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Editors

Persistent Pollution – Past, Present and Future

School of Environmental Research – organized by Helmholtz-Zentrum Geesthacht

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Foreword

Environmental problems and tasks are complex, and their solution requires interdisciplinary cooperation. Emissions may be local, but transport of pollutants – especially of persistent organic pollutants (POPs) – are transboundary. Thus, our activities to minimize these environmental impacts have to be international.

The identification and assessment of pollutants is an evident challenge for a more sustainable world. Great efforts in identifying, assessing and managing chemical pollutants have already been made within the last decades – often with legal consequences. On the other hand, we observe a long time from early evidences on environmental impacts of harmful chemicals to regulatory decisions, with e.g., more than 50 years from the first evidence of ecotoxicological effects of polychlorinated biphenyls (PCB) until their legal limitation. Since new classes of chemical compounds, e.g., nanomaterials or ionic liquids, are continuously developed and sooner or later "disseminate" in the environment, many problems for the environment will remain.

The idea of Green or Sustainable Chemistry can contribute to achieving sustainability in two key areas. First, the resources and reagents used by the chemical industry must increasingly be obtained from renewable sources. Second, polluting technologies and products must be replaced by benign, safe and inherent alternatives. According to its current guidelines, the German Federal Environmental Foundation (DBU) can support projects in these fields, comprising the topics of

- Sustainable Chemistry
- Renewable Materials
- White Biotechnology

Further on, our scholarship programme awards about 60 Ph.D.-scholarships per year in all fields of science, e.g., biology, chemistry, engineering, economics and law. Apart from this German programme meanwhile comparable programmes exist for students from Poland, Czech Republic, Baltic States, Hungary, Romania and Bulgaria. We are convinced that current and upcoming environmental tasks can only be solved by a generation of well educated scientists, engineers and politicians, who are able to act in a holistic and integrated way.

This book is mainly the result of the Fifth School of Environmental Research (organized by Helmholtz-Zentrum Geesthacht) “Persistent Pollution – Past, Present, Future”, sponsored by the DBU and held in summer 2007. The School of Environmental Research focused on persistent organic pollutants (POPs), heavy metals and aerosols. This workshop combined practical tools and lectures in the field of description, comparison and assessment of environmental data and their causes and consequences with respect to different time scales in a convenient and skillful way. The result is very impressive, with authors from international leading institutes and excellent reputation. I thank the organizers Ralf Ebinghaus, Markus Quante and Götz Flöser, for preparing the Fifth School of Environmental Research, and the editors and authors for this readable work.

Hempel

Osnabrück, Germany

Dr. Maximilian Hempel

Preface

The contamination of the global environment by persistent pollutants is one key feature of the “Chemical Anthropocene”. This is the time period starting around the 1950s, where the distribution of chemical substances in our environment reached global dimensions, i.e., chemical analysis could demonstrate that these substances accumulate in ecosystems far away from the locations of their production and usage. For an assessment of possible future changes it is imperative to understand how the “system environment” has responded to past pressures and changes induced by human activity. These human drivers include the input of chemical substances, metals and aerosols, but also policy action aiming at the regulation of the releases of harmful substances in order to reduce their impact on environmental health.

From past research it is evident that numerous factors are involved and influence the time frame in which pollution of the environment with a particular chemical substance reaches global dimensions. On the other hand, the response time of contaminated environments to political measures taken to reduce pollution is also strongly dependent on various physico-chemical and environmental parameters.

This book evolved from the Fifth School of Environmental Research entitled “Persistent Pollution – Past, Present and Future”, which has set a focus on persistent organic pollutants (POPs), heavy metals and aerosols. The Summer School was held from May 9 to 18, 2007 in the Göhrde Hunting Castle, about 50 km south of Hamburg, Germany. Thirty-six Ph.D. students and post-docs from 25 countries attended the school in the middle of a large northern German forest area.

Research topics covered by the Fifth School included the

- Reconstruction of past changes based on the scientific analysis of natural archives such as ice cores and peat deposits
- Evaluation of the present environmental state by the integration of measurements and modelling and the establishment of cause-effect-patterns
- Assessment of possible environmental future scenarios including emission- and climate change perspectives

Leading scientists in the field of marine and atmospheric chemistry, meteorology and modelling, environmental chemistry and physics, as well as environmental policy and management were invited lecturers at the Fifth School of Environmental

Research and a large number of them have prepared manuscripts published in this book. In order to complement some of the covered topics additional authors have been invited to contribute to the book in their special field of expertise.

The present book consists of 20 contributions prepared by more than 40 authors. The structure of the book has been outlined according to the topics addressed by the school and includes synthesis chapters which look into the history and reconstruction of environmental pollution, address emission questions, provide a closer look on selected persistent pollutants, deal with transport and modelling aspects, shed light on some health issues related to persistent pollutants, and discuss emerging contaminants in the atmospheric and marine environment.

The editors thank all authors contributing to this volume and are grateful to the *German Federal Environmental Foundation* (DBU) and the Association "Gesellschaft zur Förderung des Helmholtz-Zentrums Geesthacht" (friends and supporters of Helmholtz Centre Geesthacht), who substantially supported the school. Many other persons have helped us to make the school and the book possible, in particular Mrs. Sabine Hartmann, Mrs. Ilona Liesner, Mrs. Beate Gardeike and Dr. Merja Schlüter. Thanks a lot to all of them.

Geesthacht, Germany
The editors, 31 July 2010

Dr. Ralf Ebinghaus
Dr. Markus Quante
Dr. Götz Flöser

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Part I
Introduction, History and Reconstruction

Chapter 1
A History of the Causes and Consequences of Air Pollution

Peter Brimblecombe

Persistent pollutants remain in the environment for a long time. This obvious statement makes historical analysis important. Such analysis can be useful at times for even very practical issues such as the record of the activity at old industrial sites, which are planned for redevelopment. Because the atmosphere has a relatively rapid turnover, persistent materials are frequently found as deposits on the earth's surface. This means there is a transition in the way we approach air pollution in comparison to earlier concerns over the pollutants smoke and sulphur dioxide from coal burning. These have relatively short lives in the atmosphere. There are long-lived pollutants such as nitrous oxide or carbonyl sulphide from aluminium production, that account for an increasing interest in such pollutants and their potential impact on the stratosphere. The best known example of persistence among the long-lived gases is the issue of CFCs and their relation to the widespread concern over the impacts they have on global climate and stratospheric ozone depletion.

The historical review here will not be limited to persistent pollutants, but rather look at how pollutants have been generated over time and how societies have viewed this process. There will be a special focus on the cities of London, Lüneburg and Los Angeles which show features that characterise certain aspects of human activity in relation to the atmosphere.

1.1 Antiquity of Understanding

Pollution was known from the earliest times and smoke frequently drew negative connotations. In the ancient Persian world:

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> Don’t cause the oven in a man’s house to smoke . . . it will ruin the bread.
> Proverbs from Nibru: c.6.2.1
> my mood and heart. As if during the night watch
> . . . like excrement. . . . my countenance like smoke.
> A hymn to Inana for Išme-Dagan: c.2.5.4.

It wasn’t simply an aesthetic concern because in the ancient world, air and health were strongly linked. Not surprisingly because the act of breathing is so readily associated with life. More thoughtfully classical medical writers linked air and health perhaps most notably in The *Hippocratic Corpus* which has a major section on air and health, although for the modern reader much of this would seem to be related to climate rather than air pollution. Nevertheless there is a continued miasmatic approach to disease origin (Brimblecombe 1987b). This view saw disease associated with the foul air and odours from swamps. It is clear that architects such as Vitruvius argued for the proper choice of location for dwellings. Nero’s tutor Seneca blamed the culinary odours of Rome for his ill health. The survival of this classical learning in the Middle East gave a particular focus on air pollution among and health in Arabic medical writings tenth century (Gari 1987). Evidence is also found in the Hebrew *Bava Batra* and *Ktubot* which describe a law that: “You can’t take a wife out of the village to a city . . .” which Rabbi Shlomo Yitzhaqi (“Rashi” 1040–1105) interpreted as arising “because the city is crowded and has no air . . . in the village the air is nice”. The blackening of buildings was another effect of air pollution recognised in the ancient world e.g.,

> Your fathers’ guilt you still must pay,
> Till, Roman, you restore each shrine,
> Each temple, mouldering in decay,
> And smoke-grimed statue, scarce divine
> Odes and Carmen Saeculare
> Horace

Along side this recognition of the effects of air pollution a variety of laws developed (Brimblecombe 1987a). In Aristotle’s *Athenian Politics* the duties of the astymomoi (controllers of the town) are described, among other things, as ensuring that for rubbish to be deposited beyond city walls. The Roman Governor of Britain from AD75–78, Sextus Julius Frontinus, was later appointed as Curator Aquarum in Rome. He improved Rome’s water supply and argued, presumably through a miasmatic connection that he also reduced the effects of the city’s “infamis aer . . . [or] gravioris caeli . . .”. It also marked the rise of the professional administrator, as he saw his position as a very important one and left a book about the administration of Rome’s water supply: De aquis urbis Romae. Roman nuisance law which treated issues of neighbourly responsibility in cities were known as the urban servitudes and these treated smoke as though it was water arguing: you could no more let water drain across a house than smoke. Relatively few solutions were available to solve air pollution problems in the ancient world, but the idea of zoning was apparent and in Rome glass making was moved to the suburbs where it caused less offence.

In addition to documentary materials there is archaeological evidence of past pollution. Tissue from Egyptian mummies shows evidence of air pollutants through the presence of anthracotic pigmentation in the lungs. This hints at anthracosis and silicosis in the ancient population, as mild forms of the occupational lung diseases that arise from inhalation of dusts. Capasso (2000) has argued that lesions found of the ribs of victims of the eruption of Vesuvius suggest that pleurisy was common in Roman times and this may be evidence of indoor pollution from burning vegetable matter lamp oils. There is skeletal evidence that Anglo-Saxon Britain had a high incidence of sinusitis and Wells (1977) believed this was related to the lack of chimneys in huts at the time which meant that the interiors became filled will smoke and thus aggravating the disease.

1.2 Air Pollution in Medieval Europe

Industries in the ancient world were often small, but some were large. Strabo notes the pollution from Spanish mining activities that occasionally spread over large areas. Mieck (1990) has termed the emissions from smaller localised industries as *pollution artisanale* and distinguished this from *pollution industrielle*. This distinction can be relevant when considering the development of legislation, as smaller scale enterprises can be controlled at a local level through by-laws, but large-scale pollution requires national legislation that did not arise until the nineteenth century.

A substantial shift in air quality medieval London came about through the use of coal after the depletion of convenient nearby wood supplies. This can be seen clearly in orders for building operations at Westminster in 1253 Henry III specify oak brushwood, while just 11 years later an order of 23 July 1264 reads "purvey for the King in London … a boat load of sea-coal". Large quantities of fuel were required for the production of lime that was used as a mortar. While there were economic pressures to change fuel, coal gave rise to a smoke with an unfamiliar small and the triggered miasmatic concerns over its effects on health (Brimblecombe 1987b).

One response was to promulgate legislation forbidding the use of coal and requiring a return to wood. Punishments were likely fine or confiscation of tools and destruction of the kiln, more than the death sentences imagined in more colourful accounts of medieval pollution (Brimblecombe 1987b). There is some evidence that chimney heights were of relevance in fourteenth century London as a case before the *Assize of Nuisance* reads "… the chimney is lower by 12 feet than it should be …. And the stench of smoke from the sea-coal used in the forge penetrates their hall and chambers so that (earnings drop to a third)". Clearly there were also economic reasons for this case being brought. It may also be that some groups recognised that greater stability at night increased the potential for air pollution as the *Calendar of Early Mayor's Court Rolls for London* (1301–1431) reveals that a group of black smiths in fourteenth century thought that sea-coal should not be burnt at night. However this might have been a noise issue as there are many complaints of the noise blacksmiths made late into the night (Brimblecombe 1987b).

Even where coal was not used large wood-burning industrial activities could create pollution problem, as it did in Imperial Rome. It is interesting to explore the situation during the medieval and early modern period of salt making in Lüneburg. This city is far enough north in Germany to make solar evaporation an inefficient method of salt production, so brines were heated to extract the salt. Lüneburg's salt was first mentioned in the year 956, when Emperor Otto the Great gave the customs for to the monastery of St. Michael's. Salt became a key product and important from 1276.

The mean production between 1554 and 1614 (the most productive time) was about 21,300 t per year. This required a wood consumption in the fifteenth and sixteenth centuries that is estimated between 48,000 and 72,000 m^3 per year (Lamschus 1993; Witthöft 1989). At the peak of its production Lüneburg salt-brine was boiled in 54 boiling huts each with four lead pans (see Fig. 1.1) at salt-works close to the now-demolished St. Lambert's Church. The boiling huts were buried in the ground, so loss of brine and heat was minimised. The huts were more or less completely made of wood. The clay kilns and the lead pans had to be replaced after about 4 weeks of use. As the boiling huts had no smoke stack, smoke and steam was lost from the entrance and windows as described in Georg Agricola's *De Re Metallica* (1556):

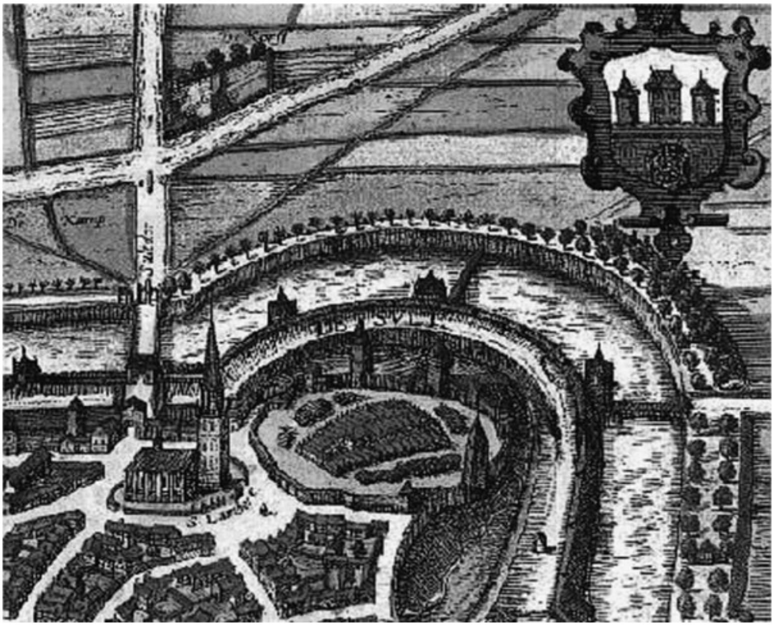

Fig. 1.1 The salt works in Lüneburg from the Braun/Hogenberg plan of the year 1574. The works with the huts are shown within a circular enclave near St. Lambert's church

Fig. 1.2 A view of Lüneburg from Braun and Hogenberg *Civitates Orbis Terrarum* (1572) in a woodcut of Sebastian Munster (1550). This shows the smoke cloud near St Lambert's church, which was close to the salt works

> At the top of the end wall are two small windows, and a third is in the roof, through which the smoke escapes. This smoke, emitted from both the back and the front of the furnace, finds outlet through a hood through which it makes its way up to the windows; (translated by Hoover and Hoover)

The works used a large amount of fuel, so pollution would have been inevitable. We can gauge the magnitude of this from early drawings of the town which show the smoke cloud above the city near St Lambert's church as especially noticeable (Fig. 1.2).

As in ancient Rome the technical control of air pollution from these early industries was difficult. Rather along the lines of the classical Mediterranean, activities such as tile, glass and brick making were moved to the outskirts and downwind of towns and cities such as York in England (Bowler and Brimblecombe 1990). Another possibility is to control the fuel type or permitted procedures, but there is no widespread evidence that this was tried, because as late at the 1660s the English environmentalist John Evelyn, was unable to raise much enthusiasm for these approaches.

1.3 Air Pollution in Early Modern Europe

The growth of interest in science characterised the seventeenth century and this was also apparent in the understanding of air pollution. In England this was seen in the work of many scientists within the early Royal Society (e.g., Brimblecombe 1978). John Evelyn in particular was noted for his pamphlet *Fumifugium* of 1661 which explored the causes and effects of air pollution in a coal burning city. However he was not alone and Sir Kenelme Digby's atomic view on the corrosive effect of coal smoke deriving from his *Discourse on Sympathetic Powder* (1658) can be traced (Brimblecombe 1987b) even earlier to Margaret Cavendish's *Poems and Fancies* (1653) who wrote:

Is, Atomes sharpe are in that coale entire
Being strong armed with Points, do quite pierce through;
Those flat dull Atoms, and their forms undo.

Evelyn's work is notable because he can be seen as modern and taking a more environmental perspective being concerned with the broader social issue of pollution and their regulation. He was aware of the health effects as were other scientists such as Nathaniel Henshaw the author of a treatise entitled *Aero-chalinos, or, A Register for the Air* (1664). John Graunt an early demographer who looked at death rates and thought the high rates in London compared to the country might be the result of the pervasive coal smoke.

The botanist Nehemiah Grew wrote to the Secretary of the Royal Society in 1682, on the effect of pollution from lead smelters on health (Brimblecombe 1978). This was much in line with a long concern over the general health problems for miners. The issue is much discussed by Georg Agricola in the mid sixteenth century in *De Re Metallica*, although illustrations of the salt-workers from Lüneburg do not show them wearing a face-cover that Agricola had recommended. Nevertheless the salt-workers of Lüneburg were well cared for and they had access to the Hospital of the Holy Ghost. This dates from the thirteenth century and was locate near to old St. Lambert's Church, adjacent to the salt workings. The ready access salt-workers had to the hospital may well suggested they needed its services, but this could well have been because of workplace accidents rather than problems of industrial hygiene.

The descriptions of the smoke in salt huts described by Agricola would indicate that workers were exposed to high concentrations of combustion-derived particulate materials. Our knowledge of the importance of fine particles suggests this would have exacerbated a range of health impacts, either respiratory health directly or cardio-vascular health via the oxidative stress imposed after fine particles that make their way into the alveoli of the lung.

There may also have been contaminants on the particles that could have enhanced their health impact. The high chloride concentrations of the process of salt-making could lead to the production of chlorinated compounds such as the polychlorinated dibenzodioxins and polychlorinated dibenzofurans. These have the potential to cause chloracne and induce cancers.

The medieval and early modern period saw the first of industrial epidemiology with the work of Agricola and the seventeenth century Italian physician, Bernardino Ramazzini (*De Morbis Artificum Diatriba*). However, occupational cancer was not recognised till the late eighteenth century when Percival Pott made studies of scrotal and nasal cancers among chimney sweeps who were exposed to coal tars in the soot. Chloracne, an industrial disease, which reveals itself as blackheads, cysts, and pustules, often noticed around the cheeks, was not discovered until 1897 when Von Bettman noticed its occurrence among German industrial workers.

Initially it was thought to be the result of chlorine and only later associated with chlorinated aromatic hydrocarbons.

There was also an early awareness of air pollutant damage to crops from writers such as the Roman Pliny or the medieval Hildegard von Bingen (1140) who regarded salt and dust as unhealthy for plants. John Evelyn wrote of damage to plants in *Fumifugium* (1661) and Fabri (1670) that volcanic acid rain damages fruit (Brimblecombe 1987b; Camuffo 1992).

We cannot ascertain the importance of any impact of the air pollutants from Lüneburg's salt-making. Nevertheless it would be worth looking for descriptions of chloracne among its salt-workers and although agricultural practice was hardly likely to be affected by the deposition of pollutants the soils around the site might well still show evidence of deposits of carbon, and the polychlorinated dibenzodioxins and dibenzofurans. The history of these chlorinated aromatic compounds in agricultural soils is now well known, but also leads to the surprising conclusion that there are widespread natural sources of polychlorinated dibenzodioxins and dibenzofurans (Green et al. 2004).

1.4 Sanitary Reform and National Regulation

The growing industrialisation of late eighteenth century Europe, most particularly the wide adoption of the steam engine meant that regulators had to consider a more formal approach to controlling air pollutants. Early regulations can be found in France and England from the beginning of the 1800s. These regulations were driven by a growing enthusiasm for sanitary legislation to improve urban health. Although much of this legislation was concerned with housing and sewage, in England it was frequently accompanied by smoke abatement clauses from the late 1840s. These were not effective, but signalled a political awareness that grew through the century (Brimblecombe 2003c), so by the early twentieth century it was clear that the key to controlling smoke was controlling furnaces, especially with automatic stoking (Brimblecombe 2003b), although Germany had earlier emphasised training of stokers.

There was also a need to incorporate science into policy and ensure that legislation was national rather than local in extent. In England this was characteristic of the Alkali Act (1863) which regulated the emissions of hydrogen chloride from a growing industry that produced sodium hydroxide for soap making etc. The hydrochloric acid emissions had destroyed vast tracts of vegetation and a national approach to its control came to be overseen by a government scientist the Alkali Inspector, Robert Angus Smith. The sources of air pollution from large chemical plant and smelters were of increasing concern in the latter half of the nineteenth century, with important scientific developments in Germany, especially science of pollution damage to crops (Schramm 1990) along with work by the US Bureau of Mines (Holmes et al. 1915).

The changes we see reflect a growing professionalisation that characterised the late nineteenth century. The men, and by the 1890s women (Brimblecombe 2003a), who regulated environmental health in cities needed a considerable amount of training. The specialist role for smoke inspectors emerged by the first years of the twentieth century to add to the improved academic understanding of air pollution (Brimblecombe 2003b).

The First World War, economic crises and another war slowed the arrival of legislation, although these years were not without developments such as studies of the problem of burning coal waste piles (Sheail 2003). After the Second World War and particularly the London smog of 1952, legislation appeared in terms of the Clean Air Act 1956. This legislation was one of the first purely modern pieces of air pollution regulation and although it may not have been as successful as some imagine as a key factor in improved air quality, it was an important step. It seems to have gone beyond mere legislation and affects our concept of environment – it has made us aware that personal freedom may have to be limited if we desire environmental improvement (Brimblecombe 2006).

1.5 Increasing Complexity

The twentieth century witnessed new forms of air pollution and health impacts that were quite unique. Air pollution increasingly derived from liquid fuels, mostly used in automobiles, became mediated by atmospheric photochemistry. Photochemical pollution was first recognised in Los Angeles of the 1950s by Haagen-Smit and was later to be found almost everywhere. The ozone in smog has no ground level sources, but is a product of atmospheric chemistry. Thus pollution became separated from the precursor pollutants via complex chemistry. The sophistication and high level of technical input required to manage modern air pollution has raised concern among politicians and decision makers (Brimblecombe and Schuepbach 2006), especially when results of the modelling seem counter-intuitive as it might when increasing roadside nitric oxide concentrations can react with ozone thus lowering its concentration.

We can also trace parallels in the health impacts of air pollutants. In the past they often seemed to have respiratory impact, but the modern understanding of the effects of fine particles indicates that they impose a broad cardio-vascular insult (Brimblecombe 2009). The carcinogens also create uncertainty over the problems whether they have thresholds for injury. Lead has been identified as a neurotoxin. Persistent organic pollutants have been seen as endocrine disruptors have been associated with a range of reproductive problems, behavioural problems and impaired immune functions. More recently exposures to a widening range of chemicals have promoted the controversial issue of multiple chemical sensitivity. Such complications draw attention to the increasing need to sound science to be able to integrate with well informed policy.

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Chapter 2
Modelling Air Pollution in Sixteenth Century Lüneburg

Peter Brimblecombe

As part of the workshop the students were presented with an exercise concerned with estimating the concentration and deposition of air pollutants around the salt works of Lüneburg during the sixteenth century.

We began with a short exercise that allowed students to reflect on issues that concerned late medieval Lüneburg from the perspective of influential civic groups (mostly merchant's guilds). Students were divided into groups representing urban guilds of: (1) saltmakers, (2) doctors and surgeons, (3) carters and haulers, (4) butchers, (5) bakers, (6) mayor and other elites. They discussed and ranked issues of concern to their guild considering issues such as: wood, food, trade, water, smoke, war and health or plagues.

During an excursion to the German Salt Museum at Lüneburg with an original boiling house from medieval times the students convinced themselves of the severe working conditions in the small rooms containing the boiling pans made out of lead. Figure 2.1 gives an impression of these working conditions, clearly indoor pollution was an important topic those days not because of incomplete combustion of the fire wood but also because lead from the pans entered air in considerable amounts.

Later in a computer laboratory they were provided with copies of SCILAB (similar to MATLAB) and two programs and their linked functions to model pollution. This allowed atmospheric dispersion of the pollution from the salt works to be modelled. Two approaches were adopted:

1. The average deposition flux of large particles was determined by considering the fall rate of the particles along with their dispersal by wind – (deposition model).
2. The concentrations in the air was estimated from a simple Gaussian plume models – (plume model).

The results gave a picture of air pollution in Lüneburg when it was a great salt producing town.

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Fig. 2.1 Worker at a lead pan in a salt boiling house. Photographic reconstruction of the medieval working conditions (Photo provided by Lüneburg Marketing)

2.1 Emissions

The models required that we estimate emission from the salt works Qp from the fuel use. This was available from historical data for the annual firewood use and overall salt production (Witthöft 1989; Lamschus 1993). Emission factors were required for relevant pollutants to determine emissions. These were taken as:

- Soot from wood 12 g/kg
- Particulate matter from wood 15 g/kg
- NOx from wood 0.2 g/kg
- PAH from wood 41,000 ng/kg
- Benzo(a)pyrene 1,200 ng/kg
- PCB from wood 550 ng/kg
- PCDD/PCDF from salt production 130 ng/kg – this has been enhanced tenfold over typical values for wood to allow for the large chloride concentration in the salt works

2.2 Deposition Model

In the case of long term deposition of particulate material we calculated the particle deposition around the sources using the early Bosanquet et al. (1950) model for the dispersion and deposition of large particles about a point source. This allows the flux of particles to the ground to be determined from as:

$$\mathrm{F_{bosanquet}} * \mathrm{F_{wind}} * \mathrm{Q_p} * \mathrm{a} * \mathrm{p} * \mathrm{p}/\mathrm{He}^2$$

Input, along with some initial guesses of values, includes:

- x = distance from source
- Q_p = source strength in g/s
- r = 25; particle radius in μm
- ρ = 1; particle specific gravity
- He = 10; emission height in m
- p = 0.05; dispersion factor
- u = 4.6; average wind velocity in m/s
- f_i = the wind probability along eight compass points. N, NE, E, etc.
- v_f = fall velocity this includes Stokes settling plus the Cunningham correction with radius, mean free path (La, 0.065) in μm, i.e.,
- $vf = 1.210^{-4} * \rho * r * r * (1 + La/r * 1.26 + .4 * \exp(-1.1 * r/La))$

There are also two functions to be executed in SCILAB,

1. The Bosanquet function treats the fall of the particles to the ground and utilises the gamma function (Γ) available in SCILAB:

$$F_{bosanquet} = (v_f/p * u) * (He/p * x)(2 + v_f/p * u) * \exp(-He/p * x)/\Gamma(1 + v_f/p * x)$$

2. F_{wind} which determined wind direction in 45° sectors at each point on the grid from an averages from a year's modelled meteorological data.

The calculations, although not especially difficult, can be rather tedious, particularly if we need to determine the concentration and deposition at a range of locations and do this for many salt-pans (49 were used in the modelling exercise). SCILAB allowed these to be done rapidly for multiple pans and for many deposition points and then plotted out as contoured deposition fields, using one of the numerous plotting functions available in SCILAB.

2.3 Plume Model

The concentration of pollutants downwind from the salt works is determined using a simple plume model (e.g., Pasquill and Smith 1983). As the emission height is very low with little plume rise so a ground level source approximation was adopted (although this simplification was not possible under the deposition model).

$$c = Q_p/(\pi\sigma_y\sigma_z U) * \exp(-y^2/(2 * \sigma_y))$$

c is the concentration and the whole expression has to be multiplied by a conversion factor to go from g m^{-3} to more comprehensible units such as from μg m^{-3} or ng m^{-3}.

y is the distance off the plume axis in metres, z is the height above the plume axis in metres, σ_y and σ_z are measures of dispersion in the cross-wind and vertical directions (perhaps thought of as standard deviation widths). These are functions of the distance from the source and the atmospheric stability, usually expressed as the Pasquill class. In the model these are calculated by a function called pasquill.

The meteorological input to the model for came from hourly meteorological data for the region Lüneburg (interpolated to the centre of a grid at: 10.4 °E, 53.25 °N) which was calculated using the MM5 model driven by ERA 40 reanalysis for the year 2000. It contained wind direction (degrees at 10 m), wind speed (m/s at 10 m), temperature at 2 m in K and incoming short wave radiation in W m^{-2}.

2.4 Results

The results suggested that the largest deposits of particulate materials occurred to the north east towards St Lambeth's Church, now dismantled. In Fig. 2.2 this is shown as an overlay on an inverted version of the pictorial map from Fig. 1.2. It was possible residual carbon and other recalcitrant deposits might be evident from soil cores. We also discussed the possibility of deposition of polychlorinated compounds in the fields to the beyond the nearby city wall. Plans were also developed for how this work might be used in a small brochure on pollution impacts for visitors to the Deutsches Salzmuseum.

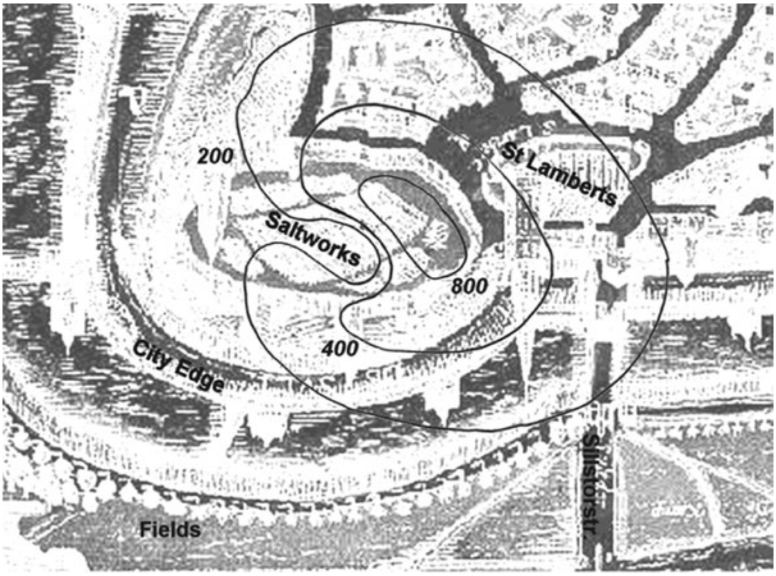

Fig. 2.2 The annual deposit of soot estimated from the model (g m^{-2}) as estimated from the deposition model plotted on an inverted and negative image of the pictorial map from Fig. 1.2

Although the models were not sophisticated it gave the students a flavour of what might be done with historical data. Students with experience of dispersion modelling had many, quite justifiable objections to the simplicity, those who had not done modelling or even programming before were excited with their achievements.

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Chapter 3
Heavy Metals in Antarctic and Greenland Snow and Ice Cores: Man Induced Changes During the Last Millennia and Natural Variations During the Last Climatic Cycles

Claude Boutron, Carlo Barbante, Sungmin Hong, Kevin Rosman, Michael Bolshov, Freddy Adams, Paolo Gabrielli, John Plane, Soon-Do Hur, Christophe Ferrari, and Paolo Cescon

In this chapter, we give an overview of some of the most interesting results which have been obtained by studying the changing occurrence of heavy metals in Antarctic and Greenland snow and ice cores. After recalling the pioneering role of Clair Patterson in this field, we describe first briefly the conditions which must be fulfilled to obtain fully reliable data, especially regarding the cleanliness of the

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samples and the use of specially designed clean laboratories. We present then some of the most interesting data which have been obtained on man induced changes during the past millennia/centuries. They show clear evidence of a global pollution of the atmosphere of our planet for heavy metals, which can be detected even in the most remote areas of the Southern Hemisphere and can be traced back to Roman times in the Northern Hemisphere. Finally, we present some recent data on past natural changes in heavy metals in ice dated back to 670 kyr BP, with pronounced variations during the successive interglacial/glacial climatic cycles.

