence of respiratory and cardiovascular diseases.

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Health Risks of Urban Airborne Particles

Andreas D. Kappos

1 Introduction

Adverse health effects of ambient airborne particles are of major concern to environmental health regulators. In recent years a tremendous amount of research on health effects of airborne particles has been published and evidence is well established, that even small concentrations of fine particles in air breathed by humans contribute significantly to their morbidity and mortality. These data prompted the European Parliament and Council to strengthen the limit values for particular matter with their new directive 2008/50/EC of 21 May 2008 on ambient air quality and cleaner air for Europe.

Extended reviews of the scientific evidence collected so far have been published amongst others by the World Health Organization (WHO-Europe 2005) and by the US Environmental Protection Agency (US-EPA 2004). A more recent review by the latter is in the process of external reviewing (US-EPA 2008[1]). This chapter draws extensively from these comprehensive syntheses.

Most evidence about the effects of airborne particular matter on human health has been produced by epidemiology. Additionally laboratory studies have been published, that involved both animals and human volunteers using concentrated ambient particles (CAPs). Toxicological studies on animals using instilled particles in high concentrations complete our knowledge on health effects of particular

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[1] A second external review paper is available since May 2009 via Internet: http://oaspub.epa.gov/eims/eimscomm.getfile?p_download_id=491199. Accessed Oct 12, 2009.

F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_27,

matter (PM). The toxicological evidence is complementary to the observational findings of epidemiological studies, providing the framework for assessing the biological plausibility of epidemiologically observed associations.

Epidemiological and clinical studies have linked particular matter (PM) to the following adverse health effects (WHO-Europe 2005):

- Mortality and hospital admission in patients with chronic obstructive pulmonary disease (COPD) or cardiovascular diseases (CVD)
- Exacerbation of symptoms and increased use of therapy in asthma
- Mortality and hospital admission in diabetes mellitus
- Increased risk for myocardial infarction
- Development of atherosclerosis
- Increased incidence of infection
- Increased risk for lung cancer.

In this chapter only effects of major relevance for public health will concisely be reviewed. For more details and completeness refer to the comprehensive reviews mentioned above.

2 Deposition of Airborne Particles in the Respiratory Tract

Airborne particles in order to have an effect on human health have to come into contact with cells and tissues of the human body. The main route of intake is inhalation. To a certain amount inhaled particles will be deposited at the surface of the extra- and intra-thoracic airways and in the alveoli of the lung. The amount and site of deposition depends on the aerodynamic and thermodynamic properties of the particles inhaled, particularly on their size and shape. On the contrary the interaction of the particle with the cells and tissues of the body is determined by its physical, chemical and biological properties. During their passage through the airways small hydrophilic particles adsorb immediately water vapour and grow significantly in size.

The probability of deposition and retention of particles at the surface of the different parts of the respiratory tract depends on their physical properties but also on the breathing pattern at inhalation and on the anatomic features of the respiratory tract. Figure 1 illustrates schematically the airway anatomy with distal progression into the lower respiratory tract. Natural growth in childhood, age and thoracic diseases, like asthma or chronic obstructive bronchitis, may influence the anatomy of the respiratory tract and as a consequence the deposition and retention of inhaled particles. In a healthy adult breathing through the mouth most of the larger particles with an aerodynamic diameter of more than 5 μm are deposited in the extra-thoracic airways (mouth, larynx and pharynx) and the large bronchi. Smaller particles reach the periphery of the lung where they might settle at the surface of the small bronchi, the respiratory bronchioli and the alveoli. Breathing through the nose notably changes the deposition pattern. The nose filters most of the particles larger

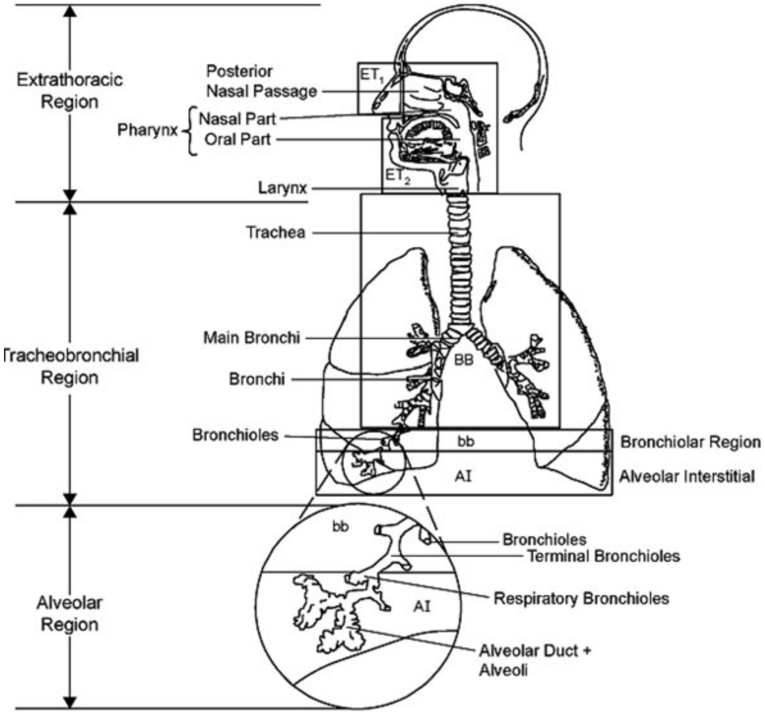

Fig. 1 Schematic depiction of the human respiratory tract (based on ICRP 1994; US-EPA 2004). *ET*$_1$ anterior nasal passages, *ET*$_2$ oral airway and posterior nasal passages, *BB* bronchi, *bb* bronchioli, *Al* alveoli

than 2.5 µm and a relevant part of the particles with an aerodynamic diameter of 1–2.5 µm and in this way fewer particles of those sizes reach the deeper regions of the lung reducing the exposure of the bronchioli and alveoli (Heyder et al. 1986).

Figure 2 shows the deposition of particles of different sizes in the various regions of the respiratory tract during quiet breathing. The data presented in Fig. 2 are calculated on the basis of a theoretical model developed by the International Commission on Radiation Protection (ICRP 1994). It takes into account that particle deposition in the lung is predominantly governed by three physical processes: impaction, sedimentation and diffusion. The model reproduces quite well the available experimental data[2]. The efficiency of deposition in the respiratory tract may generally be described as a “U-shaped” curve on a plot of deposition efficiency versus the of log particle diameter as in Fig. 2. Total deposition shows a minimum for particle diameters in the range of 0.1 to 1.0 µm, where particles are small enough to have minimal sedimentation or impaction and sufficiently large so

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[2] For a detailed discussion of the model and its limitations refer to the original ICRP-report or to US-EPA (2004).

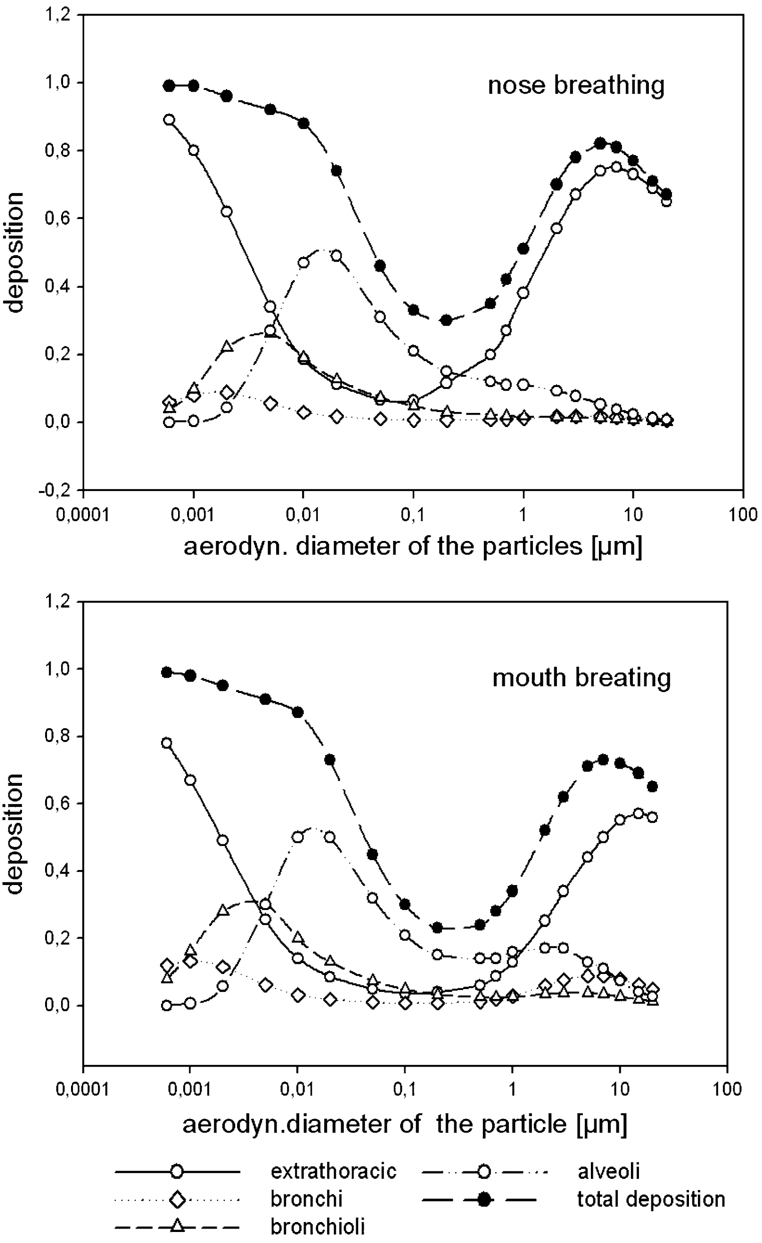


Fig. 2 Total and regional deposition of particles in the respiratory tract dependent on log particle size (aerodynamic diameter) during quite breathing of an healthy individual (based on ICRP 1994)

as to have minimal diffusive deposition. Total deposition does not decrease to zero for any sized particle because of mixing between particle laden tidal air and residual lung air. The particles mixed into residual air remain in the lung following a breath and are removed on subsequent breaths or gradually deposited. Total deposition of ultrafine particle increases with falling diameter nearly up to 100 % due to their rising diffusivity (see left side of Fig. 2). In contrary alveolar deposition exhibits a maximum at approximately 20 nm. Yet smaller particles settle increasingly in the upper airways due to their specific diffusion characteristics and will not reach the periphery of the lung anymore.

In the various regions of the respiratory tract different physiological mechanisms exist to remove foreign material. In the extra-thoracic airways, the trachea and the bronchi there is a thick liquid lining and the synchronous movement of microscopic hairy cila at the surface of the bronchial epithelial cells rapidly moves deposited particles toward the larynx, where they are swallowed (mucociliary clearance). Normally this takes 1–3 days. Only highly soluble material moving from the air into the liquid layer will have systemic access via the blood.

With distal progression, the protective liquid lining diminishes and clearance rates slow down. Soluble compounds as well as some poorly soluble ultrafine particles may cross the air–liquid interface to enter the tissues and the blood especially in the alveolar region. Depending on the solubility of the particle retention may take years. Alveolar clearance is not a linear process and half live increases with the elimination time.

Macrophages on the alveolar epithelium may recognize foreign particles and phagocyte them, determining their further kinetic fate. Phagocytosis is rather effective for particles between 0.3 and 5 μm with an optimal rate for particles of 1–2 μm. The removal rate is much slower for smaller particles (overview in WHO-Europe 1997). If the macrophage moves toward the bronchi, the particle will be removed by the mucociliar clearance. During one year approximately one third of insoluble particles in the human alveoli will be removed by this way (Kreyling et al. 1990). The remaining two thirds stay on the alveolar epithelium or are kept in the interstitial space of the lung, under the pleura or in the lymphatic system of the thorax. According to their larger number ultra fine particles are distributed more evenly on the epithelium of the alveoli than larger particles. Ultra fine particles are less frequently phagocytized by alveolar macrophages and are present as well in the epithelium as in the interstitial lung tissue (Ferin et al. 1992). The incorporated particles may stay there or be transported toward the connective tissue or in to the bloodstream.

3 Short-Term Effects of Airborne Particles on Human Health

Most of the current body of evidence about short-term effect of particulate air pollution arises from epidemiological studies examining the association between exposure to airborne particular matter (PM) of various size fractions (e.g. PM_{10}, $PM_{2.5}$ or ultra fine particles) and the health effect in question or outcome (e.g. various symptoms or diseases, medication use, hospital admissions or visits to an emergency department, additional deaths). The methods used include time series studies, "panel studies" or short-term cohort studies of susceptible groups, and cross-sectional studies. In time-series analysis the investigators observe the health indicator (e.g. the daily number of death) in a city or region and correlate them with the simultaneous registered indicator of the concentration of PM at the same location. An other type of studies follows a panel of selected subjects (e.g. asthmatic children or patients with chronic obstructive bronchitis) over a certain time period and evaluate the health indicator of interest (e.g. daily deaths, hospital admissions, lung function and/or respiratory symptom) in relation to changes in ambient PM. In some recent studies the risk for acute events, including myocardial infarction and stroke, has been assessed using the case-crossover design. In this design, the individual bearing the event is the unit of analysis and exposures are compared in the "case" period during which the event of interest took place and in one or more matching event-free "control" periods. The time series analysis study designs applied aim to disentangle the PM-health effect through complex modeling, the case crossover design by appropriate matching strategies.

3.1 Short-Term Mortality

Various health effects have been reported from short-term studies. Increased mortality associated with short-term exposure is the most important health outcome in these studies. A multiplicity of studies from various settings in the US, Canada and Europe attest the association of different metrics of particular matter (PM_{10}, $PM_{2.5}$, $PM_{10–2.5}$ or ultrafine particles) with general and cause specific human mortality. In the first line are daily time series studies from single cities (e.g. Schwartz 1991). More relevant are analyses that pool data from several locations, using a common protocol for analysis of the within-city data and then combining estimates from various locations in order to gain precision and to evaluate the heterogeneity of the effect of particulate matter across the cities.

The APHEA (Air Pollution and Health—An European Approach) project studied air-pollution effects in 15 and later with the APHEA 2 project in 34 European cities (Katsouyanni et al. 1995, 1997, 2001). The NMMAPS (National Morbidity, Mortality, and Air Pollution Study) project in the United States focused on time-series analyses of PM_{10} effects on mortality during 1987–1994 in the 90 largest US cities (Samet et al. 2000a, b, c), and in the 20 largest US cities in more detail (Dominici et al. 2000a, b). These data have been summarized in the US-EPA's particulate matter criteria document (US-EPA 2004) and in a met analysis carried out by a WHO-Europe task group (Anderson et al. 2004).

The WHO task group used the updated estimates for those studies with reanalyzed data. Estimates of the effect of PM_{10} on all-cause mortality were taken from 33 separate European cities or regions. The summary relative risks of all cause deaths, deaths from cardiovascular and from respiratory causes for these 33 results is shown in Fig. 3. 21 of theses estimates were taken from the APHEA 2 study (Katsouyanni et al. 2001) and hence the summary estimate derived from this review is dominated by this multicity study. There were no cause specific mortality data available from the APHEA project at the time of met analysis and the summary risk estimate for cause specific mortality was calculated on the basis of 17 multicity studies mainly conducted in France, Italy and Spain. Therefore care has to be taken interpreting the differences in the risk estimates. The estimates for all-cause mortality and cause-specific mortality taken from European studies are comparable to those reported from the NMMAPS based upon the 20 largest cities in the United States (Samet et al. 2000a) (Fig. 3). Air pollution risk estimates were relatively robust to different modeling approaches (Samoli et al. 2008).

All-cause mortality associated to $PM_{2.5}$ were reported only in three studies from Erfurt, Germany (Wichmann et al. 2000), the Czech Republic (Peters et al. 2000) and the West Midlands conurbation in the United Kingdom (Anderson et al. 2001). Evidence from Europe of an effect of fine particles on daily mortality is therefore sparse. Of the five estimates from three studies available, none showed a statistically significant positive association and one was significantly negative. The risk

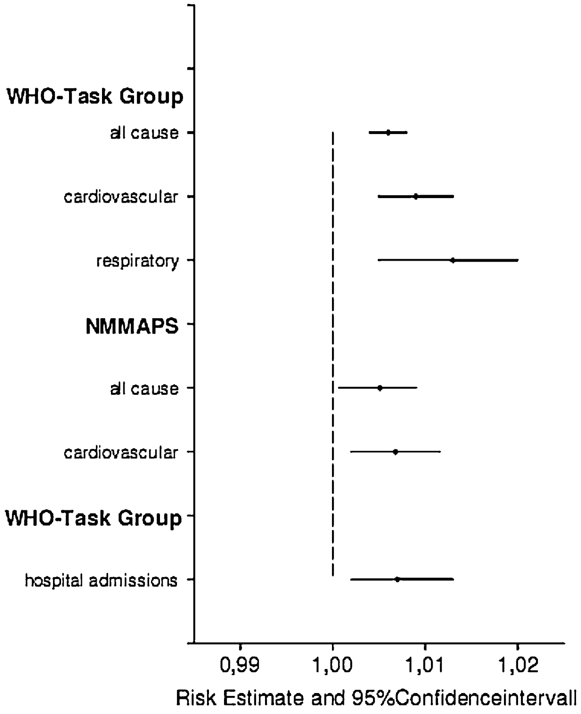


Fig. 3 Risk estimates of short-term mortality for a 10 μg/m^3 increase of PM_{10} from WHO-Task Group (Anderson et al. 2004) and US-National morbidity, Mortality, and Air Pollution Study—NMMAPS (Samet et al. 2000b)

estimates for North American cities were larger than those for Europe and their summary estimates were statistically significant, the cause-specific mortality for respiratory diseases being larger then the mortality for cardiovascular diseases or all-cause mortality (US-EPA 2008).

An analysis of the lag structures (time lag between change in concentration of PM and death) used in the studies found that the greatest effects were observed at lag 1 or lag 0–1 day, and the use of a distributed lag model resulted in slightly larger (by ~30%) risk estimates compared to single-day lags (Zeka et al. 2005).

It has been considered, that the associations between PM and daily mortality observed in the time series studies could reflect only a brief advance in the time of death, perhaps among those already frail because of underlying heart and lung disease. This possibility, referred to as "harvesting", implies that the associations observed in the daily time series studies are not indicating an effect of public health significance. Analytical approaches to assess the extent of "harvesting" have been developed and their results indicate that any advance of the time of death caused by PM is more than just a few days (Zeger et al. 1999; Schwartz 2000).

3.2 Short-Term Respiratory Morbidity

A great variety of epidemiological studies investigated the association of different indicators of respiratory health with particulate mater (US-EPA 2004) specifically in asthmatic children (Roemer et al. 2000).

3.2.1 Deterioration of Respiratory Disease

Investigators discovered significant associations of PM_{10} and to a lesser extent of $PM_{2.5}$ and $PM_{10-2.5}$ with hospital admissions for pneumonia (Ito 2003), for chronic obstructive pulmonary disease (Zanobetti and Schwartz 2003; Moolgavkar 2003), for asthma (Nauenberg and Basu 1999; Sheppard 2003) and general for all respiratory diseases (Burnett et al. 1997). Significant associations of PM with exacerbations and emergency department visits for asthma (Choudhury et al. 1997; Sheppard 2003) and for respiratory diseases in general (Stieb et al. 2000; Burnett et al. 1997) were also reported.

According to the WHO-met analysis (Anderson et al. 2004) the risk for hospital admissions with respiratory diseases in individuals age 65 years and older for a 10 µg/m^3 increase in PM_{10} increased by 0.7% (see Fig. 3) based upon 8 estimates mostly provided by the APHEA 2 project (Atkinson et al. 2001). A re-analysis of the APHEA 2 data confirmed the robustness of the original results (HEI 2003b). For the other two age categories, ages 0–14 and 15–64 years, the met analysis indicated a trend of increased frequency for hospital admission, which was not significant. For fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) particles only the West Midlands study (Anderson et al. 2001) provided results for the respiratory hospital admissions. There was a trend for an association of hospital admissions in the youngest age group with $PM_{2.5}$, but it was not statistically significant too.

3.2.2 Lung Function and Respiratory Symptoms

Numerous studies report short-term PM exposure effects on lung function and respiratory symptoms. Lung function was usually measured daily, both in the morning and afternoon. Most studies included forced expiratory volume in one second (FEV_1), forced vital capacity (FVC) and peak expiratory flow rate (PEF), which are indicators of bronchial obstruction. Additionally various respiratory symptoms were registered, including cough, phlegm, difficulty breathing, wheeze, and medication use. Detailed summaries of these studies are presented in US-EPA (2004).

The results for asthmatic children tend to show small decrements of lung function associated with PM_{10} and $PM_{2.5}$ as seen in studies by Gielen et al. (1997), Peters et al. (1997), and Pekkanen et al. (1997). For PM_{10}, the available point estimates for morning PEF showed decreases lagged one day, but the majority of the studies were not statistically significant. PM_{10} and $PM_{2.5}$ both appear to affect lung function in asthmatics, but there is only limited evidence for a stronger effect of fine versus coarse fraction particles; ultrafine particles do not appear to have any notably stronger effect than other larger-diameter fine particles. Of the studies provided, few if any analyses were able to clearly separate out the effects of PM from other coexisting pollutants.

The effects of PM_{10} on respiratory symptoms in asthmatics tended to be positive, although they are somewhat less consistent than PM_{10} effects on lung function. Most studies showed increases in cough, phlegm, difficulty breathing, and bronchodilator use, although these increases were generally not statistically significant for PM_{10}. For example, Vedal et al. (1998) reported that increases in PM_{10} were associated with increased reporting of cough, phlegm production, and sore throat. Children with diagnosed asthma were more susceptible to the effects than were healthy children. Similarly Gielen et al. (1997) studied a panel of children, most of whom had asthma. Low levels of PM increased symptoms and medication use. Ostro et al. (2001) studied a panel of inner-city African American children using a model with several measures of PM, including PM_{10} (both 24-h average and 1-h max.) and $PM_{2.5}$, demonstrating positive associations with daily probability of shortness of breath, wheeze, and cough.

The effects on respiratory symptoms in non-asthmatics were similar to those in asthmatics. Most studies showed that PM_{10} increases cough, phlegm, difficulty breathing, although these were generally not statistically significant. Vedal et al. (1998) reported no consistent evidence for adverse health effects in their non-asthmatic control group.

Several recent panel studies conducted in Europe have examined effects of daily exposures to air pollution on adults with asthma, chronic bronchitis or cardiovascular diseases. As part of the multicenter ULTRA (Exposure and Risk Assessment for Fine and Ultrafine Particles in Ambient Air) study (de Hartog et al. 2003) enrolled 131 older adults with coronary artery disease in three cities [Amsterdam, Erfurt (Germany), and Helsinki]. Pooling data from all three cities, significant associations were observed between $PM_{2.5}$ and shortness of breath and phlegm. In a study from Erfurt, Germany (von Klot et al. 2002), examined daily, winter time exposure to ambient $PM_{10–2.5}$, $PM_{2.5–0.01}$ and $PM_{0.1–0.01}$ and respiratory health effects in 53 adult asthmatics. The authors examined associations between wheeze, use of inhaled short-acting β_2-agonists or inhaled corticosteroids and exposure to particles in single and multipollutant models. Particle exposure metrics examined included same-day, 5-day and 14-day averages. No significant effects were observed for wheeze and exposure to $PM_{10–2.5}$ or $PM_{2.5–0.01}$ for any averaging time. The strongest association between wheeze and exposure to ultrafine particles was for a 14-day average: each 7,700 increase in the number count (NC) increased the risk of wheeze by 27% (RR 1.27, 95% CI: 1.13–1.43). The effect was attenuated in co pollutant models that also included $PM_{2.5–0.01}$.

In Paris, Segala et al. (2004) recruited 78 adults from an otolaryngology clinic and followed them for three months. Both PM_{10} and Black Smoke [which were very highly correlated ($r = .88$)] were associated with cough. Also in Paris, 60 severe asthmatics were followed for 13 months and the relationship between daily air quality (including 24-h PM_{10} as measured at the site nearest to the subject's home) and asthma attack (defined as the need to increase rescue medication use and one or more positive signs of obstruction on clinical examination) were examined (Desqueyroux et al. 2002). Each 10 $\mu g/m^3$ increase in PM_{10} increased the risk of asthma attack, but only after lags of 3 to 5 days. Boezen et al. (2005) enrolled 327 elderly adults in the Netherlands. For subjects with both airways hyperreagibility and high total immunoglobulin E ($IgE > 20$ kU/L) an indicator of atopic disposition, each 10 $\mu g/m^3$ increase of PM_{10} was significantly associated with an increased risk of upper respiratory symptoms for males and cough for females with different lags. The strongest association in both cases was for the 5-day mean. The authors suggest that the sex differences of the lag observed may be explained by differential daily exposure to traffic exhaust experienced by men compared to women.

3.3 Short-Term Cardiovascular Morbidity

Surprisingly a number of epidemiology studies in the early nineties showed associations between ambient particulate matter and increases in cardiac-related deaths and/or morbidity indicators and that the risk of PM-related cardiac effects may be so great or greater than those attributed to respiratory causes. These effects appear to be induced via direct particle uptake into the blood and/or via mediation by the nervous system. Such effects may be especially deleterious to individuals compromised by diseases such as ischemic heart disease, cardiac arrhythmias, and chronic obstructive pulmonary disease (COPD).

3.3.1 Hospital Admissions

The US-EPA-Air Quality criteria document (US-EPA 2004) quotes more than twenty studies relating daily hospitalizations with primary discharge diagnoses of cardiovascular diseases (CVD) to the effect of urban particulate matter. The NMMAPS study evaluated the effect of daily changes in ambient PM levels on total CVD hospitalizations among elderly Medicare beneficiaries in 14 US cities and found a $\sim 1\%$ excess risk per 10 $\mu g/m^3$ increase in PM_{10} (Samet et al. 2000b; Zanobetti and Schwartz 2003). Recent large studies conducted in the US (Dominici et al. 2006; Bell et al. 2008) and Europe (Host et al. 2008; von Klot et al. 2005) have confirmed these findings for PM_{10}, and have also observed consistent associations between $PM_{2.5}$ and cardiovascular hospitalizations. It is apparent from these studies that the observed increases in cardiovascular hospitalizations are largely due to admissions for ischemic heart disease and congestive heart failure rather than for stroke.

3.3.2 Heart Rate, Heart Rate Variability, Arrhythmia, Blood Pressure

Heart rate (HR), heart rate variability and blood pressure are regulated, in part, by the sympathetic and parasympathetic nervous systems. Changes in one or more may increase the risk of cardiovascular events (e.g. arrhythmias, myocardial infarction). Decreases in heart rate variability have been associated with cardiovascular mortality/morbidity in older adults and those with significant heart disease. Fine particles in ambient concentrations have recently been implicated in decreases of heart rate variability (Timonen et al. 2006), increased risk of arrhythmias (Metzger et al. 2004; Lanki et al. 2006) and increased blood pressure (Timonen et al. 2006) in particular in older subject with compromised health. Additionally inhaled particles seem to enhance blood coagulation (Rückerl et al. 2007a, b).

4 Long-Term Effects of Airborne Particles on Human Health

4.1 Mortality

Long-term exposure to urban airborne particles over many years or decades implies serious consequences for human health. These include shorter life expectancy caused by higher mortality for cardiovascular diseases and lung cancer as well as increased infant mortality in polluted regions. The influence of PM on human mortality was investigated by several large and expensive cohort studies first published in the late eighties and nineties of the last century. Most of our knowledge is based on these. They were supplemented and extended by more recent studies and the data reanalysed with more sophisticated modelling.

The Harvard Six Cities Study (HSC) (Dockery et al. 1993) monitored approximately 8,000 adults over 14–16 years in six US-Cities with varying air pollution. The study investigated the influence of TSP, $PM_{2.5}$, SO_4^-, H^+, SO_2 and ozone on different health indicators. The strongest association of mortality was found with sulfate and $PM_{2.5}$. In the city with the highest $PM_{2.5}$ the mortality exceeded the mortality in the city with the lowest $PM_{2.5}$ by 26%. The results were confirmed by reanalysis of the data (Krewski et al. 2000). Laden et al. (2006) studied the effect of improvements in particle exposure with the methodology oft the HSC. They extended the mortality follow-up for 8 years in a period of reduced air pollution concentrations. From their data they found a decrease in overall mortality, cardiovascular and lung cancer deaths associated with decrease in $PM_{2.5}$ modelled either as the overall mean or as exposure in the year of death.

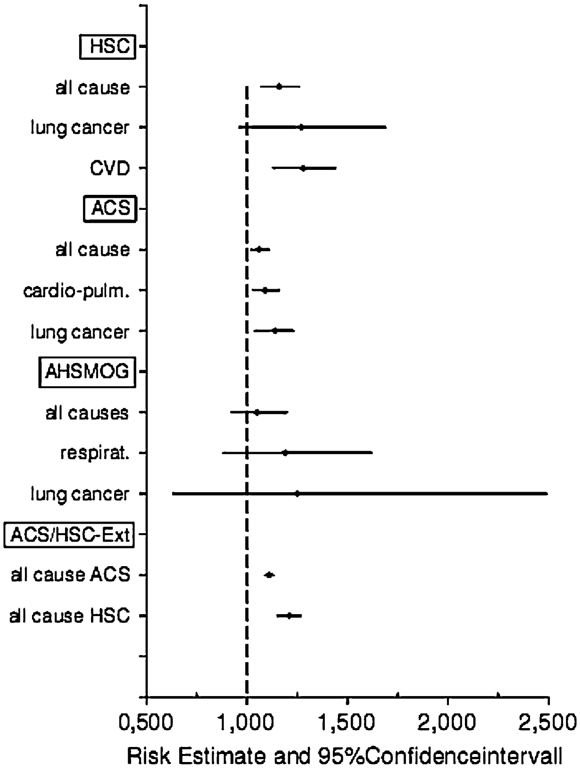
The Study of the American Cancer Society (ACS) (Pope et al. 1995) included approximately 550,000 adults in 154 North American cities for a time period of 8 years, later extended to 16 years of follow up (Pope et al. 2002). An association of mortality with sulfate was found but where measurements of $PM_{2.5}$ were available, this parameter exhibited the strongest association with mortality. These data were extended with better PM-data and reanalyzed by Krewski et al. (2005).

Eftim et al. (2008) extended the HSC and ACS studies using US-Medicare data for the period 2000–2002. They assessed the association of $PM_{2.5}$ with mortality for the same locations included in the HSC and ACS studies. The adjusted risk estimates are somewhat higher than those reported by the original investigators (Fig. 4).

The Adventist Health Study of Smog (AHSMOG) (Abbey et al. 1999; McDonnell et al. 2000) included 1977 6300 non-smoking white Seventh Day Adventists age 27–95 years living in California. Mortality was followed up 15 years. PM_{10} showed a strong association with mortality for any mention of non-malignant respiratory disease or lung cancer on the death certificate, adjusting for a wide range of potentially confounding factors, including occupational and indoor sources of air pollutants. The risk estimates for a change in $PM_{2.5}$ of 10 μg/m^3 of the three US long-term studies cited above are depicted in Fig. 4.

The Veterans' Administration Cohort Mortality Study (VA) (Lipfert et al. 2000) studied 70,000 men with light to medium elevated blood pressure and age 39–63. The investigators did not find any significant correlation of mortality with any PM-metric. $PM_{2.5}$ exhibited a negative association with mortality. On the contrary a positive, consistent and significant association with ambient concentrations of NO_2 and ozone was found.

Fig. 4 Risk estimates for long-term mortality associated with a 10 μg/m^3 increase in $PM_{2.5}$ HSC refers to the extended Harvard Six Cities Study (Laden et al. 2006), ACS to the American Cancer Society Study (Pope et al. 2002), AHSMOG to the Adventist Health Study of Smog (McDonnell et al. 2000) and ACS/HSC Ext to the extended study of Eftim et al. (2008) at the same locations as ACS and HSC. *CVD* death caused by cardiovascular disease



In the Dutch Traffic Cohort Study (NL) (Hoek et al. 2002; Beelen et al. 2008) cardio-pulmonary mortality was significantly associated with living near a major road (relative risk 1.95, 95% CI: 1.09–3.52). Total deaths and lung cancer were not significantly associated with traffic exposure (RR 1.41, 95% CI: 0.94–2.12 and RR 1.03, 95% CI 0.88–1.20 respectively).

The Nurses' Health Study (Puett et al. 2008) examined the association of chronic particulate exposures with all-cause mortality, incident nonfatal myocardial infarction, and fatal coronary heart disease (CHD) in a prospective cohort of 66,250 women from the Nurses' Health Study in north-eastern US metropolitan areas. In an age- and season-of-the-year-adjusted models, 10 μg/m^3 increases in 12-month average exposures to PM_{10} were associated with increased all-cause mortality (RR 1.16, 95% CI: 1.05–1.28) and fatal CHD (1.43, 95% CI: 1.10–1.86).

The North Rhine-Westphalia State Environment Agency studied a cohort of approximately 4800 women and assessed whether long-term exposure to air pollution originating from motorized traffic and industrial sources was associated with total and cause-specific mortality (Gehring et al. 2006). Cardiopulmonary mortality was associated with living within a 50-meter radius of a major road (adjusted RR = 1.70; 95% CI: 1.02–2.81), and with PM_{10} concentrations calculated from air monitoring station data (RR = 1.52 [95% CI: 1.09–2.15] per 10 μg/m^3 PM_{10}).

In spite of some inconsistencies in the relative strength of the associations of mortality with fine ($PM_{2.5}$) or coarse (PM_{10}) particles and the negative results of the VA study the overwhelming evidence speaks for an causal relationship of long lasting exposure to respirable airborne urban particles and premature deaths specifically deaths due to cardiopulmonary diseases or lung cancer. The evidence for increased number of CVD deaths is much stronger than for lung cancer.

4.2 Cardiovascular Effects of Long-Term Exposure to Airborne Particles

Künzli et al. (2005) were the first to report an association of an indicator of atherosclerosis with $PM_{2.5}$. They used data on 798 participants from two clinical trials to investigate the association between atherosclerosis and long-term exposure to ambient $PM_{2.5}$. For a cross-sectional exposure contrast of 10 μg/m^3 $PM_{2.5}$, the atherosclerosis indicator used in the study (carotid intima-media thickness or CIMT) increased by 5.9% (95% CI: 1–11%). Several recent studies showed comparable results with other indicators of atherosclerosis (Diez Roux et al. 2008; Hoffmann et al. 2007).

Zanobetti and Schwartz (2007) studied 196,000 persons from 21 US cities discharged alive following an acute myocardial infarction (MI), using within-city between-year exposure to PM. They constructed city-specific cohorts of survivors of acute MI using Medicare data between 1985 and 1999, and defined three outcomes on follow-up: death, subsequent MI, and a first admission for congestive heart failure. Yearly averages of PM_{10} were merged to the individual annual follow-up in each city. Significant associations were found with adjusted risk of 1.3 [95% CI: 1.2–1.5] for mortality, of 1.4 (95% CI: 1.2–1.7) for a hospitalization for congestive heart failure, and of 1.4 (95% CI: 1.1–1.8) for a new hospitalization for myocardial infarction per 10 μg/m^3 PM_{10}.

Baccarelli et al. (2008) studied in a case–control study 870 patients with deep vein thrombosis (DVT) and 1210 healthy controls from the Lombardy region in Italy, who were examined between 1995 and 2005. They estimated exposure to PM_{10} in the year before DVT diagnosis (cases) or examination (controls) through area-specific mean levels obtained from ambient monitors. Each increase of 10 μg/m^3 in PM_{10} was associated with a 70% increase in DVT risk (OR 1.70; 95% CI: 1.30–2.23).

Miller et al. (2007) examined the association of long-term exposure to particulate $PM_{2.5}$ with cardiovascular events. They studied 65,893 postmenopausal women without previous cardiovascular disease in 36 US metropolitan areas from 1994 to 1998, with a median follow-up of 6 years and assessed the women's exposure to air pollutants using the monitor located nearest to each woman's residence. 1816 women had one or more fatal or nonfatal cardiovascular events, including death from coronary heart disease or cerebro-vascular disease, coronary revascularization, myocardial infarction, and stroke. Each increase of 10 μg/m^3 PM$_{2.5}$ was associated with a 24% increase in the risk of a cardiovascular event (CI: 9–41%) and a 76% increase in the risk of death from cardiovascular disease (95% CI: 25–147%). The risk of cerebro-vascular events was also associated with increased levels of PM$_{2.5}$ (OR 1.35; 95% CI: 1.08–1.68).

Hoffmann et al. (2006) studied the relationship between the long-term residential exposure to traffic and prevalence of coronary heart disease (CHD). For 3,399 participants from two German cities they assessed the long-term personal traffic exposure and background air pollution, comparing residents living within 150 m of major roads with those living further away. The principal outcome variable studied was clinically manifest coronary heart disease (CHD). 242 (7.1%) had CHD. The odds ratio (OR) of CHD after adjusting for cardiovascular risk factors and background air pollution at high traffic exposure was significantly elevated (OR 1.85, 95% CI 1.21–2.84). Subgroup analysis showed stronger effects for men (OR 2.33, 95% CI 1.44–3.78), participants younger than 60 years (OR 2.67, 95% CI 1.24–5.74) and never-smokers (OR 2.72, 95% CI 1.40–5.29).

4.3 Respiratory Effects of Long-Term Exposure to Airborne Particles

Children living in communities with higher particulate air pollution exhibit higher frequencies of respiratory symptoms and bronchitis (McConnell et al. 1999); specifically children with asthma (McConnell et al. 2003). Declining levels of PM$_{10}$ in Switzerland were associated with declining prevalence of chronic cough, bronchitis, common cold, nocturnal dry cough, and conjunctivitis symptoms in school children (Bayer-Oglesby et al. 2005). Brauer et al. (2007) assessed the development of asthma, allergic symptoms, and respiratory infection in relation to long-term traffic related air pollution at the home address. PM$_{2.5}$ was associated with doctor-diagnosed asthma, respiratory infections and some measures of allergy during the first 4 years of life.

Longitudinal cohort studies have evaluated the relationship between long-term exposure to PM and changes in measures of pulmonary function (FVC and FEV$_1$, and measures of expiratory flow). Lung function increases in healthy subjects continually from infancy to early adulthood with growth and development, then declines with aging. Within the Children's Health Study of 1,600 Californian school children (Gauderman et al. 2002) found that the estimated growth rate for children in the most polluted communities as compared with the least polluted was reduced: 3.4% for the FEV$_1$ (forced expiratory volume in 1 s) and by 5.0% for MMEF (maximal midexpiratory flow) over the 4-year study period. The estimated deficits were generally larger for children spending more time outdoors.

Nordling et al. (2008) examined the relationship between estimated PM exposure levels and respiratory health in a Swedish birth cohort ($n = 4{,}089$) of preschool children. Persistent wheezing (cumulative incidence up to age 4) was associated with exposure to traffic-generated PM_{10} (OR 2.28, 95% CI: 0.84–6.24 per 10 $\mu g/m^3$ increase). Peak expiratory flow (PEF) at age 4 was associated with exposure to traffic-PM_{10} too. PEF was 8.93 L/min lower in children with the higher PM exposure [95% CI: -17.78 to -0.088].

Gotschi et al. (2008) examined the relationship between air pollution and lung function in adults within the European Community Respiratory Health Survey (ECRHS). FEV_1 and FVC were assessed at baseline and after 9 years of follow-up from 21 European centers (followed-up sample $n = 5610$). $PM_{2.5}$ was measured in 2000–2001 using central monitors. Despite sufficient statistical power no significant associations were found between city-specific annual mean $PM_{2.5}$ and average lung function levels in adults.

4.4 Lung Cancer

A limited number of epidemiologic studies evaluated associations between long-term exposure to PM and the incidence of cancer. Though several studies have reported an association between lung cancer mortality and long-term PM exposure (e.g. Dockery et al. 1993; Beelen et al. 2008), the single study that looked at lung cancer incidence found no association with $PM_{2.5}$ (Beelen et al. 2008). There are known constituents of PM that have varying levels of toxicity, including some that have been classified as possible or probable carcinogens. An epidemiologic study looked at PM (using TSP as a surrogate for PAHs) and found a positive association (Bonner et al. 2005). Overall, there is limited evidence available to evaluate the relationship between relevant PM exposures and cancer incidence.

4.5 Low Birth Weight

Parker et al. (2005) investigated the associations between birth weight and air pollution among full-term infants in California. They found a significantly increased odds ratio of neonates small for gestational age and a small difference in birth weight with increased $PM_{2.5}$ at mother's residence at pregnancy after controlling for CO. Similar results were obtained in other studies in the US (Wilhelm and Ritz 2005; Chen et al. 2002), in Munich (Slama et al. 2007) and in the Czech Republic (Dejmek et al. 1999).

5 Limitations of Epidemiological Studies

The limitations of the epidemiological studies have been carefully considered. Issues in interpreting the findings have been those relevant to any body of observational evidence, which are exposure misclassification and the potential for uncontrolled confounding.

Exposure misclassification is a far reaching concern. In general, this type of misclassification tends to reduce estimates of effect towards the null, i.e. finding no effect. A detailed analysis for daily time series studies led to the conclusion that measurement error would lead to an underestimation of effect under most conditions (Zeger et al. 2000). One critical uncertainty in interpreting the epidemiological studies is the question of the contribution of particles in outdoor air to total personal (and population) exposure. In moderate climate, where the studies were predominantly conducted most time is spent indoors. Ambient particles would make a substantial contribution to personal exposure only if they penetrated into the indoor spaces. Personal exposure studies carried out in the United States and Europe showed that particles in outdoor air contributed substantially to personal exposures and to temporal variation in personal exposures (NRC 2004). These findings provide support for using central site measurements of ambient particle concentrations as a surrogate for changes in personal exposures in epidemiological studies.

Confounding is always of concern in interpreting the findings of observational studies. Confounding arises when the effect of a factor other than that being studied biases the effect of the factor under study; for confounding to occur, the potential confounding factor needs to be both associated with the outcome of interest and the factor under investigation (Rothmann and Greenland 1998). In carrying out studies, epidemiologists use both design and analytical strategies to control for any bias from confounding. The potential for confounding to have biased the findings of the daily time series studies has been explored in a number of ways. Temperature and humidity, along with season, have been controlled in the daily time series studies with approaches that involve inclusion of temperature (and relative humidity) variables in the models and the use of temporal smoothing methods that account for the well-known seasonality of mortality. Because influenza epidemics, are a particular concern, models have been used that incorporate this factor and also temporally smooth its effects. The sensitivity of findings to the degree of smoothing provides one indication of potential confounding. Even with very sophisticated models it is some times difficult or impossible to separate the effects of particulate matter from the effects of other concomitant and heavily correlated pollutants like NO_2, ozone or sulfate.

Particularly with regard to the time series and other longitudinal studies, critics have questioned the statistical models used, both with regard to the selection of particular models and to the specification of the variables in the models. Various models have been used to assess the extent to which control of confounding is model-dependent (HEI 2003a). But in general the risk estimates presented turned out to be rather robust. Because of identification of the potential for bias from default settings in widely used statistical software a number of key data sets have been reanalyzed (HEI 2003b). The reanalysis gave similar results as the original analysis, but showed lower effect estimates and larger standard errors.

6 Toxicological Evidence of PM Health Effects

Considering the epidemiological evidence of the health effects of particulate matter, the main purpose of toxicological studies was to prove the plausibility of the statistical associations, to elicit the components of particulate matter responsible for the health effects and to analyze the mechanisms of action and the dose-effect relationship. A vast body of data has accumulated during the past 10 years (for an overview see, US-EPA 2004, 2008).

Evidence related to underlying mechanisms and the plausibility of the effects observed in epidemiological studies comes from a range of clinical studies on human volunteers and toxicological studies on animal models and cell systems. In principal, the toxicological in vitro and animal experiments give clear hints as to the mechanisms of the effects observed in the epidemiological studies but the exposures in these experiments are by up to two magnitudes higher than the exposures observed in epidemiology. Additionally it has to be considered that experimental studies only partly reproduce the year- or life-long exposure of populations in observational studies.

Inhalation or instillation of particles induces oxidative responses at the bronchial and alveolar surfaces and local inflammation. At least at higher concentrations (e.g. CAP or instillation) pulmonary injury may result. At concentrations lower than 100 $\mu g/m^3$ no morphological changes in the lung of the exposed animals were observed. Some constituents of the particles are more toxic than other. Instilled residual oil fly ash (ROFA) produces significant cell damage and inflammation in animal lungs depending on its content of transition metals (Fe, Ni, V, Zn) but in concentrations much higher than in ambient air (Dreher et al. 1997; Kodavanti et al. 1997). Water soluble components, rich on metals were most toxic (Dye et al. 2001; Ghio and Devlin 2001).

The production of reactive oxygen species (ROS) by particles in contact with epithelial and cellular surfaces in the bronchial tree and the lung is considered to be the first step in a cascade to generate inflammation and lung injury. Numerous studies have demonstrated the oxidative potential of PM in vitro assay systems (Ayres et al. 2008). Both redox active surface components such as metals and organic species and the surface characteristics of crystal structures have been shown to contribute to the oxidative potential (Warheit et al. 2007). In this way, PM may be a direct source of ROS in the respiratory tract. PM may also act as an indirect source of ROS in the respiratory tract by stimulating cells to produce ROS (Tao et al. 2003). Li et al. (2002) proposed a model in which at the beginning mild oxidative stress enhances antioxidant defenses by upregulating antioxidant enzymes. Subsequently further increase in oxidative stress induces inflammation and cell death.