3.1 Introduction

The last decades have been the golden age for the study of heavy metals in the successive dated snow and ice layers which have been preserved in the large Antarctic and Greenland ice caps.

The impetus in this field came from the pioneering work of Clair Patterson (Fig. 3.1) and his colleagues at the California Institute of Technology. Clair Patterson (Davidson 1999; Bertsch Mc Grayne 2002a) had already gained international

Fig. 3.1 Clair Patterson in his clean laboratory at the California Institute of Technology (Photo C. Boutron)

recognition for a study published in the 1950s that established that Earth and the solar system were 4.6 billion years old (see for instance Patterson et al. 1955; Patterson 1956) when he became interested in determining how much of the lead which was ubiquitous in the environment was natural and how much had been introduced by human activities. He realized soon that this could be achieved by sampling snow and ice in Greenland, comparing Pb concentration in ancient ice several thousand years old and recent snow. He also understood that reliable measurements could be obtained only if using sophisticated ultraclean procedures both for field sampling and analysis inside special clean laboratories, because of the extremely low concentrations to the measured (Patterson and Settle 1976).

The results were published in 1969 in a remarkable paper (Murozumi et al. 1969), which showed that Pb concentrations in Greenland snow dated from the mid-1960s were two orders of magnitude higher than in Greenland ice about 3 kyr old. This enormous increase was mainly linked to the huge increase in the use of Pb additives in gasoline from the 1930s onward (Nriagu 1990, 1999; Bertsch Mc Grayne 2002b).

The samples analysed by Murozumi et al. (1969) were large size snow and ice blocks collected from open snow trenches or shallow ice tunnels. Clair Patterson realized that it was going to be necessary to also analyse Pb in deep ice cores in order to better assess past natural levels of Pb against which modern time trends can be evaluated. He was then the first to tackle the key problem of the decontamination of deep ice cores drilled in holes filled with a wall retaining fluid. The method which he developed consisted in mechanically chiselling successive concentric ice layers from the contaminated outside of the core towards its inner parts using sophisticated ultraclean procedures, and checking the efficiency of the method by determining changes in concentrations from the outside to the center of each individual core section (Ng and Patterson 1981; Boutron and Patterson 1986; Boutron et al. 1987).

Since that, a wealth of fascinating data have been obtained for a wide range of heavy metals both in Antarctica and Greenland, mainly thanks to an international collaboration between our research groups in France, Italy, Korea, Australia, Russia and Belgium.

In this article, we shall give first a brief description of the field sampling procedures and analytical protocols which have been developed for the reliable determination of heavy metals in Antarctic and Greenland snow and ice. Then, we shall give a general overview of some of the most significant results which have been obtained so far.

3.2 Field Sampling and Laboratory Analysis

3.2.1 The Purest Natural Water on Earth

A major issue when dealing with heavy metals in Antarctic and Greenland snow and ice is contamination. This is because heavy metal concentrations in polar ice and snow are exceedingly low. As an illustration, Pb concentration in Antarctic Holocene ice 7 kyr old is about 0.2 pg/g (1 pg = 10^{-12} g) (Vallelonga et al. 2005), while Ir concentration in Antarctic ice 150 kyr old is about 0.5 fg/g (1 fg = 10^{-15} g) (Gabrielli et al. 2006). It means that 1,000 metric tons of Antarctic ice contains only 0.5 µg of Ir!

The main problem when dealing with such extremely low concentrations is contamination during field sampling and/or laboratory analysis. Uncontrolled contamination can easily lead to data which are erroneous by orders of magnitude and have then no scientific meaning at all.

3.2.2 Clean Samples

For shallow snow, it is possible to obtain clean samples from the walls of pits or trenches which are hand dug by operators wearing full clean room clothing, using acid-cleaned digging and sampling tools. An example is the 8.3 m snow pit which was dug by Wolff and Suttie (1994) in Coats Land in Antarctica, 200 km from the nearest manned station and 30 km from the line of previous traverses (Fig. 3.2). It allowed to obtain continuous series of large size snow blocks (~40 × 30 × 33 cm) covering a 66 year period from 1920 to 1986. A detailed description of the digging and sampling procedures is given in Planchon et al. (2001).

Clean samples can also be obtained using special mechanical augers made of plastic (polycarbonate), which are extensively cleaned with acids before use and are

Fig. 3.2 Excavation of a clean snow pit in Coats Land, Antarctica, for the collection of snow blocks for heavy metals analysis. The operator is wearing clean room clothing over his warm clothing, and uses an acid cleaned spade (Photo E. Wolff)

handled by operators wearing clean room clothing, Fig. 3.3 (Boutron and Patterson 1983; Boutron et al. 1991).

The depths which can be reached with such approaches are however limited (generally not more than about 10 m). Deeper samples can be recovered only as cores obtained with electromechanical or thermal drills operated in holes which are generally filled with a wall retaining fluid (the use of such fluids is mandatory when great depths are to be reached, in order to counterbalance the enormous pressure on the walls of the drilling hole). The fluids are often made of a mixture of kerosene and Freon or Freon substitutes. Examples of such deep ice cores are the 3,626 m long core which was drilled at Vostok station in East Antarctica and the 3,270 m long ice core which was drilled at Dome C in East Antarctica as part of European Project for Ice Coring in Antarctica (EPICA). They cover the past 420 and 800 kyr, respectively (see for instance Petit et al. 1999; EPICA Community members 2004).

The outside of such deep ice cores is strongly contaminated for heavy metals because of the contact with the drill and the fluid. The analysis of such contaminated

Fig. 3.3 Collection of a 10 m snow core in central Greenland (Summit) using an acid cleaned hand operated polycarbonate auger (Photo C. Rado)

ice cores appeared to be hopeless until Clair Patterson and his co-workers successfully developed sophisticated procedures to decontaminate them. Successive concentric veneer layers of ice are mechanically chiselled in progression from the contaminated outside of each core section (initial diameter of about 8–10 cm) towards its center, in order to obtain the uncontaminated inner part of the core (Ng and Patterson 1981; Boutron and Patterson 1986; Boutron et al. 1987). Sophisticated ultraclean procedures are used in order to prevent the transfer of outside contamination towards the central part of the core when chiselling the successive veneer layers, Fig. 3.4 (Candelone et al. 1994; Hong et al. 2003).

The efficiency of the decontamination procedures has to be checked for each individual core section, by analysing separately each veneer layer and inner core and determining radial concentration changes of each heavy metal from the outside to the center. Only if a concentration plateau is found can data obtained from the inner parts of the core section be accepted (see Fig. 3.5). If a continuous decrease in concentrations is observed (see Fig. 3.5), it means that concentrations measured in the central part of the core should be considered as representing only an upper limit of the original concentrations in the ice.

These decontamination procedures have now been successfully used for the decontamination of numerous sections of various deep ice cores drilled in Antarctica and Greenland (see for instance Boutron and Patterson 1986; Boutron et al. 1987, 1990, 1993; Vandal et al. 1993; Hong et al. 1994, 1996a, b, 2003, 2004, 2005; Gabrielli et al. 2004a, 2005a, b, 2006; Vallelonga et al. 2005; Burton et al. 2007; Marteel et al. 2008; Jitaru et al. 2008).

Fig. 3.4 Decontamination of an ice core by chiselling veneer layers of ice in progression from the outside towards the center inside a laminar flow clean bench in a cold room (Photo C. Boutron)

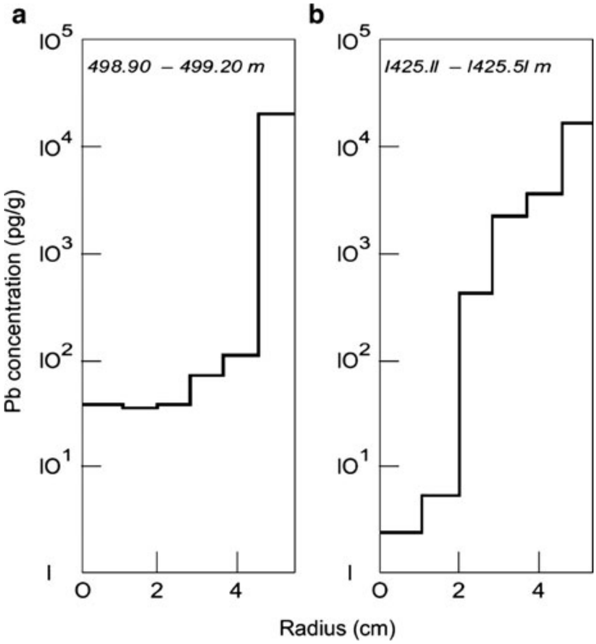


Fig. 3.5 Variations in Pb concentrations from the outside to the center of two sections of the 2,083 m Vostok (Antarctica) ice core. Each section is a cylinder, 10 cm in diameter and 30–50 cm long. (**a**) Section from a depth of 499 m, dated 26,000 years BP; (**b**) section from a depth of 1,425 m, dated about 100,000 years BP (From Boutron et al. 1987)

3.2.3 *Clean Laboratories*

The reliable determination of such extremely low concentrations of heavy metals can be achieved only if using special ultraclean laboratories. Description of such laboratories can be found for instance in Moody (1982), Boutron (1990), Vallelonga et al. (2002a) and Rosman et al. (2005). They are similar to the clean rooms which are extensively used in microelectronics. As an example, Fig. 3.6 shows a general view of the clean laboratory of the Laboratoire de Glaciologie et Géophysique de l' Environnement which was specially designed for the analysis of heavy metals in Antarctica and Greenland snow and ice.

Of particular importance are the cleaning procedures used both for field sampling equipment and labware (mostly made of Low Density Polyethylene (LDPE) and FEP and PFA Teflon). They involve the use of series of diluted nitric acids baths of increasing purity, prepared using high purity acids and water (see for instance Paulsen et al. 1988; Boutron 1990; Vallelonga et al. 2002a).

Special attention must be given to the determination of procedural blanks, especially by processing artificial ice cores made by freezing ultra pure water whose heavy metal content is known beforehand.

Fig. 3.6 General view of the clean laboratory of the Laboratoire de Glaciologie et Géophysique de l' Environnement in Saint Martin d'Hères/Grenoble, specially built for the analysis of heavy metals in polar snow and ice (Photo C. Boutron)

3.2.4 Ultrasensitive Analytical Techniques

Various techniques have been used for the determination of heavy metals in Antarctic and Greenland snow and ice. They include Isotope Dilution Thermal Ionization Mass Spectrometry (ID-TIMS, Fig. 3.7; see for instance Boutron and Patterson 1983, 1986; Chisholm et al. 1995; Vallelonga et al. 2002a; Jimi et al. 2008), Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SF-MS; see for instance Barbante et al. 1997a, 1999; Planchon et al. 2001, 2004; Gabrielli et al. 2004b), Laser Excited Atomic Fluorescence Spectrometry (LEAFS; see for instance Apatin et al. 1989; Bolshov et al. 1989, 1991, 1994), and Graphite Furnace Atomic Absorption Spectrometry (GFAAS; see for instance Görlach and Boutron 1990; Hong et al. 2000).

Of special interest is the determination of the isotopic composition and speciation of some metals. It is now possible to determine Pb isotopic ratios on picogram-sized samples (Chisholm et al. 1995; Vallelonga et al. 2002a; Jimi et al. 2008). Great efforts were also devoted to the determination of ethyl and methyl Pb compounds (Lobinski et al. 1993) and methyl-Hg (Jitaru and Adams 2004).

3.3 Man-Induced Changes in Antarctic and Greenland Snow and Ice During the Last Millennia/Centuries

We shall briefly present in the following sections some of the most interesting results which have been obtained so far, with special emphasis on Pb.

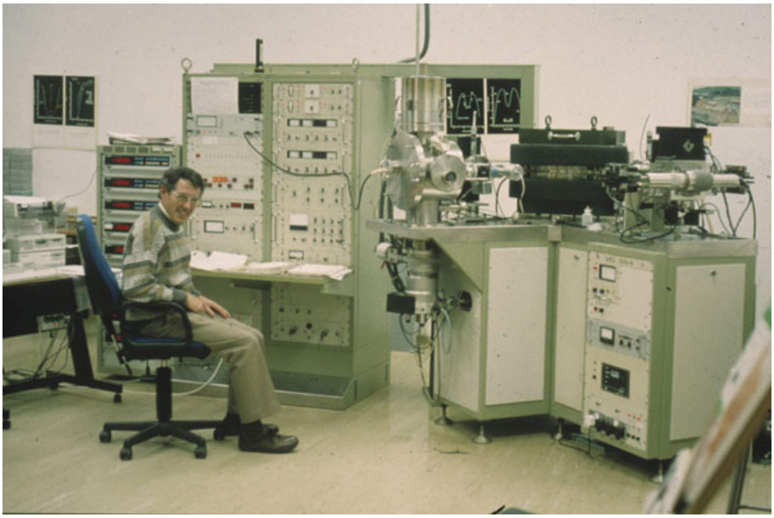


Fig. 3.7 The VG 354 (Fisons Instruments) thermal ionization mass spectrometer of the Department of Imaging and Applied Physics, Curtin University of Technology, Perth, Australia (Photo C. Boutron)

3.3.1 Pb in Greenland Ice Dated from the Greek and Roman Antiquity

In a famous study, Hong et al. (1994) have measured Pb in various sections of the 3,028 m long ice core drilled at Summit (72°34′N, 37°37′W) in the center of Greenland as part of the Greenland Ice Core Project (GRIP). The age of the sections ranged from 7,760 year BP (depth of 1,286 m) to 470 year BP (depth of 129 m interval), with special emphasis on ice sections dated from the time of the flourishing of the Roman Republic and Empire. The results are shown in Fig. 3.8.

7,760 years ago, Pb concentration in Greenland ice was about 0.5 pg/g. At that time, Pb was entirely natural and originated from sources such as rock and soil dust and volcanoes. The situation was about the same 3,000 years ago, with concentrations still close to 0.5 pg/g, see Fig. 3.8.

The data then clearly show an increase in Pb concentration from ~500 year BC (2,500 year BP) onwards, and they remain above natural values during more than eight centuries, with values as high as 3 pg/g at the apogee of the Roman Empire, i.e., 6 times higher than natural values. Concentrations then decrease down to natural values around 500 year AD (1,500 year BP), before increasing again during Medieval times, Fig. 3.8.

Elevated concentrations observed during the Greek and Roman Antiquity are not due to changes in inputs from natural sources, as shown by the observed changes in Pb isotopic ratios in the ice (Rosman et al. 1997). They are the consequence of a large scale pollution of the atmosphere of the Northern Hemisphere for Pb two

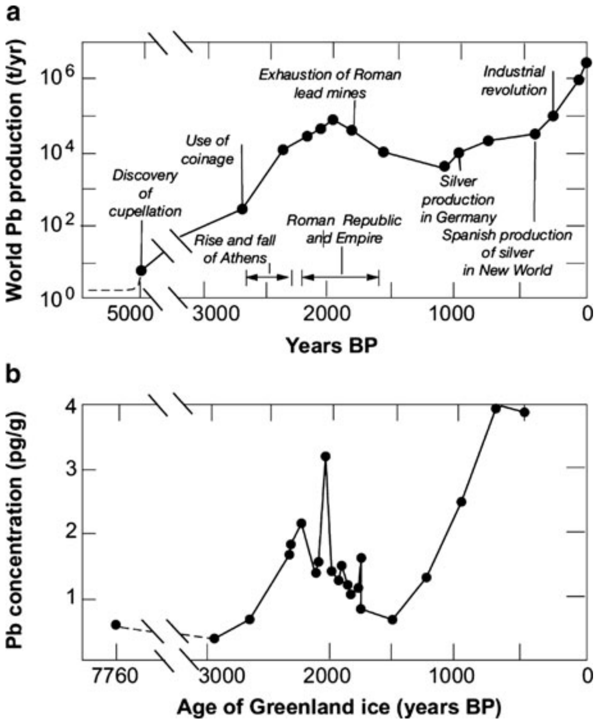


Fig. 3.8 (**a**) Worldwide Pb production (in metric tons/years) during the last five millennia (From Settle and Patterson 1980); (**b**) changes in Pb concentration in ice from central Greenland (Summit) from 7,700 to 500 years ago (From Hong et al. 1994)

millennia ago, long before the Industrial Revolution. This pollution was linked with Pb and Ag production activities in ancient Greece and Rome (see for instance Nriagu 1983a, b), and Greenland ice shows that it was strong enough to be detected in the Arctic, at an altitude of more than 3,000 m, far away from the Mediterranean basin. It is the oldest large scale atmospheric pollution ever evidenced.

Also shown in Fig. 3.8 are past changes in world Pb production during the last 5,000 year, i.e., since the discovery of Ag cupellation (Settle and Patterson 1980). It can be seen that the peaks in Pb concentration in the ice and Pb production occur at about the same time.

The isotopic composition of Pb in Greenland ice can be compared with the isotopic signature of the different Pb/Ag mines which were worked during ancient times, especially in Southern Spain (Rio Tinto and Cartagena and Mazarron regions) and Greece (Laurion and the Aegean), Rosman et al. (1997). It shows that on the average 70% of Pb in Greenland ice can be assigned to Rio Tinto type Pb between 366 year BC and 36 year AD. Such information is of great interest for archaeologists and historians since the history of metal production was instrumental in the rise and fall of human societies and empires.

In addition, it is important to mention that the determination of Cu in the same Greenland ice samples analysed for Pb has evidenced an early pollution for Cu, beginning ~2,500 years ago (Hong et al. 1996a). It is attributed to emissions from the crude, highly polluting smelting procedures used for Cu production during Roman and Medieval times, especially in Europe and China (Hong et al. 1996c).

3.3.2 Pb and Other Metals in Greenland Snow from the Industrial Revolution to Present

It is Clair Patterson and his colleagues Masayo Murozumi and Tsaihwa Chow who reported the first reliable data on past changes in Pb concentration in Greenland snow during the last few centuries, in their famous paper published at the end of the 1960s (Murozumi et al. 1969). Although the number of data points was very limited, it clearly evidenced for the first time the pronounced increase in Pb concentration from the 1750s (~10 pg/g) to the mid-1960s (~240 pg/g), Fig. 3.9. In addition, they also analysed a single sample of ice ~2,800 years old collected from an ice tunnel at Camp Tuto, near the large air force base of Thule in North West Greenland. Pb concentration in the ice was found to be ~1 pg/g. When combined with the snow data, it showed that Pb concentration in snow dated from the mid-1960s were ~200 times higher than natural values. A major part of the observed increase was ascribed to the massive use of Pb additives in gasoline from the 1930s onwards (Nriagu 1990, 1999; Bertsch Mc Grayne 2002b).

These outstanding data excited universal interest, and were the basis for the fight against Pb additives in gasoline (Bertsch Mc Grayne 2002a; Davidson 1999), which resulted ultimately in the ban of these additives (Nriagu 1990, 1999; von Storch et al. 2003).

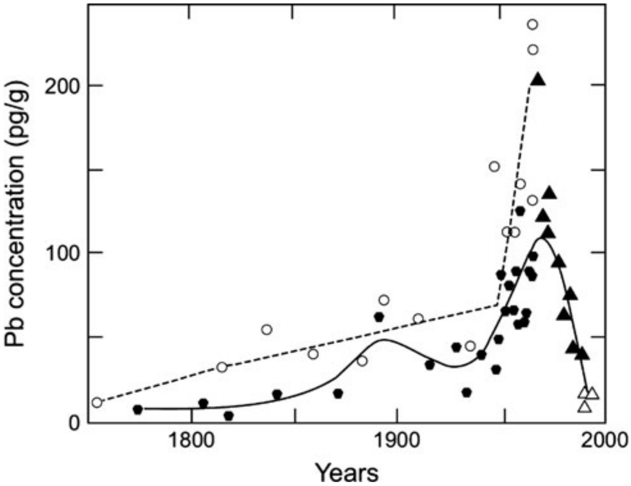


Fig. 3.9 Changes in Pb concentration in Greenland snow from the eighteenth century to the 1990s. *Open circles* and *dotted line*: data from North-West Greenland published by Murozumi et al. 1969. *Black circles*, *triangles* and *continuous line*: data from central Greenland (Summit) by Candelone et al. (1995)

It took more than 20 years before these pioneering data were replicated and extended (Boutron et al. 1991; Candelone et al. 1995; McConnell et al. 2002). As an illustration, the data obtained by Boutron et al. (1991) and Candelone et al. (1995) are shown in Fig. 3.9. They confirmed that Pb concentrations in snow dated from the 1700s were about 10 pg/g, and indicated that Pb concentrations peaked in the 1960s, with values which are ~200 time higher than natural values. They showed that Pb concentrations strongly decreased from the 1970s onward, in parallel with the rapid fall in the use of Pb additives in gasoline at that time, Fig. 3.9.

The key role played by Pb additives in the rise and fall of Pb concentrations in Greenland snow was further confirmed by the direct measurement of ethyl and methyl Pb compounds in Greenland snow dated from the late 1940s to the late 1980s, Lobinski et al. (1994).

Furthermore, the study of Pb isotopic ratios allowed to determine that ~2/3 of Pb in Greenland snow dated from the 1970s originated from the United States (Rosman et al. 1993). In the 1980s, the contribution from Europe became predominant because of the fall in the use of Pb additives in the United States at that time (Rosman et al. 1993).

If particular efforts were devoted to the study of Pb, which was a priority pollutant because of the enormous emissions associated with the massive use of Pb additives in gasoline, it should however be mentioned that data are also available for various other heavy metals, especially Cd, Cu, Zn and Bi (see Boutron et al. 1991; Candelone et al. 1995; Ferrari et al. 2000), Hg (Boutron et al. 1998) and Pt, Pd, Rh and Ir (Barbante et al. 2001; Gabrielli et al. 2008). We shall now briefly describe the data obtained by Barbante et al. (2001) for Pt, Pd and Rh.

3.3.3 Pt, Pd and Rh in Greenland Snow During Recent Decades

While Pb pollution has now strongly declined, a rather new pollution has been rapidly increasing during recent decades: it is the pollution for Pt, Pd and Rh, which is largely linked with the rapid increase in the use of these metals, especially as catalysts in automobile catalytic converters (see for instance Bartholomew and Farrauto 2006; Barbante and Cescon 2000).

In order to assess if the emissions of Pt, Pd and Rh from automobile catalytic converters and other anthropogenic sources have now resulted into a large scale contamination of the atmosphere, Barbante et al. (2001) have determined these metals in a series of ice and snow samples collected at Summit in Greenland: (a) 2 sections of the 3,028 m GRIP ice core dated 7,260 and 7,760 years ago (depths of 1,230 and 1,286 m, respectively), which will allow for the assessment of pre-human influence natural Holocene concentrations; (b) snow samples dated from 1969 to 1975, which will be used to assess pre-automobile converters anthropogenic changes; (c) snow samples dated from 1976 to 1995, which will be used to identify the possible influence of emissions from automobile catalytic converters. The results are shown in Fig. 3.10.

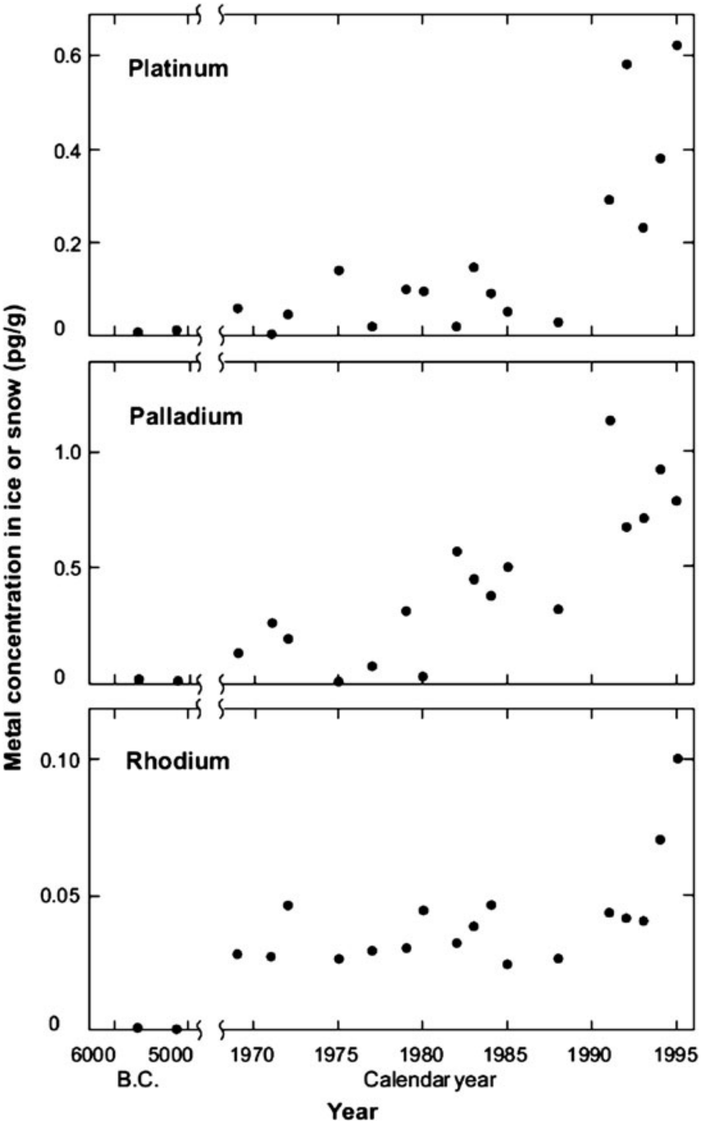


Fig. 3.10 Changes in Pt, Pd and Rh concentrations in snow from central Greenland (Summit) from the late 1960s to the mid-1990s. Also shown are data points for ancient Holocene ice dated 7,260 and 7,760 years ago. (From Barbante et al. 2001)

Seven millennia ago, Pt, Pd and Rh concentrations were extremely low in Greenland ice (~0.01 pg/g for Pt and Pd and 0.0007 pg/g for Rh). At that time, these metals were totally natural. For snow dated from1969 to 1975, i.e., just before the introduction of automobile catalytic converters, the data show that Pt, Pd and Rh concentration levels were already ~6, 15 and 45 times the Holocene natural values (Barbante et al. 2001), indicating that there was already at that time a large scale contamination of the atmosphere of the Northern Hemisphere for these metals. Possible sources include mining and smelting activities especially in the Russian Arctic, the use of these metals in the chemical industry as catalysts, incineration of refuse, steel and iron manufacturing, and the combustion of fossil fuels.

The data then show contrasting situations from 1976 to 1995, i.e., the period which corresponded to the development in the use of automobile catalytic converters, Fig. 3.10. For Pt and Rh, they indicate rather constant concentrations to the late 1980s, followed by higher values for snow dated from the mid-1990s. For Pd, they rather suggest a steady increase during these 20 years. On the whole, the data published by Barbante et al. (2001) suggest that concentrations of Pt, Pd and Rh in Greenland snow dated from the mid-1990s are ~40, 80 and 120 times above natural Holocene values, respectively, then suggesting a very large contamination of the atmosphere of the Northern Hemisphere for these metals.

For Pt and Rh, Barbante et al. (2001) suggest that the high concentrations observed in the 1990s are mainly linked with increasing emissions from automobile catalytic converters. This interpretation was supported by observed changes in Pt/Rh mass ratios. For Pd, the steady increase observed from 1969 onwards was thought to mainly result from increasing emissions of this metal from mining and smelting, especially in the Russian Arctic.

It should however be mentioned that a recent study by Gabrielli et al. (2008) suggests that Pt concentrations in Greenland snow dated from the 1990s might be lower than indicated by Barbante et al. (2001), with an increase in Pt concentrations from several millennia ago to the 1990s by only ~5 times.

The ever increasing world demand for Pt, Pd and Rh during recent decades is illustrated in Fig. 3.11. Also shown is the demand for automobile catalytic converters, which represents an increasing percentage of the total demand.

3.3.4 Pb in Antarctic Snow Since the Nineteenth Century

Time series for Pb in Antarctic snow during the last few centuries are now available for three locations: Coats Land, in the sector of Antarctica facing the South Atlantic Ocean (Wolff and Suttie 1994; Planchon et al. 2003); the Law Dome, in the sector of Antarctica facing Australia (Vallelonga et al. 2002b); and Victoria Land, in the sector of Antarctica facing the Pacific Ocean (Barbante et al. 1997b; van de Velde et al. 2005).

Figure 3.12 shows the time series obtained for the years 1834–1990 at the Coats Land site (77°34′S, 25°22′W) by Planchon et al. (2003). For convenience, Pb concentrations have been converted here into crustal enrichment factors (EFcrust) using Ba as crustal reference element, using the relation: EFcrust (Pb) = [Pb/Ba] snow/[Pb/Ba] upper crust [using the data for the upper continental crust given by Wedepohl (1995)].

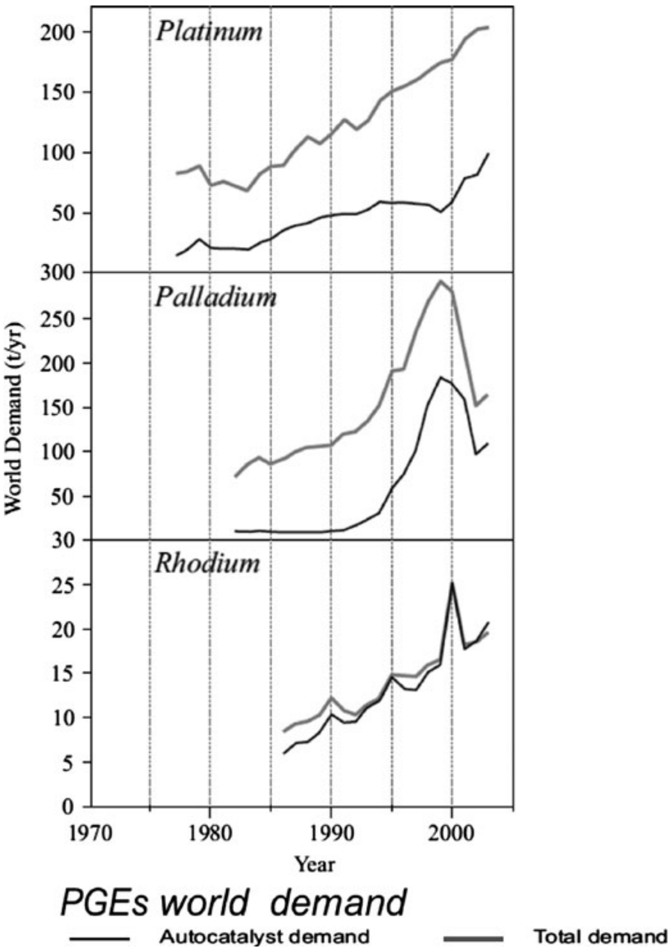


Fig. 3.11 Changes in world demand (in metric tons/year) for Pt, Pd and Rh during recent decades (expressed in metric tons per year). *Grey* (*upper*) *curve*: total demand. *Black* (*lower*) *curve*: demand for automobile catalytic converters (Data from Johnson Mattey, London, various reports)

As shown in Fig. 3.12a, EFcrust (Pb) values close to unity are observed from the 1830s to the late 1880s (time period 1 in Fig. 3.12), with Pb concentrations (~0.4 pg/g) close to those observed in Antarctic ice several millennia old. It indicates that Pb in Antarctic snow was mainly natural at that time, with a dominating contribution from rock and soil dust.

Enhanced EFcrust (Pb) values are then observed from the late 1880s to the mid-1920s (time period 2 in Fig. 3.12), with two maxima in the early 1900s and the 1920s, respectively, Fig. 3.12a. During these 30 years, mean Pb concentration was ~2.8 pg/g, i.e., ~6 times higher than concentrations observed before the late 1880s.

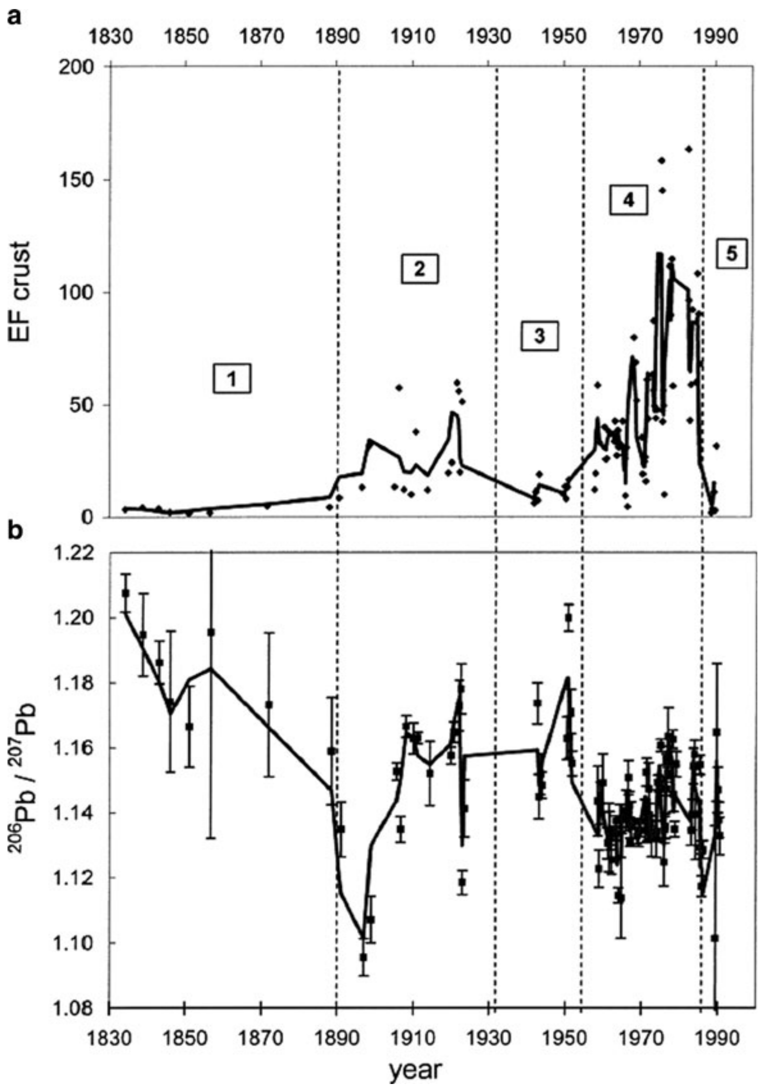


Fig. 3.12 Changes in Pb crustal enrichment factor (EFcrust) and 206Pb/207Pb isotopic ratio in snow from Coats Land, Antarctica from the 1830s to the 1990s. Uncertainties for the ^{206}Pb/^{207}Pb ratio are 95% confidence intervals (From Planchon et al. 2003)

It shows that Antarctica was already polluted for Pb one century ago, before the conquest of the geographic South Pole by Amundsen, Scott and their companions. At that time, Pb pollution was already global, reaching even the most remote areas of the Southern Hemisphere.

Interestingly, the first maximum in the early 1900s is characterized by very low values of the ^{206}Pb/^{207}Pb isotopic ratio, down to 1.10, while the ratio is much higher for the second maximum in the 1920s, see Fig. 3.12b.

Possible causes for this early pollution for Pb in Antarctica are discussed in detail by Planchon et al. (2003). A significant contribution could have been linked with the use of coal both for whaling stations and whaling ships, especially along the Antarctic Peninsula. Another contribution could be from the numerous coal-powered ships that crossed the Cape Horn. The traffic was important at that time, before the opening of the Panama Canal in 1914. At least part of this pollution could have also originated from non-ferrous metal production (Pb, Cu and Zn) in South America, South Africa and Australia. The corresponding emissions of Pb to the atmosphere of the Southern Hemisphere were estimated at ~1,500 t/year by Wolff and Suttie (1994).

Figure 3.12 shows that EFcrust (Pb) values were then lower during the 1930s–1950s (time period 3 in Fig. 3.12). It suggests that there has been a pronounced weakening in anthropogenic inputs of Pb to Antarctica during that period. At least part of this observed decline could be linked with the opening of the Panama Canal, which resulted in a collapse of ship traffic around Cape Horn. Other explanations could be linked with the great economic recession during the 1930s and World War II, which resulted for example in a decline of Pb production in Peru mines and rationing in the use of leaded gasoline in Australia (Wolff and Suttie 1994).

The data then show a clear increase in EFcrust (Pb) values from the early 1960s to the early 1980s (time period 4 in Fig. 3.12a). Mean Pb concentrations in the late 1970s–early 1980s are ~4 pg/g, i.e., ~10 times the concentrations observed in the mid-nineteenth century. It is mainly the consequence of the very large rise in the use of leaded gasoline in the Southern Hemisphere during that period, combined with the continuous increase in non-ferrous metal production in South America, South Africa and Australia. Just to give an example, the number of passenger cars in Australia and New Zealand increased about 8 times during that period, and the Pb content of the gasoline was very high in these countries at that time.

Finally, the data show a sharp decrease at the beginning of the 1990s (time period 5 in Fig. 3.12a), largely because of the fall in the use of Pb additives in gasoline in various countries of the Southern Hemisphere, especially in Brazil and Australia (Barbante et al. 1997b; Wolff and Suttie 1994).

Figure 3.13 compares the variations in the $^{206}Pb/^{207}Pb$ isotopic ratio observed at the three locations where Pb time series for the last few centuries have been obtained: Coats Land (Planchon et al. 2003), the Law Dome (Vallelonga et al. 2002b) and Victoria Land (Barbante et al. 1997b; van de Velde et al. 2005). The same general features are observed at these three widely separated sites, with especially the same dip in isotopic ratio around 1900.

3.3.5 *Other Heavy Metals in Antarctic Snow Since the Nineteenth Century*

In addition to Pb, various other heavy metals have been determined in the series of snow samples, covering the period from 1834 to 1990, collected in Coats Land. They include V, Cr, Cu, Zn, Ag, Cd, Bi and U (Planchon et al. 2002; Wolff et al. 1999).

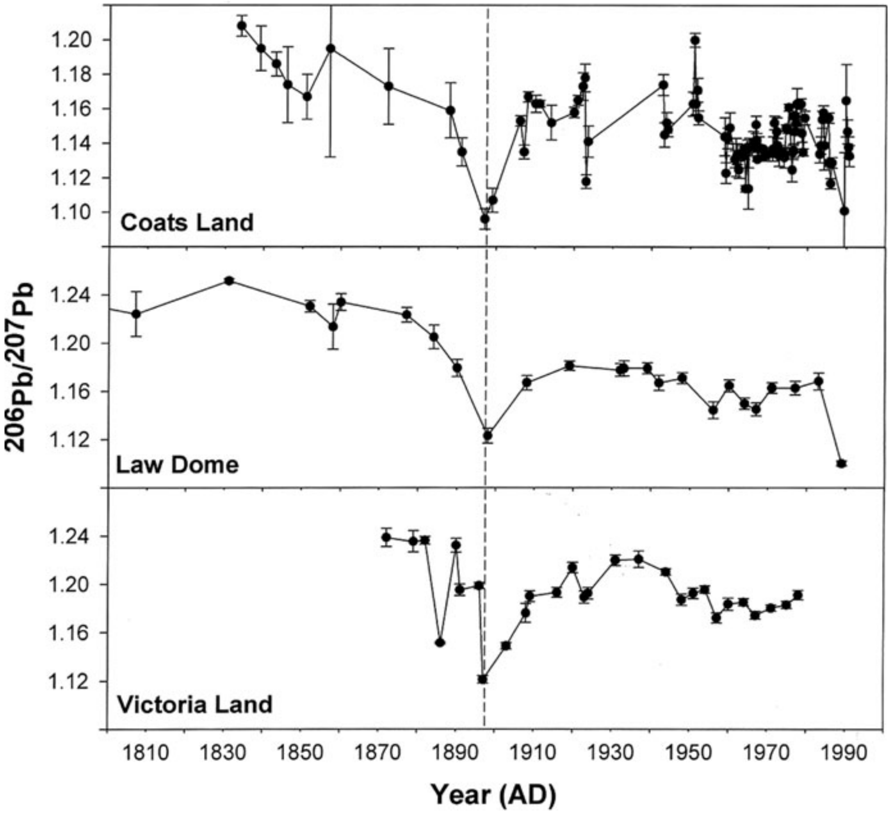


Fig. 3.13 Comparison of changes in ^{206}Pb/^{207}Pb isotopic ratio over the past 200 years at three Antarctic sites: Coats Land (Planchon et al. 2003), Law Dome (Vallelonga et al. 2002b) and Victoria Land (van de Velde et al. 2005)

For Cr, Cu, Zn, Ag, Cd, Bi and U, the data show a pronounced increase in concentrations during the second half of the twentieth century (Planchon et al. 2002). This is illustrated in Fig. 3.14, which shows changes in crustal enrichment factors EFcrust for Cu, Bi, Zn and U in Coats Land snow from the 1830s to 1990. On the average, EFcrust values are found to have increased by 4 times for Cu and Zn, 5 times for U and10 times for Bi. It shows that atmospheric pollution for heavy metals in the remote Antarctic continent is not limited to Pb, but also affects various other heavy metals. It further confirms that atmospheric pollution for heavy metals is global, reaching even the most remote areas of our planet.

These increases are attributed to emissions of heavy metals to the atmosphere from human activities in the Southern Hemisphere [see for instance the emission inventories published by Pacyna and Pacyna (2001)], especially non-ferrous metal mining and smelting in Chile, Peru, Zaire, Zambia and Australia.

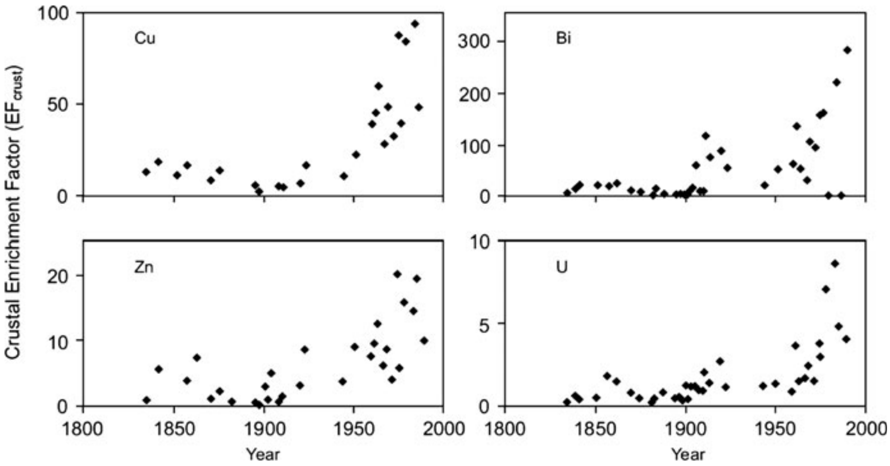


Fig. 3.14 Changes in Cu, Bi, Zn and U concentrations in snow from Coats Land, Antarctica from the 1830s to the 1990s (From Planchon et al. 2002)

No data are available on changes in these emissions during the twentieth century. Planchon et al. (2002) tentatively used changes in ore and/or metal production as a surrogate to changes in emissions. As an illustration, Fig. 3.15 shows the reconstruction of ore production for U, Zn and Cu in the Southern Hemisphere and the contributions from South America, South Africa and Australia. Both ore and metal productions are found to have strongly increased during the twentieth century (Planchon et al. 2002).

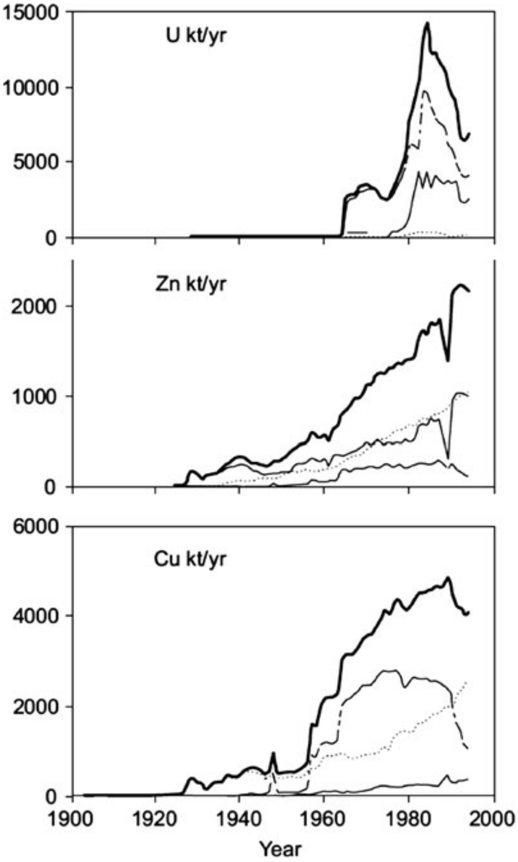
3.4 Natural Changes in Antarctic and Greenland Ice During the Successive Climatic Cycles

We shall now briefly present some of the most interesting data which are now available on past natural changes in the occurrence of heavy metals in Antarctic and Greenland ice during the last climatic cycles. They were obtained by analysing various deep ice cores, especially the 3,028 m GRIP Greenland ice core (which covers the last 100 kyr; see Hong et al. 1996b; Gabrielli et al. 2004a; Burton et al. 2007), the 3,626 m Vostok Antarctic ice core (which covers the last 420 kyr; see Hong et al. 2003, 2004, 2005; Gabrielli et al. 2005b, 2006), and the 3,270 m EPICA/ Dome C ice core (which covers the last 800 kyr; see Gabrielli et al. 2005a, 2006; Vallelonga et al. 2005; Marteel et al. 2008; Jitaru et al. 2008).

3.4.1 Ir and Pt in Greenland Ice During the Last Climatic Cycle

Ir and Pt have been determined by Gabrielli et al. (2004a) in various sections of the 3,028 m long ice core which has been drilled at Summit (72°34′N, 37°37′W)

Fig. 3.15 Historical changes in ore production for U, Zn and Cu in the Southern Hemisphere during the twentieth century (*thick continuous upper line*). Production is given in metric tons/year for U, and 103 metric tons/year for Zn and Cu. Also shown are contributions from South America (*dotted line*), South Africa (*dots and dashes*) and Australia (*thin continuous line*) (From Planchon et al. 2002; Minerals Year Book, US Bureau of Mines, Washington D.C., USA, various issues)



in central Greenland as part of the European Greenland Ice Sheet Project (GRIP). Parts of the sections were dated from the period between ~700 and 11,500 year before present, covering the current interglacial period (Holocene). The other sections, spanning from ~13 to 100 kyr BP, covered the last glacial age (LGA).

The data show low and remarkably constant concentrations both for Ir (average concentration of 0.3 fg/g) and Pt (average concentration of 0.6 fg/g) during the Holocene, with high crustal enrichment factors (EFcrust) values for both metals. These high EFcrust values indicate that contribution from terrestrial dust is negligible for both metals during the Holocene, and there are various indications that contributions from explosive and quiescent volcanisms are unlikely (Gabrielli et al. 2004a). Very interestingly, the Ir/Pt ratio is very close to 0.5, i.e., the chondritic ratio (Anders and Grevesse 1989). It strongly supports a common extraterrestrial origin for Ir and Pt in Greenland Holocene ice. This cosmic input arises from the deposition of the nanometric meteoric smoke particles formed from the recondensation of ablated meteoroids in the mesosphere.

A dominant feature of mesospheric circulation is the seasonal wind flow from the summer to the winter pole, so that meteoric smoke particles are transported to the winter polar vortices and are preferentially deposited pole wards of 55° latitude. When taking this feature into account, extrapolation of the Greenland ice data to the whole Earth gives a global input of ~15 × 10^3 t/year of extraterrestrial matter to the Earth (Gabrielli et al. 2004a).

EFcrust values are found to be much lower during the last glacial age, because of greatly enhanced inputs of Ir and Pt from the terrestrial crust at that time which mask the cosmic flux (Gabrielli et al. 2004a). The last ice age was indeed characterized by a high crustal dust loading in the Earth's atmosphere, especially because of enhanced dry and windy conditions and the exposure of large areas of the continental shelves because of lower ocean level.

Comprehensive data on Ir and Pt in Antarctic ice dated from the last two climatic cycles (back to 240 kyr BP) have now also been obtained from the analysis of various sections of the Vostok and EPICA/Dome C ice cores. They are presented and discussed in Gabrielli et al. (2006).

3.4.2 Pb, Cd, Cu, Zn, As, Bi, U and Hg in Antarctic Ice During the Last Climatic Cycles

Data are now available on past natural changes in the concentrations of various heavy metals in Antarctic ice during the last climatic cycles. They were obtained from the analysis of numerous sections of the 3,626 m long Vostok ice core and the 3,270 m long EPICA/Dome C ice core. The Vostok data now cover the last four climatic cycles (past 420 kyr), back to Marine Isotopic Stage ("MIS", see for instance Bassinot et al. 1994) 11.3 (Hong et al. 2003, 2004, 2005; Gabrielli et al. 2005b). The EPICA/Dome C data cover the last eight climatic cycles (past 670 kyr), back to MIS 16.2 (Gabrielli et al. 2005a; Vallelonga et al. 2005; Marteel et al. 2008; Jitaru et al. 2008).

As an example, Fig. 3.16 shows changes in Pb and Cu concentrations in EPICA/Dome C ice from 670 kyr BP (depth of 3,062 m) to 0.5 kyr BP (depth of 32.5 m) (Marteel et al. 2008; Gabrielli et al. 2005a). Also shown at the top of the figure is the deuterium concentration profile (deuterium concentrations are expressed in per mil delta units) from EPICA Community Members (2004) and related papers.

Deuterium is used as a proxy of temperature, with less negative values indicating higher temperatures during warm periods, and more negative values showing cold climatic stages. The deuterium profile of Fig. 3.16 shows that the 3,062 m cover the last eight climatic cycles, with a series of interglacial and glacial periods. The interglacial periods are identified by odd MIS numbers. The most recent one is the current Holocene interglacial period (MIS 1), which began ~10,000 years ago. The previous ones were MIS 5.5, 7.5, 9.3, 11.3, 13.1, 13.3, 15.1 and 15.5 (~600 kyr BP), see Fig. 3.16. Amongst these interglacials is MIS 11 (~400 kyr BP),

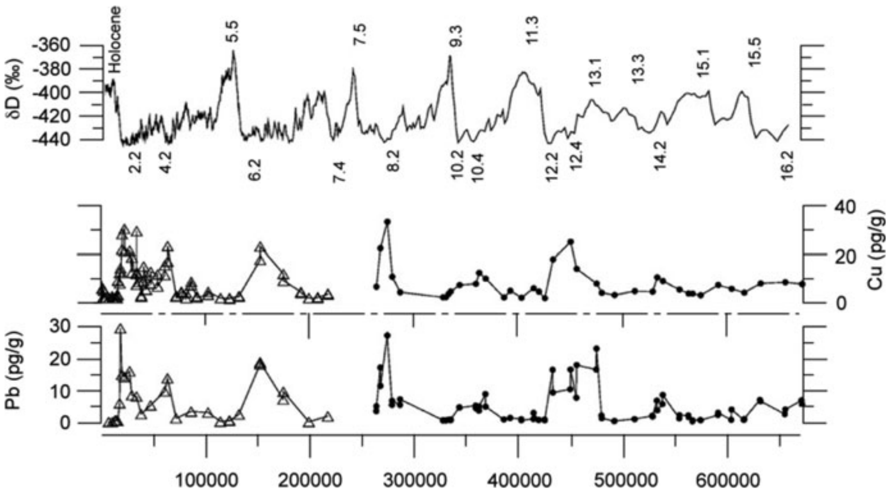


Fig. 3.16 EPICA/Dome C Antarctic ice core: changes in Pb and Cu concentrations during the past 670 kyr (open triangles: data from Gabrielli et al. (2005a); black dots: data from Marteel et al. (2008)). Also shown at the top of the figure are the deuterium profile (in δD per mil unit) and Marine Isotopic Stages (MIS) numbers (From EPICA Community Members 2004 and related papers; Adapted from Marteel et al. 2008)

which is easily recognized in paleo-climate records as an exceptionally long interglacial. It exhibited warm interglacial climatic conditions during at least 30 kyr, a duration twice as long as the most recent interglacial periods, with orbital parameters (low eccentricity and consequently weak precessional forcing) similar to those of the present (Berger and Loutre 2003). The glacial periods are identified by even numbers. They included both very cold periods (glacial maxima characterized by δD values down to ~−440‰, see the top part of Fig. 3.16) and less cold interstadials with less negative δD values. The 670 kyr time period includes a series of glacial maxima, especially MIS 2.2 (also identified as the "Last Glacial Maximum" [LGM]), 6.2, 7.4, 8.2, 10.2, 10.4, 12.2 and 16.2, see the top part of Fig. 3.16.

Figure 3.16 shows that Pb and Cu concentrations have strongly varied during the last 670 kyr, with high values during the coldest periods such as MIS 2.2 (Last Glacial Maximum), 4.2, 6.2, 8.2, 10.4, 12.2 and 12.4, and low values during interglacial periods such as the Holocene, MIS 5.5, 9.3, 11.3, 15.1 and 15.5. The maximum/minimum concentration ratio is ~40.

Figure 3.17 shows changes in Cu and Pb concentrations as a function of δD. Concentrations of Cu and Zn are found to remain very low for δD values between ~−380‰ and −420‰, i.e., during interglacial periods and warm interstadials during glacial periods. They increase strongly when δD values fall below ~−420‰, especially during glacial maxima (Marteel et al. 2008).

These large natural variations as a function of climate appear to be mainly linked with changing inputs of rock and soil dust to the Antarctic continent during the

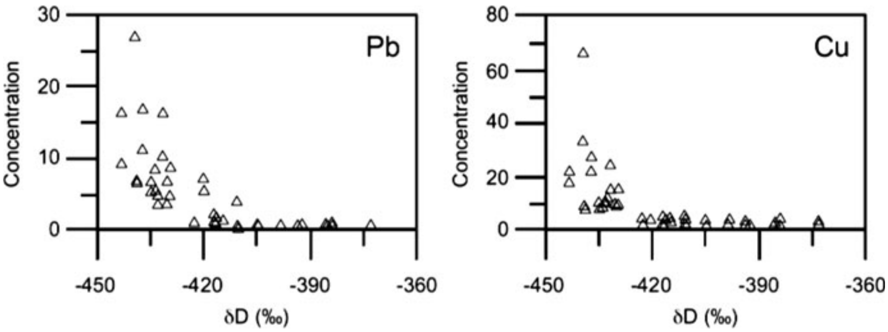


Fig. 3.17 EPICA/Dome C Antarctic ice core: changes in Pb and Cu concentrations (expressed in pg/g) as a function of the deuterium content of the ice (expressed in delta per mil unit) from 263 to 670 kyr BP (From Marteel et al. 2008)

successive climatic cycles. Dust fallout to Antarctica is indeed found to be rather small during warm periods such as interglacials, but much larger during glacial periods, especially during glacial maxima (EPICA Community Members 2004; Wolff et al. 2006; Fischer et al. 2007). This enhanced dust input to Antarctica during the coldest periods was linked with several concomitant factors which favoured the production of dust particles in the continents of the Southern Hemisphere, especially in Patagonia, and their transport to Antarctica during the coldest stages of the glacial periods (see for instance Delmonte et al. 2004). Amongst these factors is the lowering of ocean level, resulting in the exposition of larger portions of the continental shelves to wind erosion, especially along South America. Another factor was the increased aridity of the soil, which favoured emission of dust particles to the atmosphere. Also, the enhanced thermometric and barometric gradients between mid and high latitudes strengthened poleward atmospheric dust transport.

These large variations in dust inputs to Antarctica are the main driver for the past natural variations in Pb and Cu concentrations, since rock and soil dust is the main natural source of these two metals (Nriagu 1989). Rock and soil dust indeed explains virtually 100% of Pb and Cu measured in Dome C ice during glacial maxima. During interglacials, it remains a major source of Pb, and a significant source for Cu. Sea-salt spray contribution is negligible whatever the period, while volcanoes could be a significant source for Cu during interglacial periods when rock and soil dust contribution is low.

We shall not discuss here the data which have been obtained for other heavy metals. We would like however to mention that highly interesting data have recently been obtained on the past natural variations of Hg during the past 670 kyr, with additional data for methyl Hg during the past 210 kyr (Jitaru et al. 2008). The data show enhanced Hg deposition from the atmosphere to the ice cap during the successive glacial maxima, implying that polar regions might have acted as an important sink for Hg during the coldest climatic stages.

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Part II
Emissions

Chapter 4
Environmental Emissions of Selected Persistent Organic Pollutants

Jozef Pacyna

4.1 Introduction

Persistent Organic Pollutants (POPs) are chemicals that are recognized as persistent, bio-accumulative, toxic and susceptible to long-range atmospheric transport (PBT-LRT). POPs generally fall into two classes dependent on their origin; intentionally produced chemicals (typically organo-chlorinated pesticides and industrial chemicals, such as hexachlorobenzene – HCB) and unwanted by-products of combustion (such as, polycyclic aromatic hydrocarbons – PAHs, and dioxins – PCDD/Fs).

Elevated concentrations of several POPs have been observed in remote environments far from global source regions, such as the Arctic (AMAP 2004). Ottar (1981) hypothesized that several chlorinated hydrocarbons have a potential for reversible atmospheric deposition, and that they therefore may be subject to a systematic long-term transport from warmer to colder regions. This theory was further elaborated by Wania and Mackay (1993) who offered more detailed explanations how the temperature-dependent partitioning of persistent and low volatility compounds could lead to an enrichment in the Arctic through global fractionation and cold condensation processes. Later, several modelling studies have been undertaken to understand and predict source-receptor relationships for POPs on a European (e.g., Van Jaarsveld et al. 1997; Prevedouros et al. 2004), hemispherical (e.g., Malanichev et al. 2004; Hansen et al. 2004), and global scale (e.g., Wania and Su 2004). International agreements are now also coming into force to reduce further environmental exposure to POPs on a regional and global scale. One of such international agreements is the Stockholm Convention on POPs (UNEP 2001). The Stockholm Convention entered into force in May 2004 (151 signatories and 118 parties as of February 17, 2006). The Stockholm Convention targets 12 POPs (the so-called dirty dozen) for reduction and eventual elimination, and sets up a system for evaluation of additional chemicals for consideration. Another

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international agreement is the 1979 Geneva Convention on Long-range Transboundary Air Pollution (LRTAP), which has 49 parties (UN/ECE 1979). The LRTAP Convention has been extended by the 1998 Aarhus Protocol on Persistent Organic Pollutants (POPs), which entered into force by the end of 2003 (25 ratifications as of January 13, 2006).

Information on POP emission sources and magnitude is of utmost importance for providing justification for new international agreements of emissions and exposure reductions, as well as for verification of existing agreements. This paper reviews our knowledge on sources and current emission levels of selected POPs in Europe on the basis of information collected within the EU SOCOPSE project on Source Control of Priority Substances in Europe. Environmental releases of POPs have been studied with the use of Material Flow Analysis (MFA) diagrams.

4.2 Material Flow Analysis

Material Flow Analysis (MFA) is a technique, which is applied to provide quantitative information on how the flow (mass per time) of materials or substances behaves within a well-defined system. The central part of the methodology is basically related to the first two physical laws of thermodynamics. The first law indicates that the total amount of materials and energy is constant, meaning that materials or substances extracted from the natural environment somehow must return to the environment (usually in a degraded form). The second law states that eventually, energy dissipates to a lower quality, meaning that the natural environment in the future will absorb materials or substances (Scott and Redclift 1995). In combination with the two first laws on thermodynamics, the MFA method applies to the concept of industrial ecology and it should indeed be well suited for modelling the interrelation between production (the economy) and the environment, justified by the fact that the production systems are subsystems of the environment. The European Environmental Agency (EEA) defines MFA as an evaluation method which; "…. helps to identify waste and natural resources and other materials in the economy which would otherwise go unnoticed in conventional economic monitoring systems" (EEA 2007).

In the SOCOPSE project, the use of MFA and substance flow accounting can be justified by the development of economy- or production-wide indicators to better integrate environmental and economic decision-making tools. In this case, static modelling can be useful to assess the origin of specific flows and to compare policy measures on the basis of their effect on problem flows. In other words, through analyzing the flow of a single substance through the economy and the environment, it is a point to obtain an overview to where problem emissions occur or accumulate. This is thus the basis for providing guidelines and establishing a decision support tool for the management of priority pollutants.

The system design is flexible enough to account for differences between release patterns and pathways for individual priority substances in addition to provide quantitative information on production, use and release. The quantification is limited to emissions that are emerging from inside the system boundaries of Europe, meaning that produced or emitted substances outside the system boundaries are not taken into account. Emissions to air, water and soil are outputs into the environment and inputs into the mass balance. The advection flows are the flows, which are exported outside the system boundaries.

4.3 Application of MFA to Study Sources and Amounts of POP Emissions

The MFA method is very powerful for studying emissions and pathways of POPs in the environment. Two examples of MFA application are presented here for hexachlorobenzene (HCB) and polycyclic aromatic hydrocarbons (PAHs).

4.3.1 Hexachlorobenzene

Hexachlorobenzene (HCB) is a chemical which is recognized as both bio-accumulative and persistent in the environment. In fact, the chemical is persistent enough to be transported over long distances through the atmosphere which means that levels measured today are likely to have occurred in the past (Breivik et al. 2002). The emission sources of HCB can be classified into deliberated produced chemicals for field application in agriculture and wood production, and into the accidentally formed chemicals found in solvent production, industrial production processes and in combustion processes.

The usage of agrochemicals for prevention of fungal disease on grains was extensive from the beginning of the 1950s, until it was discontinued in most countries when it was banned in the 1970s (Jones 2005). HCB has also been used as a flame retardant in woods and plastics in addition to being a wood protective (Pacyna et al. 2003).

The accidentally (unintended) formed HCB is emitted mainly from chemical processes that result in dioxins/furans formation such as metal smelting/production, pulp and paper production as well as cement production. HCB emissions can also result from production and use of chlorinated solvents. Additionally, combustion of fossil fuels and waste incineration usually are sources of HCB air emissions.

The information on sources and emissions of HCB in Europe in 2000 was used to prepare a diagram presenting MFA for this compound. This diagram is presented in Fig. 4.1.

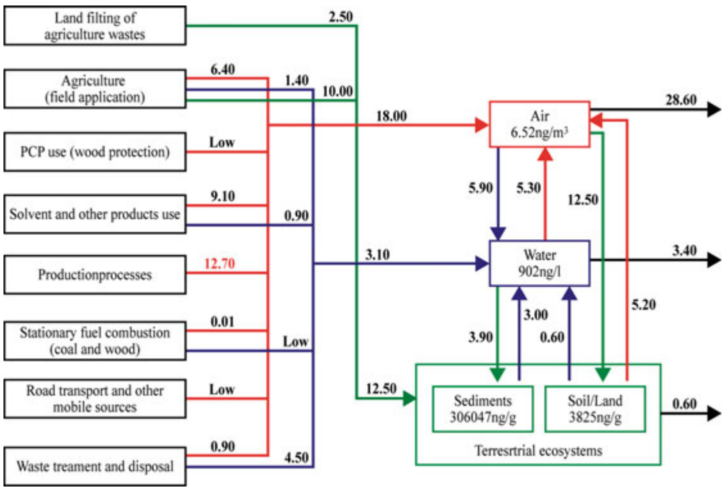

Fig. 4.1 MFA diagram for HCB in Europe in 2000 (numbers in tonnes/year, unless indicated otherwise)

The largest amounts of HCB are emitted to the atmospheric compartment. In the 1990s (1993–1995) the emission estimate was about 18.2 t HCB per year (van der Gon et al. 2007) whereas the most important source category was the agricultural sector accounting for about 80% of the emission. Solvents and other product use counted for 13% while production processes contributed to about 7% and waste treatment and disposal contributed less than 1% (Pacyna et al. 2003). At present, the largest source category is the production processes including cement- and sinter production, which is responsible for more than 13 t of HCB to the atmospheric compartment. Further, the solvent and other products use account for about the half of the emissions to the atmosphere. The field application in agriculture is counting for about 35% while waste incineration is responsible for about 5%. Low contributions can be traced to fossil fuel consumption, road transport and PCP use.