Mechanisms underlying the extra-pulmonary cardio-vascular or systemic effects are incompletely understood. However, pulmonary inflammation can lead to systemic inflammation and pulmonary reflexes can activate the autonomic nervous system. Many animal studies confirm the systemic cardiovascular toxicity of particles and give hints regarding the underlying mechanisms (Godleski 2006; Muggenburg et al. 2000; Salvi et al. 1999; Thomson et al. 2006). The hypothesis is that particles induce a reversible increase of coagulation and an inflammation reaction. Elemental composition seems to be an important factor influencing these effects (Costa and Dreher 1997). The experiments show effects mostly in older animals and in animals of impaired health supporting the epidemiological findings of increased mortality and morbidity predominantly of persons with respiratory or cardiovascular diseases.

Whether particles are capable of crossing the epithelial barrier and reaching capillary endothelial cells or the circulation is in question. To date, the evidence for ultrafine or other PM size fractions accessing the circulation by traversing this barrier is not convincing. The effects of ultra fine particles evoked special interest because of their large surface area per mass. Oberdörster et al. (1994) and Li et al. (1999) compared the effects of fine and ultra fine particles. At equal mass concentration ultra fine particles seem to be more toxic than fine particles producing oxidative stress reactions. The effects depend on the chemical composition of the particles, e.g. ZnO-particles being more toxic than MgO-particles (Kuschner et al. 1997). But the experimental evidence is insufficient for firm conclusions about the role of ultra fine particles regarding the health effects of particulate matter.

6.1 Allergic Responses

Laboratory and toxicological studies have shown that PM can modulate immune reactivity in both humans and animals to promote allergic sensitization and exacerbate allergic responses (US-EPA 2004). Exposure to diesel exhaust particles for example was shown to increase the allergic response among atopic adults (Bastain et al. 2003). Numerous forms of PM, including inert materials, have been shown to function as adjuvants in laboratory studies. Although studies of relatively homogeneous materials demonstrate greater adjuvancy for smaller particles than for larger, this could not be reproduced by analyses of ambient PM. Particle composition might be more influential than size (Steerenberg et al. 2006; Gavett et al. 2003), but few if any studies have compared size fractions of well-characterized ambient PM for adjuvant activity in a direct, controlled fashion via inhalation exposure.

6.2 Host Defense

Toxicological studies demonstrated increased susceptibility to infectious agents following exposure to PM. These studies evaluated the effect of high concentrations of particles inhaled (CAP) or of suspensions of particles instilled in rodents.

They observed e.g. an increase in susceptibility to influenza infection in mice (Ciencewicki et al. 2007). Similar effects of ambient particles may be partly responsible for the observed increase of hospital admissions with pneumonia cited above.

7 Conclusions

Evidence has grown over the last decade, that urban airborne particles at ambient concentration levels common in many cities in Europe, America and Asia exert adverse effects on human health. Short- or long-term exposure to particulate matter (measured as PM_{10} or $PM_{2.5}$) is associated with an increase risk of cardiovascular and respiratory morbidity and mortality. Collectively the toxicological and epidemiological studies provide sufficient evidence that a causal relationship is likely to exist between exposure to ambient concentrations of PM_{10} or $PM_{2.5}$ and specific human morbidity (exacerbation of chronic bronchitis, asthma or coronary heart disease) and premature deaths.

For various health outcomes of PM, there has not been any indication of a threshold below which adverse effects would not be anticipated. Anyways a reduction of present levels of urban air pollution by particulate matter seems to be warranted.

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Airborne Particulate Matter, Platinum Group Elements and Human Health

Clare L. S. Wiseman and Fathi Zereini

1 Introduction

Exposures to ambient particulate matter (PM), especially fine PM with an aerodynamic radius of 2.5 μm ($PM_{2.5}$), have been consistently related to increases in mortality and morbidity (Dockery et al. 1993; Burnett et al. 1999). The effects of ambient PM exposures on certain vulnerable populations such as the elderly, those with compromised cardiopulmonary health and children are of particular concern. A number of studies have demonstrated, for instance, that exposure to air pollution is associated with reductions in lung function and growth, asthma, allergic rhinitis and respiratory infections in children (Janssen et al. 2003; Brauer et al. 2007). Among other things, their susceptibility can be attributed to the immaturity of their respiratory defence mechanisms and higher permeability of their airways to air pollutants compared to adults.

Although the exact mechanisms involved are not known, PM exposures appear to induce oxidative stress, pulmonary inflammation and modulate the immune responses of the lungs. Respiratory infections such as pneumonia, for example, have been found to increase significantly among individuals following exposures to higher levels of PM, especially in the elderly (Schwartz 1995; Zelikoff et al. 2002). The toxicity of PM has often been related to particle size and not the constituents per se (Höhr et al. 2002). In recent years, however, evidence has been mounting that the composition of PM strongly determines its toxicity. Burnett

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_28,

et al. (2000) found, for instance, that daily mortality in eight Canadian cities was more strongly associated with the constituents of fine PM than the fine mass alone.

Urban PM has been found to contain significant amounts of metals (Zereini et al. 2005), which may mediate the health related effects of PM exposures, as demonstrated in a number of studies (e.g. Carter et al. 1997; Costa and Dreher 1997; Zelikoff et al. 2002). Ionisable or bioavailable metals in airborne PM have been particularly associated with enhanced airway hyperresponsiveness, altered immune resistance and pulmonary inflammation (e.g. Hatch et al. 1985; Costa and Dreher 1997). Most attention has been paid to metals that typically occur in higher amounts in ambient PM such as Fe, Zn and Ni. Much less is known about the health effects of exposures to platinum group elements (PGE), metals which are also found to occur in the PM_{10} and $PM_{2.5}$ fractions found to pose a risk to humans. Increases in the environmental levels of PGE, notably platinum (Pt), palladium (Pd) and rhodium (Rh), have been particularly due to their use as catalysts in automotive catalytic converters. Documented increases of PGE in the environment have stimulated much interest and debate regarding the potential of these metals to impact human health. This chapter assesses current environmental exposures to PGE in airborne PM of biological concern in light of more recent evidence regarding the toxicity and bioavailability of these metals. In the following section, we will first discuss evidence regarding the potential health effects of ambient PM and exposures to PM-associated metals, especially with respect to identified vulnerable populations. Section 2 will present data on PGE concentrations in ambient PM. Data on PGE toxicity in ambient PM will be presented in Sect. 3. Section 4 will then discuss current knowledge regarding the environmental behaviour and bioavailability of PGE and its relevance in terms of the possible health risks of exposures. The final section will conclude with an assessment of the potential health risks associated with environmental exposures to PGE.

2 Traffic-Related PGE Emissions and Ambient Concentrations

The chemical and thermal characteristics of PGE make them highly useful as catalysts in a wide variety of industrial, chemical, electrical and pharmaceutical processes (Johnson Matthey 2007). Their use as catalysts in automotive catalytic converters to reduce noxious emissions from the burning of fossil fuels has undoubtedly been one of the most far-reaching and important applications. Automobiles have been equipped with catalytic converters since 1975 and 1986 in the US and Europe, respectively. Initially, Pt and Pd were used to reduce hydrocarbon and carbon monoxide emissions. Since the early 1990s, Rh has also been used in various combinations and ratios with Pt and Pd in three-way catalytic converters to reduce NO_x emissions. PGE appear to be emitted together with alumina particles from the washcoat as a result of various chemical, physical and thermal stresses such as mechanical abrasion and high temperatures (Schlögl et al. 1987; Artelt et al. 1999, 2000; Palacios et al. 2000). The amount and rate of PGE emissions are also dependent on speed of driving, type and age of the catalyst and engine type (Artelt et al. 1999, 2000).

A number of studies have demonstrated elevated PGE levels in various environmental media such as airborne PM (Zereini et al. 2001, 2005; Rauch et al. 2001; Gomez et al. 2002), soils (Zereini et al. 1997, 2007; Whiteley and Murray 2003), street dust (Jarvis et al. 2001; Gomez et al. 2002; Whiteley and Murray 2003) and in run-off sediments (Zereini et al. 1997; Zereini and Golwer 1999). PGE have also been found in vegetation (Schäfer et al. 1998; Djingova et al. 2003) and organisms such as the freshwater invertebrate *Asellus aquaticus* (Moldovan et al. 2001) and raptors (Ek et al. 2004). Elevated PGE concentrations have also been measured in remote areas such as central Greenland (Barbante et al. 2001), which reflects their potential to be transported over long distances.

Although diet has been determined to be a relatively important exposure route for PGE in humans (Vaughan and Florence 1992), the inhalation of PGE-containing PM is likely of greater significance in terms of their potential health risks (WHO 1991, 2002). This is also supported by recent studies conducted by Columbo et al. (2008a, b) which demonstrate that PGE uptake in the human body is likely to be significantly higher via respiratory exposure versus ingestion. This was also observed by Moore et al. (1975) in their study on rats exposed to Pd and Pt salts. As discussed previously, ambient PM with an aerodynamic diameter of less than 10 μm (PM_{10}), especially the $PM_{2.5}$ fraction, has been associated with an increase in morbidity and mortality (Dockery et al. 1993; Burnett et al. 1999). As such, PGE pose a potential health risk given the fact that 30–57% of the total measured PGE in air samples has been found to be fall in this fraction (Artelt et al. 1999; Gomez et al. 2002; Zereini et al. 2004). While most of the available data relates to levels in ambient PM_{10}, there have been several studies which also measured PGE levels in $PM_{2.5}$, which is a greater human health concern. Table 1 provides an overview of PGE concentrations that have been measured in PM_{10} and $PM_{2.5}$ over the last 10 years. Schierl (2000), one of the first to measure Pt in PM_{10}, measured an average Pt concentration of 21.5 pg m^{-3} in buses and tramways in Munich, Germany. Rauch et al. (2001) measured PGE concentrations in PM_{10} and $PM_{2.5}$ at two different sites in Göteborg, Sweden in 1999. For the high traffic site, PM_{10} collected from a site with a high traffic volume of 70,000 cars per day was found to contain a mean of 14.1 pg Pt m^{-3}, 4.9 pg Pd m^{-3} and 2.9 pg Rh m^{-3}. The $PM_{2.5}$ fraction had lower concentrations of PGE, with a mean of 5.4 pg Pt m^{-3}, 1.5 pg Pd m^{-3} and 1.6 pg Rh m^{-3}. The low traffic site with less than 10,000 cars per day had lower levels of PGE, with a mean of 2.1 pg Pt m^{-3}, 1.8 pg Pd m^{-3} and 0.6 pg Rh m^{-3} for PM_{10} and 2.7 pg Pt m^{-3}, 1.4 pg Pd m^{-3} and 0.5 pg Rh m^{-3} in $PM_{2.5}$.

In Madrid, Pt content varied according to sampling site and associated traffic volumes and speed limits, ranging from <0.1 to 57.1 pg m^{-3} (Gomez et al. 2001). The average Pt value was 12.8 pg m^{-3}. Rh varied from <0.2 to 12.2 pg m^{-3}, with an average value of 3.3 pg m^{-3}. PM_{10} collected from ring-road sites in Madrid,

Table 1 PGE concentrations in airborne PM_{10} and $PM_{2.5}$ (were measured) (adapted from Wiseman and Zereini (2009))

City/Country (Sample year)	Sample type	Location/Description	Average PGE concentrations in pg m^{-3} (median given were specified) (ranges in brackets)	References
Munich, Germany (1995/1996)	PM_{10}	Buses & tramways	Pt: 21.5 (±6.5) (max. 62)	Schierl (2000)
Göteborg, Sweden (1999)	PM_{10} & $PM_{2.5}$	Two sites: 1. High volume (70,000 cars per day) 2. Low volume (<10,000 cars per day)	High volume site PM_{10}: Pt: 14.1 (7.6–19.2) Pd: 4.9 (1.3–9.7) Rh: 2.9 (1.3–4.3) $PM_{2.5}$: Pt: 5.4 (3.9–7.2) Pd: 1.5 (0.7–2.2) Rh: 1.6 (1.0–2.7) Low volume site PM_{10}: Pt: 2.1 (0.9–3.0) Pd: 1.8 (<0.6–4.4) Rh: 0.6 (0.3–1.2) $PM_{2.5}$: Pt: 2.7 (1.4–6.3) Pd: 1.4 (0.7–2.5) Rh: 0.5 (0.3–0.6)	Rauch et al. (2001)
Madrid, Spain (1998/1999)	PM_{10} (7-stages)	City suburb with medium traffic density	Pt: 8.19 (<0.1–57.1)	Gomez et al. (2001)
Madrid, Spain (1998/1999)	PM_{10}	Five sites	Pt: 12.8 (<0.1–57.1) Rh: 3.3 (<0.2–12.2)	Gomez et al. (2001)

Table 1 (continued)

City/Country (Sample year)	Sample type	Location/Description	Average PGE concentrations in pg m^{-3} (median given were specified) (ranges in brackets)	References
Madrid, Spain (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown: Pt: 7.3 Rh: 2.8 Ring-road sites: Pt: 17.7 Rh: 4.6	Gomez et al. (2002)
Göteborg, Sweden (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown: Pt: 13.1 Pd: 4.6 Rh: 2.7 Ring-road sites: Pt: 4.1 Pd: 1.6 Rh: 0.8	Gomez et al. (2002)
Rome, Italy (1999/2000)	PM_{10}	Downtown and ring-road locations	Downtown: Pt: 8.6 Pd: 42.7 Rh: 2.2 Ring-road sites: Pt: 8.1 Pd: 54.9 Rh: 3.0	Gomez et al. (2002)

(continued)

Table 1 (continued)

City/Country (Sample year)	Sample type	Location/Description	Average PGE concentrations in pg m^{-3} (median given were specified) (ranges in brackets)	References
Frankfurt, Germany (2001/2002)	PM_{10}	Three sites: 1. Major street (high t raffic, 32,550 cars/day), 2. Side street (low traffic, <1,000 cars/day), 3. Nonurban site	Major street: Pt: 15.7 (8.7–28.4) Pd: 25.1 (9.4–29.3) Rh: 2.9 (1.8–4.5) Side street: Pt: 6.2 (4.1–9.5) Pd: 8.9 (5.1–15.6) Rh: 0.7 (0.7–1.1) Nonurban site: Pt: 5.2 (3.0–7.9) Pd: 7.8 (4.7–11.7) Rh: 0.8 (0.3–1.5)	Zereini et al. (2004)
Buenos Aires, Argentina (2001)	PM_{10}	Seven inner city sites	Pt: 12.9 (2.3–47.7) Rh: 3.9 (0.3–16.8)	Bocca et al. (2006)
Vienna, Austria (2002)	PM_{10} (6-stages)	Downtown, heavy traffic area	Average sum of stages: Pt: 4.3 (±1.7) Pd: 2.6 (±0.6) Rh: 0.4 (±0.1)	Kanitsar et al. (2003)

Table 1 (continued)

City/Country (Sample year)	Sample type	Location/Description	Average PGE concentrations in pg m^{-3} (median given were specified) (ranges in brackets)	References
Boston, USA (2002/2003)	PM_{10}	Two sites: 1. 20,000 cars/day 2. 10,000 cars/day	Site 1: Pt: 9.4 (0.6–17) Pd: 11.0 (1.0–26) Rh: 2.2 (0.5–5.9) Site 2: Pt: 6.2 (0.6–36) Pd: 7.1 (0.8–39) Rh: 1.3 (0.3–5.9)	Rauch et al. (2005)
Mexico City, Mexico (2003)	PM_{10}	Five sites with various traffic volumes	9.3 (±1.9) pg Pt m^{-3} 11 (±4) pg Pd m^{-3} 3.2 (±2.2) pg Rh m^{-3}	Rauch et al. (2006)
Neuglobsow, Deuselbach & Frankfurt am Main, Germany (year 2008/2009)	PM_{10}	Three locations with different traffic volumes	Neuglobsow (rural site): Pd: 1.15 (median) (0.06–7.4) Deuselbach (rural site): Pd: 2.2 (median) (0.1–9.7) Frankfurt am Main (high traffic): Pd: 30.4 (median) (3.3–102.8)	Alsenz et al. (2009)

were found to contain higher amounts of Pt and Rh compared to downtown (Gomez et al. 2002). While PM_{10} from the downtown location contained 7.3 pg Pt m^{-3} and 2.8 pg Rh m^{-3}, the PM_{10} from the ring-road site had 17.7 pg Pt m^{-3} and 4.6 pg Rh m^{-3}. Conversely, PGE measured in PM_{10} from downtown sites in Göteburg in the same study had higher levels of Pt and Pd compared to ring-road sites, with 13.1 pg Pt m^{-3} and 4.6 pg Pd m^{-3} and 4.1 pg Pt m^{-3} and 1.6 pg Pd m^{-3}, respectively (Gomez et al. 2002). Rh levels were also found to be higher for downtown with 2.7 pg Rh m^{-3}, compared to the ring-road site with 0.8 pg Rh m^{-3}. For PM_{10} collected in Rome, Pt and Rh concentrations did not vary much between the downtown and ring-road locations, with 8.6 pg Pt m^{-3} and 2.2 pg Rh m^{-3} and 8.1 pg Pt m^{-3} and 3.0 pg Rh m^{-3} for the two sites, respectively. Pd levels were found to be high for both sites in Rome, with concentrations of 42.7 pg m^{-3} for samples collected downtown and 54.9 pg m^{-3} for samples from the ring-road site.

In other PM_{10} samples collected from a site with a heavy traffic load in Frankfurt, Germany, Pt, Pd and Rh concentrations ranged from 8.7 to 28.4 pg m^{-3}, 9.4 to 29.3 pg m^{-3} and 1.8 to 4.5 pg m^{-3}, respectively (Zereini et al. 2004). Average concentrations of 15.7 pg Pt m^{-3}, 25.1 pg Pd m^{-3} and 2.9 pg Rh m^{-3} were measured for PM_{10} for this site, which were the highest observed concentrations for samples collected at three different sites with varying traffic densities in this study. PGE concentrations were considerably lower for the side street with less than 1,000 cars per day, with an average of 6.2 pg Pt m^{-3}, 8.9 pg Pd m^{-3} and 0.7 pg Rh m^{-3}. Unlike the coarse PM samples collected in this study (i.e. <22 μm), the PM_{10} samples had considerably higher average amounts of Pd compared to Pt. This suggests that Pd is more commonly associated with finer particle size fractions of biological concern. For Buenos Aires, Pt and Rh in PM_{10} samples were determined to have a mean of 12.9 and 3.9 pg m^{-3}, respectively (Bocca et al. 2006). For the US, where the first automobile catalysts were introduced, very little is known about PGE in aerosols. In the only known study of PGE in US urban air, Rauch et al. (2005) measured PGE concentrations in PM_{10} samples collected at two locations in Boston. Samples from the site with higher amounts of traffic were determined to have an average concentration of 9.4 pg Pt m^{-3}, 11.0 pg Pd m^{-3} and 2.2 pg Rh m^{-3}. Values for both sites ranged from 0.6 to 36 pg m^{-3} for Pt, 0.8 to 39 pg m^{-3} for Pd and 0.3 to 5.9 pg m^{-3} for Rh. Rauch et al. (2006) measured concentrations of 9.3 pg Pt m^{-3}, 11 pg Pd m^{-3} and 3.2 pg Rh m^{-3} for PM_{10} collected at five sites in Mexico City in 2003. PGE concentrations in airborne PM were found to be considerably higher compared to that measured in 1993; two years after the mandatory use of automobile exhaust catalysts was introduced. Using a novel method to measure Pd involving the use of helium as a collision gas in combination with isotope dilution Q-ICP-MS after reductive co-precipitation with mercury, Alsenz et al. (2009) analysed PM_{10} samples collected in Neuglobsow, Deuselbach and Frankfurt am Main, Germany. For Neuglobsow and Deuselbach, rural sites considered to be more representative of background concentrations for PGE, median levels of 1.15 and 2.2 pg Pd m^{-3} were measured in PM_{10}. Samples collected in Frankfurt am Main, which is characterized by a high traffic volume, were found to contain a median of 30.4 pg Pd m^{-3}. Concentrations of Pd for this site ranged from 3.3 to a high of 102.8 pg m^{-3}.

No definitive conclusions can be made regarding the distribution pattern of PGE among various $<PM_{10}$ size fractions from the few studies that have examined this, due to inconsistencies in results. Gomez et al. (2001) found that the highest Pt values were generally associated with the very fine <0.39 μm fraction, which can penetrate deep into the lungs and elicit a toxic effect due to their greater surface reactivity and potential to induce the production of reactive oxygen species (Wilson et al. 2002). Zereini et al. (2001) determined that most of the Pt and Rh occurred in the coarse fraction of 2.1–10 μm (i.e. 75% Pt and 95% Rh) for PM_{10} samples collected in the Botanical Gardens in downtown Frankfurt, Germany. Kanitsar et al. (2003) found that the highest Pt, Pd and Rh concentrations were measured in the size fraction of 1–2.15 μm (ca. 1.4 pg Pt m^{-3}, 1.0 pg Pd m^{-3} and 0.17 pg Rh m^{-3}), followed by PM with an aerodynamic equivalent diameter of 0.46–1.00 μm (ca. 1.0 pg Pt m^{-3}, 0.6 pg Pd m^{-3} and 0.11 pg Rh m^{-3}) in their samples collected in Vienna, Austria.

In sum, studies have demonstrated repeatedly that PGE levels in airborne PM of biological concern tend to fall in the low pg m^{-3} range, with Pt normally exhibiting the highest concentrations. Rh levels in ambient PM tend to be the lowest of all PGE. Values of as high as 62 pg Pt m^{-3} (Schierl 2000) and 102.8 pg Pd m^{-3} (Alsenz et al. 2009) have been reported for PM_{10} collected in urban areas and could be considered to represent a more “worst case” scenario. Distribution patterns for PGE among various particle size fractions have been somewhat inconsistent. The highest Pt levels among PM_{10} have been measured for the fine and ultrafine particle size fractions in two separate studies (Gomez et al. 2001; Kanitsar et al. 2003).

3 PGE Toxicity

Although a number of studies have demonstrated that various metals may play a primary role in mediating PM-related cardiopulmonary health effects and autoimmunity, less is known regarding the potential impacts of environmental exposures to PGE. In particular, very little data is available regarding the sub-clinical effects of chronic low dose exposures. This is especially relevant regarding attempts to assess the effects of exposures to low concentrations of PGE that are being continuously emitted into the environment.

Most of the available information regarding PGE toxicity relates to Pt and the use of Pt-containing substances in chemotherapy. Less is known about Pd and Rh and the toxicity and behaviour of particle-bound PGE emitted from catalytic converters. As for other metals, the acute toxic effects of PGE are dependent on metal speciation, with soluble compounds being the most toxic. Hexachloroplatinic acid, for instance, is highly nephrotoxic in rats (Ward et al. 1976), while metallic Pt appears to be only mildly toxic (WHO 1991). Several Pt compounds have been found to be mutagenic in bacterial systems, especially the commonly used anti-neoplastic agent cis-platin, which is an IARC group 2A carcinogen ["probably carcinogenic" (IARC 1981)]. Pd salts appear to have a lower genotoxicity in bacteria and mammalian cells compared to Pt (Gebel et al. 1997). This was confirmed in a recent study using human lymphocytes, which demonstrated that soluble Pt ($(NH_4)_2PtCl_4$, $PtCl_2$, $PtCl_4$) and Rh ($RhCl_3$) compounds were more genotoxic than Pd salts ($(NH_4)_2PdCl_4$, $PdCl_2$), likely mediated by an ability to induce oxidative damage (Migliore et al. 2002).

In rats exposed to various concentrations of Pt salts per gavage over a 4-week period, Pt was found to cause DNA damage, shrinkage of the glomeruli in the kidney and induce the development of eosinophil inclusion bodies in the adrenal glands (Gagnon et al. 2006). This same study also showed a heightened immune response to Pt, as indicated by a hyperactivity of the lymphocytes (i.e. pulp size of the spleen increased with increases in Pt dosage). In another study, male Wistar rats exposed to sub-chronic levels of Pd (as K_2PdCl_6) in drinking water were found to have elevated levels of the cytokines interleukin (IL)-2 and interferon (INF)-γ (Iavicoli et al. 2008), an indication of the potential of this metal to exert an immune-modulating effect.

Although very little is known about the autoimmune effects of PGE exposure, metal ions which possess a high redox potential such as Pt(IV), do have the ability to denature proteins by oxidizing the sulphur-containing amino-acid side chains. Further, metal ions such as Pt(II) may also form coordination complexes with proteins, which could also serve to interfere with the processing and presentation of self-proteins and -peptides, resulting in activation of autoreactive T cells. Only one known epidemiological study has demonstrated an association between PGE exposures and rates of autoimmune diseases in humans. As part of the German Environmental Specimen Bank program, which collects, measures and stores environmental and human samples of medical students, urinary samples from 367 participants were examined for Pd in 2000 (Helm 2002). It was found that those who reported to have autoimmune diseases such as Type 1 diabetes and hypo-/hyperthyroidism had elevated levels of Pd. Given the low sample number, however, further study would be needed to confirm the existence of such a relationship.

Some in vitro studies suggest that Pd(II), Pt(II) and Rh(III) complexes are able to inhibit a variety of cellular functions, which can be attributed to their capacity to form strong complexes with various organic and inorganic ligands. A number of older studies already demonstrated that PGE can affect cellular fluidity, membrane integrity and permeability and interfere with protein synthesis (Binet and Volfin 1977; Wataha et al. 1995), inhibit mitochondrial enzyme production and alter the structure of the mitochondrial lipid bilayer (Rosen et al. 1992). Their ability to impact cell viability and cellular processes and function has also been confirmed in more recent in vitro studies. Frazzoli et al. (2007) investigated the potential of $PdCl_2$, $PtCl_2$ and $RhCl_3$ to interfere with aerobic respiration at a cellular level using suspended yeast cells (*Saccharomyes cerevisiae*). Metal concentrations were found to closely correlate with acute respiration inhibition. The lowest experimental doses found to induce an adverse effect were 161 ng g^{-1} for Pd, 120 ng g^{-1} for Pt and 60 ng g^{-1} for Rh. Interestingly, they found that Rh was more toxic (i.e. EC50%, steepness of curve) than Pd and Pt.

Schmid et al. (2007) used human bronchial epithelial cells (BEAS-2B) to examine the effects of PGE exposure on cellular viability and their capacity to induce the release of reactive oxygen species as an indicator of oxidative stress. Inorganic PGE salts were used ($Pt(NO_3)_2$, $PtCl_4$, $PdSO_4$, $RhCl_3$) and compared to the effects of Cd, Cr and Ag salts. The LC_{50} for Pt(IV) was 0.05 mmol L^{-1} and Pt(II) and Pd(II) had a LC_{50} of 0.4 mmol L^{-1}, which is similar to heavy metal species such as Cd(II) and Cr(IV). Rh demonstrated a low toxic potential. Pt(II) and Pt(IV) were found to lead to an increase in the production of reactive oxygen species, while no effect was observed for Pd(II) and Rh(III).

Similar to other metals such as Hg, Pb and Cd, PGEs have also been found to be among the most potent inducers of metallothionein (MT) protein synthesis, a commonly used indicator of metal toxicity which appears to play a role in detoxification (Klaassen and Lui 1998; Park et al. 2001). The possible effects of PGE exposures in utero and on neonates or infants are unclear. An earlier study on rats exposed to Pd and Pt salts through various routes, Pd and Pt were shown to be capable of passing through the placental barrier in pregnant rats (Moore et al. 1975). Gagnon and Patel (2007) recently demonstrated that Pt accumulated at a higher rate in the brain of chicken embryos compared to the liver, which is likely due to the absence of a fully developed blood–brain barrier. Induction of MT synthesis in the brain and liver of chick embryos exposed to PGM was also observed. As the blood–brain barrier is also not fully developed in humans at birth, it is possible that PGEs are also able to penetrate the brain of newborns, which, of course, elevates the potential for these metals to induce neuro-developmental effects. Given more recent evidence regarding an association between environmental exposures to metals during this highly vulnerable early stage of development and a variety of later health effects ranging from attention deficit hyperactivity disorder (ADHD) to Alzheimer's (Makri et al. 2004; Wigle et al. 2007), the possible effects of chronic exposures to PGE in children deserves our attention.

One major concern regarding PGE exposures is the sensitization potential of these metals, especially that of their salts (WHO 1991; Merget and Rosner 2001; Ravindra et al. 2004). Pt salts have been particularly associated with an increased incidence of asthma, rhinoconjunctivitis and dermatitis and urticaria among workers occupationally exposed to these metals such as those in catalyst production and refineries (Santucci et al. 2000; Cristaudo et al. 2005; Watsky 2007). In a Pt refinery where levels in air were determined to be generally less than 0.08 μg m^{-3}, 20% of exposed workers displayed skin sensitization (Merget et al. 1988). For Pd, patch testing in various clinics have shown that as many as 13% of tested individuals reacted positively with this metal (Orion et al. 2003). In one large study conducted by Kränke et al. (1985) with over 10,000 individuals, Pd was demonstrated to be one of the most potent sensitizers among the metals. The respiratory sensitization potential of environmental exposures to PGE among the general population, a primary toxic endpoint of concern, is however unclear. A study conducted in Nordrhein-Westfalen, Germany, showed that ambient Pt levels significantly correlated with the number of neutrophils and epithelial cells in the nasal lavage fluid of children, which have been established to be good biomarkers for upper airway inflammation (Shins et al. 2004). No relationship was observed between nasal inflammation and nasal Cr levels. Although environmental levels of PGE are generally much lower than that found among those who are occupationally exposed, such studies indicate that ambient exposures to these metals may elicit effects on a subclinical level that are not readily detected among the general population.

4 PGE Behaviour and Bioavailability

Generally, guidelines and policies to regulate environmental levels of metals to protect human health have tended to focus on their general concentrations. However, in the assessment of risk, a metal's speciation and related bioavailability are critical factors for consideration (Peijnenburg et al. 1997). Today, we generally have a good idea regarding concentrations of PGE in various environmental media, due to the efforts of a number of individuals that have conducted measurements over the last 10–20 years (e.g. Zereini et al. 1997; 2005; 2007; Rauch et al. 2001, 2005; Gomez et al. 2002; Kanitsar et al. 2003). In contrast, our knowledge regarding the transformation behaviour, speciation and bioavailability of PGE in the physical environment and in organisms once they are taken up is limited. In the past, it has generally been assumed that PGE are not bioavailable to any significant extent, as they appear to be emitted primarily in metallic form. Initial studies which examined PGE emissions determined that only about 1% of Pt in exhaust is released in a soluble form, likely as Pt^{4+} (Schlögl et al. 1987; Artelt et al. 1999). Although most PGE appear to be emitted in an inert state, more recent studies have shown that a significant fraction of these metals in the environment may be bioavailable.

Zereini et al. (2001) determined that about 10% of the Pt measured in airborne PM collected in Frankfurt and Offenbach, Germany is soluble in 0.1 M HCl. Similarly, Moldovan et al. (2002) determined that less than 10% of PGEs emitted in the exhaust from a new catalyst was soluble. For older catalytic converters, the soluble fraction was found to be higher, especially for Rh and Pd. Although Alt et al. (1993) determined the soluble fraction of Pt in a tunnel dust sample to range between 2.5 and 6.9%, as much as 43% of dust samples collected in areas further away from roadways was found to be soluble. This shows that finer dust fractions, which are likely to be carried further distances via wind, are more soluble due to their particle size.

In addition to the solubility of metals in emissions, some recent studies have demonstrated the importance of considering the role of various environmental parameters in enhancing or reducing the bioavailability of PGE. Dahlheimer et al. (2007), for instance, showed that the presence of siderophores can significantly increase the solubility of PGEs at various pH levels, particularly that of Pd. The siderophores were found to enhance the dissolution of not only PGE oxides but also that of metallic Pd and Pt. As these compounds are commonly present in soils, being produced by plants and microorganisms to increase the availability of iron (Kraemer 2004), this is a particularly important finding and suggests that they may serve to enhance the bioavailability of PGE once deposited in the environment.

The presence of complexing agents in the environment is also an important factor in determining the solubilisation potential of metals and their bioavailability. For instance, EDTA has been shown to remobilise heavy metals found in sediments (Nowack et al. 2001) and appears to increase the lipid solubility of Pt, Pd and Rh (Zimmermann et al. 2003). Humic substances have also been shown to increase the water solubility of Pt and Pd (Wood 1996; Lustig et al. 1998; Zimmermann et al. 2003). Of all the PGE, Pd appears to be particularly soluble and mobile in the environment and has been demonstrated to have greater potential for uptake in organisms (Jarvis et al. 2001; Moldovan et al. 2001; Sures et al. 2001; Zimmermann et al. 2003). Jarvis et al. (2001) found that 35% of the total palladium in road dust dissolved in a solution with a pH of 3, similar to rain. This was much higher than that for Rh (1.2%) and Pt (0.5%). They suggested that Pd can be rapidly transformed from a metallic to a chloride species in the environment and is thus highly mobile.

In addition, the transformation behaviour of metals upon uptake by organisms is an important factor in the determination of risk (Peijnenburg et al. 1997). Unfortunately, our knowledge of PGE bioavailability upon inhalation or ingestion is even more limited compared than that regarding how these metals behave in the environment. There are a handful of studies that have examined the body burdens of PGE in humans, mostly measuring metal levels in urine. For instance, Iavicoli et al. (2004) examined the urinary Pt concentrations of 103 traffic police officers in Rome and found that they were not significantly different from levels measured for another 58 individuals who work primarily indoors (0.28–13.67 ng Pt l^{-1} in occupationally exposed police officers compared to 0.20–15.29 ng Pt l^{-1} in the control group). This was comparable to concentrations measured in urine samples from children living in Rome (<0.6–9.5 ng Pt l^{-1}), the levels of which were found to correspond with traffic density in the area of residence (Caroli et al. 2001). In a study of bus and tram drivers, Schierl (2000) reported median urinary Pt values of 2.8 and 1.3 ng l^{-1}, respectively, which were somewhat lower than that measured in the Iavicoli et al. (2004) study. Although urinary levels can be a good indicator of exposure levels, definitive conclusions regarding toxicity or their toxicodynamics cannot be made.

Recent advances made using simulated body fluids to examine the bioavailability of metals are highly valuable and provide a better picture of the risks associated with environmental exposures. In examining the bioavailability of PGE upon inhalation, Columbo et al. (2008a) exposed various simulated lung fluids to road dust, milled vehicle catalyst and solic PGE hydroxides to estimate the metal amounts solubilised in the human respiratory tract. Of all the test materials, they found that the road dust samples contained the greatest amount of bioavailable PGE when exposed to artificial lysosomal fluid (pH 4.5) (36% of Pt and 88% of Rh was solubilised). For the auto catalyst and hydroxide samples, less than 8 and

10% of the PGEs were solubilised, respectively. Despite the higher solubility and mobility of Pd and Rh, the higher amount of Pt in road dust accounts for the highest release of this metal in the respiratory tract in absolute terms. In another study on the solubility of PGE in the gastrointestinal tract, Columbo et al. (2008b) demonstrated that a higher uptake for PGE is likely to occur through respiration (36% for Pt) compared to digestion (17% of Pt). They also found that the bioavailability of these metals in catalyst and the hydroxide samples increased slightly from the stomach to the intestinal phases. For the catalyst and hydroxide samples, the percent bioavailability of the PGEs decreased in the following order: Pd > Rh > Pt. For road dust, considerably more Rh was bioavailable in relative terms compared to Pt (64–68% vs. 15–17%). The dissolution of PGE in the respiratory and gastrointestinal tract may involve the formation of PGE-chloride complexes, due to the presence of chloride in both lung and stomach fluids (Columbo et al. 2008a, b). As halogenated PGE salts have been shown to be highly toxic in lab tests (WHO 1991, 2002), this is a critical consideration in toxicological terms and demands further study.

5 Assessing the Health Risks of Environmental Exposures to PGE

An earlier study conducted by Rosner and Merget (2001), which calculated a ‘safe concentration’ of between 15 and 150 ng Pt m^{-3}, has often been used as the point of reference in assessing the risks of current environmental levels of PGE (e.g. Ravindra et al. 2004). Rosner and Merget’s (2001) assessment was based on a study of observed incidences of sensitization among workers in a catalyst production plant and a “worst-case scenario” that halogenated Pt salts comprise 1% of total Pt emissions. As environmental concentrations of PGE are typically much lower, they concluded that they are unlikely to pose a health risk.

For Pd, WHO (2002) calculated that ambient air levels of this metal can be expected to be below 0.100 ng m^{-3} in urban areas where PGE catalysts are used. At this concentration, exposed individuals would inhale a total of 2.2 ng Pd per person on a daily basis (assuming an average inhaled volume of 22 m^{3} of air per day). Of the studies reviewed here, we calculate a maximum possible daily intake of about 2.3 ng Pd per person (average inhaled volume of 22 m^{3} per day), using the highest value of 0.103 ng m^{-3} from the Alsenz et al. (2009) study on PM$_{10}$ collected in Frankfurt am Main, Germany. This would exceed that assumed by WHO for urban areas in their report from 2002 (WHO 2002). Together with the maximum values of 0.062 ng m^{-3} (Schierl 2000) and 0.004 ng m^{-3} (Bocca et al. 2006) measured for Pt and Rh, respectively, we estimate a total potential PGE intake of approximately 3.7 ng m^{-3} via inhalation of PM$_{10}$ on a daily basis. This is higher than that calculated by Wiseman and Zereini (2009) in their recent review of PGE exposures and associated health risks. The possible health risks associated with this exposure level cannot be adequately assessed, however, given the data on PGE toxicity and bioavailability, despite the advances that have been made in research in recent years. Current environmental exposure levels to Pt do fall below that estimated by Rosner and Merget (2001) to be a ‘safe concentration’ for the workplace.

However, recent evidence regarding the environmental behaviour and bioavailability of Pt, Pd and Rh suggests they are indeed a human health concern. As indicated by the studies reviewed here, PGE may pose a greater health risk than once thought for a variety of reasons. First, despite the fact that PGE may be emitted primarily in a metallic state, they may be easily mobilised and solubilised by various compounds commonly present in the environment (e.g. Wood 1996; Zimmermann et al. 2003; Dahlheimer et al. 2007). This, of course, serves to increase their bioavailability and hazard potential. Second, PGE may be transformed into more toxic species upon uptake by organisms (Columbo et al. 2008a, b). The presence of chloride in lung fluids, for instance, may lead to the formation of halogenated PGE complexes that have a greater potential to induce cellular damage. Third, a significant proportion of PGE is present in the finer particle size fractions of airborne PM which have been found to be associated with increases in morbidity and mortality (Dockery et al. 1993; Burnett et al. 1999). Hence, PGE are also a human health concern to the extent that they contribute to that suite of metals found in fine PM suspected to pose a health risk, especially in vulnerable populations such as children. Further, PGE emissions will likely continue to rise as increasingly more automobiles are equipped with exhaust catalysts, leading to even greater exposure levels. This will be exacerbated by the fact that current technological advances being made to further reduce exhaust emissions, such as attempts to increase the performance of exhaust catalysts in reducing NO_x emissions by accelerating converter heat-up and elevating core catalyst temperatures (Winer and Behrentz 2005), may actually create conditions that are conducive to even greater releases of PGE. All these factors highlight the need to monitor environmental levels of PGE and continue research on their bioavailability, behaviour, speciation and associated toxicity to enable us to better assess their potential to elicit health effects in humans.

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Part VI
Protecting Human Health: Policy, Regulation and Scientific Uncertainty

Clare L. S. Wiseman and Fathi Zereini

As discussed in many chapters of this book, there is a large body of evidence which demonstrates the potential for airborne particulate matter (PM) to negatively impact human and environmental health. Given this, there is a critical need for air quality policy and emissions regulations that minimize PM exposures and health risks as much as possible, while considering the interests of industry and society in general (e.g. energy requirements, travel). Despite the advances which have been made in our knowledge of airborne PM and its potential to impact human health, existing knowledge gaps and the attendant scientific uncertainty complicates decisions regarding air quality and emissions regulations. Airborne PM is perhaps one of the most difficult environmental contaminants to regulate in the interest of protecting public health. This is due, in part, to the fact that airborne PM can originate from a large number of natural and man-made sources and its prevalence and composition can be highly variable through both time and space as a consequence of many factors. Our ability to develop good public health policy is made even more difficult by the lack of established threshold levels between PM dose and response and existence of mathematical models which adequately describe the relationship between PM exposure and health effects. The ability for airborne PM to be transported further distances from the emission source, especially the finer fractions of PM, adds even more complexity to the issue of air quality regulation, highlighting the need for cross-jurisdictional cooperation.

This concluding part includes two chapters, which grapple with different aspects of the above issues and questions. In the first chapter, Grahame critically examines a variety of methodological issues as they relate to population-based studies undertaken to investigate the relationship between airborne PM exposures and effects. He further discusses how these issues may be addressed, emphasizing a need to systematically examine the constituents of PM and their sources. Grahame argues for an interdisciplinary approach to better describe exposure-response relationships and to provide a basis for policy that more adequately protects human health. In the second chapter, Morawska et al. provide a comprehensive overview of existing regulations and policy measures to regulate air quality and reduce airborne PM levels in various political jurisdictions. As part of this, they detail a number of problems which are inherent to the regulation of emissions and air quality, including the quantification of source contributions and confounding factors such as the nature of particle formation. Similar to Grahame, Morawska et al. discuss problems with current approaches to air quality policy and emissions regulations, which are based on the mass of certain particle size fractions, notably $PM_{2.5}$ and PM_{10}.

Distinguishing Health Effects Among Different $PM_{2.5}$ Components

Thomas J. Grahame

1 Introduction

Particulate matter (PM) is regulated in the U.S. under the original Clean Air Act of 1970, as amended. At the time of passage, although it was apparent that large concentrations of smoky or industrial emissions in the air harmed the public health, little was known about how PM harmed health, what size fractions were most important, or which chemical or physical properties caused harm. In 1971, US Environmental Protection Agency (EPA) initiated regulations of TSP (total suspended particulates), generally in the 25–45 μm size range (Martineau et al. 2005). Subsequent research suggested smaller size fractions independently posed health risks, leading to regulation in 1987 of PM_{10} (particulate matter 10 μm or less in diameter) and in 1997 of $PM_{2.5}$.

Among the most seminal studies for establishing associations between adverse human health effects and $PM_{2.5}$—particles about 1/100th the width of a human hair—were two early studies, the "Six Cities" study of 1993 (Dockery et al. 1993) and the American Cancer Society (ACS) study of 1995 (Pope et al. 1995). These two studies linked exposure to elevated $PM_{2.5}$ concentrations with increased long term (chronic) risks to longevity. Other studies found pollution associations with elevated risks of mortality and morbidity on a daily (acute) basis.

The Six Cities and the ACS studies were designed before concerns about health effects of different specific components of $PM_{2.5}$, including black carbon and $PM_{2.5}$ species with little ambient mass (such as metals), had become a major research focus. Perhaps for this reason, the only chemically-speciated type of

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The analysis provided in this chapter is the work of the author alone and does not necessarily represent views of the US Department of Energy

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_29,

$PM_{2.5}$ included in the monitoring data used by both studies was sulfate, a geographically widespread and major constituent of $PM_{2.5}$ which had already been monitored for some years (the Six Cities study also included a measure of acidity).

Many studies of PM, especially early ones, examine health associations only with measures of PM mass. Some of the other investigations which draw associations between PM concentrations (i.e. mass) and mortality include Pope et al. (2009); the National Morbidity, Mortality, and Air Pollution (NMMAPS) Study (Health Effects Institute 2000); and a follow-up of the Six Cities study with more years of data (Laden et al. 2006). A recent paper of interest estimates the monetized health damage per ton of emission of different $PM_{2.5}$ species, based upon how many people are exposed to the emissions, while continuing to assume constant toxicity across all components of $PM_{2.5}$ (Fann et al. 2009). While these studies demonstrate clear associations between $PM_{2.5}$ mass exposures and patterns of mortality and morbidity, the most important question facing pollution researchers has yet to be adequately addressed: what pollutants are the ones we need to preferentially regulate to benefit the public health, and which ones, perhaps, cause little harm to the public health? This question becomes more important if $PM_{2.5}$ species with relatively little mass, especially widespread species, turn out to be particularly harmful, because if $PM_{2.5}$ is regulated on the basis of mass, species with relatively little mass are not likely to be targets for reduction.

1.1 Multi-City, Multi-County and Site-Specific Studies

Table 1 reviews examples of three types of studies: (1) multi-city studies, such as the Six Cities and ACS studies; (2) multi-county studies; and (3) studies of a particular location, in this case the Atlanta area (chosen because of the wealth of studies in this area). Health outcomes examined are restricted to all-cause and cardiopulmonary mortality, and cardiovascular disease hospital or emergency department admissions, in order to retain focus. Although additional studies could be included, these studies were chosen because, in concert, they are among the best to illustrate with the least amount of complexity how epidemiology studies with some similarities can reach different conclusions about which pollutants are harmful. In particular, the multi-county and Atlanta studies were chosen because they monitored for many types of $PM_{2.5}$. Table 1 generally does not include factor analyses (such as those of Mar et al. [2000, 2006]), because (as discussed in Sect. 1.4) such analyses typically come to inconsistent conclusions, because of varying inputs and methodological factors.

Two points stand out with regard to the two multi-city studies. First, $PM_{2.5}$ components such as BC (black carbon) or EC (elemental carbon, virtually the same as BC), OC (organic carbon), and metals (such as iron [Fe], nickel (Ni], and vanadium [V]) are not monitored. Secondly, these studies find health associations with sulfate, the only $PM_{2.5}$ species monitored by both studies.