The industry emissions to the aquatic environment were estimated to be 8.5 kg/year in 2002 (Barber et al. 2005). The largest source of emissions to the aquatic environment is however atmospheric deposition (65%). Water can be directly contaminated by HCB-emissions from HCB producing plants and run-off from agricultural fields (Barber et al. 2005). The field application in agriculture is responsible for about 15% of the emissions and the solvent and other products use is responsible for about 10%. The domestic waste disposal is contributing to about 5% while combustion of fossil fuels gives a relatively low contribution.

In soil, the pollutants mainly result from atmospheric deposition and direct pesticide application. Atmospheric deposition of HCB counts for about the half of the contamination while the field application in agriculture counts for about 40%. Land-filling of agricultural waste is thus an additionally source responsible for about 10% of total emissions to the compartment.

Subsequent transfer between compartments may have significant implications to the mass balance and thus material flow. To investigate the fugacity between the compartments, it is applied a steady state fugacity model which employs the fugacity concept for the bulk compartments air, water, soil and bottom sediment (Mackay 2001). The results show that the major receiver for HCB is the compartment for air and the compartments for land and sediments. The major portion of the atmospheric emissions of HCB in Europe is deposited with wet and dry deposition to aquatic and terrestrial discharges and the largest amount of HCB is ending up in the compartment for land and sediments (25 t). Still, HCB have the propensity for being re-emitted into the atmosphere from aquatic compartments in addition to leaching from sediments. If assumed no advective inflow concentrations, the most important fate process is the flux between soil and air counting for about 5 t. HCB does not generally leach to water.

The estimated concentrations are compared with the measured values in order to validate the material flows. Monitoring data on HCB shows that in marine waters, the concentration is most likely below 1 ng/l while concentrations measured in sediments are below 24 μg/kg dry weight. Background measures in air show concentrations to about 51 pg/m^3 on an average in Norway and a global average of 40 pg/m^3. In water the global average of concentrations are 10 pg/l or less (Jones 2005). When allowing for advective inflow concentration (54 pg/m^3) to the air compartment in the steady state fugacity model, the concentrations for air and water seems to be about 54 pg/m^3 for air and 9 pg/l for water.

4.3.2 Polycyclic Aromatic Hydrocarbons

PAHs occur in products used intentionally and as byproducts discharged to the environment. Releases of PAHs to the environment occur from a multitude of point and diffuse sources. Major sources of PAH emissions include fossil fuel combustion in residential and industrial units, road transport (mainly petrol but also diesel engines), wood burning, and a variety of industrial processes (e.g., coke ovens, aluminium production, iron and steel production, anode baking, wood impregnation). Other sources include accidental discharges during the use, transport and disposal of petroleum products, waste incineration and disposal, run-off from roads, and natural sources such as forest fires and geothermal activity. For those PAHs which are manufactured intentionally, there may also be inputs associated with their production, storage and use PAHs used intentionally as products are complex mixtures: coal tar and coal tar-containing products (paints, waterproof membranes, etc.), and creosote. Recent estimates put the amount of creosote used in the EU at approximately 107,000 t/year. Only anthracene is produced as pure substance. In recent years the production of pure anthracene is thought to have dropped to around 1,000 t/year.

The majority of emissions initially occur into the atmosphere. Atmospheric deposition can therefore be a significant pathway of soil and surface water contamination. Direct contamination of the aquatic environment is most frequently associated with discharges from the chemical, metal and petroleum industries and accidental spillages or leakages of petroleum products to land or water. Small amounts of PAHs may be released to soils and surface water from wood products treated with creosote.

Material Flow Analysis was prepared for the following compounds:

- Benzo(a)pyrene
- Benzo(k)fluoranthene
- Benzo(b)fluoranthene
- Indeno(1,2,3-cd)pyrene
- Benzo(ghi)perylene

PAHs are released to the atmosphere, aquatic environment and terrestrial environment. The assessment of atmospheric emissions is more advanced and accurate than the assessment of discharges to the two other compartments of the environment.

The atmospheric data for the above mentioned components were prepared on the basis of information on emission factors from the EMEP/CORINAIR Atmospheric Emission Inventory Guidebook. They were cross-examined using the EPER data and the emission factors from other sources. Quite essential discrepancies were noticed in this comparison, caused mainly by different PAH profiles in these inventory systems. The difference is also caused by the emission factors used in different countries at present. The emission factors prepared in this study take into account also technological changes.

Water loads are based on the EPER data and calculation based on the discharge factors of PAH to water and the geostatistical parameters such as population, territory area, production sets, etc. The results were also cross-examined to check the uncertainty of the assessment carried out.

Land depositions were calculated on the basis of the waste disposal factors.

The information on sources and emissions of PAHs in Europe at the beginning of the 2000s was used to prepare a diagram presenting the MFA for these compounds. The diagram for the sum of Benzo(a)pyrene, Benzo(k)fluoranthene, Benzo(b)fluoranthene, Indeno(1,2,3-cd)pyrene, and Benzo(ghi)perylene, called 5 PAHs, is presented in Fig. 4.2.

4.4 Concluding Remarks

The following concluding remarks can be drawn from the analysis of POP emissions in Europe and the application of Material Flow Analysis (MFA) in this analysis:

1. Material Flow Analysis has proven to be a very useful method to describe sources, fluxes, and end points in the environment for POPs. The MFA can be

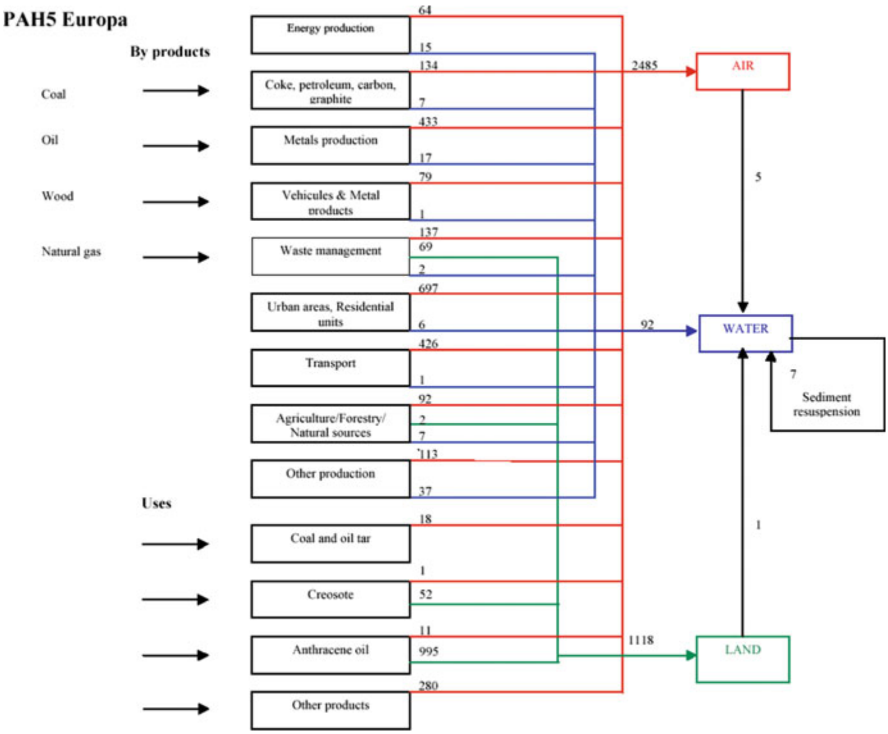

Fig. 4.2 MFA diagram for 5 PAHs in Europe at the beginning of the 2000s (numbers in tonnes/year)

used to describe cycling of these substances in the environment. Such information is very important for policy makers for their work applied at all geographical levels. The MFA can be used to describe past and current cycling of POPs and define solutions for reductions of fluxes if the biogeochemical cycling for a given substance undergoes serious alterations due to various anthropogenic stressors. The MFA can also be used to project future changes of the POPs cycling in the environment in order to reduce environmental exposure to these POPs.

2. Atmospheric deposition has been found to be a major pathway for many POPs entering the aquatic environment. Thus, solutions for reduction of atmospheric emissions and direct discharges of POPs to the terrestrial ecosystems can be the major step towards reducing the contamination of the aquatic environment in Europe for pesticides, compared to the reduction of direct releases to the aquatic ecosystems.
3. The amount of information on sources and fluxes of many POPs has been very limited for proper development of complete and accurate transfer paths of substances in the MFA diagrams. This is a serious problem limiting the application of the MFA method for policy making tasks.

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Chapter 5
Curbing the Omnipresence of Lead in the European Environment Since the 1970s: A Successful Example of Efficient Einvironmental Policy

Hans von Storch

5.1 Introduction

For the foreseeable future, the atmosphere and the environment in general will remain to serve as a dump for various anthropogenic substances. Some substances will have negative properties so that society will sooner or later begin regulating their emissions. To that end, science must provide society with the tools for the retrospective evaluation of the physical and economical impacts of past regulations, and for the predictive evaluation of alternative scenarios of future regulations.

We have developed such a tool for reconstructing past lead air concentrations and depositions across Europe (1958–1995), made up of a detailed emissions, a regionalized history of weather events (with the help of a regional climate model using global weather re-analyses as input), and an atmospheric transport model (for a summary, refer to von Storch et al. 2002, 2003).

We used this tool in conjunction with lead measurements in biota and human blood, and with an economic analysis to assess past European gasoline-lead regulations. Some of the specific questions asked were: How did lead emissions, atmospheric concentrations and depositions develop since the 1950s? Was the decline in air concentrations matched by corresponding declines in plants, animals and humans? Did the regulations result in considerable economic burdens in Germany? How was the media coverage of the issue of lead in gasoline?

We have chosen lead for several reasons. Lead, specifically tetraethyl-lead has been used for a long time as an anti-knocking additive in gasoline (cf., Berwick

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1987; Seyferth 2003). The use of lead in gasoline underwent significant changes, from an unabated increase of emissions to a series of sometimes drastic reductions of emissions since the 1970s. Thus, there is a strong and well-defined signal to be detected. Second, once released into the atmosphere, lead will accumulate and persist almost indefinitely in some environmental compartments, such as aquatic sediments. What might the ecological and human health impacts be when this neurotoxin is present in the environment? Finally, airborne lead behaves to a first order approximation as inert, so that the simulation of its transport and deposition is relatively simple. In principle, our tool can be used for any other particle-bound substance of limited reactivity.

It turns out that this approach is successful in describing the temporal evolution of the spatial distribution of lead deposition in Europe. Demonstrating the effectiveness of gasoline-lead policies, the reconstructed concentrations in the atmosphere, in plant leaves and in human blood show a steady decline since the early 1980s, while concentrations in marine organisms along the North Sea coast, however, seem to remain unaffected – at least until recently. Contrary to initial expectations, the German mineral oil industry was not negatively affected. While competition conditions changed in the German gasoline and automobile markets, no impacts of the regulations could be identified in the macro-economic indicators.

While lead pollution has successfully been curbed in Europe and North America, the problem persists in many parts of the world, including Africa.

5.2 Gasoline-Lead Regulations in Europe

Air pollution problems related to automobile traffic in the 1960s were addressed in the US by the 1963 Clean Air Act.[1] In Europe, concern with the resulting risks to human health would only gain momentum in the 1970s. Lead in particular, which was added to gasoline for its anti-knocking properties, was perceived as a health threat at this time, given the then new evidence of its severe neurotoxicological effects, especially to children. After lead-based paint and lead solder in water pipes and food cans was prohibited, gasoline lead (tetraethyl and tetramethyl lead additives) became the next target.

In the 1970s, the German government was the first in Europe to regulate gasoline lead. A maximum content of 0.4 g Pb/l was imposed in Germany in 1972 (down from the usual 0.6 g Pb/l) and lowered further to 0.15 g Pb/l in 1976. A preliminary analysis of newspaper coverage found that the topic of gasoline lead health dangers entered the German press in the 1960s. British articles did not focus on lead but on urban smog instead. Also, in 1972, a group of experts from the French government

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[1] Actually, the debate about the health implications of using lead in gasoline began already in the United States in the 1920s. An account of this exciting and sometimes harrowing history is provided by Kitmann (2000). See also Seyferth (2003).

did not acknowledge any automobile emissions to be dangerous (Kolb 2005). Starting only in 1981, the European Union (EU) fixed its limit modestly at 0.4 g Pb/l (Council Directive 78/611/EEC of 1978; Hagner 2000).

In the 1980s, the discussion of automobile air pollution in Europe moved to concerns relating to forest protection and the effects on forests of massive NO_x, CO, and C_xH_y emissions. This discussion was also initiated by Germany, concerned with the death of the 'German Forest' from acid rain and photo-oxidation (Kolb 2005). In 1985 Germany passed a law to reduce total automobile emissions. This law included the introduction of unleaded gasoline since the largest reductions in NO_x, CO, C_xH_y and other pollutants could only be achieved with catalytic converters (already in use in the US) and these were incompatible with lead. Opposing reactions expressed in the media of some European countries are reviewed by Kolb (2005; for a short English account refer to von Storch et al. 2003). The press coverage in the 1980s emphasized the expected economic problems in the automobile industry and the difficulty in finding a compromise solution in Europe.

A detailed account of the socio-political process which led to the regulation of lead use in gasoline in Switzerland is given by Breu et al. (2002) and Mosimann et al. (2002). A pan-European account of the introduction of unleaded gasoline is provided by Berwick (1987).

Despite the opposition, in 1985 the EU mandated all member states to offer unleaded gasoline starting October 1989, and recommended a maximum of 0.15 g Pb/l. While some countries promptly adhered to this directive, others lagged behind (see Hagner 2000). The Aarhus Treaty, signed in 1998 by nearly all European countries, stipulated the exclusive use of unleaded gasoline in automobiles by the year 2005.

5.3 Reconstructing Regional Pathways of Lead

For running a model of atmospheric lead transport, regional weather information including wind speed and direction, precipitation rate and boundary layer depth, are required. Since the global weather analyses are available from NCEP (Kalnay et al. 1996) since 1958 at 2° spatial resolution were considered too coarse, the regional atmospheric model REMO was used to 'downscale' to a 0.5° grid (roughly, 50 km scale) covering all of Western Europe and parts of the North Atlantic (Feser et al. 2001).

Emission estimates disaggregated to the 0.5° grid were provided by Pacyna and Pacyna (2000) for the years 1955, 1965, 1975, 1985, 1990 and 1995. Figure 5.1 shows the yearly totals, peaking at nearly 160,000 t in 1975, and shows the predominance of automobile emissions. The sharp decrease since the 1970s resulted from the gasoline-lead regulations as well as from the abatement of fixed-source lead emissions (industrial and others).

Using these emission estimates and the regionalized atmospheric forcing, lead concentrations and depositions over Europe were computed using a two-dimensional

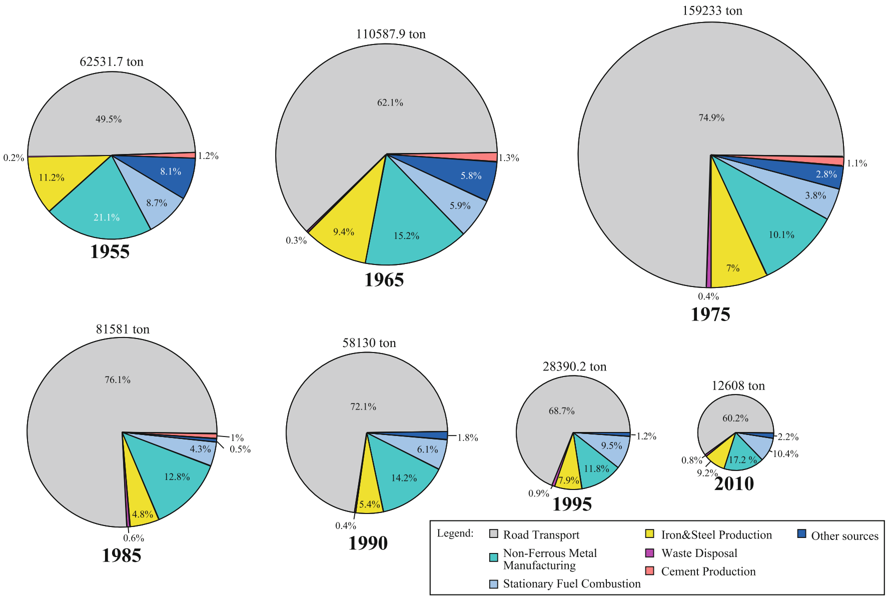

Fig. 5.1 European lead emissions estimates by source category (From Pacyna and Pacyna 2000)

Lagrangian model (Costa-Cabral 1999), with a 6-hourly time step and a 0.5° spatial resolution. It was assumed that lead remains within the well-mixed planetary boundary layer, where it is horizontally advected by wind and deposited to the surface by turbulent transport and precipitation scavenging. The dry settling velocity used was 0.2 cm s^{-1} and the precipitation scavenging constant was 5×10^5.

To validate the model results, a comparison was made with local measurements of lead concentrations and depositions obtained from EMEP (for details refer to von Storch et al. 2003). The general pattern of deposition since the beginning of monitoring activities in 1960 are reproduced very well by the model, particularly those of the early 1980s. The added value provided by the model is the complete space-time coverage, extending over 2 decades (1960–1980) while using hardly any observations.

Simulation results indicate that most of the deposition within a given country originates from its own emissions. Only smaller countries such as Switzerland or the Netherlands have suffered from substantial depositions originating in neighbouring states (von Storch et al. 2003). For the Baltic Sea, for instance, 23% of the total depositions originate in Poland, 20% in Germany, and 16% in Finland. According to our estimation, total input peaked in the mid-1970s, surpassing 3.500 t annually, and declined to under 500 t in 1995 (Fig. 5.2). Simulations compare favourably with comprehensive analyses of the overall deposition of lead into the Baltic Sea based on observational evidence obtained during the second half of the 1980s (Fig. 5.2).

Schulte-Rentrop et al. (2005) extended the analysis – by simulating the overland transport of lead after it had been deposited at the earth's surface. They considered the catchment area of the river Elbe and described the transport of lead into the river

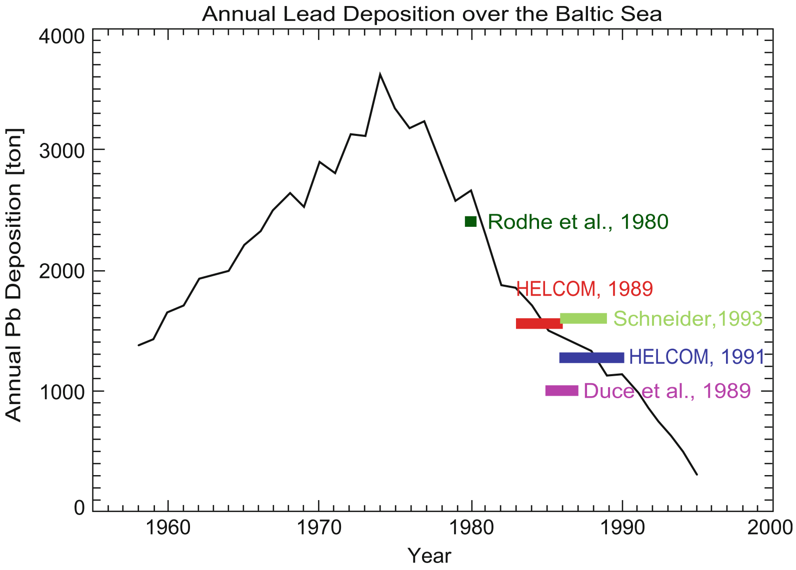

Fig. 5.2 Simulated input of lead into the Baltic Sea (*line*) and estimates based on comprehensive analyses of observational data (*coloured bars*) (von Storch et al. 2003)

by way of atmospheric deposition onto the surface of the river, by erosion and by runoff. A major finding of this study was that the flux of lead into the river diminished since the 1970s, but that the ongoing deposition, with decreasing rates since the 1970s, was associated with a steady accumulation of lead in soils (see also Johansson et al. 2001). Accordingly, the soil released (via erosion and runoff) increasing amounts of lead into the river. Only the atmospheric depositions into the river decreased in parallel to the decreasing atmospheric loads. The overall effect was, however, a reduction in the flux of lead into the river (Fig. 5.3).

5.4 Some Environmental and Economical Impacts

Measurements made in Germany between the 1980s and 1990s showed that atmospheric lead concentrations halved approximately every 4.5 years (Hagner 2000). The same trend could be observed in plants, for example, between 1985 and 1996 a decline in lead concentrations was observed in annual spruce needles and poplar leaves in Germany. However, in marine organisms, such as, for example, the blue mussel and fish in the German Wadden Sea, lead levels have not diminished since the 1980s (Fig. 5.4; Hagner 2002).

Between 1979 and 1997, several studies investigated the levels of lead in human blood in Germany (see Hagner 2002). During this period, levels remained consistently below those indicated as hazardous to adults by medical experts. In Fig. 5.5,

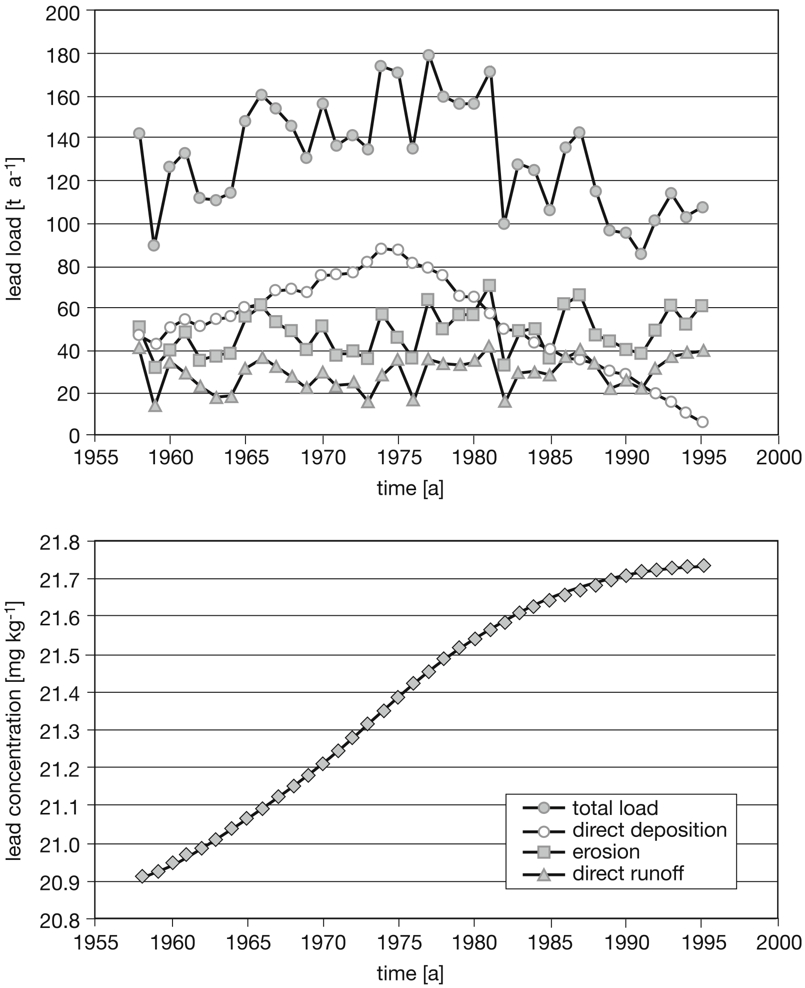

Fig. 5.3 *Top*: Simulated lead loads via the three pathways into the river – direct deposition, erosion and run-off. *Bottom*: Mean simulated lead concentration of the soils in the Elbe catchment

blood lead levels are crudely estimated back to the year 1958. To do this, a regression-type model was constructed using the recorded lead concentrations in adult human blood and the simulated aerial lead concentrations in one grid box (von Storch and Hagner 2004). Data on sample mean concentrations (i.e., mean values across a sample of many people) as well as the 90 and 95%iles were available, so that it could be concluded that 10% (or 5%) of the people sampled had lead concentrations above the 90%ile (95%ile) in their blood, and 90% (95%) had levels below this number. In Fig. 5.5, the coloured backgrounds indicate the critical levels as stipulated by the German Human Biomonitoring Commission. For levels above

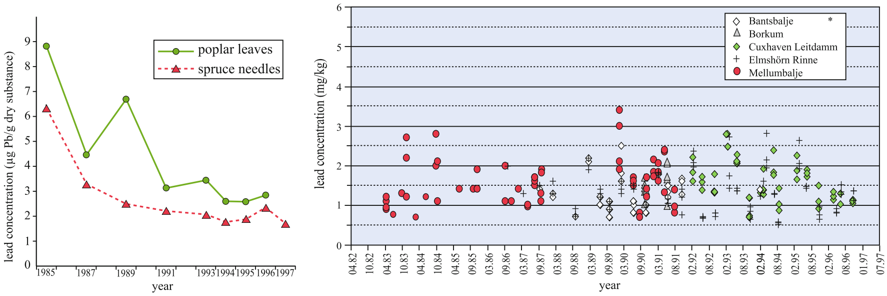

Fig. 5.4 *Left*: Lead concentrations (mg/g) in spruce (Picea abies) sprouts and poplar (Populus nigra) leaves in urban areas in Saarland (Germany), 1985–1996. *Right*: Lead concentration (mg/kg) in Blue Mussels (Mytilus Edulis) along the southern in North Sea coast, 1982–1997 (Hagner 2002; reproduced with permission from the Royal Swedish Academy of Sciences)

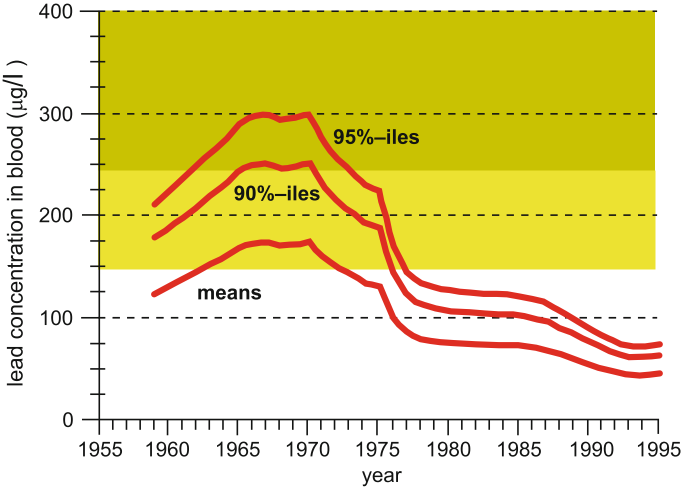

Fig. 5.5 Estimated lead concentration in adult human blood in Germany. The lowest curve relates to the population mean, so that half of the adults have blood concentrations below the cure, and half above. The uppermost curve refers to the 95%ile, so that 5% of all adults have concentrations above the curve. The middle curve describes the 90%ile. The three coloured backgrounds refer to the domains used by the German Human Biomonitoring Commission to classify health risks – in the white domain no dangers are expected, and in the upper class (*densely stippled*) a health risk prevails (von Storch and Hagner 2004)

250 µg Pb/l, health risks for adults are expected, and for levels above 150 µg Pb/l, monitoring is advised (Hagner 2000). For pregnant women and for children, a critical value of 150 µg Pb/l was adopted as indicative of a potential risk to health.[2]

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[2] Interestingly, some American researchers believe that the intellectual development of children is already disturbed at a blood lead level of 100 µg Pb/l.

The estimated mean blood levels of lead reached a peak level of about 150 μg Pb/l in the early 1970s (von Storch and Hagner 2004). This implies that it is highly likely that the lead concentrations in the ambient air in the mid-1970s may have been high enough to raise serious medical concerns for half of the population. The 90%ile reached a level of 250 μg Pb/l, and the 95%ile reached a level of 300 μg Pb/l. Thus, 10% of the entire population was exposed to a serious health risk in the early 1970s.[3] After this period the levels diminished and have now reached much lower levels, well below the critical levels recommended by the Human Biomonitoring Commission. For an international comparison, refer to Thomas et al. (1999).

An assessment of the most immediate economical impacts of the lead regulations is a difficult task. Hagner's (2000) analysis indicates that despite the concerns voiced by the German mineral oil industry that petrol production would become costlier following the first regulation in 1972; the costs have actually dropped thanks to the savings resulting from lead additives. It was only after the second regulation in 1976 that production costs rose slightly and this was due to the fact that new additives with high octane numbers were now required for maintaining gasoline performance (Hagner 2000).

The impacts of introducing unleaded gasoline in 1985 were more complex. Tax incentives for unleaded gasoline and for low-emission cars increased the sales of both products. Many independent gasoline traders went bankrupt, as gas-station reconstruction represented a higher financial strain for them compared to the large multinational companies. Favourable terms of competition were experienced by car manufacturers with the highest technical standards, and who had already gathered experience with catalyst systems on the U.S. market (Hagner 2000).

Aside from these shifts in market competition conditions, no significant impact could be detected in the German macro-economic indicators including gross national product, economic growth, price stability, unemployment level, or foreign trade balance.

5.5 Conclusion and Outlook

We have developed a tool for reconstructing past lead air concentrations and depositions across Europe. With the help of regionalized atmospheric data, spatially disaggregated lead emissions from road traffic and point sources, and various local data, an attempt was made to reconstruct the airborne pathways and deposition of gasoline lead in Europe since 1958. We have also analyzed trends in concentrations in biota and human blood, and evaluated the most direct economic impacts of gasoline-lead regulations.

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[3] At least for the site where the blood monitoring was carried out, namely the city of Münster in Nordrhein-Westfalen.

We have demonstrated that for the case of lead our tool is functioning well. Our modelled data show that European gasoline-lead reduction regulations may be considered a good example of successful environmental policy. However, the success of lead policies is limited to atmospheric pathways, and did not have the effect of lowering concentrations in some marine biota and soil concentrations.

One should, however, not forget that the large amounts of lead emitted in the past 50 years have not simply vanished but ubiquitously reside for good in the global environment. The use of lead in gasoline was indeed a large-scale geophysical pollution exercise, and it remains to be seen if long-term effects may emerge at a later time.

The major conclusion to be drawn from our analysis is that the regulation to remove lead as an anti-knocking additive in gasoline after 2 decades of unabated increase was mostly successful. The regulation solved the problem for the atmospheric pathway, and that part of the ecosystem in which the toxin essentially ‘passes through’ in relatively short time. Thus, a relatively short residence time is a necessary condition for substance abatement through emission regulations in a given environmental compartment once considerable amounts of the substance have already been released. For other parts of the ecosystem, which accumulate and store the toxin for an extended period of time, such a regulation is better than nothing but is certainly insufficient. For such systems, the prevention of such pollution actually occurring is the only solution.

The success of the environmental protection policy was mostly limited to the developed world (Fig. 5.6; Thomas 1995; Thomas et al. 1999; Kwong and Kwong

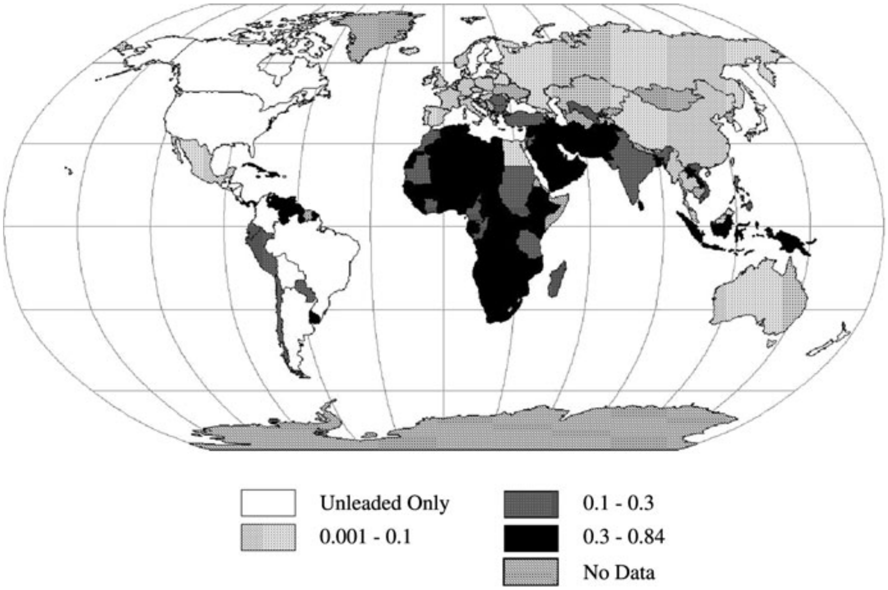

Fig. 5.6 Use of leaded gasoline in different countries of the world (After Thomas and Kwong 2001). The unit is g Pb/l. Values in most of Europe are 0.0015 g Pb/l – which is sold as ‘lead-free’

2001). Almost everywhere in Africa and the Near East, where lead was still in use as an anti-knocking additive up until the early 2000s and on a large scale, the lead concentrations were mostly 0.3 g Pb/l and higher. For instance, Thomas et al. (1999) report about 0.39 g Pb/l in gasoline and 156 μg Pb/l in human blood for Caracas in 1991; in Mexico City the concentration went down from 0.2 g Pb/l in gasoline and 122 μg Pb/l in human blood in 1988 to 0.06 g Pb/l in gasoline and 70 μg Pb/l in human blood in 1993. For Cape Town the latest concentrations available are from 1990 with 0.4 g Pb/l in gasoline and 72 μg Pb/l in human blood. In Egypt all gasoline had lead in it in 1994, with 0.35 g Pb/l (Thomas 1995); the same account reports 0.66 g Pb/l in Nigeria (no year given) and 0.84 g Pb/l in Equador (in 1993). One would hope that the situation has improved in these countries.

Our methodology is presently being extended to more ‘interesting’ chemicals, in particular to benzo(a)pyrene (Matthias et al. 2007; Aulinger et al. 2007).

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For further information refer to: http://coast.gkss.de/G/Mitarbeiter/blei/. The annual emissions, and modelled concentrations and depositions data are available for download from a link on this page.

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Part III
Persistant Pollutions: A Closer Look

Chapter 6
A Historical Record of Heavy Metal Pollution in Alpine Snow and Ice

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This chapter is dedicated to our friend and colleague Kevin Rosman, who passed away in March 2009.

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Heavy metals and trace elements are ubiquitous throughout the environment, some are essential for life (e.g., Fe), others are micronutrients (e.g., Se) and others are considered as toxic elements (e.g., Hg). Levels of these elements in the environment are determined by the local geochemistry and anthropogenic emissions, with implications for human and environmental health. Records from Alpine ice cores have demonstrated to be among the best tools in paleoenvironmental studies to reconstruct past emissions of heavy metals and persistent organic pollutants. From the comparison of trace element records in the snow and ice with the emission inventories compiled in recent years it is also possible to reconstruct the past trends in the emission of these compounds. We present here some trace elements records from the European Alps and in particular from the Mont Blanc and Monte Rosa regions. The study of levels of these elements in alpine regions allows us to begin to understand their biogeochemistry and their effects on a global and regional scale. However, without advances in clean working techniques and the outstanding improvement in instrument sensitivity that have occurred over the last two decades, none of these studies would have been possible.

6.1 Introduction

Metals and their compounds are widespread throughout the environment and are constantly cycled through it, due to chemical and mechanical weathering as well as re-mobilization by human activities that also accelerate their speed of emission. Some of these elements are considered to be essential for life, while others are micronutrients, that are beneficial in small quantities but toxic in higher amounts and others are toxic at all concentrations. An ever increasing range of elements are becoming economically important as uses are found for them, and mankind is having a deep effect on their geochemical cycles, by mining them out of the crust and utilizing them, or releasing them from other materials (e.g., burning fossil fuels).

Human activities perturb the atmosphere and thereby influence the global climate. A prominent example is aeolian mineral dust originating from changes in land use and land cover, which affect the radiative balance at the surface of the Earth. Given these ongoing anthropogenic changes, understanding the past record of atmospheric composition is extremely important. Over the past 100 years it is not always an easy task to separate atmospheric changes induced by human activities from those related to natural variability. Only the longer term past record, going back in time to when there was negligible anthropogenic influence on the environment, provides the context of natural variability within which recent anthropogenic perturbation has taken place. In this respect, ice cores from polar and alpine regions are extraordinarily valuable proxies for past climatic, environmental and atmospheric conditions.

As the third millennium opens, it is clear that human beings are having a discernible impact on the environment and profound changes are underway. Population growth increase economic activity, with all their implications in terms of

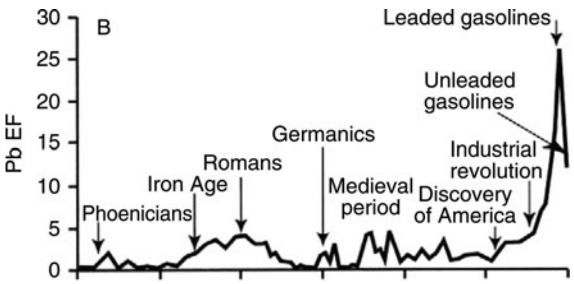


Fig. 6.1 The lead Enrichment Factor (EF) record from Penido Vello, a peat profile in Northern Spain (Martinez Cortizas et al. 1999) sets against a series of historical events and cultural stages from 3,000 BP onwards

higher demands on energy, water and a wide range of resources, both renewable and non-renewable. Discernible widespread impacts of human activities on atmospheric chemistry begin with the early days of intensive metal smelting (Nriagu 1996). Although there are indications of these impacts from the Bronze Age onwards, they become much stronger during the time of the Greek and Roman Empires for which there are clear signs of enhanced atmospheric concentrations of lead, copper and other trace metals in Greenland ice (Hong et al. 1994) and in European lake sediments (Renberg et al. 1994) and peat bogs (Shotyk 1996; Shotyk et al. 1998; Martinez Cortizas et al. 1999; Fig. 6.1).

Over the last 40 years great efforts have been devoted to assess the occurrence of toxic metals such as Pb, Hg, Cd, As, Cu and Zn in the successive well-preserved snow and ice layers deposited in alpine and polar ice caps, in order to obtain historical records of atmospheric concentrations of these elements in the remote areas of both hemispheres from prehistoric times to present. Due to the purity of polar snow and ice, it is extremely difficult to collect the samples in the field and to analyze them for these elements in the laboratory without introducing contamination.

This article highlights the most recent results obtained in the field of the reconstruction of heavy metal emissions in the Alpine region, considering in details the sources and fates of these substances in the environment as well as the correct approach for the sampling, treatment and chemical analysis of ice cores, through state of the art analytical techniques.

6.2 Sources and Fate of Heavy Metals in the Environment

The interactions between the atmosphere and the various geochemical reservoirs of the biosphere (hydrosphere, cryosphere, lithosphere) are numerous and lead to the formation of many types of aerosols containing heavy metals. Aerosols have two principal origins: natural (dust, sea salt spray, volcanism, etc.) or anthropogenic (industrial combustions, smelting, mining, automobile emissions, domestic heating, etc.). Aerosols may be divided into two main classes, arising from two different basic processes: (1) primary aerosol derives from the dispersal of fine materials from the earth's surface, such as sea salts and dust; (2) secondary aerosol is formed by chemical reactions and condensation of atmospheric gases and vapours. Heavy metals, emitted as primary and/or secondary aerosol, can be transported for long distances by wind, generally in the troposphere, through sometimes by stratospheric pathways. Aerosol particles are incorporated in snowflakes by nucleation scavenging at cloud level, by below-cloud scavenging and by dry deposition.

Anthropogenic activities increase the quantity of secondary aerosols in the atmosphere due to the chemically unstable nature of many anthropogenically emitted compounds. The majority of anthropogenic aerosols exist in the form of sulphates, carbonates and nitrogen compounds. Presently, anthropogenic activity contributes approximately 20% of the global aerosol mass burden, but up to 50% to the global mean aerosol optical depth (Raynaud et al. 2003).

6.2.1 Natural Emissions of Heavy Metals into the Environment

Mineral dust particles are mostly generated by winds in arid continental regions and, sporadically, by explosive volcanic eruptions which emit huge amounts of ash particles and by a negligible input of extraterrestrial materials (Gabrielli et al. 2004). Minerals entrapped in snow and ice (at the end of the dust cycle) mostly reflect the geochemical characteristics of the sources.

In order to assess the importance of the rock and soil dust contribution for the trace elements studied, the Crustal Enrichment Factor (EFc) is frequently used. EFc is defined as the concentration ratio of a given element to that of Al, Mn or Ba (which are good proxies of continental dust) in the snow or ice, normalized to the same concentration ratio characteristic of the upper continental crust (UCC). Usually, data for the upper continental crust given by Wedepohl (1995) are used. It should however be noted that the choice of other published crustal composition data (for instance Rudnick and Fountain 1995 or McLennan 2001) would not make any significant change in the interpretation of the data.

For example, the EFc for Pb is calculated as:

$$EF_c = \frac{\frac{[Pb]_{ice}}{[Mn]_{ice}}}{\frac{[Pb]_{UCC}}{[Mn]_{UCC}}}$$

Despite the fact that the composition of rock and soil dust reaching the high elevation Alpine site may significantly differ from the composition of the mean upper continental crust, EFc values close to unity (up to ~5) will indicate that the corresponding element mainly originated from the continental dust. Conversely, EFc values much larger than unity will suggest a significant contribution from other natural or anthropogenic sources. Although EFc is not an exclusive or precise tool for data interpretation, it is quite useful when comparing different proxies and records of past atmospheric pollution from heavy metals, as we will see in the following sections.

The main possible natural sources of trace elements other than continental dust are sea salt spray, volcanic emissions and marine biogenic activity (Nriagu 1989). Most sea salt particles are produced by evaporation of spray from breaking waves at the ocean surface (Raynaud et al. 2003). Trace elements show very variable content in sea water with concentrations fluctuating between ng/g to pg/g (Table 6.1). These elements can be grouped by their “oceanic behavior”. This behavior governs their repartition in the water column, and so concentration at the sea surface where the sea salt spray is formed.

Amongst the trace elements studied in Table 6.1 only U shows a conservative behavior, probably due to its ionic form and constant concentration regardless of depth (Chen et al. 1986). V, Cr, Cu, Zn, Cd and Ba follow the distribution of nutrients. Biological activity tends to lower concentrations in surface layers and to enrich deep water by mineralization of the organic material (Donat and Bruland 1995). Mn, Cu, Pb and Bi are enriched in the surface layer. Their great affinity for particulate matter deposits them quickly into deeper waters (Donat and Bruland 1995). Cr and Cu have hybrid behavior. Cr is influenced by both biology and redox potential whilst Cu is influenced by biology as well as tending to be adsorbed onto particles.

As well as the influence of mineral dust, the contribution from sea-salt spray can be estimated in snow and ice from Na concentrations measured in the samples (Wolff et al. 2006) and metal/Na concentration ratios in bulk ocean water (Yoshiyuki 1999)), after subtracting the Na contribution from crustal dust. Earlier studies considered the possible enrichment of trace elements in ocean derived

Table 6.1 Mean concentration (in pg/g) of trace elements in seawater (North Pacific, North Atlantic, Southern Ocean) and oceanic behavior in the water column

	Mean concentration (North Pacific; Yoshiyuki 1999)	Surface concentration (North Pacific and North Atlantic; Donat and Bruland 1995)	Surface concentration (Southern Ocean)	Oceanic behavior
V	2,000	1,100–1,700		N
Cr	210	150		R + N
Mn	20	25–160		S
Co	1.2		1.8[a]	N
Cu	150	30–80	120[a]	S + N
Zn	350	6–12	260[a]	N
Cd	70	0.1–1	100[a,b]	N
Ba	15,000			N
Pb	2.7	2.8–3.0	2[a,c]	S
Bi	0.03	0.05		S
U	3,200			C

C conservative, *N* nutrients, *R* controlled by redox potential, *S* scavenged

[a] Westerlund and Öhman 1991

[b] Capodaglio et al. 2001

[c] Flegal et al. 1993

aerosols relative to bulk ocean water, but recent studies have put doubt on the magnitude of such enrichments (Hunter 1997) so the current tendency is to not overestimate the importance of surface micro-layer enrichment.

Volcanoes are also another important source of gases and aerosol to the atmosphere. Large volcanic eruptions which penetrate the stratosphere affect global climate on the order of 1–3 years and can produce significant climatic changes (Rampino and Self 1992). Small, passively degassing volcanoes, for which there are many currently active at any time, also contribute significant amounts of volatile elements as gases and aerosols to the troposphere (Zreda-Gostynska and Kyle 1997).

There are other possible natural sources for heavy metals into the environment. They include emissions from forest fires, biological activities and other minor sources, which are difficult to quantify and generally limited to local or regional scales of influence and brief time intervals (<1 year).

6.2.2 Anthropogenic Emissions of Heavy Metals into the Environment

Many studies have been devoted to the estimation of anthropogenic fluxes of trace elements into the atmosphere on global (Nriagu 1990a, b; Nriagu and Pacyna 1988; Pacyna and Pacyna 2001) and regional scales (Barbante et al. 2004). All these studies confirm that emissions stemming from human activities largely exceed natural fluxes for the present period and in particular since the 1950s.

For example, since the development of civilization demand for Pb and other metals has steadily increased, with increasing exploitation of lead-bearing ore bodies (Nriagu 1996). The discovery of alkyllead additives for gasoline in the 1920s and their subsequent introduction worldwide has seen a further increase in demand for Pb in the twentieth century, and has also greatly increased the quantity of Pb emitted to the atmosphere (Bollhöfer and Rosman 2000, 2001a, b). Despite the withdrawal of alkyllead additives from gasoline, Pb fluxes were still significantly perturbed by anthropogenic activities in 1995. This trend is shown by lead concentrations in firn dated from the last centuries, with peak concentrations in the 1970s and a steady decline in the last three decades (Schwikowski et al. 2004).

6.2.3 Atmospheric Transport of Aerosols

Heavy metals are transported through the air mostly in the form of particulates, and as such their transport is dependent upon the size, shape, mass and other physical and chemical properties of the particle. During long-range transport, the decrease in particle concentration from the source (a) to the sink (b) can be described as:

$$C_b = C_a \cdot f \cdot e^{\frac{-t}{T}},$$

where t is the transit time between the source and the sink, T is the residence time of the particle in the atmosphere, governed by wet and dry deposition processes en route, C_a and C_b the atmospheric concentrations at the source and the sink respectively, and f a correction factor. Therefore, for a given atmospheric residence time, longer transport times will result in lower concentrations of trace elements at the sink.

Particles carrying heavy metal and their compounds can be removed from the atmosphere by dry or wet deposition. Dry deposition includes gravitational settling, where the settling velocity depends on the square of particle size, and turbulent mixing to the surface, while precipitation-related events like sub-cloud scavenging and in-cloud removal control wet deposition processes.

The removal efficiency is size dependent; hence during transport the size distribution changes. For sands and coarse silts the gravitational settling alone (dry deposition) determines the sedimentation velocity, while for clays and fine particulates the lifetime in the atmosphere is mainly controlled by wet deposition and turbulent mixing.

6.3 Snow and Ice Archives of Past Atmospheric Pollution

The study of the atmospheric composition in the past, prior to instrumental records, is based on the interpretation of environmental archives. Several of these archives exist and all of them contain so-called proxies that are in some way related to climate. The most important climate archives are historical data, polar and temperate ice sheets and glaciers, tree rings, speleothems, oceanic and lacustrine sediments, peat bogs, surface and subsurface temperature profiles (from boreholes).

All these archives have their individual weaknesses and strengths such that it is often helpful to combine many of them to compensate for spatial and temporal (if not biological) variability, thereby ensuring redundancy. This strategy has recently become very popular and is referred to as multi-proxy approach.

Ice cores are among the best climate archives because they provide information on many different parameters of the climate system. Moreover, ice cores from polar regions cover a useful time range, up to nearly 800,000 years (EPICA 2004) at high temporal resolution. Ice cores allow for the reconstruction of gaseous composition of the atmosphere (including concentrations of greenhouse gases, like CO_2, CH_4 and N_2O), ambient aerosol concentration and composition (mineral and anthropogenic dust), past temperatures and changes in atmospheric circulation, and in precipitation. No other climate archive allows for the simultaneous determination of such a variety of different parameters. Further, ice and snow are “clean” environmental matrices, assuring low background for many analytical determinations and relatively simple chemical preparation.

Ice core drilling has a long tradition in polar regions and started in 1960 with the recovery of an ice core in Camp Century, Greenland (Dansgaard et al. 1969). Later, ice coring was extended to mountain glaciers in the mid and low latitudes (outside polar regions). These glaciers are remarkably different to those in polar regions. They generally experience higher annual accumulation (typically 0.5–2.5 m water equivalent per year) and their thickness in the accumulation area is typically 100–300 m which is less than 10% of the thickness of the ice sheets in Greenland and Antarctica. Therefore, they generally cover a much shorter time period ranging from less than 110 years as observed for an ice core from Col du Dome, France, 1890–1994 (Preunkert et al. 2001), to more than a glacial cycle (100,000 years) for an ice core from the Tibetan Plateau (Thompson et al. 1997), the only time glacial climate has been recorded outside the polar regions. The higher accumulation rates commonly found on mid and low latitude glaciers also have the advantage of allowing sub-annual resolution. The type of climate signal recorded is much more local compared to polar glaciers which archive climatic variations on a global or hemispheric/regional scale. Therefore changes in regional moisture and temperature are assessable, information that cannot be gained from polar ice cores.

Another strength of non-polar glaciers is that they are located much closer to sites of human habitation and industrialization (Fig. 6.2). Mountain glaciers from such regions provide important records of anthropogenic air pollution especially for species with a short atmospheric residence time. Mountain glaciers are excellent archives of anthropogenic air pollution, documenting accurately the environmental

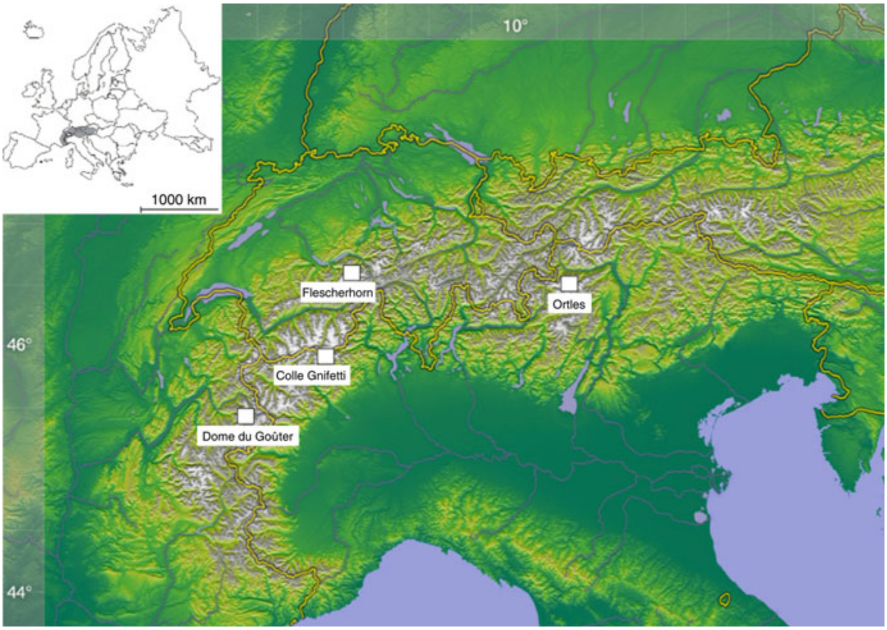


Fig. 6.2 Some of the high altitude sampling sites in the Alps

impact of anthropogenic emissions over the last centuries and the efficacy of recent air pollution control.

6.3.1 Snow and Ice Sampling

Surface or near surface samples (to about 10–15 m depth) are collected directly from hand dug pits or by drilling shallow firn cores. The scientists wear clean room clothing over their warm weather gear and use ultra clean shovels and tools to collect block samples, or push ultra clean plastic cylinders into the pit walls to take discrete samples.

Sampling of deeper firn or ice requires electromechanical or thermal drilling due to the difficulty and impracticality of working in snow trenches or hand drilling below depths of 15 m. As drilling contaminates the outer core, and various fluids are used (like kerosene mixed with Freon or n-butyl acetate) to keep the borehole from collapsing, outer sample contamination is unavoidable, so the cores have to be carefully decontaminated. This is done in a cold (−15°C) clean laboratory on a lathe with plastic or stainless steel tools, where the outer contaminated layers are successively removed until a plateau of elemental concentrations is reached (Planchon et al. 2001).

6.3.2 Decontamination of Alpine Snow and Ice

There is no point in taking such precautions in the field if the samples of snow and ice are contaminated once they arrive in the laboratory. Contamination can come from the labware, the reagents used, from the operators and the laboratory itself (Planchon et al. 2001).

The working environment where samples are prepared must be at least a Class 100 clean room as classified by Federal Standard 209 (1988). In these environments two distinct areas should be organized: the first for sample handling, standard solution preparation and rinsing of the plastic labware; the second for ultrapure reagent production (e.g., nitric acid by subboiling evaporation) and the arrangement of acid baths used for cleaning plastic labware. Clean laboratories must have an entrance-room which acts as a transition area, allowing the operators to put on particle-free clothing, including plastic gloves and shoes. These items decrease the number of potentially-contaminating particles produced by the operators as they work in the inner ultra-clean area. The clean room is ideally built with walls of Polyvinyl chloride (PVC) or other acid-resistant, particle-free material, and the air is pressurized, preventing the admission of contaminated external air. Furthermore the pressurized air must be filtered through high efficiency particulate filters, able to remove 99.999% of particles greater than 0.5 μm. In these conditions the transfer of airborne particulate matter to the samples is kept to a minimum.

Within such a clean working environment, it is imperative that ultra pure reagents are used and labware is cleaned to a level suitable for ultra trace analysis. Various water systems exists capable of delivering suitably clean water, the main manufacturers being Millipore (Bedford, MA, USA) and Elga (High Wycombe, Bucks, UK), acid can be bought from various manufacturers in ultra pure analytical grades and can be further purified by sub boiling distillation if required.

Labware is cleaned in the following fashion, after an initial rinse with tap water to remove dust; the apparatus are degreased with chloroform and rinsed in ultra pure water. They are then immersed in a series of acid baths maintained at 50°C for 2-week periods with rinsing in between. The first bath is 1:3, nitric acid:water (v/v), the second and third are 1:1000 nitric acid:water baths (v/v), after the 6 week washing period the bottles are filled with 1:1,000 nitric acid:water (v/v) and stored in double polyethylene bags until required for use (Planchon et al. 2001).

6.3.3 Age Assignment

Age dating of Alpine ice cores is a complicated task. The main dating tool, applied to such archives is the counting of annual layers or of one or more seasonally varying parameters. Most often ice cores are dated by combining these methods: counting of annual layers from continuous concentration profiles of seasonally varying species, such as ammonium (Döscher et al. 1996), calcium, sulphate and stable isotopes of hydrogen and oxygen; use of stratigraphic markers, such as large Saharan dust events, atmospheric nuclear tests (identified from tritium an plutonium profiles) and major volcanic eruptions; ^{210}Pb measurements for the post-1900 period; and a three dimensional ice flow model (Döscher et al. 1996). More recently a novel approach that uses ^{14}C dating of the carbonaceous particles entrapped in ice cores has been proposed (Jenk et al. 2006, 2009).

6.4 Alpine Ice Core Record of Past Anthropogenic Pollution by Heavy Metals

The Alps are a very promising study site for ice core research as a dense network of observational data is available (e.g., temperature, precipitation, stable isotopes), allowing for the calibration of glaciochemical data obtained. Some of the instrumental temperature data reach over 250 years back in time (e.g., Böhm et al. 2001). The Alps represent the largest barrier to southern air flow in Europe, strongly influencing the weather and hence the distribution of atmospheric trace components. Typically, northern regions are more influenced by polar-maritime air masses whereas on the southern side, tropical-maritime air masses dominate.

6.4.1 Seasonal Variation of Heavy Metals in Alpine Ice

As an example, the seasonal variations of some trace elements (Pb, Zn, Cu, Cd, Bi, Mn and Al) were determined in selected samples of an ice core from Col Dû Goûter (Mont Blanc, 4,304 m asl) covering the time period from 1960 to 1968 (van de Velde et al. 1998). Figure 6.3 shows the variations of the concentrations as a function of the depth for the years 1966–1968. Also shown are the variations of the D/H isotopic ratio (expressed as δD in units of per mil, ‰) which can be used to identify the different periods of the year: more-negative δD values are associated with cooler temperatures indicating winter layers while less-negative values are associated to warmer temperatures and indicate summer layers.

Figure 6.3 shows pronounced seasonal variations for all investigated heavy metals with extremely low winter concentrations and much higher summer

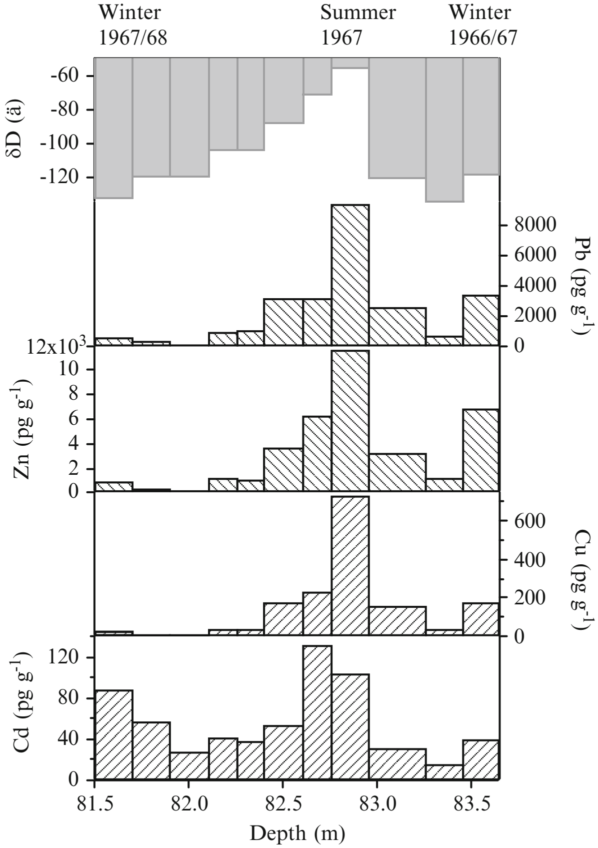


Fig. 6.3 Seasonal variations in the concentrations of selected metals and δD (‰) (*in grey*) in high altitude ice dated from 1966 to 1968 collected near the summit of Mont Blanc in the French-Italian Alps. Depth scale is shown at the bottom and the isotopic seasons are shown at the top

concentration. The summer/winter ratio is ~180 for Pb, ~330 for Zn, ~850 for Cu, ~120 for Cd, ~90 for Bi, ~32 for Mn and ~10 for Al. It is interesting to mention that the ratio is especially high for Cu, Zn, Pb and Cd. For Bi, Mn and Al on the other hand the amplitude of the variations is smaller.

Table 6.2 compares the concentration values observed for Pb, Zn, Cu, Cd and Bi in Mont Blanc ice from the 1960s with those observed in snow deposited in Central Greenland dated from the same decade (Candelone et al. 1995; Boutron et al. 1991). The very low winter concentrations observed for Mont Blanc are comparable with the lowest concentrations observed in Central Greenland snow. On the other hand, the very high summer concentrations at Mont Blanc are higher by about one order of magnitude than the higher Greenland values.

There are two main factors which can explain this very strong variability in heavy metals concentrations in Mont Blanc ice from the 1960s. The first one is linked to the seasonal variability in the emissions of heavy metals from natural and anthropogenic sources to the atmosphere. The second is related to the variability in meteorological conditions, especially regarding thermal inversions.

When comparing natural versus anthropogenic sources of heavy metals emitted into the atmosphere (van de Velde et al. 1998), it appears that the seasonal patterns in source strength would rather favour enhanced emissions during winter which should result in maxima of heavy metal concentrations in Mont Blanc ice in winter. Clearly it is not what is observed in Fig. 6.3.

The key parameter to explain the observed seasonal variations in the ice is the changing vertical structure of the regional troposphere. Simplifying the meteorology, in winter and early spring, precipitation in the western part of the Alps is associated with frontal systems mainly arriving from West, Southwest or Southeast, while in late spring and summer, snowfalls on alpine relief are mainly caused by convective stormy systems, which play an important role in the vertical exchange between the boundary layer and the free troposphere. Winter times are characterized by stable low altitude thermal inversions which strictly limit the transportation of ground emitted pollutants to high altitude locations such as the summit areas of Mont Blanc (Anquetin et al. 1999a, b).

During winter the high altitude areas of the Alps are influenced very little by local or even regional anthropogenic emissions. Winter air in this area rather represents continental background conditions. It is a key parameter to understand why the measured concentrations in winter ice are extremely low.

Table 6.2 Comparison between heavy metals concentrations in ice from Greenland (Candelone et al. 1995; Boutron et al. 1991) and the Alps (van de Velde et al. 1998) dated from the 1960s

	Measured concentrations (pg/g)				
	Pb	Zn	Cu	Cd	Bi
Greenland lowest concentration	60	20	3	0.5	0.028
Greenland highest concentration	320	490	30	15	0.28
Alps lowest concentration	50	35	1	0.7	≤ 0.1
Alps highest concentration	8,540	11,700	900	130	37

The situation is very different during the rest of the year: the meteorological situation is indeed often characterized by important vertical exchanges between the boundary layer and the high altitude locations such as Mont Blanc. It allows pollutants to easily reach high altitude locations with likely significant contributions from local or regional sources. This is certainly one of the main factors responsible for the high concentrations observed in summer ice. It appears therefore that the vertical extension of the continental boundary layer is one of the most important controlling factors of the air and precipitation quality in the high altitude areas in the Alps.

6.4.2 Historical Record of European Emissions of Heavy Metals to the Atmosphere

In Barbante et al. (2004), the concentrations of many heavy metals (Cr, Cd, Zn, Co, Ni, Mo, Rh, Pd, Ag, Cd, Sb, Bi, Pt, Au, U) were determined in a 109 m ice core drilled in 1982 on Colle Gnifetti, Monte Rosa Group at 4,450 m asl of altitude (the so called Blue Core), Fig. 6.4. The Blue Core was particularly important because it

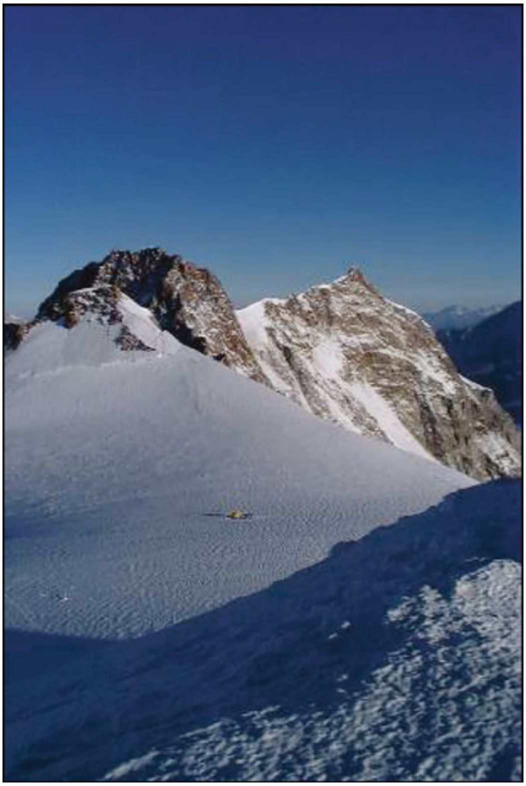


Fig. 6.4 The drilling site at Colle Gnifetti, in the heart of Europe at 4,450 m a.s.l. altitude. The 109 m deep ice core drilled in 1982 covers a time period of about 350 years, from 1650 to the mid-1990s

covered a 350-years time period, from 1650 to 1994, representing the oldest glaciological record over the Alps at that time. The elements were chosen because they are emitted by human activities to the atmosphere and might pose a threat to the environment, especially in populated areas such as Europe (Nriagu and Pacyna 1988; Pacyna and Pacyna 2001; Pacyna et al. 1984).