The multi-county studies are different from the multi-city studies in that they (1) monitor for several more $PM_{2.5}$ components; (2) are done at a smaller

Table 1 Multi-city studies, multi-county studies, studies in Atlanta area: varying conclusions regarding which particle components are associated with all-cause mortality, cardiopulmonary mortality, or emergency department visits for cardio-vascular disease

Study	Geographic basis	Temporal basis	Particle components studied	Associations found
Multi-city studies				
1. Six Cities Study (Dockery et al. 1993)	6 Eastern and Midwestern localities	Prospective cohort study, survival since enrollment	$PM_{2.5}$, sulfate, acidity	Significant mortality associations found for all-cause, cardiopulmonary mortality for locality with highest $PM_{2.5}$ vs. lowest (RR = 1.26, 1.37); acidity not associated. Sulfate and $PM_{2.5}$ were very highly correlated (0.98), sulfate associations nearly identical to $PM_{2.5}$ associations.
2. ACS Study (Pope et al. 1995)	151 U.S. localities	Prospective cohort study, survival since enrollment	$PM_{2.5}$, sulfate	Significant mortality risks found for all-cause, cardiopulmonary mortality with both $PM_{2.5}$ (RR = 1.17, 1.31) and sulfate (RR = 1.15, 1.26)
Multi-county studies				
1. Bell et al. 2009	106 counties	Time series study (same day hospital admissions)	20 $PM_{2.5}$ components (those in Peng et al. (2009) below, plus 13 elements which are minor components of $PM_{2.5}$, mostly metals)	Significant associations in cardiovascular hospital admissions found for interquartile range increase in vanadium, nickel, and elemental carbon components of $PM_{2.5}$, but not for other $PM_{2.5}$ components
2. Peng et al. 2009	119 counties	Time series study (daily emergency hospital admissions)	7 largest $PM_{2.5}$ components (sulfate, nitrate, silicon, elemental carbon, organic carbon, sodium and ammonium ions)	Significant associations in cardiovascular hospital admissions found only for elemental carbon, not for other $PM_{2.5}$ components (0.80% increase in hospitalizations per one IQR (interquartile range increase) in EC

(continued)

Table 1 (continued)

Study	Geographic basis	Temporal basis	Particle components studied	Associations found
3. Lipfert et al. 2006a	206 rural and urban counties	Prospective cohort study, survival since enrollment	$PM_{2.5}$, sulfate, traffic density (surrogate for traffic emissions)	Consistent significant mortality risk associations with traffic density in 19 single and multi-pollutant models; significant $PM_{2.5}$ association in one of two single pollutant models, but not in any of four multi-pollutant tests; sulfate not associated with elevated mortality risks
4. Lipfert et al. 2006b	206 rural and urban counties	Prospective cohort study, survival since enrollment	15 elements (mostly metals), EC, OC, nitrate, sulfate, $PM_{2.5}$, traffic density (surrogate for traffic emissions)	Significant mortality risk associations with traffic density in 9 of 12 single and multi-pollutant models[1]; nitrate, EC, V, and Ni associated with elevated mortality risk in single pollutant, occasional multi-pollutant models; sulfate and $PM_{2.5}$ not associated with elevated mortality risks
Atlanta area studies				
1. Metzger et al. 2004	31 hospitals in Atlanta area	Time series study (daily emergency department admissions)	PM_{10}, $PM_{2.5}$, 10 to 100 nm particle count, water soluble metals, sulfate, acidity, OC, EC	Emergency department admissions for cardiovascular disease associated with EC, OC, and $PM_{2.5}$ in single pollutant models, but not with other $PM_{2.5}$ components
2. Tolbert et al. 2007	41 hospitals in Atlanta area	Time series study (daily emergency department admissions)	$PM_{2.5}$, sulfate, OC, EC, total carbon, water soluble metals (1998-2004 period of study)	Emergency department admissions for cardiovascular disease associated with EC, OC, total carbon, but not with other $PM_{2.5}$ components

(continued)

Table 1 (continued)

Study	Geographic basis	Temporal basis	Particle components studied	Associations found
3. Sarnat et al. 2008	27 hospitals in Atlanta area	Time series study (daily emergency department admissions)	In factor analysis, following factors identified: gasoline, diesel, wood smoke, soil, secondary sulfate 1 and 2, cement kiln, railroad, and metal processing. Particles include EC, OC, Se, nitrate, sulfate, K and Zn	In factor analyses, emergency department admissions for cardiovascular disease associated with sources of carbonaceous emissions (gasoline, diesel, wood smoke). PM components associated with CVD hospital admissions were EC, OC, and K (a tracer for wood smoke). Sulfate, nitrate, Se, and Zn not associated.

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[1] In the three models of 12 in which traffic density was not significantly associated with elevated mortality risks, EC was also a variable. Like traffic density, EC is a proxy for vehicular (mainly diesel) emissions

geographic scale; (3) find health associations with components of vehicular emissions such as EC (and with a proxy for traffic emissions, traffic density), which could not have occurred in the multi-city studies because such emissions were unmonitored; and (4) do not find associations with sulfate. Studies which include metals such as V and Ni are uncommon, but these emissions are often significantly associated with health endpoints when included (as with two of the multi-county studies, Bell et al. (2009), and Lipfert et al. (2006b)). In general, most researchers would expect that a majority of $PM_{2.5}$ components are likely to cause health effects, although effects may differ in type and severity.

Studies in the Atlanta area also monitor for many pollutants, including components of traffic emissions such as EC, and report similar findings as the multi-county studies.

Because these are population-based epidemiology studies, covering broad geographic areas and millions of people, exposure misclassification for pollutants with spatial variability across a metropolitan area will occur to some degree in each. For pollutants whose concentrations vary significantly over a locality, such exposure misclassification is expected to reduce the size and significance of effect estimates, as explained below. Therefore health risk associations found for locally variable emissions such as BC/EC may be larger than reported in these studies. Yet, because of exposure issues, results of these studies cannot be definitive regarding causality, without additional evidence from toxicology and from studies with better exposure information.

1.2 Progress in Identifying Health Relevant Sources and Components of $PM_{2.5}$

The Clean Air Scientific Advisory Committee (CASAC) is the scientific body charged with advising EPA on proposed regulation of the six "criteria" air pollutants, including PM. In their June 13, 1996 letter to the EPA Administrator, CASAC members reflected diverse opinions about whether to regulate $PM_{2.5}$, and if so, at what level to set the standard (CASAC 1996). Among the issues raised in the letter were exposure misclassification (the first issue identified in the Abstract above), the influence of confounding pollution variables (the 3rd issue in the Abstract), and the lack of understanding of toxicological mechanisms (also discussed in the Abstract).

In 1998 and in later years, the NRC emphasized the need to identify which components of $PM_{2.5}$ are most, or least, toxic (National Research Council 1998, 2004).

Despite these concerns, progress was slow with regard to differentiating health effects among $PM_{2.5}$ constituents until 2002, when several studies of different aspects of highway pollution came forward.

Zhu et al. (2002a, b) demonstrated that concentrations of ultrafine emissions, black carbon, and carbon monoxide (CO) were highly elevated adjacent to freeways in Los Angeles, but dropped by up to an order of magnitude 150 m away.

This study caused many in the air pollution health research community to focus more clearly on near-roadway emissions.

Concomitantly, the small cohort study of Hoek et al. (2002) was the first of many "highway proximity" studies to show elevated health risks from close exposure to vehicular emissions. Hoek et al. (2002) found highly elevated risks of cardiopulmonary mortality for those living within 100 m of a freeway or within 50 m of a major urban arterial, versus those living further away, after taking personal and sociological factors into account. Risks were significantly elevated for near-highway BC concentrations, but not for background BC concentrations. Another cohort study, the Canadian study of Finkelstein et al. (2004), found a "mortality rate advancement period" of 2.5 years for those living in such close proximity to major roads, a health risk comparable to having chronic ischemic heart disease.

The combination of the results of the Zhu et al. (2002a,b) studies, showing elevated vehicular emissions in close proximity to major roads, with the results of the early "highway proximity" studies, showing elevated mortality and morbidity risks for those living within this zone of high pollution, sparked increased research of how vehicular emissions might cause observed harm. Extant studies associating various cardiac and cardiovascular outcomes with close proximity to major roads are reviewed by Grahame and Schlesinger (2009).

Several studies by Li et al. (2002a, b, 2003) found oxidative stress to be caused by diesel emissions in human bronchial epithelial lung cells in vitro, with the smallest (ultrafine) particles, highly correlated with polycyclic aromatic hydrocarbon (PAH) content, causing the most damage. Due to their tiny size, these ultrafine particles easily penetrate walls of lung epithelial cells. Once inside, the chemical toxicity of the ultrafine PM causes oxidative stress. These findings were later replicated in vivo by McDonald et al. (2004), who also found that removing most carbonaceous matter in diesel exhaust (including 100% of BC) abrogated the oxidative stress as well as inflammation. Carbonaceous matter was removed with a catalyzing filter of the type required by EPA in 2007 for new on-road diesel vehicles.

Salvi et al. (1999) found in healthy human volunteers an increase in neutrophils in airway lavage after 1 h of exposure to diluted diesel exhaust. This same effect was also found by Huang et al. (2003), in a study which examined effects of two subsets of soluble components and took place near major roads, but which did not measure for diesel emissions or organic $PM_{2.5}$ species.

These and ensuing studies led many researchers to focus more on vehicular emissions in analyzing health effects of air pollutants. Just as importantly, they came to understand the importance of research methodologies which emphasized relatively accurate subject exposure to pollutants—in large part because the highway proximity studies showed that only with better exposure to vehicular emissions, were elevated risks consistently found with such emissions. With this understanding, researchers were motivated to develop new methodologies, such as those which enabled the mapping of a pollutant "surface" over a geographical area, such as Los Angeles, and then associate health outcomes with the more precise measure of a pollutant at a subject's home (Jerrett et al. 2005; Kuenzli et al. 2005; Maynard et al. 2007).

Increased emphasis on exposure was not limited to vehicular emissions, although vehicular emissions are usually the dominant source of local emissions where the majority of people live, in large urban areas. NYU researchers found associations between V and Ni in residual oil emissions and inflammatory effects in vitro (Maciejczyk and Chen 2005), and between Ni from a distant smelter and cardiovascular effects in vivo (Lippmann et al. 2006). Both studies utilized strategies, including the relatively new step of backcasting wind trajectories, to better characterize the sources of the metals which were associated with each health effect.

Increasingly sophisticated research has taken place, particularly in the last five years, suggesting risk of harm from specific components or sources of $PM_{2.5}$. For example, vehicular emissions—including ultrafine carbonaceous emissions, various organic gases, and $PM_{2.5}$ black carbon—have been suggested as presenting cardiovascular health risks in reviews (Samet 2007; Adar and Kaufman 2007; Grahame and Schlesinger 2009). Emissions containing nickel, such as those of Ni smelters and of residual oil, in studies with good exposure information, also appear likely to have cardiovascular consequences (Lippmann et al. 2005, 2006; Bell et al. 2009).

Distinguishing characteristics of newer research include:

- More accurate exposure information in population, based and human panel epidemiological studies.
- Examination of a wide variety of emissions, both particle phase and gaseous, in the same study.
- Combining information from toxicological studies with information from epidemiological (including panel) studies with the above characteristics.

We will now turn to the first of these characteristics.

2 Importance of Accurate Exposure Information in Epidemiological Studies

A fundamental epidemiological principle is that random exposure misclassification biases results towards the null, i.e., results in an underestimation of an input variable's true relative risk (Hennekens and Buring 1987). In an air pollution setting, more accurate measurement of subjects' exposure to a harmful pollutant in an epidemiology study produces effect estimates which are larger and more often statistically significant. For example, Zeger et al. (2000) used both daily ambient and personal exposure measurements in the PTEAM study, and found a smaller coefficient for mortality risk in regressions using measured ambient levels, such as from a central monitor, than when using personal exposure data. In Van Roosbroeck et al. (2008), effect estimates were two to three times higher for schoolchildren when personal exposure measures of soot and NO_2 were used, than when measurements taken outside the school were used. These examples show that the better the estimate of a subject's exposure to a pollutant, the larger the risk estimate of a damaging pollutant is likely to be.

For a single pollutant, these observations are straightforward. But what about studies examining effects of two or more pollutants, which have different measurement errors? Goldberg and Burnett (2003) suggest that exposure misclassification of consequential input variables could actually lead to "transference" of causal effects "from less precisely to more precisely measured variables." If in studies of two or more pollutants, associations are not only reduced for the poorly measured pollutants, but also transferred from the poorly measured to the better measured pollutants, then this exposure misclassification might explain why some studies find associations with emission X but not emission Y, while other studies find the opposite. Further, if such transference occurs, then the importance of relying more heavily on studies with reasonably accurate exposure information is magnified.

In the world of published journal articles, can we demonstrate both that associations are stronger when subject exposure is well characterized, and that there may be transference of associations from the poorly measured to the better measured emissions? Grahame (2009) addressed this question for heart rate variability (HRV), an easily measured cardiac health endpoint. Perhaps because of the non-invasive nature of this measure, there appear to be more human panel studies of this endpoint than of other cardiac and cardiovascular endpoints. HRV changes appear not only to have medical relevance in their own right for those with a history of heart disease, but also to cause and be a marker for oxidative stress, e.g. in the heart, a chronic risk factor for cardiovascular disease (Rhoden et al. 2005; Chahine et al. 2007).

Grahame (2009) found that in studies where subject exposure to BC was reasonably well characterized, it was almost always strongly and significantly associated with changes in HRV. In such studies, regional air masses containing large amounts of sulfate but few urban emissions were not associated with changes in HRV. However, BC was significantly associated with HRV changes only infrequently in studies where subject exposure across a city was characterized by central monitor readings. In the study with the poorest subject exposure information, there appeared to be transference of associations from BC (with no associations) to sulfate (large and significant associations). Grahame and Schlesinger (2009) made similar but preliminary findings in studies of ST-segment depression and arrhythmias, e.g., the better the subject exposure to traffic emissions, the stronger the associations with either endpoint. However, insufficient empirical work has been done on such transference of associations, when considering groups of studies; thus further investigation is a research priority.

3 Examining Wide Variety of Pollutants in the Same Study

Concentrations of various pollutants are often well correlated in epidemiological studies. This can mean that taken individually, each pollutant might show a significant positive association with a given health endpoint. On a stagnant day, most pollutant concentrations will be elevated, and thus many might show associations with a daily health endpoint.

For example, in Tolbert et al. (2007), four of the five pollutants examined for the 1993–2004 time frame (CO, NO_2, PM_{10}, and ozone) were significantly associated with daily respiratory disease emergency room visits. In two-pollutant models, ozone and PM_{10} remained significant in all tests, and in three-pollutant models, only ozone retained significance. Tolbert et al. (2007) point out that there are important issues with multi-pollutant models, some due to measurement error for one or more of the pollutants. Tolbert et al. (2007) point out that when two pollutants are thought to be independent risk factors for a given health endpoint, and when they are correlated with each other, then it may be "appropriate to use a two-pollutant model to adjust the effect estimate of each pollutant for confounding by the other pollutant." Tolbert et al. (2007) also note that "while it should be kept in mind that there may be residual confounding as a result of model misspecification or measurement error, the risk estimates from this model are likely to be more valid than those from each pollutant's single-pollutant model."

In general, use of single pollutant models will be suspected of finding associations which may not be causal, unless it can be shown that the pollutant in question is not correlated with other pollutants thought to be risk factors, and that there is toxicological evidence suggesting biological mechanisms by which the pollutant could cause the observed harm. Multi-pollutant models also have issues, such as properly dealing with collinearity of various pollutants. Despite these difficulties (and taking into account exposure misclassification and the possibility of transferring associations "from less precisely to more precisely measured variables"), multi-pollutant models (especially two pollutant models) may allow us to better identify the most harmful emissions (or the least harmful ones) compared to single pollutant models. Again, however, these results by themselves are insufficient to confirm causality of a given $PM_{2.5}$ species, absent additional evidence, in particular when exposure misclassification is present.

3.1 Factor Analyses

Factor analyses have been developed as a method of reducing large amounts of correlated data to a smaller number of "factors." In air pollution research, such factors are often thought to represent sources of emissions. Yet in practice such factors often represent a mix of sources, especially in earlier, less complete analyses. Factor analysis is a multivariate receptor modeling approach, using pollutant concentrations obtained from a monitoring site. For a description of a popular method of factor analysis (Positive Matrix Factorization, or PMF), see Paatero and Tapper (1993, 1994) and Paatero (1997). Unmix is another type of factor analysis. These methods of identifying factors, and potentially sources, possibly may be helpful in distinguishing health effects among sources of pollutants. A similar method, not a type of factor analysis, is chemical mass balance (CMB), which can be used to determine source contributions but requires a priori knowledge of major sources and characteristics of their emissions.

Like the other epidemiology models in Table 1, exposure misclassification is a given, because central monitor readings are used to develop the “factors.” That said, it is useful to review the findings of different factor analyses and to see how factor analyses have developed over time. The next two subsections briefly illustrate some of the characteristics and issues with contemporary factor analyses.

3.2 Factor Analyses in Phoenix Area

The many factor analyses done in the Phoenix area can be distinguished from each other by the differences in their results, which in turn depend upon which emissions are monitored as well as upon differing methodologies.

Mar et al. (2000) found five factors, which they identified with apparent sources: vehicular emissions (enriched in Fe, Zn, OC, EC, NO_2, and CO); soil dust (enriched in Si, Al, and Fe); vegetative burning (highly enriched with K); a local SO_2 source; and sulfate enriched factor, thought to represent regional coal, fired power plants.

Ramadan et al. (2000) explored sources of $PM_{2.5}$ in and nearby Phoenix during the same time period, also using PMF. By utilizing more PM components, Ramadan et al. (2000) found eight factors. Three large smelters were operating approximately 100–170 km from Phoenix in the mid to late 1990s. In contrast to Mar et al. (2000), which didn’t utilize copper PM data, Ramadan et al. (2000) found a factor associated with “nonferrous smelting.”

Using one data set (DFPSS), Ramadan et al. (2000) found the level of S in the smelter factor to be about half the level of S in the “secondary sulfate or (coal fired power plant)” factor (Fig. 1 in Ramadan et al.), suggesting that perhaps one-third of the sulfate in the Mar et al. (2000) analysis could come from regional copper smelters. Using a second data set (DICHOT), Fig. 8 in Ramadan et al. (2000) suggests that the average amount of fine PM in the smelter factor and the coal power plant factor may have been about equal. Thus the inclusion of an additional metal—copper—appears to have added to understanding of regional sources of sulfate.

Lewis et al. (2003) used Unmix to analyze sources of $PM_{2.5}$ in Phoenix and surroundings. Lewis et al. (2003) did not identify a factor associated with smelter emissions, but found a factor associated with diesel emissions substantially larger than did Ramadan et al. (2000). Whether the divergence in findings between Ramadan et al. (2000) and Lewis et al. (2003) is the result of different factor analysis models (PMF and Unmix) or some other reason is not clear.

Mar et al. (2006) reported on results of a workshop in which factor analyses from nine different practitioners were generated for the Phoenix area. Six groups identified six factors (soil/crustal material; traffic [gasoline and/or diesel]; secondary sulfate; biomass/wood combustion; sea salt; and copper smelters). Two of the factor analyses identified four factors, and one identified but two factors.

A later study, Brown et al. (2007), also using PMF, differed from the preceding studies in several ways. Probably the two most important differences are (1) use of emissions data from both sides of the US–Mexico border, and (2) an incremental probability analysis linking factor strengths and receptors using wind direction.

Brown et al. (2007) found a total of nine factors. A new factor is the "secondary transport" factor, enriched moderately with sulfate but mostly with bromine (Br), and accounting for 7% of $PM_{2.5}$ mass. This factor is associated with sources west of Phoenix with strength in southern California and northern Mexico, possibly suggesting the use of methyl bromide in agriculture as well as miscellaneous urban emissions. This factor is in addition to a regional power generation factor with higher sulfate loadings.

The regional power factor in Brown et al. (2007) suggests that the two largest sources of sulfate from power plants in the Phoenix area, based upon the combination of source emissions and the use of incremental probability analysis, are (1) a large coal plant in Nevada near the California/Nevada/Arizona border, and (2) a large residual oil, fired power plant in Puerto Libertad, Sonora, Mexico, on the Gulf of California.

Thus, among the many factor analyses for Phoenix we now find four distinct potential sources of sulfate: (1) coal fired power plants; (2) copper smelters; (3) a "secondary transport" factor from west of Phoenix, with sources on the California/Mexico border; and (4) residual oil emissions from the Puerto Libertad plant in Sonora. All of these factors will have different co-emissions co-mingled with the sulfate (most of which is not directly emitted, but is the product of atmospheric transformation of SO_2 to sulfuric acid to neutral ammonium sulfates). This diversity of findings indicates the need not merely to monitor for a widespread emission such as sulfate, but also to employ sophisticated methods to distinguish among sulfate sources, before examining health effects. These issues are discussed at greater length in Grahame and Hidy (2007).

3.3 Factor Analyses in the Southeast US

This same sensitivity to nuance in the types and number of pollutants measured can be seen in a pair of studies in the southeastern US. The first study (Liu et al. 2005) used 19 particle components (mostly metals) to identify factors at four locations (2 urban/rural pairs). Eight factors were resolved at the urban sites, and seven at the rural sites. A motor vehicle factor was identified which had high concentrations of both EC and OC.

The second study (Liu et al. 2006) utilized several more pollutant components, in addition to the components in the first study, to aid in determining factors. Concentrations of 4 gas components (CO, SO_2, HNO_3, and NO_y) were used, and both EC and OC were split into temperature-resolved fractions (4 OC fractions, 3 of EC).

Major differences in factors between the studies occurred with the addition of added pollutant information in the second study. First, instead of a single motor vehicle factor, separate diesel and gasoline emission factors were identified. Secondly, several factors changed in their percentage contribution to $PM_{2.5}$ mass between the two studies. At a downtown Atlanta site, there was a decrease of 8.6% in secondary sulfate contribution (from 37.0 to 28.4%); an increase in wood smoke contribution from 13.0 to 22.2% (prescribed agricultural burning in spring and residential wood burning in winter are the main contributors); and a decrease in the non-sulfate coal combustion factor from 3.0 to 1.9%. In a rural area (Yorkville), the secondary sulfate contribution changed little, but the secondary nitrate factor increased from 7.0 to 15.3%; wood smoke dropped from 20.0 to 16.6% contribution; and non-secondary sulfate coal combustion dropped from 6.0 to 0.7%.