The only other data to which these data can be compared to are those obtained from Dome du Goûter, Mont Blanc massif (van de Velde et al. 1998, 1999, 2000; Barbante et al. 2001, 2002). Colle Gnifetti and Dome du Goûter are ~80 km apart (Fig. 6.2) and they are at nearly the same altitude. It should however be kept in mind that the snow accumulation rate is much higher at Dome du Goûter than at Colle Gnifetti. It can be seen in Table 6.3 that the concentrations are rather similar at the two locations, which is reasonable when remembering that the two locations are such a short distance from each other.

An interesting feature of the data set is that there is a pronounced variability in concentrations. As an example, Fig. 6.5 shows the whole data set for Zn and Cu, which are the only metals that were measured in all the samples. Concentrations are reported in log scale and differ by two to three orders of magnitude in adjacent core sections. This confirms that there are pronounced short term (inter-annual and intra-annual) variations in heavy metal inputs to Colle Gnifetti as was previously observed for other species such as ammonium, sulphate and nitrate (Döscher et al. 1995, 1996; Schwikowski et al. 1999) as well as aerosol concentrations in ambient air (Lugauer et al. 1998). This fact was explained by seasonal changes in the efficiency of vertical transport of boundary layer air to high-alpine sites (Lugauer et al. 1998; Baltensperger et al. 1997).

Table 6.3 Concentrations (in pg g^{-1}) of trace metals in recent snow and ice from Colle Gnifetti (Monte Rosa, Swiss – Italian Alps, Barbante et al. 2004) and from Dome du Goûter (Mont Blanc, French – Italian Alps) (From van de Velde et al. 1998, 1999, 2000; Barbante et al. 2001, 2002)

Element	Colle Gnifetti		Dome du Goûter	
	Range (min–max)	Mean	Range (min–max)	Mean
Cr	83–920	320	7.7–830	142
Cu	1–14,500	460	2.0–900	142
Zn	15–38,200	2,280	35–11,700	1,790
Co	1.0–1,080	156	16–1,040	155
Ni	1–1,530	127	6.5–710	136
Mo	3.1–66	17	0.44–50	9.3
Rh	0.01–0.43	0.12	0.01–0.4	0.10
Pd	0.7–17	3.7	0.5–10	2.5
Ag	0.01–35	2.4	0.15–12	1.6
Cd	0.1–270	52	1.1–130	25
Sb	2–690	48	0.2–110	22
Pt	0.08–2.7	0.35	0.08–0.6	0.27
Au	0.06–0.3	0.13	0.07–0.4	0.22
Bi	2.1–8.4	4	0.18–24	3.5
U	0.2–28	5.0	0.2–37	4.6

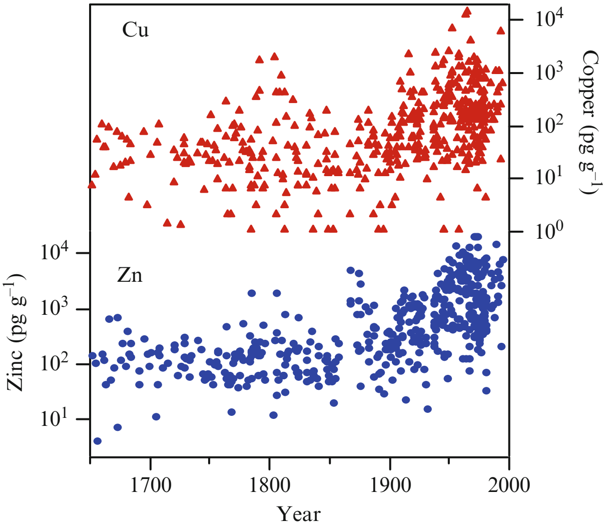


Fig. 6.5 Changes in Cu (*red triangles*) and Zn (*blue circles*) concentrations in dated snow/ice from a high altitude Alpine site (Colle Gnifetti, Monte Rosa massif, Swiss-Italian Alps; Barbante et al. 2004)

Previous investigations on seasonal variations of heavy metals in the Dome du Goûter snow/ice core (van de Velde et al. 1998, 1999, 2000; Barbante et al. 2001, 2002) have confirmed that such short-term variations are largely linked with seasonal changes in the vertical structure of the regional troposphere. Winter is indeed characterized by frequent low altitude thermal inversions limiting the transportation of pollutants from low altitude source areas to high altitude locations. The pollutant content of high altitude winter snow is then largely derived from distant sources. Conversely, there are stronger vertical exchanges in the troposphere during summer, which allow locally and regionally emitted pollutants to reach the high-altitude areas (Schwikowski et al. 2004).

Figure 6.6 shows long-term changes in the concentration of Cu and Zn from the 1650s onward. To isolate the long-term time trends, we have averaged individual data points over periods of several years to compensate for the pronounced short-term variations discussed in the previous section. Five year averages were used for the period 1900–1995; averaging times of 10 years were applied for the pre-1990 period, because less data were available for that period.

Although the profiles show elevated concentrations for both metals during the twentieth century, they differ markedly for several time periods. For instance the Cu profile shows elevated concentrations around 1800, which are not seen in the Zn profile. Conversely, the Zn profile shows elevated concentrations around 1870, which are not observed for Cu.

The only other ice/snow time series to which the Colle Gnifetti data can be compared are those obtained at Dome du Goûter (van de Velde et al. 1999, 2000; Barbante et al. 2001). It should however be remembered that the Dome du Goûter

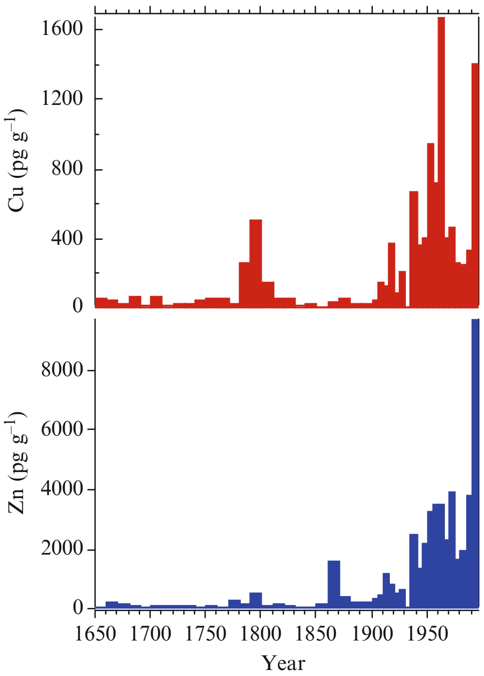


Fig. 6.6 Changes in copper and zinc concentrations in dated snow/ice from Colle Gnifetti, Monte Rosa massif. The individual data have been averaged over periods of 5–10 years, thereby compensating for short-term variations

core was dated with good precision only for the post-1940s period, although the ice at the bottom was at least 200 years old. There are many common features between the Colle Gnifetti and Dome du Goûter concentration profiles. Notably, both data sets show enhanced concentrations for many metals during the second half of the twentieth century.

Table 6.4 gives the mean factors of increase of concentrations for the various metals from the pre-1700 period to the post-1970. The post-1970 period was chosen because it corresponds to the period with the highest concentrations for many metals; conversely, the pre-1700 period was selected because it corresponds to low anthropogenic inputs, before the Industrial Revolution. The highest factor of increase is observed for Cd (~36), followed by metals such as Zn (~19), Bi (~16), and Cu and Ni (~10). This is not observed for Au, with a factor that is close to one. These pronounced increases of concentration for most metals reflect the increasing pollution of the atmosphere by emissions of heavy metals in Europe.

The trace element concentrations found in Colle Gnifetti have also been used to reconstruct emissions into the atmosphere in the past, when direct data or atmospheric inventories were not available (Barbante et al. 2004). Inventories of metal emissions from anthropogenic sources in Europe during recent decades have been published by several authors, especially Pacyna and co-workers (see e.g., Pacyna and Pacyna 2001; Pacyna et al. 1984; Pacyna 1984, 1996; Olendrzynski et al. 1996). They give estimates of total European emissions and in some cases also of emissions for individual countries and/or different source categories for various metals considered in this field (especially Cr, Cu, Zn, Co, Mo, Cd and Sb).

Table 6.4 Colle Gnifetti: average concentrations (in pg g^{-1}) in ice dated from before 1700 and snow dated from after 1970; increase factors between these two periods are also reported

	Average concentrations		Increase factor
	Before 1700	After 1970	
Cd	1.6	58	36.3
Zn	171	3,176	18.6
Bi	0.25	3.9	15.6
Cu	39	412	10.6
Ni	24	218	9.1
Mo	3.4	18.0	5.4
Pd	0.86	3.7	4.2
Cr	144	350	2.4
Co	70	144	2.1
Rh	0.030	0.10	3.3
Ag	0.34	1.16	3.4
Sb	21	53	2.5
Pt	0.15	0.40	2.7
Au	0.16	0.13	0.8
U	2.9	4.7	1.6

To determine if changes observed in the Colle Gnifetti snow/ice atmospheric archives do faithfully reflect changes in emissions from the nearby European countries, snow/ice data from Colle Gnifetti were compared to the emission data from the literature, by using a normalization approach described in detail in (Barbante et al. 2004). For emissions, data from Italy, Switzerland, Germany, France, Belgium and Austria were selected. These countries are likely to be important contributors for heavy metal inputs to Colle Gnifetti (Schwikowski et al. 2004).

Considering this approach, the changes in concentrations in Colle Gnifetti snow and ice since 1650 (Fig. 6.6) have been considered as good proxies of past changes in the emissions of metals to the atmosphere in a large portion of Western Europe. This opens the way to a quantitative reconstruction of past changes in emissions during periods before emission inventories became available. Using this approach, we have estimated a mean yearly Cu emission for the area of Western Europe noted above, for the period between 1650 and 1750, of ~340 t/year (Barbante et al. 2004).

To test this hypothesis, Cu production in Europe in 1750 was estimated at ~3,000 t/year by Hong et al. (Hong et al. 1996). Cu emission factors for mining and smelting activities at that time were estimated at ~15% (Hong et al. 1996; Tylecote 1992). When combining these figures, it comes to an emission of Cu in Europe of ~450 t/year in 1750. This value is in remarkable agreement with the value of ~340 t/year obtained from Colle Gnifetti data, which validates the approach of using the Alpine time series to reconstruct past changes in emissions.

6.4.3 Lead Isotopic Compositions in Alpine Snow and Ice

Lead is a ubiquitous pollutant – like zinc and copper, it has been mined and used since the beginning of civilization and is still commonly found in many industrial products and processes (Nriagu 1996). For example, the ancient Greek and Roman empires used lead extensively for coinage and plumbing, while more recently lead has been used for printers' type, batteries and as a paint additive, among many other applications. During the twentieth century, widespread lead pollution resulted from the use of tetraethyl lead additives in gasoline. It is only in the last few decades that global Pb concentrations have begun to decrease.

Lead isotopes can be used to study natural and anthropogenic processes on Earth because its isotopic composition varies by up to 30%. Three lead isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb) are being constantly produced by the radioactive decay of Uranium and Thorium which have half-lives on the order of 10^9 and 10^{10} years respectively. As a result, old Pb ore bodies have different isotopic compositions to more recently formed ones. This isotopic information has been used to study the lead deposited in Alpine snow and ice to better understand the origins of environmental contamination (Rosman and Walton 2001).

The first study of Pb isotopic compositions in Alpine snow and ice was a 200 year record from Mont Blanc. Rosman et al. (Rosman et al. 2000) evaluated the sources of Pb pollution in Europe, with emphasis on the period 1911–1991. The samples were prepared using the chiseling decontamination technique described above, with Pb isotopes measured by Thermal Ionization Mass Spectrometry (TIMS). Figure 6.7 shows the isotopic composition of Pb in Mont Blanc snow and ice since 1750. In the figure, it can be seen that the ratio of two lead isotopes, ^{206}Pb/^{207}Pb, is steady at a value of approximately 1.175 until the early twentieth century, representing the isotopic signature of early industrial emissions principally from coal burning as well as mining and smelting of European lead ores. The Pb isotopic ratio drops below 1.17 after 1900, then below 1.16 in the 1960s, to a minimum of 1.13 in the late 1970s.

Decreasing Pb isotope ratios in the twentieth century reflect imports of older, isotopically distinct Pb sourced principally from the Broken Hill ore mine in Australia. In the first half of the twentieth century this lead was used in industrial processes, whereas the rapid decrease in ^{206}Pb/^{207}Pb during the 1960s and 1970s is

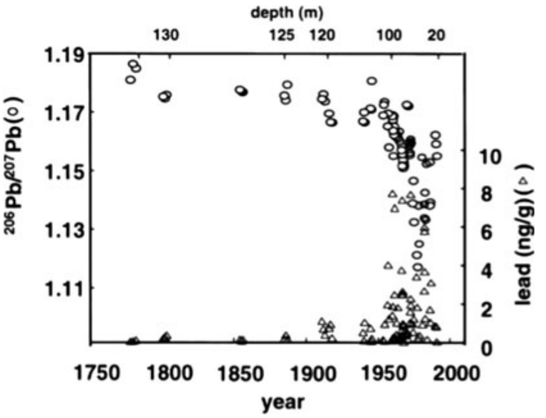


Fig. 6.7 The ^{206}Pb/^{207}Pb isotopic ratio and lead concentration in the 140 m Mont Blanc snow/ice core (From Rosman et al. 2000)

a result of emissions of gasoline lead additives. An interesting feature of the record results from the Italian Isotopic Lead Experiment (IILE) conducted in Turin from 1975 to 1981. For 6 years the city of Turin exclusively used lead with an isotopically distinctive ratio of 1.04, much less than the European mean of about 1.14. The effect of the Turin experiment is clearly visible in the Mont Blanc snow (the city is about 110 km from Mont Blanc) with ^{206}Pb/^{207}Pb ratios sharply dropping to 1.12–1.13 in the late 1970s.

More recently, Schwikowski et al. (2004) reported Pb isotopes in a 300-year snow/ice record from Colle Gnifetti, allowing the sources of European Pb pollution to be investigated in greater detail. Samples were prepared using Continuous Flow Analysis (CFA): a technique in which the ice core sections are placed on a heated plate and sequentially melted, with the meltwater then introduced directly into the analytical instrument – in this case an Inductively-Coupled Plasma Mass Spectrometer (ICP-MS). The combination of CFA with ICP-MS resulted in a far greater sampling resolution than that reported by (Rosman et al. 2000), offering far greater detail in the temporal variations of Pb isotopes and allowing a statistically valid apportionment of Pb pollution sources with time.

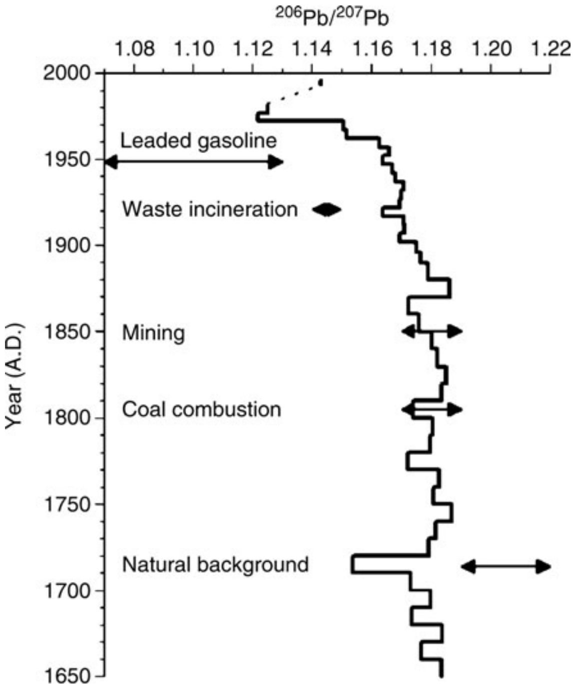
Schwikowski et al. (2004) found similar Pb isotopic compositions to those reported in (Rosman et al. 2000), with ^{206}Pb/^{207}Pb ratios about 1.18 prior to the twentieth century, lower values of 1.16–1.17 from 1870 to about 1960 and the lowest values 1.10–1.12 in the 1970s (Fig. 6.8). Recent snow deposited in the 1990s featured a much lower Pb concentration (about 1 ng/g) than the 1970s peak of about 3 ng/g, but still contained about 80% anthropogenic Pb.

Lead isotopic systematics can be used to apportion Pb inputs from various sources, and thereby reconstruct the historical emissions budgets for various industrial activities. Schwikowski et al. (2004) employed representative ^{206}Pb/^{207}Pb ratios of various types of anthropogenic Pb sources, including coal combustion (1.17–1.19), Pb mining (1.17–1.19), waste incineration (1.14–1.15) and leaded gasoline (1.07–1.13), to compare to a natural ^{206}Pb/^{207}Pb ratio of 1.19–1.22. Considering the ^{206}Pb/^{207}Pb ratios observed from 1650 to 1938 to consist of a mixture of natural Pb and anthropogenic Pb from mining and coal combustion, they showed that as early as 1650, anthropogenic activities accounted for 50–60% of Pb deposited, and since 1900, anthropogenic Pb sources consistently account for over 95% of total Pb. Of the anthropogenic Pb sources, leaded gasoline emissions were less than 40% of total anthropogenic Pb emissions in 1940, but rapidly increased in the 1960s to about 80% of total anthropogenic Pb emissions in the 1970s and early 1980s.

6.5 Conclusions

Snow and ice records from the Alps have allowed the reconstruction of the history of European atmospheric pollution from trace elements. One important prerequisite in these kinds of studies is that of having a suitable site to investigate, where

Fig. 6.8 Paleo record of ^{206}Pb/^{207}Pb, given as 5-year (period 1892–1982) and 10-year averages (period 1760–1890). Typical ranges of ^{206}Pb/^{207}Pb ratios of different atmospheric lead sources are indicated (From Schwikowski et al. 2004)



atmospheric deposition is faithfully registered year by year. Unfortunately only a few high altitude sites are suitable to these purposes and sometimes some of the annual layers deposited are blown away by the strong high altitude winds. Paleo-records obtained from Alpine snow and ice cores by chemical analysis of aerosol related ionic and carbonaceous species, reveal a pronounced concentration increase from pre-industrial to modern times, thus reflecting emissions by human activities. This also applies to a number of trace elements, such as Zn, Cd, Cu, Pb and platinum group elements, testifying a marked alteration of atmospheric composition due to anthropogenic activities that followed from the onset of the industrial revolution at the end of the eighteenth century. Since the mid 1970s, concentrations of most of the trace elements in the Alpine cores have started to decrease, as a consequence of the stringent emission regulations put in place by the European Union. This trend has been also confirmed by studies of lead isotopes which allow accurate apportionment of pollution sources.

New studies are underway, aiming for a better understanding of biogeochemical cycles of trace elements in the Alpine environment (Gabrieli 2008). These advancements are principally oriented to the application of high resolution analysis of ice cores through the use of novel decontamination techniques directly coupled to instrumental devices. These will allow the detection of trace elements at high resolution, looking in detail at seasonal and sub-seasonal changes. Such technology also enables discontinuous sampling for the determination of persistent organic pollutants which are an important new threat to human health as well as alpine ecosystems.

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Chapter 7
METAALCIUS: A Whole Ecosystem Experiment to Study the Environmental Fate of Mercury

Holger Hintelmann

7.1 Introduction

Atmospheric mercury depositions have increased approximately by a factor of three since industrialization, which also led to increase of methylmercury (MeHg) levels in fish, spawning a large number of health advisories. Mercury is now the most common contaminant responsible for fish consumption advisories in the United States and Canada. Almost all US states have regulations against fish consumption due to high mercury levels. Unacceptable fish mercury concentrations exist in all Canadian provinces, including remote "pristine" lakes. Because of the many human and environmental health risks associated with mercury exposure via fish consumption, implementation of effective Hg emission control regulations is discussed in many nations. However, such measures are expected to be very costly and at the same time, safe emission levels are difficult to establish because the available science is still not able to answer if and to which degree reductions in atmospheric mercury deposition translate into changes in fish mercury concentrations. This relationship cannot be understood by examining historical or regional data, mainly because of confounding effects of other environmental factors. Laboratory experiments provide good control over test conditions, but fail to simulate the complex links in the real world that connect atmospheric mercury deposition and fish mercury. To overcome this conundrum two unique experimental approaches were combined in the Mercury Experiment To Assess Atmospheric Loading In Canada and the United Sates (METAALICUS). This experiment is carried out at he whole ecosystem scale by loading an entire lake and its watershed with isotopically labeled mercury providing full-scale realism plus the control necessary to examine the effects of one critical factor: mercury loading. The overriding question METAALICUS set out to answer is: *What happens to fish mercury concentrations when there is a change in atmospheric mercury deposition?*

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7.2 METAALICUS

METAALICUS is a whole-ecosystem experiment. It is critical to emphasize that the experiment is not designed as a tracer experiment to study the fate of Hg, but as a mercury loading study. Key is an at least experimental doubling of the Hg load to the lake to simulate initially an increased Hg deposition and later an Hg emission reduction during the ensuing recovery phase, when Hg additions cease. METAALICUS represents *the first whole-ecosystem addition of isotope enriched Hg anywhere*. Mercury was added in the form of stable, non-radioactive isotopes of inorganic mercury, Hg(II). The power of using isotope enriched rather than natural Hg lies in the ability to follow the newly deposited mercury separately from "old" background mercury. To further increase the predicting ability, the watershed is not only dosed with one, but three different isotope enriched materials: ^{200}Hg is added to the upland, ^{198}Hg to the wetland and ^{202}Hg directly to the lake surface to determine the relative contributions of these sources to fish mercury levels (Fig. 7.1).

Prior to the whole ecosystem addition of Hg, which started in 2001, 2 years of pilot and baseline studies were conducted. Considering the considerable costs of the investigation, it was crucial to establish the feasibility of the experimental design prior to adding Hg to the entire ecosystem. Three pilot studies were carried out: small scale additions of isotope enriched Hg to well characterized forested upland and wetland plots, and a mesocosm study using four large limnocorals. These experiments were invaluable for range finding purposes and testing of analytical protocols. As well, 1 year of baseline studies in the experimental lake was crucial to document the status quo prior to adding any Hg. The full-scale experiment eventually started in 2001 and has been running for 7 years. Hg loading stopped in 2008, which is the first year of lake recovery, simulating an at least twofold reduction in Hg deposition to the watershed.

In METAALICUS, mercury concentrations are being tracked in all major compartments including lake, watershed, and atmosphere. In addition, mechanistic

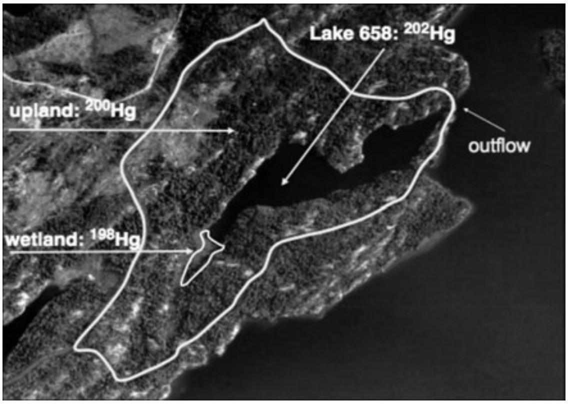

Fig. 7.1 Aerial view of Lake 658 at the Experimental Lakes Area showing compartments receiving different isotopes of mercury

process studies on mercury transport, reaction and bioavailability are also being conducted to corroborate the whole field data. The inclusion of process studies is essential to develop an understanding of the general factors governing the accumulation of mercury in fish. In this way, the results of the study will be useful for interpretation beyond the conditions at the study site. The effects of mercury loads, geochemical factors and the role of the food web will all be examined closely during the study. One general limitation of whole ecosystem loading studies is that often only one dose level is economically feasible, which makes the investigation of dose-response relationships difficult. To overcome this challenge, separate Mesocosm Simulations of Atmospheric Deposition to Aquatic Ecosystems (MESOSIM) were initiated in nearby Lake 240, in which 11 large limnocorals were loaded with 10 different Hg levels (Orihel et al. 2007; Orihel et al. 2006).

Modeling is also an important part of the study. Existing mass balance models for mercury cycling and bioaccumulation in lakes are employed (Harris and Bodaly 1998; Hudson et al. 1995) to help identify information gaps, synthesize the multidisciplinary field study into a single framework, test different mercury loading scenarios and eventually condense all data into a predictive model to extrapolate METAALICUS results to other ecosystems.

7.3 METAALICUS Research Team

The project team includes more than 50 scientists, including leading mercury researchers from the United States and Canada (Table 7.1). The group has extensive experience with whole ecosystem mercury experiments and a history of successful collaboration.

7.4 Study Areas and Sites

The Study is conducted at the Experimental Lakes Area (ELA), situated in a remote corner of northwestern Ontario, Canada, approximately 300 km east of Winnipeg, Manitoba (Fig. 7.2). The ELA was established in the late 1960s and consists of more than 200 lakes, of which 46 are set aside for large-scale ecosystem manipulation (Fig. 7.3). ELA lakes have been used over the past 30 years to provide world-class limnological studies in freshwater lakes, including whole-lake additions of contaminants in controlled long-term experiments to investigate their impact on the environment. Famous key studies on eutrophication (Schindler 1974), and acid rain (Kerr 1998) led directly to new policies. Others included the addition of Cadmium to simulate the effect of emissions from metal smelters, wetland and boreal forest floodings to study the increase of mercury in fish after reservoir generation (St Louis et al. 2004) and greenhouse gas emissions (St Louis et al. 2000).

With respect to mercury, the ELA is a site of low deposition of mercury (approximately 3 μg/m^2/year wet deposition) (St Louis et al. 1995). Dry deposition

Table 7.1 METAALICUS principal investigators

Principal investigator	Organization
Marc Amyot	Université du Montréal
Chris Babiarz	University of Wisconsin
R.A. (Drew) Bodaly	Fisheries and Oceans Canada (DFO)
Ken Beaty	Fisheries and Oceans Canada (DFO)
Paul Blanchfield	Fisheries and Oceans Canada (DFO)
Brian Branfireun	University of Toronto
Robert Flett	Flett Research Ltd.
Cynthia Gilmour	Smithsonian Institute
Reed Harris	Tetra Tech Inc.
Andrew Heyes	Chesapeake Biological Laboratory
Holger Hintelmann	Trent University
James Hurley	University of Wisconsin
Carol Kelly	R&K Research
David Krabbenhoft	US Geological Survey
Steven Lindberg	US Department of Energy
Robert Mason	Chesapeake Biological Laboratory
Michael Paterson	Fisheries and Oceans Canada (DFO)
Cheryl Podemski	Fisheries and Oceans Canada (DFO)
John Rudd	R&K Research
George Southworth	US Department of Energy
Vince St. Louis	University of Alberta

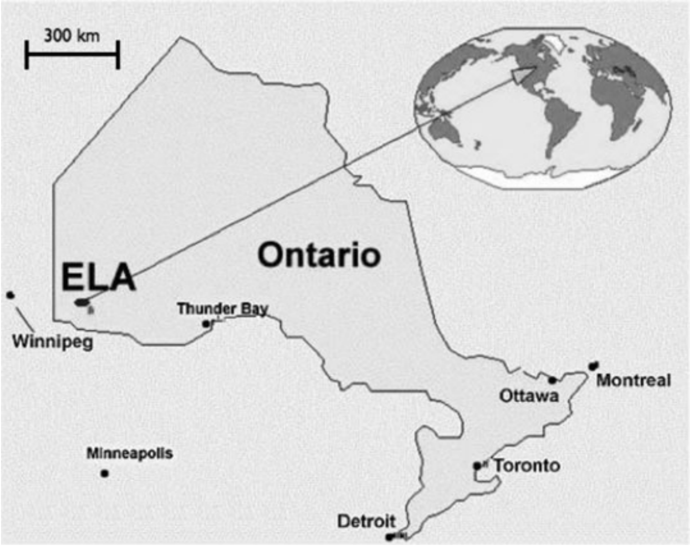

Fig. 7.2 Location of Canada's Experimental Lakes Area

rates are not well known at the ELA but are likely comparable to or less than those measured in northern Wisconsin, where rates on the order of 3–4 μg/m^2/year have been reported (Watras et al. 1995). The low mercury deposition rate at the ELA is therefore ideal for the METAALICUS study because only small amounts of Hg additions are required to achieve an increase in loadings. Approximately 12 g of

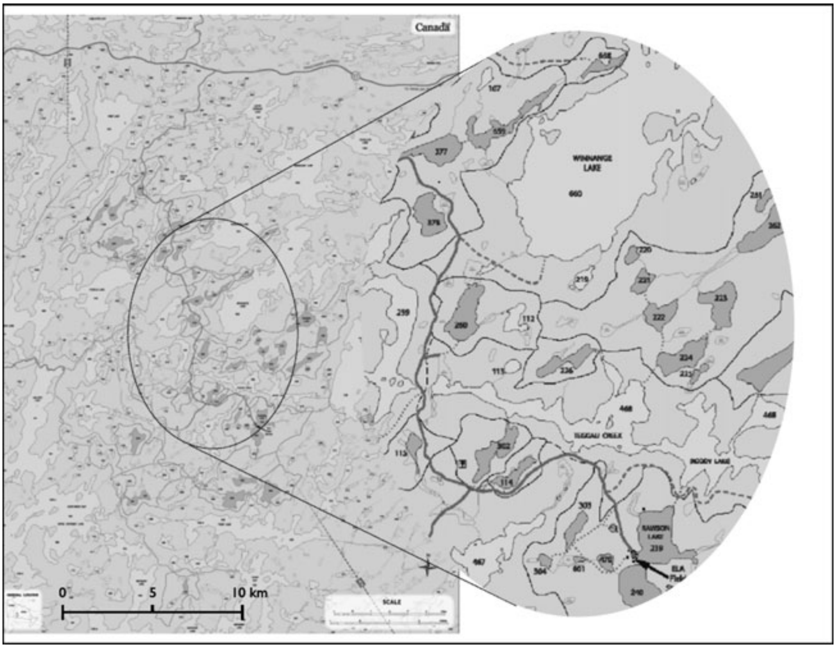

Fig. 7.3 Map of Experimental Lakes Area showing lakes, which are available or have been used in the past for ecosystem-scale experiments are shaded in *dark gray*. *Insert* identifies METAALICUS study sites within the ELA

mercury are added per year to increase Hg deposition to the 52 ha Lake 658 watershed by a factor of 4–5. The result is a mercury deposition rate to the experimental system that is comparable to rates currently observed in some parts of the northeastern US, Florida and southern Sweden. The upland, wetland and lake are receiving Hg isotopes at a rate of approximately 22 $\mu g/m^2/year^1$.

7.4.1 Upland Plot

The inorganic mercury loading was experimentally increased to a 680 m^2 forested micro-catchment, "U1f" (Figs. 7.3 and 7.4; Allan et al. 1993). A total of 8.4 mg of Hg as $Hg(NO_3)_2$ (99.2% ^{202}Hg) was first equilibrated in natural throughfall, adjusted to pH ~ 5 and manually sprayed onto ground vegetation using acid-cleaned pressurized hand-sprayers. The single application elevated the natural load by 12.5 $\mu g/m^2$. This application technique simulated a small rain event or dry deposition, since the spraying itself did not create runoff from the catchment. Concentrations of the applied isotope enriched Hg were monitored for the remainder of the year in the atmosphere above the plot, in vegetation, soil and surface runoff. Evasion and fluxes of Hg(0) to the atmosphere were measured with dynamic flux chambers by collecting volatilized Hg(0) on gold-traps. Soil profiles were sampled manually using an acrylic plastic corer (4 cm i.d.), frozen and extruded

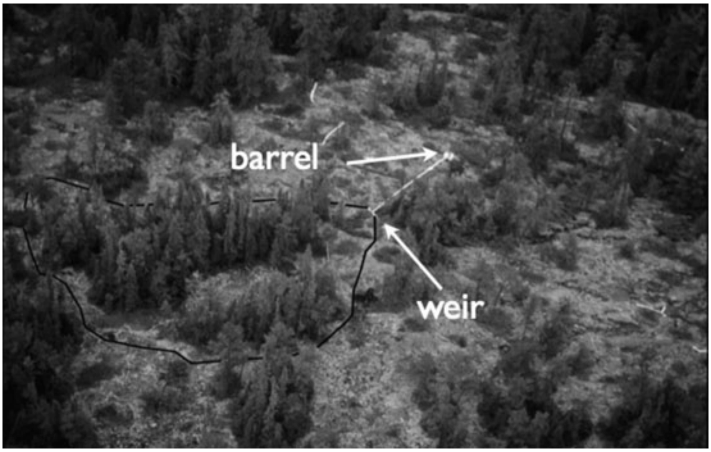

Fig. 7.4 Aerial shot of the U1F site of terrestrial pilot trial

in 3 cm sections for further analysis. Above-ground vegetation was removed before soil sampling and analyzed separately. Runoff from the sub-catchment was funneled first to a downstream weir and then directed to two large 500 L polyethylene barrels to estimate the total seasonal runoff volume.