Apparently the addition of SO_2 to the analysis enabled refinement of the coal combustion factor. The newer non-secondary sulfate coal plant emission numbers comport better with known percentages of coal fly ash in ambient air. Coal fly ash (CFA), mainly composed of aluminosilicates with calcium or sodium, iron, and trace materials, is the major primary $PM_{2.5}$ coal plant stack emission (CFA atmospheric concentrations typically are in the tens of ng/m^3, up to ~200 ng/m^3, depending on the number of coal plants in the region). The use of temperature, differentiated EC and OC fractions allowed differentiation of diesel and gasoline emissions, and also caused the contributions of other factors to change (e.g., wood smoke).

Sarnat et al. (2008), one of the Atlanta area studies and the only factor analysis in Table 1, utilizes a factor analysis most similar to that of Liu et al. (2006), one of the two most sophisticated of the factor analyses reviewed herein (Brown et al. 2007 being the other). Sarnat et al. (2008) compares the results of this factor analysis (e.g., health effect attributions) with results of other analytical methodologies, including CMB as well as using representative PM components as tracers of sources, and finds consistent results. There may be several reasons why Sarnat et al. (2008) were able to find consistent results among different methodologies, where others (e.g., Mar et al. 2000) did not. First, the factor analysis utilized was more advanced in the number and choice of input components. Secondly, there weren't significant unforeseen emission sources (e.g., large cross-border sources in the Phoenix area found only by Brown et al. (2007), in addition to copper smelter emissions identified by some analysts). Third, co-mingling of emissions from disparate sources was less likely because steel mills, coke ovens, smelters, and residual oil combustion sources are absent in the Atlanta area.

4 Different Sources of Common Pollutants

While many epidemiology studies today find associations with pollutants such as OC, EC or BC (which are virtually the same), or sulfate, it is important to recognize (1) the multiple sources of each, (2) the multiple co-pollutants which often occur with each, and (3) changes in concentrations of these emissions which have occurred over time. As a result, associations with one of these emissions could reflect confounding by other particulates or by gases. Understanding the potential for confounding will enable greater sophistication in interpretation and design of such studies.

4.1 Organic Carbon

Organic carbon can be emitted in particle phase (primary organic carbon or POC), e.g., certain semivolatile PAHs which condense to particle or liquid phase in cooler weather. However, much organic carbon is emitted in gaseous form and has two major primary sources. Anthropogenic volatile organic compounds or VOCs (e.g., toluene, xylene, etc.) are found in emissions from vehicles, filling stations, and refineries. Natural VOCs originate from vegetation (e.g., isoprene), mainly in warmer seasons. Many of the more chemically active of these various organics, such as certain PAHs and benzene among others, appear to be harmful.

Many such organic gases are converted to organic particles, via various atmospheric chemical processes, such as oxidation, and by condensation after such atmospheric processing. These are called "secondary organic aerosols" (SOA) or "secondary organic carbon" (SOC), because they were first emitted as gases and only secondarily converted to particles.

Thus, if a study finds associations with PM organic carbon, is the association due to (1) POC, (2) SOA, or (3) co-emitted pollutants such as ultrafine particles (a portion of POC)? Until recently, very few studies tried to examine differences in health impacts among OC types. Further, some effects theoretically may be caused by certain VOCs which might be correlated with some of the PM components (e.g., ultrafine BC) but which were not monitored.

The panel studies of Delfino et al. (2008, 2009) measured pollutants inside and outside the Los Angeles homes of non-smoking elderly subjects with a history of coronary artery disease. Health endpoints examined included various markers of inflammation, platelet activation, and anti-oxidant capacity. Pollutants included hourly concentrations of EC, BC, primary OC, SOA, particle number, CO, ozone, and NO_2, and daily size-fractionated PM. Thus these two studies had very good subject exposure and included a large number of health-relevant pollutants.

The studies found that POC, EC, $PM_{0.25}$ (near-ultrafine sized PM, ¼ of a micron in size or less), and particle number concentrations in Los Angeles were consistently associated with increased systemic inflammation, platelet activation, and decreased erythrocyte antioxidant enzyme active in the subjects. Effects were stronger in cooler weather, when there would be more condensed POC nanoparticles. Associations were rarely found for other PM types. Because in Los Angeles these emissions are almost entirely from vehicles (mostly diesel), the authors concluded that traffic emissions are associated with these three health endpoints, important for progression of cardiovascular disease. The study did not measure organic gases co-emitted with particulate traffic emissions, so it remains possible that these might also have effects.

Notably, the Delfino et al. (2008, 2009) studies found no associations with SOA. These studies may be the first study to explicitly analyze both POC and SOA in a health effects study. A few other studies implicitly have made this comparison, however. Schwartz et al. (2005), for example, in a study with good exposure characterization, examined HRV changes in elderly patients living in close proximity to a major urban road. The authors found that increased BC concentrations were significantly associated with reduced HRV in almost all cases, but that regional air masses with high $PM_{2.5}$ levels (which include high levels of sulfate and SOA), uncorrelated with BC, were not associated with HRV changes. Creason et al. (2001) made similar findings to those of Schwartz et al. (2005). More research is needed on the health effects of rural or regional air masses which contain little urban or industrial emissions but do contain SOA and sulfate, versus health effects of the other air masses.

Studies with small sample sizes such as Delfino et al. (2008, 2009), in contrast to population, based studies, may fail to find associations because of inadequate statistical power. However, the far better subject exposure in these panel studies argues in the opposite direction. It does seem notable that such robust findings for vehicular emissions were found in the Delfino et al. (2008, 2009) studies, despite just 60 subjects. The lack of associations with SOA, had the associations been reasonably close to significance, might suggest that the lack of association was due only to small sample size; however, all the SOA findings but one (IL-6) were far from significance.

4.2 Sulfate

In the mid-1970s, 17% of US electricity was generated in residual oil-fired power plants; today it is less than 2%. In addition, the high sulfur content of residual oils 20 and 30 years ago (typically 2% circa 1980) has now declined to about 0.3% in the few places where it is still used for power generation, such as the New York City area. Residual oil emissions contain the metals V and Ni, usually in primary metallic sulfate forms. Interestingly, V and Ni levels in residual oil rise and fall in concert with sulfur content of the fuel (Thurston and Spengler 1985). Thus sulfate would have been correlated with V and Ni in ambient air 20 and 30 years ago, in regions such as New England and the upper Atlantic coast, when sulfur levels in fuels were higher.

Steel and coke complexes were once far more widespread than today, when more steel was made domestically. Sulfate emissions from such facilities were high because large amounts of coal were coked, then consumed in steelmaking.

Sulfate emissions would have been correlated with PAH and other carbonaceous emissions from coking facilities and with metal emissions from steelmaking. Sulfate emissions from steelmaking are now down considerably for two reasons: (1) far fewer steelmaking facilities use coke, as these inefficient facilities have been retired or replaced by electric arc steelmaking, which is now used to make ~60% of US steel; and (2) stricter environmental controls for emissions from still-existing integrated steelmakers.

Coal-fired power plants are the largest emitter of SO_2 and thus the largest source of sulfate in the US (although shipping emissions can be locally large). Coal plants co-emit coal fly ash with SO_2, so that sulfate and coal fly ash are likely to be correlated in regional air masses within a few hundred miles of states with substantial numbers of coal plants.

Vehicular fuels formerly were high in sulfur, particularly diesel, but sulfur in such fuels has declined over the decades, culminating in the requirement for ultra-low sulfur in diesel starting in 2007. Thus in previous years, vehicular emissions such as EC, POC, carbonaceous ultrafines, and VOCs would have been correlated with vehicular sulfate. A 2003 study found a sulfate gradient falling with distance from a freeway near Cincinnati (Reponen et al. 2003), demonstrating that even with large amounts of sulfate from other Midwestern sources, a vehicular sulfate signature near major roads could be identified. Post 2006, with ultra-low sulfur diesel, such gradients may now be hard to detect.

As this short review suggests, sulfate associations in studies using data from previous years could have reflected possible effects from confounding pollution co-emitted with sulfate and/or with SO_2 from several different sources. Grahame and Hidy (2007) discusses this point further.

Today, however, residual oil is little used, mainly in the New York City area and in shipping. Sulfur levels in residual oil used for shipping (e.g., bunker oil) is much higher in sulfur and therefore in metals levels. There are fewer steel centers today, and emissions from remaining centers are lower than before. For example, Steubenville, Ohio in 1979 had 11 steel-making facilities and was highly polluted (Dockery et al. 1993), but today it is a clean ghost town, with one integrated mill remaining (two were still in operation in 2000). A total of 600 acres of coke ovens 3 miles downriver have been rebuilt to cleaner standards. As noted, studies post-2006 would be unlikely to have enough vehicular sulfate to confound with regional secondary sulfate, although the findings of Reponen et al. (2003) suggest otherwise for earlier time frames.

Researchers finding associations with sulfate using data from previous decades and years may find, upon re-examination, that sulfate associations may be confounded by other correlated emissions, and vice versa. Looking forward, unless shipping or local residual oil or local steelmaking facilities are present, such confounding may no longer be a large issue in epidemiological studies. Therefore health associations found with sulfate in studies using post-2006 data, especially if subject exposure for different pollutants is accurate, should be subject to less ambiguity.

5 Combining Toxicological and Epidemiological Studies

With some exceptions (some recent human panel studies, “highway proximity” studies, and some population-based studies where pollutants are modeled to a subject’s residence), epidemiology studies rarely have adequate subject exposure information to ensure that (1) associations accurately reflect underlying health effects (in strength of association and in significance), and (2) there would be very little chance of transferring an association from more poorly measured to better measured emissions. Thus, to give better confidence that epidemiological findings truly reflect effects of exposure metrics used, methodologies which have accurate exposure are crucial.

Another way to affirm epidemiological results is to link toxicological findings for the same types of $PM_{2.5}$, and thus establish biological mechanisms for how the type of $PM_{2.5}$ could cause the harm observed in epidemiology. In vitro and in vivo studies are useful in generating and testing hypotheses, and in demonstrating biological mechanisms of harm. Several important hypotheses which appear now to have been demonstrated in humans were first developed in in vitro studies. One such example is oxidative stress in human bronchial epithelial cells caused by ultrafine diesel emissions, strongly correlated with PAH content (Li et al. 2002a, b, 2003). A later in vivo study found the same effects in mice (McDonald et al. 2004). A toxicology study in which healthy human volunteers were exposed to diesel emissions in a crossover study suggests that oxidative stress in a vascular pathway may cause reduced nitric oxide (NO) availability, impairing vascular tone and function (Mills et al. 2005).

Epidemiology and toxicological studies can each reinforce the findings of the other type of study. For example, the increased oxidative stress found in the toxicological studies just reviewed is likely involved in the epidemiological findings of Kuenzli et al. (2005), who found increased atherosclerotic development for Los Angeles residents living in parts of the city with higher $PM_{2.5}$ levels (the major human-caused source of $PM_{2.5}$ in Los Angeles is vehicles, as there is little heavy industry and the power plants use natural gas). Oxidative stress, of course, is critically involved in the development of atherosclerosis.

But in vitro and in vivo studies, useful as they are, may not be adequate to demonstrate that particular pollutants cause an effect in humans. An effect observed in rodents may not necessarily occur in humans because of interspecies differences. In addition, some rodents have different reactions to an emission than other rodents (Kodavanti et al. 2005). So in addition to these studies, human panel studies are crucial.

Human panel studies, since they have a relatively small number of subjects who can be closely monitored, offer the opportunity to obtain excellent exposure information. Personal pollution monitors can be used; a mobile monitor can follow residents of a retirement community as they go about group activities; a monitor within 100 m of a major urban road can assess pollution for those living in similar proximity to the same road; monitors can be placed inside and just outside a home.

Wind trajectory analysis can be used to determine whether $PM_{2.5}$ on a given day came from rural or urban areas. If an effect is not found for a given emission in several studies with accurate exposure information, then there may be reason to question epidemiology studies which do find such an association for the same pollutant with the same health endpoint. But if the panel studies with good exposure make the same findings that the epidemiological studies do, then confidence will increase in the epidemiological studies.

Toxicology studies can have limitations. In general, the closer a toxicology study is to using pollutants as they appear in ambient air, the more likely the study's findings can shed light on biological processes triggered by exposure to air pollution people are exposed to. A toxicology review article found that inorganic salts such as sulfates and nitrates appear to not be harmful at levels two or more orders of magnitude higher than in ambient air (Schlesinger and Cassee 2003). This study put in perspective findings (such as in the Six Cities and ACS multi-city studies) of sulfate associations with early mortality, suggesting that chemically neutral salts such as ammonium sulfate and nitrate are unlikely to have consequential health effects. The studies reviewed in Schlesinger and Cassee (2003), however, do not address the atmospheric chemistry processes involving transformation of SO_2 to sulfuric acid and then to chemically neutral ammonium sulfate salts. Could these processes create compounds in SOA which might not be as prevalent but for the SO_2-related chemistry? In theory, some such compounds could have health consequences. In this case, human panel studies or toxicology studies using ambient air from locations where such compounds might be found (e.g., in rural areas not far from locations with many coal plants), but where vehicular or industrial emissions would be minimal, might shed light on whether any such compounds might be harmful. While such panel studies cannot be used to study risks of all-cause or cardiovascular mortality, they can be used to examine mechanisms which lead to both acute (daily) and chronic (long term) cardiovascular mortality.

In contrast, toxicology studies using diesel emissions would expose subjects (human volunteers or animals) to emissions quite similar to those produced near busy streets.

Grahame and Schlesinger (2009) present an analysis using in vitro and in vivo studies, together with epidemiological studies, to examine the relationships between vehicular emissions—marked by black carbon—with a panoply of cardiovascular-related endpoints. Similar comprehensive analyses should be done for other $PM_{2.5}$ species, including metals such as V and Ni, among others.

6 Conclusions and Recommendations

In this chapter, to simplify presentation, we have emphasized two types of health endpoints: all-cause (total) mortality, and cardiovascular endpoints. Other important endpoints exist, however, such as respiratory diseases. Much work has been done on relationships between particular pollutants and asthma, for example. In addition, there are susceptible subgroups, such as the elderly, and those with pre-existing diseases such as diabetes, who likely are more affected by air pollution. In researching effects of ambient air pollution, and in discussing recommendations herein, these complexities must be kept in mind.

The most important outstanding questions of air pollution research are, which pollutants are most harmful to the public health, and how do we design strategies to produce satisfactory answers?

The air pollution research community has in the past several years made large strides toward more fully recognizing the importance of specific chemical species of $PM_{2.5}$, and of different sizes of PM, such as ultrafines and occasionally coarse PM ($PM_{2.5-10}$), in causing adverse health effects. Biological mechanisms are now the focus of many research efforts to understand how ambient air pollution advances cardiovascular disease (the most important air pollution mortality endpoint in the US) and other health endpoints. In order to benefit the public health, the research community needs to identify those pollutants which are most harmful, so that they can be preferentially regulated. Continuing to regulate $PM_{2.5}$ only as mass, as if there were no difference in toxicity among $PM_{2.5}$ species, is not adequate for protecting the public health, and in fact might be harmful, if the end result of such regulatory policies is to regulate emissions which might cause little harm, and not regulate more harmful emissions which constitute a relatively small portion of $PM_{2.5}$ mass.

Small, light personal pollution monitors with the capability of monitoring many pollutants simultaneously—including not just BC, a few metals (Fe, V, Cu, Ni), sulfate, and nitrate, but also SOA, POC, ultrafines, and gases such as SO_2, ozone, and NO_2 on an hourly basis—would be very useful. Light weight is crucial because many of the subjects of panel studies are elderly, often with an existing medical condition such as diabetes or cardiovascular disease. With such lightweight personal pollution monitors, more panel studies with greater capability to associate various emissions with several important health effects, such as arrhythmias, can go forward. With such monitors, larger numbers of subjects could be followed, over larger areas, than in panel studies which require that subjects travel in a group with a portable monitor.

In epidemiology, ongoing efforts to deal with exposure misclassification should be continued. One particularly useful area of exploration might be to seek to understand the extent to which using smaller geographic areas (in terms of total size, and in terms of population density) instead of cities, in multi-locality epidemiology studies, may cause less exposure misclassification.

In establishing regulations, population-based epidemiological studies with minimal exposure misclassification which quantify the health impacts of various types of $PM_{2.5}$ will be important in establishing harmful ambient levels (although thresholds may not exist for some to many $PM_{2.5}$ species). If researchers can model several types of emissions (such as BC, Ni, V, SOA, POC, and regional sulfate) to the residences of subjects in a study, then it might be possible to create multi-pollutant analyses with accurate exposure which can be used for regulation of specific $PM_{2.5}$ components. The introduction of ultra-low diesel fuel in 2007 may now make it easier to do such a study without co-mingling regional sulfate and near-roadway sulfate, the latter of which would be highly correlated with BC.

Perhaps the best way, with current information, to identify the most harmful emissions would be to utilize the most relevant in vitro, in vivo, and epidemiology (especially human panel studies with good exposure information), in a comprehensive multi-disciplinary review of each important PM constituent, and PM source. Taken together, the biological mechanisms identified by the in vitro, in vivo, and panel studies can be an important check on findings of epidemiological studies, which as we have seen, can come to inconsistent conclusions. At the same time, epidemiological studies are necessary, because atmospheric chemistry is so complicated that replication in a laboratory is very problematic. Thus a set of human panel studies, conducted against the same health endpoints, but in different areas where particular types of emissions dominate, one of which has little pollution other than rural air masses, would likely be a better toxicology study than one using artificially generated atmospheres.

Ambient air which is essentially rural in origin will in warm months be more elevated in SOA and secondary sulfate. The mix between SOA and sulfate will vary among localities, but these would be the two common particle types in such rural air masses. These masses would contain SOA reaction products that might not exist but for the atmospheric chemistry of SO_2. If rural air masses from different parts of the country, with different combinations of SOA and secondary sulfate, were not associated with adverse health effects, then both types of particles might be seen as relatively harmless. Alternatively, air masses heavy in one of these particulate types might be harmful, but not air masses with the reverse balance between the two emissions. Such information would obviously be useful in protecting the public health.

Acknowledgment Thanks to two anonymous reviewers and especially to JoAnn Yuill for their invaluable assistance.

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Regulations and Policy Measures Related to the Reduction of Ambient Particulate Matter

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1 Introduction

A process leading to the development of regulations and introduction of policy measures to reduce concentrations of a pollutant in the environment in order to protect human health is a very complex one. Such a process is normally initiated when evidence emerges that exposure to the pollutant constitutes risk to human health. Some of the key subsequent steps of the process include quantification of both the exposure response relationship and the impact of the proposed regulations or policy measures on the actual reduction of the exposures. The entire process of risk assessment for the purpose of risk management encompasses several more steps; in particular, establishing of the exposure-dose and dose-response relationships (these two not always conducted), life time individual risk, and risk to exposed population (Naugle and Pierson 1991; Pierson et al. 1991). In relation to air quality, guidelines for the protection of human health against adverse effects of pollution are developed first based on public health studies (epidemiological, toxicological, and clinical), which in turn serve as a foundation for setting national air quality standards as the main means to enforce policies related to air quality management.

Quantification of risk due to an environmental exposure to a particular pollutant is always a complex process, since the multiplicity of other pollutants and factors have an impact on the individual at the same time, and the particular exposure investigated is only one of the factors. Risk assessment of airborne particulate matter is even more complex; in addition to the aforementioned challenges is the

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F. Zereini and C. L. S. Wiseman (eds.), *Urban Airborne Particulate Matter*,
Environmental Science and Engineering, DOI: 10.1007/978-3-642-12278-1_30,

complexity arising from the multifactorial nature of particulate matter. While some pollutants, such as carbon monoxide, have only one characteristic (i.e. their concentration) averaged over relevant periods of exposure, there are many characteristics of particulate matter which can be considered. One of the fundamental properties is size: airborne particles range in size over five orders of magnitude, from molecular dimensions to the sizes that are distinguishable with the naked eye (from about 0.001 μm to about 100 μm; Baron and Willeke 2001). Other characteristics include: number concentration, number size distribution, mass concentration, mass size distribution, surface area, shape, electrical charge or light scattering properties. Usually only some of these properties are measured, and almost never all of them, simultaneously.

In relation to some of these metrics, not only hazard has been established, but epidemiologic studies have quantified exposure–response relationships. This is particularly the case for mass concentration fractions including $PM_{2.5}$ and PM_{10} (mass concentration of particles with aerodynamic diameters smaller than 2.5 and 10 μm, respectively; more precisely the definitions specify the inlet cut-offs for which 50% efficiency is obtained for these sizes) and Total Suspended Particulate Matter (TSP). However, in relation to other metrics, for example number concentration of ultrafine particles (<0.1 μm), while there is ample evidence of hazard provided by toxicological studies, the epidemiology has not yet established an exposure–response relationship, and therefore health guidelines could not be proposed (as discussed in more detail below). In relation to other metrics, including particle surface area, there is even less quantitative evidence of effects, yet mechanisms have been proposed by which exposure to this and to other metrics can lead to health effects. However, whether the effects are independent, and whether each of the metrics should be regulated, or whether they are dependent and therefore only some of them need to be regulated, are open questions at present.

An additional issue is related to the nature of particle formation: primary versus secondary particles. A primary particle is a particle introduced from the source into the air in solid or liquid form, while a secondary particle is formed in the air by gas to particle conversion. Particles in the ultrafine and more generally in the submicrometer ranges are typically generated by combustion, gas to particle conversion, nucleation or photochemical processes with some of them primary and some secondary in nature. In contrast, supermicrometer particles are generated by a variety of mechanical processes, and as such, are primary in nature. While management of primary particles is somewhat easier, secondary particles present a far greater challenge, particularly since the scientific understanding of the secondary particle formation process is far from complete.

Quantitative assessment of individual source contribution to specific particle metrics presents another challenge. Again, there is a reasonably good understanding and quantification in relation to some of the metrics, such as $PM_{2.5}$ or PM_{10}. However, there is little information available regarding particle number (further complicated by the issue of secondary particle formation), and it is almost non-existent in relation to particle surface area. Without source apportionment it is not possible to manage the emissions in an informed way. Subsequently, the link between both source emission and air quality standards is often lacking (this will be further discussed below in relation to vehicle emissions). In general, anthropogenic combustion sources significantly contribute to ambient particulate matter, with vehicle combustion contributing approximately 90 and 65% of ultrafine and nanoparticle count, respectively, in the urban environment (Mejia et al. 2008). These particles are generally measured in terms of number concentration because their mass is very small and very little or no information about them can be gained from $PM_{2.5}$ or PM_{10} measurements.

Instrumentation and measurement techniques are an intrinsic part of the discussion of particulate matter management. Sampling of particles and choice of appropriate instrumentation and methodology is primarily based on particle physical properties. Due to different physical properties, different methods need to be used for measuring very small particles (mostly affected by diffusion) compared to those employed for large particles (mostly affected by inertia). While there are generally accepted instrumental techniques applied to some particle metrics, especially mass concentration measurements, there are no standard methods in relation to others (particle number for example). This further complicates the matter, as introduction of any regulation in regard to concentrations or emission levels has to be accompanied by setting a method by which compliance with the regulations be measured and monitored.