7.4.2 Wetland Plot

The wetland pilot study was conducted in a small, 12 by 8 m rectangular peat area of a wetland connected to Lake 115 (Fig. 7.3). It was composed of low-lying vegetation, dominated by sphagnum mosses with scattered larger plants, sedges and grasses. Floating sphagnum mosses floated on top of up to 1.5 m decomposed vegetation material a the lake edge. A total of 43.2 μg of ^{202}Hg enriched (99.2%) Hg was dissolved to a final concentration of 75 μg/L and applied to the wetland surface by using hand sprayers to simulate Hg deposition. On regular intervals, porewater samples were taken from 5 to 15 cm depths 1, 2, 8, 30 and 90 days after application. Peat cores were collected 1, 2 and 90 days post application.

7.4.3 Limnocorals

Four large decagonal enclosures of 10 m diameter and approximately 1.5 m depth, open to the lake sediments, were installed in Lake 239 (Figs. 7.3 and 7.5). ^{200}Hg enriched (96.4%) mercury solutions were added to each enclosure in two distinct fashions to determine the best dosing method for the whole scale lake addition. Two enclosures received an initial single dose of 30 μg/m^2 and two enclosures were spiked five times biweekly with 6 μg/L, so that the accumulative doses over the entire season were identical. Water was sampled from a raft in the center of each enclosure.

Fig. 7.5 One of the large enclosures used for the limnocorral pilot experiments

Table 7.2 Characteristics of Lake 658

Lake area	8.3 ha
Wetland area	1.9 ha
Upland area	42 ha
Drainage pattern	Surface flow headwater lake
Maximum depth	13 m
Hydraulic retention time	5 years
pH	6.5
DOC	9 mg/L
Predatory fish	Northern pike

7.4.4 Lake 658

Lake 658 was selected for METAALICUS (Fig. 7.1). It is a small, oligotrophic, headwater lake on the Canadian Shield and one of the reserved lakes for research at ELA. Main characteristics are shown in Table 7.2. It typically stratifies during the summer at a depth of 4–5 m and the bottom 2 m of the hypolimnion become anoxic during the summer. The oxygen depletion can even extend to the bottom 6 m in some years. The lake is surrounded by typical boreal forest with mainly jack pine, balsam fir, red maple, poplar and paper birch. The adjacent wetland of sphagnum moss is dominated with black spruce. Adding Hg isotopes to the watershed of Lake 658 proved to be a logistically very challenging. Owing to the large upland, which consisted in mainly of dense brush, most of the area was inaccessible by foot. Likewise, the wetland vegetation was rather fragile and easily damaged by simply walking over it. Hence, it was decided to apply the Hg load by fixed wing aircraft once each year for 6 years (2001–2006). To prevent overdrift of sprayed Hg to the lake itself, a buffer zone of approximately 30 m around the shoreline was avoided by the plane and sprayed later manually with gas-powered water pumps and fire hoses. Lake spike was added every 2 weeks at dusk during the ice-free season from an electrically powered boat.

7.5 Hg Determinations

Since natural mercury consists of seven stable isotopes, multi-labeling experiments are possible and exploited in METAALICUS. Stable isotopes are non-radioactive and do not decay. Once added, they remain in the system and will be detectable forever, making long-term studies possible, which is particularly critical during the recovery phase of METAALICUS. To follow the movement of the applied isotope enriched mercury through the ecosystem the study relies on isotope ratio measurements using ICP-MS instrumentation. Most procedures used methods, which are already well developed and established for conventional mercury species analysis. Total Hg (HgT; all species of Hg combined) is measured using cold vapor techniques followed by gold amalgamation ICP-MS. Detection limits are as low as 0.1 ng/L for water samples 10 ng/g for sediments. MeHg determinations are carried out after distillation and aqueous phase ethylation, followed by gas chromatography ICP-MS. Hg(0) is measured after amalgamation on gold trap. Details of these techniques can be found elsewhere (e.g., Hintelmann 2003; Hintelmann and Ogrinc 2003). To correct for variations in analytical recoveries (especially those associated with MeHg determinations), a third isotope of Hg, typically in form of $CH_3{}^{201}HgCl$ or $^{201}HgCl_2$, is added at the time of sample processing. The use of this "internal standard" significantly improves the accuracy and precision of the measurements.

In contrast to conventional studies, the limit for detecting the added mercury isotopes does not depend on the absolute sensitivity of the ICP-MS detector, but rather on the ability to measure changes in isotope ratios. Hence, the overall detection is limited by the precision of the mercury isotope ratio measurement, which can be determined with very high precision using modern ICP-MS instruments, making these experiments extremely powerful. Overall mercury concentrations (ambient background and spike) have to increase by only 0.5% to detect and quantify the added mercury isotope; i.e., a fish having 100 ng/g methylmercury needs to accumulate only 0.5 ng of methylmercury originating from the added mercury isotope (Hintelmann and Evans 1997; Hintelmann et al. 1995).

7.6 Results

7.6.1 Upland Response

Newly deposited mercury was initially reactive and mobile through runoff, volatilization and methylation pathways (Hintelmann et al. 2002). Soon after spike addition, a heavy rainstorm caused substantial runoff with relatively high spike

Hg levels of up to 1.6 ng/L, which comprised >10% of the overall Hg in runoff (spike + ambient Hg). However, the spike mobility exponentially decreased with time, presumably owing to a rapid equilibration with the large ambient pool of mercury. By the end of the season, less than 1% of the applied spike appeared in runoff. Fluxes of mercury to the atmosphere were also highest immediately after application of the Hg load and reached values of up to 7 ng/m^2/h, but decreased already 30 min post-spike by ~50% and were near the limit of detection at the end of the season (<0.2 ng/m^3/h). In total, only 8% of the added ^{202}Hg volatilized to the atmosphere. In soils, the added mercury was initially (first 48 h) only detectable in the surface layer. Concentrations varied greatly and were on average 4.68 ± 3.39 ng/g (dw). Levels decreased by the end of the season to 0.69 ± 0.10 ng/g, but were now also detectable in deeper soil layers. However, levels of added Hg were close to the detection limit, which made it difficult to accurately quantify the amount that migrated into the soil. Clearly, the huge pool of stored ambient Hg overwhelmed the relatively small load of the isotope enriched application. As a result, it was decided to use at least twice the amount applied at U1F for the whole scale addition experiment to increase the chances of following the spike, even after it mixes uniformly with the stored ambient Hg.

The mass balance for the whole season is shown in Fig. 7.6. The total export of spike Hg (~0.03 mg) represented only 0.3% of that applied. A small but significant amount of Hg volatilized form the test plot (8% of applied Hg). The majority of the spike was still tightly associated with vegetation and to a lesser extent with the underlying soils 4 months post addition. The reminder of the applied isotope rapidly equilibrated with the comparatively large pool of ambient mercury previously stored in soil and vegetation of the catchment, and was indistinguishable from it in reactivity and mobility. This suggests that terrestrial runoff will respond very slowly to changes in Hg deposition that are received through small rain events or dry deposition producing no or very little runoff.

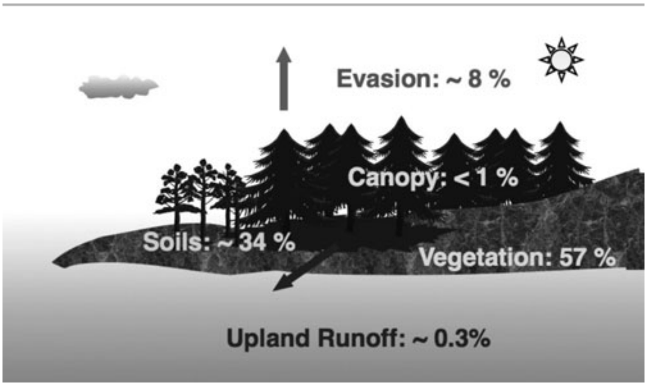

Fig. 7.6 Diagram of estimated mass fluxes for spike Hg during the first season of the U1F pilot experiment

7.6.2 Wetland Response

The added ^{202}Hg spike was detected in both solid peat and pore water, again confirming the feasibility of the experimental design for the whole ecosystem study (Branfireun et al. 2005). Immediately after spiking, ^{202}Hg was detected in pore water up to 10 cm deep, suggesting rapid migration into the wetland peat. ^{202}HgT surface concentrations decreased from approx. 1.8 ng/L 1 day after spiking to as low as 0.03 ng/L 90 days post addition. At the same time, 0.06 ng/L of spike Hg appeared outside the applied area. ^{202}HgT was also readily detected in the solid phase within the experimental plot. However, as can be seen from Fig. 7.7, spike mercury is distributed somewhat unevenly, e.g., 1 day after application, no spike was found at location #2. Nevertheless, initial concentrations in vegetation of up to 8.4 ng/g (dw) had evenly distributed throughout the top 13 cm peat core, showing an average concentration of 1.0 ng/g (dw) by the end of the summer.

Although ^{202}Hg was added in form of inorganic Hg only, also ^{202}Hg enriched methylmercury was evident in the wetland. Since in-situ methylation is the only mechanism by which excess Me^{202}Hg could be generated, this observation is clear evidence for the methylation potential of wetlands. Almost 4 pg/L Me^{202}Hg was detected 5 cm below the surface in pore water the day following the application. At the end of the summer, approx. 20 pg/L of isotope enriched MeHg was found throughout and even beyond the experimental plot. Similarly, Me^{202}Hg partitioned from the porewater into solid phases and was found not only throughout the peat core down to 13 cm depth, but also in above ground vegetation.

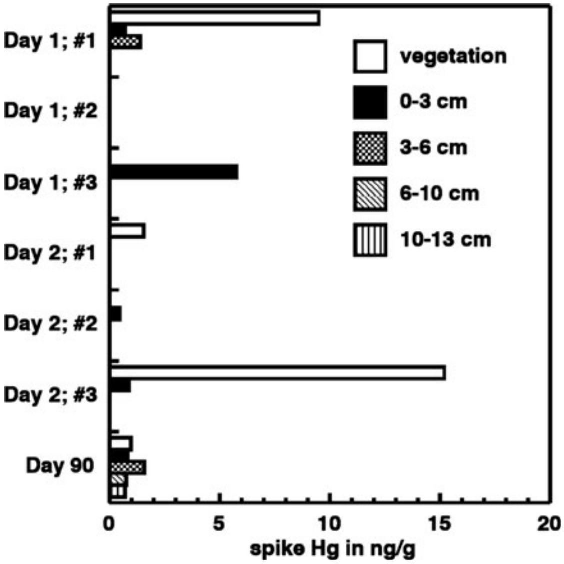

Fig. 7.7 Concentrations of spike Hg in peat cores at the Lake 115 wetland test plot

These observations demonstrated that an addition of highly enriched Hg is detectable against a large pool of ambient Hg in wetland environments. The selected spike dose of 25 μg/m^2 appears to be sufficiently high to observe the spike in aqueous and solid phases. Specifically, this pilot experiment showed the relatively high mobility of Hg in wetland environments. Added Hg spike migrated more than 10 cm into the peat within a 90 day period. As well, a small fraction of the added spike moved outside the spiked area, consistent with the main direction of the hydrological gradient in the test plot.

7.6.3 Limnocoral Response

Single Hg additions increased the initial HgT concentration in enclosures #1 and #2 to values of up to 18 ng/L, and then rapidly decreased to approximately 1.2 ng/L 3 months after adding the spike (Fig. 7.8). In enclosures receiving multiple additions, the spike increased by approximately 3–4 ng/L immediately after each addition, followed by decrease over the next 2 weeks. This created a sawtooth type pattern over the 10 week period of spike additions. These two enclosures maintained on average more consistent Hg levels during the season and final concentrations decreased only to approximately 2.6 ng/L, which is about twice as high as the final spike concentration achieved in enclosures #1 and #2. The majority of Hg added was lost by evasion to the atmosphere (Amyot et al. 2004), an average of 83 ± 3% volatilized regardless of the spike addition regime.

The inorganic Hg spike was converted to MeHg within 1 month and started to be detectable in water, zooplankton, invertebrates and fish. Although MeHg in the water column was often below the limit of detection (0.020 ng/L), sufficient MeHg was produced to accumulate to easily measurable levels in zooplankton (up to

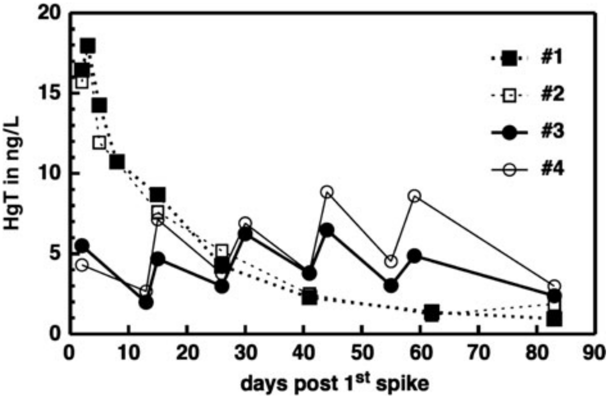

Fig. 7.8 Evolution of spike HgT added to four large enclosures. Enclosures #1 and #2 received a single dose of 30 μg/m^2 and enclosures #3 and #4 5 biweekly additions of 6 μg/m^2 each

12 ng/g dw) and fish (fine-scale dace, 6 ng/g dw) (Paterson et al. 2006). While the two spike protocols did not produce statistically different Hg concentrations at the end of the season, the rate at which Hg was accumulated differed. In enclosures receiving multiple spikes, Hg in fish increased linearly, while a single addition caused an initial sharp rise in fish MeHg, after which Hg levels remained steady. This is likely explained by a spike of initial MeHg in the single dose enclosures, which is quickly accumulated by fish at the start of the season and remained stored later on. In contrast, the multiple additions allowed continuous MeHg production over the entire season and therefore a continuous accumulation of MeHg. While the end result was the same, the multiple Hg addition approach seems to be a better simulation of natural conditions and was therefore later chosen for the whole-scale experiment.

7.6.4 Lake 658 Response

The whole ecosystem addition of isotopically labeled mercury allowed to distinguish between mercury already present in the ecosystem and newly introduced Hg. Total mercury concentrations clearly increased following spikes to the lake surface, and declined between spikes, similar to the response seen in the limnocorals receiving the biweekly additions. Figure 7.9 shows levels of HgT in the epilimnion (top 4 m of the water column) over the first 3 years. Overall, the lake spike always increases towards the end of the spiking season and declined under ice cover in the winter. It is interesting to note that initial HgT concentrations after ice-out are very similar in year 2 and 3, suggesting that spike Hg does not accumulate in the water column from year to year. A major loss pathway was the reduction and evasion of

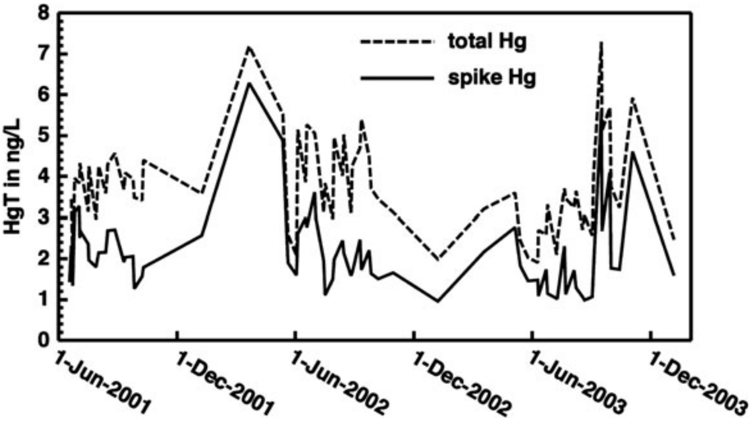

Fig. 7.9 Concentrations of spike HgT and total HgT (i.e., sum of spike and ambient Hg) in the epilimnion of Lake 658 during the first 3 years of the METAALICUS experiment

Hg(0) from the water (Poulain et al. 2004; Southworth et al. 2007), which might account for up to 30% of the added Hg being lost to the atmosphere. The conversion to inorganic spike to methylmercury began quickly, appearing in the water column within 14 days, and in sediments and young fish at low levels in the first season. During the second season, the isotope enriched Hg applied to the lake surface was clearly observable in all biota and unlike levels in water, continued to increase in following years.

The isotopically labeled terrestrial Hg spikes were detected in the areas, where they had been applied to the wetland and the upland (Harris et al. 2007). Concentrations of the upland spike in runoff to Lake 658 were initially very low with only 0.1% of the applied ^{200}Hg being exported to the lake. This proportion increased in year 2 and 3 to 0.3% and 0.6%, respectively. However, the loads of upland spike to the lake are insignificant compared to the ambient or lake spike Hg. Most of the upland spike remained bound to soils and vegetation and most of the exported Hg was pre-existing and presumably older, ambient Hg.

The initial data clearly show an annual accumulative increase of Hg in biota due to an increased load of Hg to the lake. After 3 years of Hg additions the ecosystem was not yet at a steady state reflecting the new load. These findings are relevant when speculating about the potential effects of controls (reductions) of atmospheric Hg emissions. Although the early results would also be consistent with an expected decrease of Hg in biota after lowering Hg loads, there might be a delay after which the full effect will be experienced. This delay should be short for systems, where the lake receives most of its Hg directly from the atmosphere and might be very long, (maybe centuries) in situations, where watershed inputs dominate the Hg loading. The overall contributions of old vs. new Hg to Hg in runoff, and the overall response time of watersheds to changes in atmospheric Hg deposition, will most likely depend on the balance of wet and dry deposition, as well as the fraction of rain events which are big enough to cause significant immediate runoff of newly deposited mercury.

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Chapter 8
Sources, Transport and Fate of Organic Pollutants in the Oceanic Environment

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8.1 Introductory Remarks

Industrial, agricultural and other anthropogenic activities have lead to the introduction of thousands of pollutants, most of them synthetic organic compounds to the marine environment (Dachs and Méjanelle 2010). A fraction of these organic compounds, called persistent organic pollutants (POPs), are chemicals that have become a major concern because of their toxicity, persistence, bioaccumulation tendency, and susceptibility to undergo long-range atmospheric transport. Traditionally, much attention have been given to a few families of POPs, such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) such as DDT and hexachlorobenzene (HCB) and other byproducts of industrial processes or combustion such as dioxins and furans (PCDD/Fs) and polynuclear aromatic hydrocarbons (PAHs). However, these chemicals are a small fraction of the total known pollutants in the marine environment (Dachs and Méjanelle 2010) and presumably of the total potential pollutants occurring in the environment (Muir and Howard 2006). In any case, these few families of POPs have been detected everywhere on earth in abiotic and biotic matrices (Gioia et al. 2006, 2008a; Gilman et al. 1997; Jaward et al. 2004). Today, compounds with similar or different physical chemical properties (such as the polybrominated diphenyl ethers, PBDE and other fluorinated compounds, PFs) are being manufactured and widely used,

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potentially entering the environment and providing new challenges for the maintenance of its quality. Our current knowledge indicates that the cycling of these chemicals in the environment is highly complex; indeed their local, regional and global cycle is controlled by repeated air-surface exchange and interactions with the carbon cycle, especially the organic and soot carbon fractions. Because, a fraction of these chemicals are hydrophobic, they have the potential to accumulate in all the trophic levels of ecosystems, including those far away from sources. The number of known organic pollutants in marine waters, and other environmental compartments, has increased dramatically during the last decade, in part due to important analytical developments. Nowadays, even though much of our knowledge on organic pollutants is centered on a few chemical families (PCBs, HCHs, DDT, PAHs, etc.), these families should be viewed as markers or "surrogates" of other pollutants in marine waters with similar physical–chemical properties. In addition, other chemicals with different physical–chemical properties (i.e., greater water solubility, low volatility) may reach coastal and open oceans via rivers and undergo different environmental behavior, due to their ionic character. In fact, some of newly emerging compounds have been suggested to behave as passive tracers in waters (Yamashita et al. 2008), a behavior quite different from that shown by legacy POPs such as PCBs or HCHs.

8.2 The Anthropogenic Organic Chemosphere in the Marine Environment

There are large numbers of anthropogenic organic substances in the marine environments at trace levels. Crutzen and Stoermer (2000) has introduced the term "anthropocene" for the recent last two centuries emphasizing the role of humans as a major driving geophysical force of the earth system. Steffen et al. (2007) have explored the evolution of the anthropocene, and have suggested two stages, the first being the industrial era from 1800 to 1945 and the second being the great acceleration from 1945 up to present. The number of synthetic organic substances used by humankind has increased enormously during the second half of the twentieth century, even though some substances such as PCBs, started their production during the 1920s. Obviously, chemical pollution due to hydrocarbons such as PAHs or alkanes must have started to increase during the industrial era, and even before owing to the use of fossil fuels. We can hypothesize that the second stage or great acceleration (from 1945) has represented an explosion in the introduction of chemicals to the environment, resulting in an increasing pressure to ecosystems and humans. Some chemicals, such as PAHs, have been in the environment since the initial stages of humankind due to forest fires and use of wood as an energy source. However, there are thousands of chemicals that have been introduced to the environment for the first time during the last decades and evolution has not have the opportunity to work out the mechanism to deal with them, leading in some cases to adverse effects in ecosystems and humans. The presence of synthetic organic substances in the environment can be viewed as a "new" driver that has appeared in the anthropocene. Its importance may not be linked to the occurrence of a given pollutant, or a small group of them, but by the fact that the total number of pollutants in any coastal ecosystems may be huge. A fraction of these pollutants are persistent, thus they could stay in the marine environment for decades or hundreds of years. As the use of chemicals change due to progress in industrial/agricultural applications and due to new regulatory limitations, then new chemicals are introduced in marine regions. The modification of the composition of the biosphere, in coastal and open ocean ecosystems, can be viewed as another vector of global change, one that is closely interrelated with the other vectors of global change such as social/economic changes, climate change, loss of biodiversity and perturbations in the hydrological cycle.

Since the 1970s, there has been an increasingly wider scientific field dealing with environmental risks associated with the occurrence and fate of POPs. Fifty years after the initial awareness of the potential hazard represented by synthetic chemicals, the study of the sources, transport, fate and impact on ecosystems and humans has became a major scientific field which has matured in many aspects, and has had an important impact on international legislation: for example the United Nations' Stockholm convention on POPs (UNEP 2001), the UNECE protocol (UNECE 1998), and European Union REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) Directive. However, the field is still in its infancy in terms of being able to evaluate the total contamination present in ecosystems (or humans) and the real impact that this contamination, made up by thousands of chemicals, has on individuals and ecosystems.

The chemicals introduced are numerous and come from many different applications ranging from agricultural herbicides, pharmaceuticals, detergents, flame retardants, di-electric fluids, combustion by-products and numerous other applications (Muir and Howard 2006; Schwarzenbach et al. 2003). Table 8.1 presents a list of most non-volatile organic chemicals that have been described in coastal or open ocean waters. Chemicals are classified by families and in many cases one of these families contains tens or hundreds of different compounds (for example PAHs, PCBs, etc.). The list would be larger if pollutants that have been reported in other environmental compartments such as soil, atmosphere or freshwater, had been included (see for example Kasprzyk-Hordern et al. 2008). Table 8.1 does not contain degradation products of known pollutants (Farré et al. 2008) which can be toxic as well and induce adverse effects in organisms. Usually, these degradation products are more polar than parent compounds. A few tens of these chemicals are currently regulated by various international/national laws, but many are not yet regulated. In fact, there are contradictory situations where some chemicals are of illegal use, such as cocaine and other illicit drugs, but their occurrence in continental waters is generalized and not regulated (Postigo et al. 2009).

So far no study has reported all the compounds listed in Table 8.1 in a single environment or a significant fraction of them. This is because of the analytical challenge of analyzing, detecting and characterizing all pollutants. Even for fossil-fuel residues found in the environment, the chemical structure of some fractions

Table 8.1 Non-volatile organic chemicals reported in transitional and coastal waters (Dachs and Méjanelle 2010)

Chemical family	Historical or current use application
Polychlorinated biphenyls (PCBs)	Industrial, various
DDTs (1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane)	Insecticide
Hexachlorbenzene (HCB)	Insecticide
Aldrin	Insecticide
Dieldrin	Insecticide
Endrin	Insecticide
Toxaphene (polychlorinated bornanes)	Insecticide
Chlordane	Insecticide
Heptachlor	Insecticide
Polychorinated dibenzodioxins and furans (PCDD/Fs)	Combustion byproduct
Hexachlorocyclohexanes (HCHs)	Herbicide
Polycyclic aromatic hydrocarbons (PAHs)	Combustion byproduct, fossil fuels
Polybrominated biphenyl ethers (PBDEs)	Flame retardant
Hexabromocyclododecane	Flame retardant
Nnonylphenol polyethoxylates (NPEO)	Surfactant
Nonylphenols (NP)	Degradation product of NPEO
Octylphenols (OP)	Degradation product of NPEO
Bisphenol A	Plasticizer, antioxidant
Phthalates (phtalate esters)	Plasticizer
Alkanes and other hydrocarbons	Fossil fuel, combustion byproduct
Non resolved hydrocarbons (UCM)	Fossil fuel
Chlorinated alkanes	Industrial (lubricants, flame retardants, etc.)
Organotins (Tributiltin, triphenyltin, etc.)	Antifouling agent
Atrazine	Herbicide
Simazyne	Herbicide
Diuron	Herbicide
Hexazinone	Herbicide
Endosulfan	Pesticide (insecticide/acaricide)
Linear alkylbenzene sulphonates (LAS)	Surfactant
Linear alkylbenzenes	Byproduct of LAS
Bis(4-chlorophenyl) sulphone	Plasticizer, byproduct of pesticide synthesis
Glyphosate	Herbicide
Irgarol	Antifouling agent
Methyl tertiary-butyl ether (MTBE)	Gasoline additive
Benzotriazoles	UV stabilizers, pharmaceuticals and others
Trialkylamines (TAM)	Surfactant byproduct
2-ethylhexyl 2,3,4,5-tetrabromobenzoate (TBB)	Flame retardant
Bis-(2-ethylhexyl)-tetrabromophthalate (TBPH)	Flame retardant
Perfluorinated compounds (PFOS, PFOA and others)	Industrial and other
Polychloronaftalenes	Industrial and other
Drugs of abuse (cocaine, etc.)	Illicit drugs
Pharmaceuticals (various)	Pharmaceuticals
Veterinary antibiotics	Antibiotics
Musk fragances	Fragrances, day care products

(*continued*)

Table 8.1 (continued)

Chemical family	Historical or current use application
Sucralose	Sweetener
Estrone	Natural estrogen, pharmaceutical
17β-estradiol	Natural estrogen, pharmaceutical
17α-ethynylestradiol	Pharmaceutical

remains largely uncharacterized (Rowland et al. 2001; Donkin et al. 2003; Melbye et al. 2009). Furthermore, the list of chemicals present in the environment must be several orders of magnitude longer than those ever reported, since tens of thousands of organic chemicals have been used by humankind. Due to the lack of appropriate analytical methods to survey such a large number of compounds at trace levels, an unknown number of chemicals have already being introduced in the environment and have not yet been reported in the literature. A crucial characteristic of the environmental burden in organic pollutants is that their total amount in the environment is unknown. Oceans will often be the ultimate receiving compartment for such substances.

8.3 How Do Organic Pollutants Reach the Ocean? Atmospheric and River Inputs

The oceans cover 70% of the ocean surface and have important reservoirs of organic carbon (preferred sorbing phase for many POPs). Therefore, the oceans play an important role in controlling the environmental transport, fate and sinks of POPs at regional and global scales (Wania and Mackay 1996; Dachs et al. 2002). Although POP concentrations in the open ocean have been shown to be lower than those observed in coastal areas (Iwata et al. 1993; Dachs et al. 1997a), the large oceanic volume implies that they may represent an important inventory of POPs (Jurado et al. 2004). Traditionally, research on oceanic organic pollutants has been centered in hydrophobic, persistent and semivolatile pollutants, indeed POPs. Lately, other families of organic pollutants such as perfluorinated compounds have received an increasing attention (Jahnke et al. 2007). For those chemicals that can undergo atmospheric transport due to their semi-volatility as all legacy POPs, the pathway atmospheric transport – deposition – and incorporation to plankton and transfer through the food web is of key importance for understanding their fate and transport. For other ionic chemicals, or non-ionic but limited volatility, their distribution in the ocean will be dominated by water transport, even though they can also be subject to bioaccumulation processes. The fate and transport of these ionic and/or low volatility chemicals is much less understood than that of legacy POPs, but for these chemicals the atmosphere will play a negligible or small role as a source, and their inputs in the marine environment will be dominated by riverine inputs (Pistochi and Loos 2009). Even for legacy POPs, rivers can be significant sources of POPs to the coastal environment (Gomez-Gutierrez et al. 2006; Zhulidov et al. 2000), even though, it is commonly accepted that atmosphere dominates inputs to the open ocean.

The atmosphere has been regarded as the most important and rapid route of transport for POPs to surface waters. POPs partition between gas and aerosol phases and may then be removed from the atmosphere by four major mechanisms: dry deposition of particle bound pollutants, diffusive gas exchange between the atmosphere and the surface ocean, scavenging by rain (wet deposition) and OH radical degradation. Figure 8.1 is a conceptual diagram of the major processes affecting POPs in the oceanic atmosphere. Many studies have acknowledged the importance of air–water exchange in understanding the environmental fate of POPs at local, regional and global scales (Hornbuckle et al. 1995; Nelson et al. 1998; Totten et al. 2004; Rowe et al. 2007; Gioia et al. 2008a, b; Nizzetto et al. 2008). Gaseous exchange of contaminants between the atmosphere and the ocean is driven by a concentration difference and transport by molecular and turbulent motion. Air–water gas exchange is the most dominant depositional process at the global scale compared to wet and dry deposition (Jurado et al. 2004) for those POPs which atmospheric occurrence is mainly in the gas phase (PCBs, HCHs, lighter PAHs). Conversely, for some PAH and PCDD/F, which due to their planar structure have higher affinity to aerosol soot carbon (Dachs et al. 2000; Lohmann et al. 2007), dry/wet deposition can play an important role (Jurado et al. 2005). Available measurements of POP air–water exchange fluxes in remote oceanic regions are very scarce due to the difficulties associated with the sampling procedures for POPs (e.g., large volume, partition to colloids, etc.), shipboard and laboratory contamination and the costs associated with the use of ships in the open ocean. This is

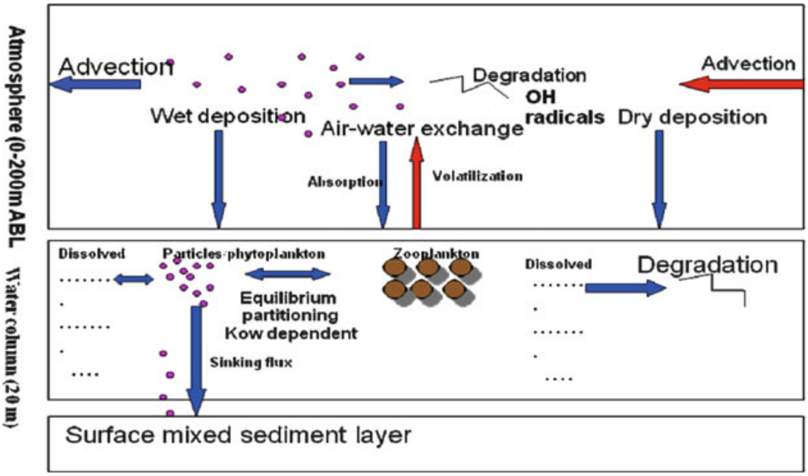

Fig. 8.1 Major processes affecting POPs in the atmosphere and the ocean

because of the inherent difficulties and very demanding sampling and analytical requirements for these compounds at ultra-trace levels which limits realistic data to output from very few laboratories around the globe.