With the above complexities in mind, the aim of this work was to review the existing health guidelines and national standards in relation to the ambient concentrations of particulate matter, as well as national source emission standards. The focus of the review was on particle physical properties of mass and number, without, however, including chemistry, which is dealt with elsewhere in this book. In addition, occupational environments, where specific production processes lead to the generation of specific types of particles (such as mining or mineral processing) are not considered here, since these are usually managed by occupational regulations.

2 Particulate Matter—Mass

2.1 Health Guidelines

Health guidelines in relation to ambient particulate matter as well as other environmental pollutants are published by the World Health Organization (WHO) and adopted based on expert panel agreements, following consideration of evidence from medical and public health studies. As stressed in the latest edition of the guidelines, they are written “for worldwide use, intended to support actions aiming for air quality at the optimal achievable level of public health protection in different contexts” (WHO 2005).

Review of the existing evidence by the WHO panel showed that a broad range of effects have been documented after both short and long-term exposures, in particularly affecting the respiratory and cardiovascular systems of children and adults, as well as some susceptible groups within the general urban population of developed and developing countries. Importantly, there is no evidence of an existence of a threshold below which no adverse health effects would be anticipated, and, in fact, the lower range of concentrations at which effects has been demonstrated is not significantly greater than the background $PM_{2.5}$ concentration (estimated at 3–5 $\mu g/m^3$) in the United States and Western Europe.

Since the majority of monitoring data as well as epidemiological evidence is based on measurement of PM_{10} as opposed to other particulate matter metrics, PM_{10} was the most obvious indicator to choose in relation to the guidelines. However, the numerical guideline value itself is based on studies measuring $PM_{2.5}$, and on a $PM_{2.5}/PM_{10}$ ratio of 0.5 (typical in developing country urban areas and at the bottom of the range in such areas in developed countries). PM_{10} includes both the coarse (PM_{10}–$PM_{2.5}$) and fine ($PM_{2.5}$) fractions and if justified by local conditions, the ratio may be changed accordingly when setting the local standards.

The composition of coarse and fine particles is likely to vary substantially between cities around the world depending in particular on the specific local sources. A major contribution to the fine particles is combustion of wood and other biomass. Since similar effect estimates have been reported across cities in developed and developing countries, despite likely differences in fractional contribution from these two sources of combustion, it was concluded that it is reasonable to assume generally similar effects of $PM_{2.5}$ from these different sources.

The values chosen for the WHO air quality guidelines, which apply to both outdoor and indoor air are:

$PM_{2.5}$:	10 $\mu g/m^3$ annual mean, 25 $\mu g/m^3$ 24-h mean
PM_{10}:	20 $\mu g/m^3$ annual mean, 50 $\mu g/m^3$ 24-h mean

The rationale for the choice of the annual average guideline value of 10 $\mu g/m^3$ for $PM_{2.5}$ was that it represents the lower end of the range over which significant effects on survival have been observed in the American Cancer Society Study (ACS) (Pope et al. 2002). Further discussion on this can be found in the document (WHO 2005), which also concludes that although adverse effects on health cannot be entirely ruled out even below that level, it is a level achievable in urban areas of developed countries, and therefore attainment to it is expected to effectively reduce the health risks. However, the experts emphasized the need to reduce exposure to non-threshold pollutants such as particulate matter, even where current concentrations are close to or below the proposed guidelines.

In addition to the guideline values, three interim targets (IT) were defined, which are achievable with successive and sustained abatement measures and helpful in gauging progress over time in the process of steadily reducing population exposures to particulate matter.

2.2 National Standards

National air quality standards are based upon the potential for health and economic effects of identified pollutants. As discussed above, the relationship between some size fractions of particulate matter and adverse health effects has been well documented. The present indicator of particulate matter is PM_{10}. Consequently, while most monitoring studies report particulate mass as PM_{10}, the majority of epidemiological studies use it as the exposure indicator. In many cities, especially in the developing world, the average annual levels of PM_{10} exceed 70 $\mu g\ m^{-3}$; a level that is known to result in adverse health effects. It has been estimated that reducing PM_{10} levels from 70 to 20 $\mu g\ m^{-3}$ can reduce mortality rates attributed to air quality by 15% (WHO 2005). However, there is no level below which damage to health has not been documented. Therefore, in specifying national standards, the aim is to achieve the lowest concentrations possible.

Particulate matter standards were first introduced in the US in 1971. In 1987, the indicator of the standards was changed from TSP to PM_{10}. In 2006, it was decided to retain the existing 24-h PM_{10} standard of 150 $\mu g\ m^{-3}$ and, “due to a lack of evidence linking health effects to long-term exposure to coarse particle pollution”, the annual PM_{10} standard of 50 $\mu g\ m^{-3}$ was revoked (USEPA 2006).

Figure 1 presents the 24-h mean PM_{10} standards currently adopted by various countries. It should be noted that some countries like China and India specify different standards for industrial, urban and rural areas and also for sensitive areas that require special protection. The values shown in the chart for China refer to “typical urban and rural areas”. Several other countries that are not shown in the chart use indicators based on total particulate matter (TPM) or TSP and not PM_{10}. While the adoption of particulate matter standards by developing nations is to be encouraged, it is also important to ensure that the resources and facilities to make the required measurements are available.

As stated earlier, the WHO guidelines for annual and 24-h mean ambient fine particle ($PM_{2.5}$) levels are 10 and 25 $\mu g\ m^{-3}$, respectively. At present, with the exception of the US and Canada, no countries have adopted a fine particle standard. The USEPA first issued fine particle standards in 1997, when the annual and 24-h standards were set at 15 and 65 $\mu g\ m^{-3}$, respectively. In 2006, the 24-h standard was tightened to 35 $\mu g\ m^{-3}$ while the annual standard was retained at 15 $\mu g\ m^{-3}$. Note that these two current values are still well away from the WHO guidelines. Recently, the European Union (EU) has introduced a $PM_{2.5}$ standard target value of 25 $\mu g\ m^{-3}$, averaged over one year, that enters into force in 2010 (EU 2008). A target value is to be attained as far as possible by the attainment date and so is less strict than a limit value. The corresponding limit value has been set to 20 $\mu g\ m^{-3}$ to become legally binding in 2015.

The USEPA is in the process of revising the particulate matter standards, with one of the proposals being the introduction of a coarse particle standard for particulate matter between 2.5 and 10 μm (USEPA 2008b). This process and schedule of this review is based on two key components in the national ambient air quality

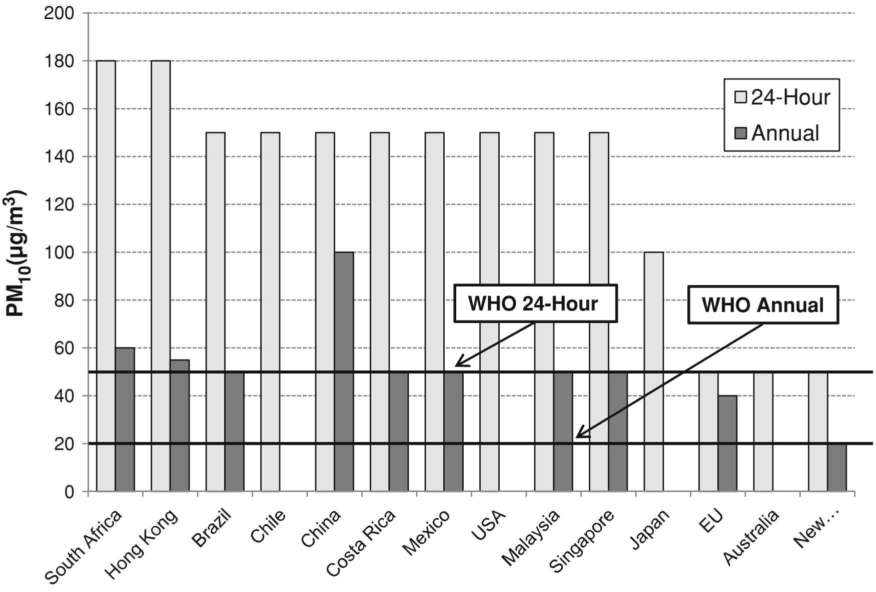

Fig. 1 24-h and annual mean PM10 standards currently adopted by various countries. The two horizontal lines show the corresponding WHO guidelines. Chile, USA, Japan and Australia do not enforce a 24-h standard at present. *Sources*: South Africa: SAGG (2005); Hong Kong: HKEPA (2006); Brazil: CONAMA (2005); Chile; China: GB (1996); Costa Rica: Mexico: DOF (1994); USA: NAAQS (2009); Malaysia: DOE (2009); Singapore: Yong (2002); Japan: MOE (2009); Ecuador; EU: EU (2008); Australia: NEPC (2003); New Zealand: NZMOE (2004)

standards review process: an Integrated Science Assessment (ISA) and a Risk and Exposure Assessment (REA), both of which are expected to be completed by July 2010 (USEPA 2009). The assessment will address concerns related to human health risk and exposure, visibility impairment as well as other welfare-related effects.

The Australian Environment Protection (Ambient Air Quality) Measure was amended in 2003 to include particles as $PM_{2.5}$, in the form of advisory reporting standards (NEPC 2003). The present annual and 24-h mean ambient $PM_{2.5}$ reporting advisory standards are 8 and 25 $\mu g\ m^{-3}$, respectively. This annual reporting standard is in fact more stringent than the corresponding WHO guideline value.

For completeness of this review it should be mentioned that there has also been discussion about introducing a PM_1 standard, as it would provide pertinent information about contributions from combustion processes and would afford improved delineation between combustion and mechanically generated aerosols compared to that provided by $PM_{2.5}$ measurements (Morawska et al. 2008a). It would thus appear that PM_1 and PM_{10} mass standards would be most desirable from the legislation point of view. The main problems, however, are that PM_1 is not routinely monitored and there are some technical challenges in relation to such measurements, and that there have been too few epidemiological studies conducted to quantify exposure-relationship in relation to PM_1.

3 Particle Number

3.1 National Standards

Unlike for particle mass concentrations ($PM_{2.5}$, PM_{10}), there are no standard methods for conducting size-classified particle number measurements. Furthermore, the impact of ultrafine particles on human health and the environment is still not fully quantified so that there is a lack of information on exposure-response relationships from epidemiological studies. These factors have prevented the development of particle number based health guidelines and any subsequent national regulations.

The main source of ultrafine particles in urban locations is motor vehicles. While particle number concentrations at clean background sites are of the order of 2,000–3,000 cm^{-3}, levels at urban sites are about four times higher. Levels at sites that are closely affected by motor vehicle emissions are even higher. Morawska et al. (2008b), in an extensive review of the literature, showed that particle number concentrations at road, roadside, street canyon and road tunnel sites are respectively 16, 18, 27 and 64 times higher than typical background values. Thus, unlike for particle mass, the range of concentrations between clean and vehicle effected environments is relatively large, varying over two orders of magnitude. This large variation across different environments has profound significance in relation to human exposure assessment and epidemiological studies, and implies that unless exposure assessment is conducted where the exposures occur; it is unlikely that epidemiological studies will provide meaningful answers based on monitoring in central locations alone. In other words, central monitoring underestimates exposures and may lead to inappropriate guidelines and standards for the management of public health risks.

3.2 Cleanroom Particle Number Concentration Standards

Cleanrooms serve various functions during the production of many items that share a common need for a highly controlled and pure environment during their manufacture. Additionally, cleanrooms or isolation rooms are often required in hospitals to prevent the spread of pathogens during surgical procedures, and to facilitate containment of infectious persons and protection of the immune-compromised. Cleanroom classes are defined on the basis of size-based particle number concentrations that are not to be exceeded within them. There are myriad cleanroom standards and guidelines around the world, although measures to rationalise the number of standards are in place (Möller 1999). The regulation, control and attendant design aspects related to particle number concentration in cleanrooms are topics discussed elsewhere, and the reader is directed to Whyte (1999) and chapter 15 of the ASHRAE Handbook of HVAC Applications (1999) for an overview of these topics. Within the context of this chapter, the key point to consider is that particle number concentrations within cleanrooms are tightly regulated by virtue of the specific criteria with which they must comply to secure and maintain a given classification. For example, to comply with Class 5 criteria under ISO 146114-1, no more than 1.0×10^5, 2.37×10^4, 1.02×10^4, 3.52×10^3, 8.32×10^2 and 2.9×10^1 particles m^{-3} may be present in room air for particle sizes equal to and greater than 0.1, 0.2, 0.3, 0.5, 1 and 5 μm, respectively (Möller 1999). The large difference between acceptable concentrations of the smallest (i.e. 0.1 μm) and the largest (i.e. 5 μm) particles within the aforementioned cleanroom class thus considers typical particle size distributions present in many indoor and outdoor environments (i.e. dominated, in terms of number, by smaller particles). Different activities necessitate varying degrees of air cleanliness, and the several cleanroom classes are designated in order to minimise the possibility of negative effects caused by airborne particles, and other parameters, on the process(es) undertaken within the cleanroom.

4 Source Emissions of Particulate Matter

4.1 Particle Mass

There are many sources that contribute to particulate matter in the environment. Figure 2 shows a breakdown of PM_{10} emissions from various sectors in the US in 2002. The total emission is 1.87×10^7 tonne, of which 50% comes from road dust. Industrial processes together with electricity generation account for about 1.6×10^6 tonne or 9%. The corresponding $PM_{2.5}$ emissions show a 27% contribution from fires, followed by 22% from industrial processes and electricity generation and 19% from road dust. Nowadays, most industrial stacks in the developing world are equipped with highly effective dust removing facilities, such as electrostatic precipitators and fabric filters, so that the total particle mass emissions are often reduced by over 99% to give concentrations of less than 1–2 mg m^{-3}. The PM_{10} component is higher than 90% when the sources are combustion or evaporative processes (Dreiseidler et al. 2000).

4.1.1 Industry

A major industrial source of particulate matter in the environment is coal-fired combustion for electricity generation. Source performance standards in the US restrict total particulate emissions from new coal-fired power plants to 6.4 ng J^{-1}

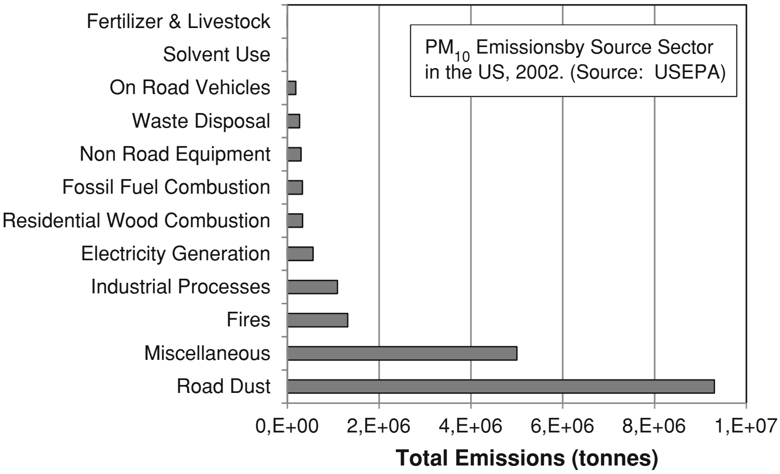

Fig. 2 PM10 Emissions by Source Sector in the US, 2002 (*source*: USEPA 2008a, b)

(USEPA 2005). The EU standards are specified for three rated thermal input ranges of 50–100, 100–500 and >500 MW and are 100, 100 and 50 mg m^{-3} for existing plants and 50, 30 and 30 mg m^{-3} for new plants, respectively. Australian standards are also based on the age of the plant, and range from 400 mg m^{-3} for plants licensed before January 1972, to 50 mg m^{-3} for plants licensed after September 2005.

Industrial sources include asphalt and cement manufacture, rock processing, fertilizer, chipboard, steel and other metal production plants. Most of these industries have their own emission standards that vary from country to country, and may be specified for individual stages in the manufacturing processes.

4.1.2 Motor Vehicles

Motor vehicle emission standards specify the maximum amount of pollutants in engine emissions. First introduced in California in 1959 to control carbon monoxide and hydrocarbon emissions from gasoline engines, they are usually regulated through government ministries and agencies responsible for the protection of the environment. While the standards dictate how much pollution vehicles may emit, it is left to the manufacturers to determine how these limits are to be achieved. In response to tighter standards, vehicle manufacturers have consistently improved engine design and equipped more sophisticated emission control devices and systems over the years.

Today, emissions, including particulate matter, are regulated in many countries and specified separately for the various emission parameters and vehicle and fuel types. Particulate mass emissions are measured by gravimetric methods over engine or vehicle test cycles, which consist of a sequence of speed and load conditions conducted on an engine or chassis dynamometer. Test cycles are designed to closely mimic the typical driving patterns of vehicles in various situations. Emissions measured on a vehicle or chassis dynamometer are usually expressed in mass per distance, such as g km^{-1} while when measured on an engine dynamometer in accordance with a test cycle, they are expressed in terms of mass per mechanical energy output, such as g kWh^{-1}. Emission test procedures are not the same across different countries and many types of drive cycles are used. Therefore, even when expressed in the same units of measure, engine emissions measured on different test cycles may not be comparable. This should be borne in mind when comparing emission standards from different countries.

4.1.3 Cars and Light-Duty Trucks

The US presently adopts the Tier 2 Standards as specified in the National Clean Air Act that were phased in between 2004 and 2009. Emissions are measured over the Federal Test Procedure (FTP-75) and expressed in g $mile^{-1}$. These standards apply to all passenger cars, minivans, light-duty trucks and SUV's irrespective of fuel type (such as gasoline, diesel or alternative fuels). However, they are structured into 11 certification levels of different stringency called ‘certification bins’ and, within certain restrictions related to type of vehicle and weight, vehicle manufacturers are given the choice of assigning vehicles to the available bins. The particulate mass emission standards for cars and light-duty vehicles range from 10 to 20 mg $mile^{-1}$.

The EU adopted emission regulations for new light duty vehicles (cars and light commercial vehicles) as specified in Directive 70/220/EEC. This basic directive has been amended a number of times from Euro 1 to the most recent Euro 6 standard, which was applied in 2009. These regulations include different emission limits for diesel and gasoline powered vehicles and are in general more stringent than the corresponding US standards. The Euro 4 standard introduced in 2005 limited the sulfur content in both fuels to 50 ppm, with the proviso that ‘sulfur-free’ ($\leq$10 ppm) be made available from 2005 and mandatory from 2009. Emissions are determined over the European 13-mode test cycle and expressed in g km^{-1}. The EU particulate matter emission standards for passenger cars and light commercial vehicles are summarised in Table 1. There were no European regulations for petrol cars until Euro 5 in 2009. Light commercial vehicles are classified into three classes according to vehicle mass. The Euro 5 and 6 standards of 0.005 g km^{-1} are to be changed to 0.003 g km^{-1} using the particle measurement programme (PMP) procedure.

Australian Design Rules (ADR) to regulate vehicle emissions are based on European standards. The current standards for all vehicles are equivalent to Euro 4. Japan introduced a regulation based on a new JC08 cycle in 2009 that limits particle mass emissions from cars and light duty vehicles to 0.005 g km^{-1}, to be fully phased-in by 2011. China presently stipulates Euro 4 standards for the Beijing region and Euro 3 for the rest of the nation.

Table 1 The European Union particulate matter emission standards for passenger cars and light commercial vehicles

		Passenger Cars		Light Commercial Vehicles					
		Petrol	Diesel	Petrol			Diesel		
Tier	Date			N1	N2	N3	N1	N2	N3
Euro I	Sep 1992	-	0.14	-	-	-	0.14	0.19	0.25-
Euro 2 IDI	Jan 1996	-	0.08	-	-	-	0.08	0.12	0.17
Euro 2 DI	Sep 1999	-	0.10	-	-	-	0.10	0.14	0.20
Euro 3	Jan 2000	-	0.05	-	-	-	0.05	0.07	0.10
Euro 4	Jan 2005	-	0.025	-	-	-	0.025	0.04	0.06
Euro 5	Sep 2009	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Euro 6	Sep 2014	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

*N*1≤1,305 kg; *N*2 1,305–1,760 kg; *N*3 >1,760 kg

4.1.4 Heavy-Duty Trucks and Buses

In the US, heavy-duty vehicles are defined as vehicles with gross weight over 8,500 lbs. USEPA emission standards for heavy duty diesel truck and bus engines controlled particle mass emissions from 0.60 g $\mathrm{bhp}^{-1}\ \mathrm{h}^{-1}$ in 1990 to 0.10 g $\mathrm{bhp}^{-1}\ \mathrm{h}^{-1}$ in 1998. A new stringent mass emission standard that took effect with the 2007 heavy-duty engine model year limits particle mass emissions to 0.01 g $\mathrm{bhp}^{-1}\ \mathrm{h}^{-1}$. This included a diesel fuel regulation that currently limits sulphur content to 15 ppm.

Emission regulations for heavy-duty vehicles in Europe were originally introduced by Directive 88/77/EEC which was followed by a number of amendments. As a result, mass emission standards for diesel heavy-duty engines were reduced from 0.36 g kWh^{-1} in 1992 (Euro 1) to 0.02 g kWh^{-1} in 2008 (Euro 5). Figure 3

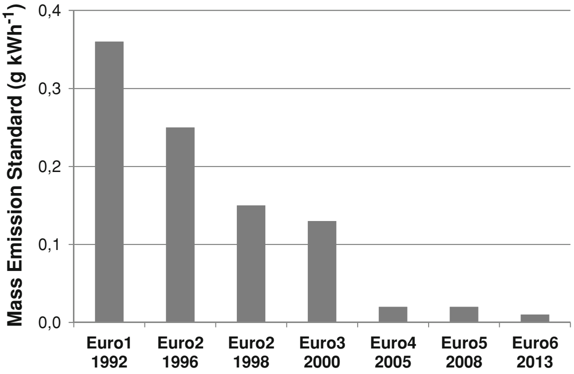

Fig. 3 European mass emission standards for heavy-duty diesel engines (data derived from Dieselnet 2009)

shows the improvement over this time. It is further expected to be reduced to 0.01 g kWh^{-1} in 2013 (Euro 6).

Emission standards for Australia are generally based on European standards. Starting from Euro 1 standards in 1995/1996, the present standard (2009) is Euro 4.

4.2 Particle Number

4.2.1 Industry

There is very little information in the literature on particle number emissions from industrial facilities. Consequently, there are no standards controlling particle number emissions from industrial sources. Dreiseidler et al. (2000) used an Anderson cascade impactor to collect particulate samples in industrial stacks in Germany. The samples were analysed gravimetrically and the peak particle number concentrations were found at an aerodynamic diameter of 0.66 μm from a hard coal combustion plant and 7.15 μm from a rock processing crusher plant, clearly illustrating that the emitted particles from combustion processes are finer than those from mechanical processes. Ohlstrom et al. (2000) measured fine particle ($PM_{2.5}$) emissions from several types of boiler plants in Finland using an electrical low pressure impactor (ELPI) and showed that the particle size distributions varied with boiler size and particle separation devices. They reported a peak particle concentration at a size of about 0.1 μm. Morawska et al. (2006) used a scanning mobility particle sizer (SMPS) to monitor particle emissions in the stack of a shale facility in Australia and showed that the particle size distributions were bimodal with average modal count median diameters of 24 and 52 nm (Fig. 4). This study also demonstrated that particle size distribution measurements have the potential to be used as source signatures of industrial emissions.

4.2.2 Motor Vehicles

In 2009, the European Union introduced a particle number limit to its Euro 5/6 emission standard for light-duty diesel vehicles. This is the first particle number standard introduced anywhere in the world. Particle number concentrations will be measured according to the PMP procedure, and emission factors will be limited to $5 \times 10^{11}\ km^{-1}$. Motor vehicle emissions often contain large numbers of volatile and semivolatile nanoparticles that are produced after emission from the tailpipe. The formation mechanisms of these nanoparticles, their associated health effects and concentrations are topics that are not well-understood; as a result, the issue of whether these nanoparticles should be included in particle number standards has been the subject of much controversy in the recent past. In order to avoid this

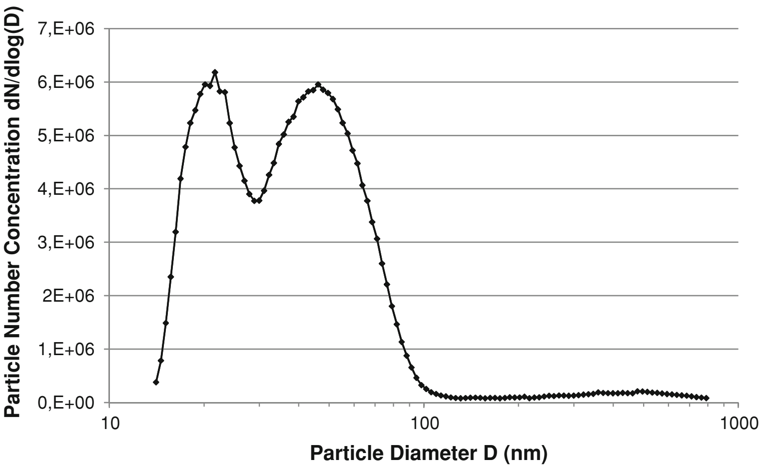

Fig. 4 Particle size distribution measured in a shale facility stack by Morawska et al. (2006)

issue, the PMP procedure eliminates all volatile material from the particles, such that only solid particles are counted.

4.3 Other Source Emissions of Particulate Matter

Whilst the contributions of vehicular combustion and industrial processes to overall particle emissions are significant, the majority of global emissions are ascribed to natural sources (Hinds 1999). Obviously, it is not possible to directly regulate the latter; only those anthropogenic emissions with which they may interact. Natural particle sources are distributed relatively evenly around the world, whilst anthropogenic emissions are largely confined to, and thus affect, populated areas (Hinds 1999). Identifying the sources of particulate matter present in ambient air in these locations is not a straightforward process. Source apportionment of particulate matter seeks to identify individual source signatures amongst what Eastwood (2008) referred to as the "almost incomprehensible anarchy" that characterises the dynamics and origin of many aerosols. Chemical mass-balance approaches are typically implemented to achieve this, and these can be divided into source and receptor-oriented techniques. In their oft-cited study, Schauer et al. (1996) used organic compounds to trace the origins of fine particulate matter collected at various urban sites in the Los Angeles area during 1982. The authors found that the bulk of primary fine particles measured at their monitoring sites were due to diesel and gasoline combustion exhaust, meat cooking, wood combustion and dust emitted from paved roads (Schauer et al. 1996). These sources also contributed substantially to overall fine ($PM_{2.5}$) particle mass (i.e. primary and secondary); although their relative importance was different to that measured in terms of primary fine particles, and road dust, wood combustion and meat cooking often made a larger combined contribution to fine particle mass than diesel and gasoline exhaust (Schauer et al. 1996). Evidently, emission sources other than automobiles and trucks can constitute a significant proportion of urban aerosols, and some of the most common of these are introduced below.

4.3.1 Roads Dust and Wear Products

Particles emitted from the surface of both paved and unpaved roads can have diverse origins, and are attributable to the mechanical wear of both vehicle tyres and the road surface at their interface in addition to products of the wear-and-tear of vehicle components (e.g. brakes, clutch, catalytic converters and exhaust systems), natural materials (e.g. mineral dust and leaf litter) and deposited combustion particles. The particles released from road/tyre interactions may thus be primary, secondary or resuspended. The characteristics of particles released via such processes, and their relationship with vehicle (Gillies et al. 2005), tyre (Dahl et al. 2006; Hussein et al. 2008) and road (Claiborn et al. 1995) parameters, in addition to the development of emission factors, is gathering momentum as a research topic. Given the potentially large contribution of road dusts (especially for unpaved roads) to ambient particle mass concentrations and their potential effects on human health (Miguel et al. 1999), such investigations are critical for emission assessment, modelling and control. Ultrafine particle release from certain road/tyre interactions have been shown to be substantial (Dahl et al. 2006), and as noted by Morawska et al. (2008a, b), this is a topic requiring further systematic research.

4.3.2 Aviation and Shipping

Non-road transportation modes, of which aviation and shipping are the most dominant in most locations, have come under increasing scrutiny with respect to their particulate emissions in recent times. Both involve the use of large combustion engines operating over extended periods at varying loads during transit and when at air or sea ports. This can have an appreciable impact on ambient particle concentration. For example, based on a study in the Mediterranean, Viana et al. (2009) estimated that proximate shipping activities contribute 14% of annual average ambient $PM_{2.5}$ mass concentration in the port city of Melilla. Global annual particle mass emissions caused by shipping have been estimated to lie between 0.4 and 3.4 Tg (Eyring et al. 2009), which marks them as a significant contributor to global anthropogenic particle emissions. Particle number emissions from shipping activities may also have a significant effect, and Sinha et al. (2003) estimated that global annual emissions of particles greater than 3 nm attributable to ocean-going ships were approximately 25% of those caused by biomass burning; which is itself a major source of particles. Notwithstanding the often substantial uncertainties inherent in emission estimates, shipping activities have the potential to have a measureable impact on particle mass and number concentration at a range of spatial scales. It is important to note, however, that in areas with multiple strong particulate sources (i.e. many urban areas), the relative contribution of shipping activities is likely to be relatively minor (Minguillón et al. 2008). It is equally important to consider, that, despite this, the mobile nature of the emission source coupled with the fact that the overwhelming majority of ship emissions occur within 400 km of land, gives rise to a scenario where shipping may affect air quality at a multitude of coastal locations (Eyring et al. 2009). Particulate emissions from ships are not directly regulated; although progressively more stringent fuel sulphur content restrictions will be adopted over the next decade, and these are expect to substantially reduce particle emissions (Lack et al. 2009).

Emissions due to aviation (which primarily relies on kerosene fuels) can have various impacts depending upon the spatial and temporal scale of interest. There are numerous research foci regarding the effects of aviation particle emissions on planetary radiative forcing and climate phenomena (Lee et al. 2009), and given the ever-increasing popularity and volume of civil aviation flights, this topic is very likely to come under even greater scientific scrutiny in the future. However, from the perspective of human health impacts, it is ground based aircraft activities (idling, taxiing and take-off) that are of paramount significance. Recent studies have indicated that particulate emissions due to ground-level such procedures can cause particle concentrations substantially elevated above background levels, especially in terms of UFPs (Westerdahl et al. 2008; Mazaheri et al. 2009; Hu et al. 2009). Aircraft particulate emissions are not directly regulated.

4.3.3 Miscellaneous Fossil Fuel Combustion

There are many non-vehicle fossil fuel combustion sources that can potentially impact upon ambient particulate concentration. Two and four-stroke garden implements (lawn mowers, edge trimmers, leaf blowers, chainsaws etc.), generators (both diesel and petrol) and non-road recreational sources such as outboard and inboard marine engines and snowmobiles, to name but a few, are all sources of particulate emissions. Additionally, in some developing countries, two-stroke road vehicles dominate transport fleets in urban areas (Eastwood 2008). Two-stroke combustion has traditionally been regarded as an emission-intensive process; owing to the large fraction of fuel and lubricant that escapes complete combustion, and despite recent technological developments that allow newly-built two-stoke engines to conform to increasingly stringent HC emission standards in developed countries, the developing regions where two-stroke combustion predominates are unlikely to utilise engines fitted with such control mechanisms (Eastwood 2008). Particulate emissions from non-road two and four-stroke engines are not regulated, although HC and NO_x emissions are in many developed countries, and it follows that regulation of these parameters will lead to associated reductions in primary and secondary particulate emissions from these sources.

In addition to its widespread use in power generation, coal is also used for heat generation in residential settings across many countries, as too are liquid and gas-phase fossil fuels (Lighty et al. 2000). Such practices can affect ambient air quality, and Junninen et al. (2009) estimated that up to 58% of PM_{10} concentrations measured in the Polish town of Zakopane were due to residential heating.

4.3.4 Cooking

Although primarily conducted indoors, certain cooking processes leave an observable signature in outdoor air and contribute to ambient fine particle mass (Schauer et al. 1996). Frying, grilling and barbecuing are the techniques most likely to generate significant particle emissions, given the high temperatures often involved. There are numerous factors affecting particle emissions due to cooking, such as food type, cooking technique, temperature, the presence and amount of oils and type of heat source (i.e. electric, gas or other); although under many permutations of these factors, the overwhelming majority of emitted particle numbers fall within the ultrafine size range (Wallace et al. 2004; Buonanno et al. 2009). The bulk of solid fuel use (fossil and biomass) for cooking and heating occurs primarily in developing world, and there are numerous attendant health implications of this practice (Smith et al. 2000). Although a significant source of ambient particles, the ethical and logistical issues associated with implementing any meaningful regulations regarding how people and businesses cook food within their own properties are numerous, such that regulation of this source seems highly unlikely in the short term.

4.3.5 Biomass Combustion

Anthropogenic biomass combustion, whether for the reduction of seasonal fire fuel loads or residential purposes, can be a major contributor to ambient particle concentration (Wardoyo et al. 2006). Under certain conditions, a substantial proportion of PM_{10} and $PM_{2.5}$ can be ascribed to wood-fired domestic heating in some cooler climates (Luhar et al. 2006; Ries et al. 2009). The emissions of fine and ultrafine particles from biomass combustion are not well-characterised, however, somewhat similarly to emissions from cooking, appear to be strongly dependent on biomass type, section (e.g. wood or leaves/branches) and combustion temperature (Wardoyo et al. 2006). Wood heater and fuel manufacturers in some countries are required to conform to allowable levels of particulate mass emission per unit mass of fuel burnt. Particle mass emissions from other types of biomass combustion are regulated indirectly in some locations via qualitative guidelines, such as limiting the number or extent of fires or not permitting biomass burning under certain meteorological conditions. Particle number emissions from biomass combustion are unregulated.

4.3.6 Miscellaneous Sources

The scope of this section has been limited to an introduction to the most widespread anthropogenic particle emission sources. There are multiple additional sources of primary and secondary particulate sources, including, but not limited to: waste incineration, construction, agricultural processes, cigarette smoke and fugitive emissions.

5 Other Policy Measures

The reduction of human exposures to particles as a preventative health care measure can have diverse applications in numerous environments. However, for the purpose of providing an example of wide relevance, the indoor environment of residential and commercial buildings located proximate to major roadways will be used as a case in point.

It is clear that, in terms of number, the overwhelming majority of freshly emitted particles from vehicular combustion reside in the ultrafine size range. The instability of many of these particles results in their relatively rapid transformation into a larger size fraction with an appreciable and readily–measured mass. How the variable time and spatial scales involved in these processes relate to human exposure to particles near this source was poorly understood until the first few years of the twenty-first century, when two separate but equally comprehensive studies were reported, based on measurements of the relationship between particle concentration and distance from roadways under various wind conditions (Sioutas et al. 2005). These studies, performed in Australia (Hitchins et al. 2000) and the USA (Zhu et al. 2002a, b), highlighted that ultrafine particle concentrations do not reach concentrations comparable to background until a distance of at least 300 m cross or downwind of major roads is reached. By comparison, these studies also noted that fine particle mass concentrations exhibited relatively small decay with distance from roadways.

The work of Hitchins et al. (2000) and Zhu et al. (2002a, b) have clear implications for ultrafine and fine particle exposure reduction as they relate to persons living and working near major roads. Depending on geographic location, residential dwellings employ either natural ventilation, or a combination of natural and mechanical ventilation. In the former case, particle ingress from outdoors to indoors via open windows, doors and through infiltration pathways occurs relatively unimpeded for accumulation mode particles, while ultrafine and coarse particles enter with reduced efficiency due to their increased susceptibility to removal mechanisms. However, where ventilation pathways are large, as is the case in most naturally ventilated buildings, the reduction in concentration of particles is typically minimal (Liu and Nazaroff 2003). Accordingly, constructing naturally ventilated dwellings proximate to major roads and freeways (especially within ~150 m), or vice versa, is likely to lead to significantly increased particle exposure for the occupants. In the case of mechanically ventilated offices and dwellings, the factors influencing exposure to outdoor particles are the particle removal efficiency of the heating, ventilation and air conditioning (HVAC) system and its associated filtration devices, and the rate at which outdoor air is delivered to the building. Most standard filtration media exhibit minimum capture efficiency for accumulation mode particles for the reasons outlined previously, and a variety of operational factors, such as dust loading and air flow rate, can further influence their efficiency (Hanley et al. 1994). The ability of the HVAC system and standard filters to reduce particle number concentrations in air delivered to commercial buildings located near major roads was shown by Jamriska et al. (2000) to be fair at best. Additionally, the height at which air is drawn into the building from outdoors can be an important determinant of particle concentrations contained in incoming outdoor air (Hitchins et al. 2002). Although occupants of mechanically ventilated buildings located near busy roads will be afforded greater exposure reduction than those in naturally ventilated buildings, the best exposure reduction policy is to separate, at the planning stage, buildings and major roads by as large a distance as practicable, preferably by 150 m or more.

6 Summary and Conclusions

The aim of this work was to review the existing regulations and policy measures related to reduction of airborne particulate matter, which is perhaps the most complex airborne pollutant to understand and manage. This is because there are many different physical and chemical (as well as microbiological) properties of the particles. This complexity is amplified by difficulties associated with simultaneous measurement of these properties and the lack of clarity regarding which are the most significant in terms of their impact on human health and the environment, and, therefore, which should be the prime target of regulations. The complexity starts when we attempt to measure one of the basic property of the particles, their size, to find out that it spans over five orders of magnitude, which is a too large range for any single measuring technique; consequently, there are only a few existing standard techniques with which to measure certain particle characteristics.

Health guidelines, the most important tool in developing national regulations, exist only in relation to one type of particle matter characteristic; its mass concentration in two size ranges: $PM_{2.5}$ and PM_{10}. Over the last few decades the studies have shown that it is the smaller particles, which potentially have higher health impact, and therefore there has been a trend in lowering the size of regulated particles. A good example of this trend is the US, where initially TSP was regulated, and was eventually replaced by the PM_{10}, with $PM_{2.5}$ regulations introduced later. It has been shown that within the current range of concentrations studied in epidemiological studies there are no threshold levels and that there is a linear exposure-health response relationship. Based on this, in the most recent review the World Health Organization Air Quality Guidelines, a new set of guidelines for particulate matter was introduced, with annual mean values for $PM_{2.5}$ and PM_{10} of 10 and 20 $\mu g\ m^{-3}$, respectively. This was based on an American Cancer Society study (Pope et al. 2002) and represents the lowest end of the range over which significant effects on survival have been observed (WHO 2005). It is important to note that these values are not much higher than the concentration levels encountered commonly in natural environments (while it should be acknowledged that, in some locations and under some circumstances, concentrations in natural environments may be well below or above those cited). If future epidemiological studies report response at lower concentration levels $PM_{2.5}$ and PM_{10}, it is likely that the guideline values will be lowered even further.

While there is a large body of toxicological evidence of the potential detrimental health impacts of UF particles measured in terms of number concentration and surface area, epidemiological studies have not yet provided any quantification of exposure–response relationships. Therefore, there are no scientific bases for setting particle number or surface area health guidelines. It has been shown in this review that vehicles are significant sources of UF particles, and it is the vehicle emissions that are commonly the most significant source of air pollution in most populated urban areas. It is therefore of particular significance to understand the magnitude and characteristics of vehicle-generated UF particles in urban air, as it is this environment which is the most likely to be considered as a target for future air quality regulations in relation to particle number. Industrial and power plant emissions have a significant impact on the environment and climate, but as they often (but not always) occur outside the most populated urban settings, their direct impact on human exposure is lower than the impact of vehicle emissions.

Despite the limitations in epidemiological studies, from atmospheric studies a picture starts emerging regarding particle number concentration levels and their spatial variation; both of significance when considering human exposure. It has been shown that the clean background levels are on average of the order of $2.67 \pm 1.79 \times 10^3\ cm^{-3}$, while levels at urban sites are 4 times higher and levels at road, roadside, street canyon and road tunnel sites are 16, 18, 27 and 64 times higher, respectively. Thus, the range of concentrations between clean and vehicle-affected environments spans over two orders of magnitude. This is very different from particle mass; for example a review by Morawska (2003) showed the decrease in mass concentration between a busy road and urban background ranges only from 0 to about 25–30%. This large variation in particle number concentration across different environments has profound significance in relation to human exposure assessment and epidemiological studies. This means that unless exposure assessment is conducted where exposures occur and at time scales that elucidate the temporal nature of the exposure, it is unlikely that epidemiological studies would provide answers based only on monitoring in central locations. In other words, central monitoring alone underestimates exposures and may lead to inappropriate management of public health risks.

As discussed above, the current state of knowledge on exposure-response relationships provides basis only for particle mass concentration health guidelines, and as a result, there are currently standards for mass only. PM_{10} includes $PM_{2.5}$, currently discussed in the US is the combination of $PM_{2.5}$ and $PM_{10\text{–}2.5}$ (fine and coarse) standards, which enable more efficient regulations of particles generated from different sources. Even more efficient would be a combination of PM_1 and PM_{10} standards in controlling combustion related ambient particles, as well as those originating from mechanical processes, however, the very limited body of epidemiological studies related to PM_1, coupled with the technical challenges of PM_1 measurements, make this combination unlikely to be considered in a foreseeable future.

While lack of UF particles exposure response relationship makes it impossible to propose health guideline for UF particles, it is important to point out that as discussed above, the current levels in environments affected by vehicle emissions are over an order of magnitude higher than in the natural environments. Thus, if there is also no threshold level in response to exposure to UF particles, as it does not relate to $PM_{2.5}$ or PM_{10}, future control and management strategies should target a decrease of these particles in urban environments to bring them closer to the background levels. This means that in many urban areas the concentrations should be lowered by one two orders order of magnitude to achieve this.

It is important to keep in mind that, unlike those relating to particle mass concentration ($PM_{2.5}$, PM_{10}), there are no standard methods for conducting size classified particle number measurements. Additionally, the number concentrations reported depend on the instrument used and its setting. This indicates the need for the development and utilization of standardised measurement procedures, thus enabling meaningful comparisons between the results of different studies. This is of particular significance for human exposure and epidemiological studies, and also regarding any future regulations of UF particles.

One additional issue in relation to UF particles is that secondary particle formation results in rapid increase of particle number concentrations by one to two orders of magnitude to concentration levels of the order of 10^5 particles cm^{-3}. This would present a challenge if there were future regulations considered based on particle number. Issues to resolve would include: (1) whether the regulations should be set around the base line concentrations without the peak concentrations, or whether they should include the peaks; and (2) how the peaks are to be defined. Developing a much better picture of particle formation dynamics in different environments, including those which are influenced by traffic, would greatly assist the formulation of such regulations.

In contrast to the above, there are cleanroom particle number concentration standards. Within the context of this review, the key point to consider is that particle number concentrations within cleanrooms are tightly regulated by virtue of the specific criteria with which they must comply to secure and maintain a given classification. This stands in great contrast to outdoor environments worldwide, where no regulation policies are in effect. Many questions are raised by this apparent discontinuity, and the casual observer is permitted to wonder why such well-defined measures are in place to quantify and assess particle number concentration in the specialised indoor environment that cleanrooms represent, yet any discussion of applying similar approaches to outdoor environments is often subject to consternation and contention. The answer to this is not simple, and a topic unto itself. However, the complex and variable nature of particle emission sources outdoors, coupled with the vicissitudes of particle generation processes and behaviour (especially towards the smaller end of the measureable size spectrum), can be held partly accountable.

Motor vehicle emission standards are derived on the basis of factors such as technological capabilities of engine design and after-treatment devices and the impact of emissions on the environment and ambient air quality standards. Emission standards and test procedures are well stipulated for both heavy-duty and light-duty vehicles in the US and in Europe. These standards are generally described in terms of total particle emission, rather than PM_{10}. Emission test procedures are not the same across different countries, and many types of drive cycles are used. Therefore, even when expressed in the same units of measure, engine emissions measured on different test cycles may not be comparable. Several countries, such as Australia and India, have adopted standards based on the Euro standards. In general, Euro standards are more stringent than those enforced in the USA.

With improvements in technology and more rigorous restrictions on air quality, motor vehicle emission standards have been getting tighter over the years. For example, between 1992 and 2008, European particulate mass emission standards for heavy-duty diesel engines have been reduced by an order of magnitude. But the most significant change occurred in 2009, when the European Union introduced a particle number limit of 5×10^{11} km^{-1} to its Euro 5/6 emission standard for light-duty diesel vehicles. In response to these increasingly stringent standards, manufacturers have been forced to consistently improve engine design and fit more sophisticated emission control devices and systems to vehicles.

Another important group of emission standards are those related to industrial emissions. There are standards in place restricting particle emissions from coal-fired power plants targeting different rated thermal inputs, as well as different age of the plants. Other industrial sources such as asphalt and cement manufacture, rock processing, fertilizer, chipboard, steel and other metal production plants usually are regulated by their specific emission standards, vary from country to country, and are sometimes specified for individual stages in the manufacturing processes. It is important to note that all these standards refer to total emissions of particulate matter, and not size specific emissions (such as $PM_{2.5}$ or PM_{10}). This constitutes a clear disparity between emission and air quality regulations, with the later being size specific. In relation to particle number emission from industrial sources, there is very little knowledge on this, and in turn, no regulations.

There are many other sources of airborne particulate matter; some of the most significant of these include aviation, shipping, biomass combustion, waste incineration, construction, agricultural processes, cigarette smoke, fugitive emissions, cooking and non-vehicle diesel, two, and four-stroke combustion None of these sources are directly regulated in terms of particle emissions.

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