In addition, most estimations of diffusive air–water fluxes are performed from the dissolved and gas phase concentrations, in effect, without measuring fluxes, but by estimation of the air–water mass transfer coefficient, a procedure that has important uncertainties associated to physical chemical properties (i.e., Henry's Law constant) and lack of enough knowledge on parameterization under high wind speeds and the role that the surface microlayer plays in air–water exchange under low wind speeds.

Generally, in the open ocean, the atmosphere is a net source of organic pollutants to water bodies. For example, Gioia et al. (2008a) observed air/water fugacity ratios higher than unity in some regions of the Atlantic Ocean. For the less hydrophobic POPs such as HCHs, Lakaschus et al. (2002) has suggested conditions close to equilibrium between the atmosphere and ocean. So far, the only clear example of net volatilization fluxes of organic pollutants is that described for lighter PAHs, such as phenanthrene, but it is presumably due to in-situ biogenic production of this hydrocarbon. For legacy POPs such as PCBs, Zhang and Lohmann (2010) have recently described a volatilization flux of PCBs from the south Pacific open Ocean.

At the coastal regions, volatilization of POPs is a generalized observation. For example, strong volatilization trends have been observed for the NE Atlantic Ocean (Yan et al. 2008) and the NE Mediterranean Sea (Garcia-Flor et al. 2009). Similar volatilisation fluxes have been observed for polar POPs such as nonylphenols in the NE Atlantic and North Sea (Van Ry et al. 2000; Xie et al. 2006). Volatilization fluxes of POPs from coastal waters may be the result of the important riverine and run-off fluxes into the marine environment. Coastal waters can also act as sources of POPs to open sea regions.

An issue that has received little attention so far is the relevant routes for the transport of pollutants from coastal ocean to open sea waters, and how important is this. For legacy POPs that can undergo transport through grasshopping (successive volatilization and deposition) these transfers of pollutants have been assessed implicitly when studying the air–water exchange. However, for chemicals with higher solubility and limited volatility, there is little work done on how ocean currents and mixing processes in the water column transport these chemicals in the marine environment. In the case of PFOS (Perfluorooctanesulfonic acid) and PFA (perfluoroalkoxy), it has been suggested that they could behave as passive tracers (Yamashita et al. 2008), even though this needs further research, because some of these chemicals can also undergo degradation in the environment (Yamamoto et al. 2007).

8.4 Cycle of Organic Pollutants in the Water Column

Once POPs enter in the water column through atmospheric transport or from riverine inputs, they undergo a series of environmental processes which are to a great extent related to the marine carbon cycle. POPs are hydrophobic compounds.

Hydrophibicity is assessed by the octanol-water partition coefficient (Kow), which for most POPs range from 10^4 to 10^8, and therefore, the concentrations in organic matter are 4–8 orders of magnitude higher than those in seawater. In the water column, POP will be associated to different organic matter pools contributing to the marine carbon cycle.

The aquatic carbon cycle, and specifically phytoplankton biomass, is known to play an important role in influencing the net air–water exchange by controlling the dissolved water concentration and consequently the fugacity gradient with the atmospheric gas-phase. Air–water exchange and partitioning to/uptake by phytoplankton act as coupled processes in aquatic environments (Dachs et al. 2000). Once POPs are in the dissolved phase, they may sorb to particles, and organisms such as phytoplankton, and can be removed from the surface waters and delivered to the deep ocean by sinking particles and by zooplankton vertical migration. Many studies including modeling work have shown that terrestrial organic matter (soil and forested surfaces) has an important influence on the dynamic and inventory of POPs (Eisenberg et al. 1998; Scheringer et al. 2000; Wania and McLachlan 2001). Therefore, it is logical to think that high productivity regions of the ocean may exert an important influence on the global distribution of POPs. Jurado et al. (2004) assessed the spatial and seasonal variability of the maximum reservoir capacity of the ocean compartment to act as a sink of PCBs and showed that temperature, phytoplankton biomass and mixed layer depth (MLD) can influence the reservoir capacity of the ocean (i.e., air–ocean equilibrium/storage issues). However, kinetically controlled processes such as particle settling, reactions and metabolism also need to be considered.

Despite these pieces of evidence, current evaluations on the role of oceans as reservoirs or sinks for POPs are limited to model assessments and few experimental data, reporting water concentrations in lakes and river (Totten et al. 2004; Rowe et al. 2007), but few studies have reported seawater concentrations in open ocean (Iwata et al. 1993; Schreitmuller and Ballschmiter 1994; Sobek and Gustafsson 2004; Gioia et al. 2008a, b; Nizzetto et al. 2008). Research in this field is one step behind what is known about biogenic gases such as dimethyl sulphide (DMS) and the Hg cycle and their coupling to the biological pump (Andreae and Barnard 1983; Andreae and Raemdonck 1983; Ayers and Gillet 2000).

POPs present in the ocean waters are distributed between the dissolved and particulate phases depending on sorption and desorption equilibrium with the suspended particulate matter (SPM) present in the water. Although the oceanic suspended particles are formed of a heterogeneous mixture materials derived from different abiotic and biotic sources (Swackhamer and Skoglund 1991), a large fraction of particles and aggregates are formed of different types of organic matrices and even inorganic fractions could be covered by organic films (Wania 2006). Natural organic matter suspended in the oceans primarily consists of altered biomolecules such as polysaccaharides and lipids that derived from the plankton and is subsequently modified in the water column. The classification of dissolved, colloidal and particulate phases is purely operational since in oceanic conditions there is a continuous load of organic matter from purely dissolved to large particulates. In the euphotic zone of oceans most particles in the water are planktonic living organisms like bacteria (Broman et al. 1996) and phytoplankton (Swackhamer and Skoglund 1993).

The complex mixture of natural organic matter may include different range of composition with both hydrophobic and hydrophilic parts, and may present portions of different binding capabilities (Schwarzenbach et al. 2003). This heterogeneity has direct implications for the kinetic and equilibration times of the sorptive process which cannot be explained as a simple equilibrium partitioning. While POPs may bind rapidly with the condensed "glassy" surface regions (adsorption process) in a few hours to few days, it takes periods of days or weeks to diffuse slowly into (and out of) the interior of the more flexible "soft" parts of the organic matrix (absorption processes) (Pignatello and Xing 1996; Xing and Pignatello 1997; Axelman and Broman 2001). The measured concentration in the solid phase is thus expected to vary with time (Seth et al. 1999). In addition to the natural organic matter, the fraction of organic carbon may also include other organic sorbents derived from anthropogenic activities. The most important one when considering the water-particle partitioning processes is the black carbon (BC). Such particles can be quite porous with high specific surface areas and exhibit a high affinity for many organic pollutants (particularly for compounds with planar molecular structure) (Jonker and Koelmans 2002). Therefore, the high sequestration capacities of this kind of organic materials could lead to an underestimation of predicted K_{oc} (partition coefficient between the organic carbon and the chemical) values from simple partitioning models (Gustafsson et al. 1997; Accardi-Dey and Gschwend 2003).

While particulate organic carbon (POC), and lately the fractions of soot carbon in sediments have been issues of intensive research, there are a number of issues that are still major bottlenecks in understanding of the POP cycling in the marine environment, among them the role of dissolved organic carbon as a sorbing phase and the role of the surface microlayer in atmosphere-ocean exchange of POPs.

8.4.1 Dissolved Organic Carbon

The bioavailability and behavior of POPs is influenced by POC and by the dissolved organic carbon (DOC) present in the water column. DOC in seawater is composed of a diversity of compounds with a wide molecular weight spectrum and various functional groups that exhibit different adsorption characteristics (e.g., humic substances, flulvic substances, etc.). There have been several studies of the binding capacity of DOC to POPs (Boehm and Quinn 1973; Niederer et al. 2007). The general observation is that DOM increases the apparent solubility of POPs (DOC bound phase) reducing the ability to be sequestered from the water column by the partitioning process into particles (Jaffé 1991).

DOC is the largest reservoir of OC in the oceanic environment. Current sampling methods do not allow a proper characterization of its capacity in accumulating POPs. This impedes efforts to assess its role in the global mass balance of POPs. Experimental distribution coefficients have frequently been normalized to the bulk filter-passing OC (commonly called DOC), although, this fraction contains both truly dissolved organic matter and the colloidal fraction (Gustafsson et al. 2001). Measurements of the number of colloid-sized particles (between 1 nm and a few μm in diameter) in the oceans suggest that this fraction may account for 20–50% of total DOC (Wells and Goldberg 1992; Kepkay 2000). In marine areas, DOC frequently represents more than 90% of the total OC content (TOT) in sea surface waters whereas colloidal organic materials exceeds other marine sources of POC (Kepkay 1994). Thus the presence of this material, if not accounted for, can lead to erroneous interpretations of estimated partition coefficients (Totten et al. 2001).

8.4.2 The Elusive Surface Microlayer

The surface microlayer is the thin layer in the top of the water column, with a thickness from few micrometers to 1 mm. It is thought to play an important role in a number of processes such as air–water exchanges, accumulation and degradation of POPs (Liss and Duce 1997; Cincinelli et al. 2001; Garcia-Flor et al. 2005a; Del Vento and Dachs 2007a). The importance of the surface microlayer has been recognized for several decades (MacIntyre 1974; Hardy 1982) but the study of the occurrence of POPs and processes affecting their fate and transport are limited by the sampling devices available and the small volumes of water that can be obtained from them.

The work performed so far shows that there is a high variability in the concentrations of POPs in the surface microlayer, even when consecutive samples are taken, and only part of this variability is driven by differences in OC (Garcia-Flor et al. 2005b). It is possible that this variability is intrinsic to the surface microlayer, but it is also possible that the sampling methods available introduce an additional source of variability. This large range of POP concentrations in the SML is also observed when the enrichment factors are considered from different studies (Wurl and Obbard 2004). In addition, the small volumes that can be sampled with the glass plate or metal screen makes their utility for oceanic regions very limited due to the need of larger sample volumes. In the future, the use of novel analytical techniques such as the stir bar sorbtive extraction and other novel techniques may allow to analysis of some POPs such as PAHs in the oceanic surface microlayer.

The processes driving the formation of a surface microlayer are complex, but its study is important if processes such as air–water exchange of POPs are to be understood. In the future, the development of new techniques to sample the surface microlayer, and new studies of the role of the surface microlayer on POP transport and fate are needed, which may allow to improve understanding of its affect on air–water exchange and other environmental processes.

8.4.3 Interaction Between POPs and Organic Carbon Cycle

The dynamics of POPs is intimately linked to the carbon cycle. Looking at the global distribution of OC stocks (Fig. 8.2), it appears that oceanic environment can represent an important reservoir for POPs. The sum of OC present in the global ocean waters (including biota, dissolved and particulate organic matter and superficial sediments) (~1,200 Gt) is comparable to that present in terrestrial environment (including biota, litter and humus) (~2,600 Gt).

It is believed (Jurado et al. 2004) that the total burden of PCBs present in the portion of world oceans included between the surface and the mixed layer depth (MLD) (averaging 10s–100s m) is in the order of hundreds of tons, with a considerable fraction of it associated to POC and DOC.

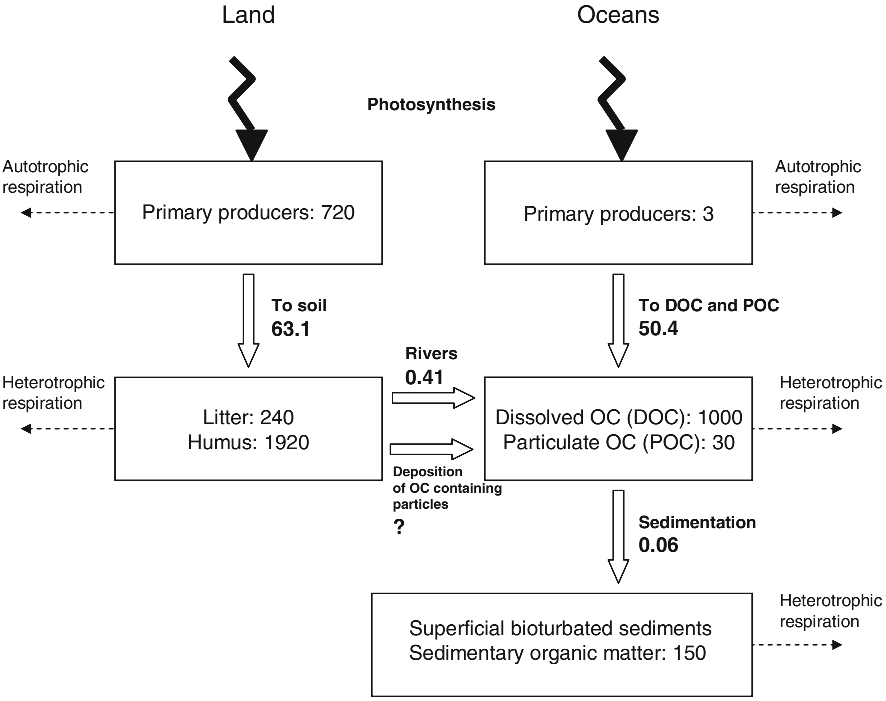

Fig. 8.2 Simplified scheme of the principal environmental stores and fluxes of OC in the biosphere. Amounts are reported in Gt (1 Gt = 10^{15} g). Fluxes are in Gt year^{-1} (Data from Ver et al. 1999; Wigely and Schimel 2000; Mackenzie and Lerman 2006)

Deeper waters are usually considered as a final sink for POPs, although an evaluation of their role in the environmental fate of POPs is not yet available. Once the POC leaves the superficial mixed waters, it sinks and supplies bounded POPs to the sediments. Sediments in coastal waters (and in particular those lying on the continental shelf) represent an important reservoir of OC and are estimated (Jönsson et al. 2003) to contain, in the superficial bioturbated layer, thousands of tons of POPs, globally.

If OC stocks control the global distribution of POPs it is reasonable to hypothesize that organic matter fluxes can serve as tracers of the potential environmental pathway of such pollutants. A key question is if it is possible to couple those two cycles in a quantitative way. Such coupling begins with the uptake on primary producers. This represents the first step for the entrance of POPs in the food webs. Autotrophic biomass is believed to be able to influence the global distribution of these pollutants, given their lipophylic characteristics and the almost ubiquitous distribution on the planet.

In the terrestrial environment this was investigated by measuring and modeling the deposition fluxes into forest ecosystems (Horstmann and McLachlan 1998; McLachlan and Horstmann 1998; Wania and McLachlan 2001). In the marine environment however, no direct observations are so far available on the potentiality of phytoplankton in influencing water column concentration. Modeling assessments (Dachs et al. 2000) suggest that phytoplankton uptake can deplete water dissolved concentration and drive significant exchange fluxes between air and water.

The OC stored in marine autotrophs, on a global scale, is much smaller than that in terrestrial phytomass (Fig. 8.2). However the net primary productivity (NPP) is comparable, because OC turnover is faster. In marine systems this can potentially make the marine primary producers a forcing parameter for the global distribution of POPs. Unfortunately, current understanding of the accumulation of POPs into phytoplankton is limited by the lack of knowledge on the actual accumulation mechanisms and the uncertainty of bioconcentration factors (Arnot and Gobas 2006). Current modeling approaches cannot adequately account for the extremely dynamic nature of the phytoplankton biomass and its interaction with the other elements of the water column. Many phytoplankton species have a life span time of 1–2 days before undergoing cellular division. The size of the phytoplankton compartment (namely: its concentration in the water) is basically the result of the balance between photosynthesis, grazing and viral lysis. Organic matter is continuously transferred to other trophic levels or to the bacterial loop and DOC is continuously generated (Handa et al. 2001). The microbial loop comprises bacteria, viruses and protozoa and controls most of the autotrophic production and grazer biomass, rather than the larger predators in the food web. The microbial loop comprises bacteria, viruses and protozoa and controls most of the autotrophic production and grazing, rather than the larger predators in the food web. However, besides the work of Wallberg and Andersson (2000) and few others, little is known about the role of the microbial loop in the fate and impact of POPs (Fig. 8.3).

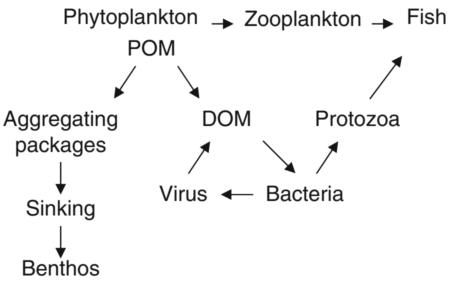

Fig. 8.3 The pelagic organic carbon pathways (Azam 1998)

During these processes, a smaller part of the POC sinks and is integrated in the superficial sediment layer, where the residual energy is basically used by the benthos. POP vertical fluxes associated to sinking particles in the water column can be directly estimated from the deposition velocity of the particles and often the fraction of OC is used as a parameter to determine the capacity in accumulating POPs. Fluxes of OC and thus of POPs associated to sinking particles are important on the continental shelves or in proximity of river estuaries, where about 97% of the total sinking organic matter deposits (Jönsson et al. 2003). In open oceanic waters most of the OC is re-mineralized within the photic zone and mesopelagic region (100–1,000 m depth).

Figure 8.3 schematizes the cycle of organic matter in the pelagic marine ecosystem. Processes occur at different spatial and temporal scales, considerably complicating the scenario. However during such processes the largest part of the organic matter (to which POP are mainly associated) entering or produced in the aquatic system is degraded and the OC is oxidized to carbon dioxide. Assuming that POPs are considerably more persistent that the organic matter, a key question concerns what happens to organic matter bound POPs during OC re-mineralization.

Recently, there has also been pointed out to the role that zooplankton has key step accumulating pollutants which are then transferred to higher trophic levels in the marine environment (Sobek et al. 2006; Berrojalbiz et al. 2009). In addition, zooplankton can accumulate organic pollutants in fecal pellets which are an important matrix for vertical transport of pollutants in the marine environment (Fowler and Knauer 1986; Dachs et al. 1996).

Current knowledge on the link between the environmental fate of POPs and OC in the biosphere is still limited. However there is evidence suggesting that autotrophic biomass accumulates a considerable fraction of the cycling POPs, and the dynamics of biomass synthesis, growth and consumption play a key role in influencing POP environmental fate. Additionally, photosynthesis, respiration and ecosystem structure are factors strictly interconnected with the climate, and therefore, sensitive to the changes occurring in it. Understanding the mechanisms linking the carbon cycle and the environmental fate of POPs is a fundamental step to assess the possible consequences which changing conditions can have on the human and ecosystem exposure to those pollutants.

8.5 Spatial Variability of Organic Pollutants in the Marine Environment

8.5.1 Geographical Variability

Data on POPs levels in the open ocean are generally scarce because sampling on research vessels requires adoption of protocols and methods to reduce contamination of the samples and the analytical challenge of measuring and detect POPs where concentrations are in the orders of pg/L in seawater and pg/m^3 in air. Generally, higher atmospheric POPs concentrations are measured in the northern hemisphere than in the southern hemisphere, which is in agreement with historical global production. For PCBs, source inventories show that the ratio of emissions between the northern and the southern hemisphere (NH:SH) is ~20:1. However, ambient levels show a smaller difference. Inaccuracies with the source inventories and/or NH "dilution" to the SH over time may explain these observations. Relatively high levels of PCBs and PAHs have been reported for the West African coast during different cruises on board two different vessels, RV Pelagia and RV Polarstern, in 2001, 2005 and 2007 respectively (Jaward et al. 2004; Del Vento and Dachs 2007b; Gioia et al. 2008a, 2010; Nizzetto et al. 2008). The sources were unknown although strong land-based emissions are suspected. Source inventories have not identified Africa as important for PCB usage raising interesting questions about unaccounted for sources/processes.

A strong latitudinal trend over the oceans is also observed within the Northern hemisphere with the highest PCB concentrations near the coasts of Europe and the lowest in the Arctic, suggests that the underlying levels in the remote Arctic atmosphere are controlled by LRAT, with deposition dominating over volatilization for PCBs in the Arctic region. Gioia et al. (2008b) raises questions about the role of ice as a compartment/buffer/source/sink for POPs in the Arctic, both in the short-term and as global climate changes occur to affect the properties and the extent of the ice sheets.

The air data show a strong decline with latitude with the highest PCB concentrations in Europe and the lowest in the Arctic. Fractionation in seawater has been observed in several studies from Europe to the Arctic Ocean (Sobek and Gustafsson 2004; Gioia et al. 2008b; Lohmann et al. 2009). In view of the different analytical procedures used by the groups, and the difficulty of comparing results from different years and somewhat different locations, the agreement between these three measurements is encouraging. However, it does restrict speculation on any trends or their absence.

8.5.2 Vertical Variability of Organic Pollutants

Unfortunately, most of the oceanic measurements of organic pollutants are made in surficial waters, usually taking advantage of the pumping systems of research ships that sample water from below the ship at 4–5 m depth. Then, the geographical variability described above is limited to samples from the upper water column, above the thermocline when the water column is stratified, and this is water influenced by atmospheric inputs as has been demonstrated by Jurado et al. (2007).

However, the oceans are notably deep, with depths of several thousands of meters in most oceanic regions. Unfortunately, there is very little information on the concentrations of POPs and the major processes affecting POPs, not only in deep waters, but also in most of the photic zone. For legacy POPs, the only vertical profiles available are those of particle phase PCBs and PAH reported for the Mediterranean and Black sea (Dachs et al. 1997a, b; Maldonado et al. 1999). These profiles show that particle phase concentrations are higher at surface and decrease with depth. Usually there is a maximum in concentrations in the photic zone that is correlated with the maximum of chlorophyll (biomass) in the water column. PCB profiles do not change through the water column, consistent with their persistence. Conversely, PAH profiles do change significantly during their transport in the water column, and while the profile of 5–6 rings PAHs is quite constant in the water column, the high predominance of 3 ring PAHs (phenanthrene, methylphenanthrenes, etc.) in the photic zone is not observed in deep waters. Low MW PAH can be degraded easily by bacteria and zooplankton (Berrojalbiz et al. 2009) and thus a major fraction of what enters the water column does not reach bottom waters.

Unfortunately, there is not a single vertical profile of dissolved phase legacy POPs available for legacy POPs. However, a few vertical profiles of emerging pollutants such as PFOS and PFOA have been recently reported (Yamashita et al. 2008). These vertical profiles show as higher concentrations at surface and an exponential decrease in concentrations with depth, the fact that these chemicals have a low affinity to sorb to particulate matter, their geographical and vertical distribution is related to marine current and the turbulent role in oceanic mixing.

8.6 Temporal Variability of Organic Pollutants in the Marine Environment

8.6.1 Long Term Trends

In general, atmospheric levels of the POPs analyzed here are declining near source regions. On the other hand, over remote areas of the open ocean it appears there is little change in air concentrations over the 15 year period (1990–2005). This points to a gradual global scale re-distribution of POPs and a shift from the dominance of primary sources to secondary sources. PCBs air concentrations over the ocean have been measured on a few different cruises in the Atlantic Ocean since 1990. Thus, a comparison of these studies may give insights into changing levels and distributions of PCBs over the Atlantic Ocean. This must be done cautiously, because they only reflect limited seasons (spring/summer in the southern hemisphere and autumn/winter in the northern hemisphere) and are subject to the uncertainties mentioned earlier (i.e., different ships, different methods and different analysts).

As mentioned earlier there are several dataset on PCBs and PAHs collected in the North and South Atlantic Ocean in the last 15 years (Schreitmuller and Ballschmiter 1994; Jaward et al. 2004; Gioia et al. 2008a, 2010). In summary, these datasets appear to have similar concentrations over the 15 year period (1990–2005), subject to the caveats made above. In contrast, several studies have shown that PCBs are declining in the atmosphere of Europe, North America and the Arctic, typically with an average half life of 4–5 years (Gioia et al. 2006). If a half life of 4–5 years is assumed to also apply to the open Atlantic Ocean, the concentration between the 1990 and 2005 should differ by about a factor of 8–10 – presumably sufficiently different to be detectable. The lack of a measured difference perhaps implies that air concentrations in these remote oceanic environments are undergoing little change, compared to the declines observed at the land-based locations close to sources. Interestingly, Panshin and Hites (1994) compared PCB in oceanic air over Bermuda in 1992/1993 with those of several studies in 1970s at the same location, and found no statistically significant difference. Hillery et al. (1997) also concluded that the atmospheric concentrations of PCBs near Lake Superior, the most remote of the Great Lakes, remained unchanged over a period of 6 years. Axelman and Broman (2001) argued that these observations indicate PCBs may be removed slowly from the environment, when viewed from a global or hemispheric perspective, with PCBs being diluted into the remote areas of the earth rather than being permanently removed from global cycling. This implies that source-region gradients would decline over time as PCBs become more uniformly distributed (Axelman et al. 2000).

8.6.2 Diel Cycling of POPs over the Ocean

Several studies on land had previously observed a strong temperature-dependent diurnal cycle for different POPs (Hornbuckle and Eisenreich 1996; Wallace and Hites 1996; Lee et al. 1998, 2000; Gouin et al. 2002; Totten et al. 2002; Lohmann et al. 2003). Jaward et al. (2004) reported for the first time a diel cycle over the open ocean for some low molecular PCBs congeners and more volatile PAHs with daytime exceeding nighttime concentrations by a factor of 1.5–2.5 in South Atlantic Ocean (Jaward et al. 2004). Such a cycle over the ocean was unrelated either to ambient or seawater temperature variations, which were insignificant between day and night. The authors suggested that the observed variability in air concentrations may be related to interactions between plankton and organic carbon concentration in the surface ocean, as a result of diel cycles in zooplankton migration, DOC cycle, and/or phytoplankton biomass turn-over, but further measurements were needed to support their hypothesis.

Since then, more data are available, confirming the presence of a diel cycle in some remote region only for more volatiles PCBs and PAHs; in contrast high molecular weight compounds did not exhibit a diurnal cycle. Ship-board atmospheric samples were collected in the North East subtropical/tropical Atlantic Ocean, at the end of spring 2003 (Del Vento and Dachs 2007b). Gas phase concentrations for some samples taken along parallel 21°N show a day/night ratios of ~1.5–2. During an Atlantic latitudinal transect in October–November 2005, air and water phases were monitoring, providing more information on the composition of the water column and its biological activity (Gioia et al. 2008a; Nizzetto et al. 2008). A diel cycle with daytime exceeding nighttime air concentrations by a factor of 1.5–3 was observed between 3°N and 27°S of the tropical South Atlantic. In this cruise dissolved phase concentrations in surface ocean also showed day/night cycled in four samples. All those observations were made on board of different ships and during different period of the year. Possible ship-borne sources were also excluded by deploy of passive samples and/or elemental and organic carbon (EC/OC) analysis. Moreover, the cycle appeared to be locally concentrated in some part of the ocean, corresponding to more oligotrophic regions, whereas ship contamination would have affected the entire datasets.

Diurnal cycling of some POPs over the ocean suggests that air concentrations, far from global source regions, are affected by some dynamic biological and/or physical processes. Water column processes affecting the carbon cycle may be drivers of air–water cycling of POPs. The influence of the “biological pump” is well documented on biogenic gases such as dimethyl sulphide (DMS) and the Hg cycle (Andreae and Barnard 1983; Andreae and Raemdonck 1983; Ayers and Gillet 2000). Phytoplankton plays an important role also on POPs, as air–water exchange and phytoplankton uptake are coupled processes (Dachs et al. 2000).

A level III/IV model, previously used to successfully interpret diel variability in PCBs air concentrations over different locations (MacLeod et al. 2007), has been used to identify possible variables that could influence the diel POPs cycle. Parameterization based on temperature, wind speed, atmospheric mixing height, and hydroxyl radical concentrations, applied to Jaward’s dataset could not explain the amplitude of diurnal POPs cycle in the atmosphere, confirming previous conclusions (Jaward et al. 2004).

Very limited information is available in the literature on other processes like zooplankton migration, microbial loop or the surface microlayer (SML) that may be involved on the diurnal cycle of POPs. The distinct chemical composition of SML promotes the accumulation of anthropogenic pollutants, such as POPs, in it and natural surfactants produced by phytoplankton can reduce air-sea gas exchange (Frew et al. 1990), but no information is available on diurnal cycles of SML properties. Existing data are therefore insufficient to explain and understand the precise mechanisms driving the diel cycle, showing that further studies are required to elucidate them.

8.7 Effects of Organic Pollutants in the Marine Environment

8.7.1 Bioconcentration, Biomagnification and Toxicological Effects

The UNEP Stockholm Convention recognizes that POPs possess toxic properties, resist degradation, bioaccumulate and are transported through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystem (UNECE 1998). As a result, they have been found in the Arctic (Bidleman et al. 1999; Harner et al. 1998; Stern et al. 1997) and shown to bioaccumulate and biomagnify in marine mammals, polar bears and humans (Kucklick and Baker 1990; Halsall et al. 2001). There is concern for the health of indigenous Arctic people and wildlife, due to the toxicity, persistence and bioaccumulation potential of these compounds (Gilman et al. 1997). Their regulation has become an international policy issue based upon their possible effects on human health and potential environmental risks (UNECE 1998).

The concentration of a POP or metabolite increases at some of all steps in the food chain. This process is called biomagnification (Fig. 8.4), which exposes animals at high trophic levels in the food webs to doses which may causes effects such as endocrine disruption, altered neurological development, immune system modulation and cancer. Most POPs and all natural compounds which have a tendency to biomagnify in food webs are neutral organic compounds that are highly substituted (or substituted at critical positions in the molecule) with chlorine or

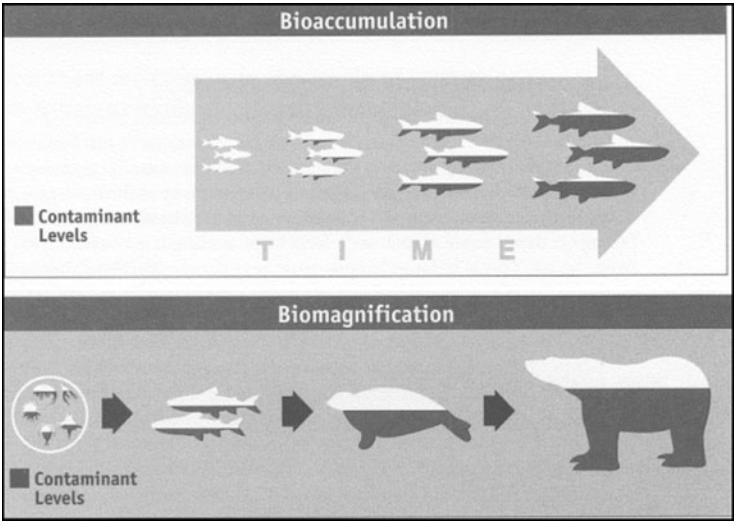

Fig. 8.4 Bioaccumulation and biomagnification

bromine. The reason for this is quite straight forward: the compounds are lipophylic and not easily metabolized. The lipophylic nature ensures efficient uptake from the diet and storage in fat depots, and the halogens block attack by enzymes. The rate of excretion of unchanged compound (usually via partitioning to feces in higher biota) is much slower than rate of uptake, so concentration in the organism becomes higher than in the diet.

It is not just the relatively non polar, lipophylic POPs and metabolites (e.g., oxychlordane and heptachlor epoxide) which bioaccumulate. Highly polar POPs (e.g., chlorophenols) are less efficiently absorbed from the gut, are relatively easily transformed into excretable metabolites, and therefore do not normally biomagnify. However, if they are formed as metabolites in the animal and protected from elimination by protein binding or some other mechanism, they may still accumulate. The first class of polar POP found to bioaccumulate was the methylsulfone metabolites of PCBs and p,p′-DDE. Methylsulfone PCBs are formed in endotherms from readily metabolized meta-/para-unsubstituted PCBs with adjacent chlorines (principally 2,5- and 2,3,6-chlorine PCBs) (Letcher et al. 1998). They are not readily further metabolized and have been shown to biomagnify in the ringed seal/polar bear food chain (Letcher et al. 1998).

Bromine is as resistant to metabolic attack as chlorine. Therefore, based on the above rules, it could have been predicted from structure alone that the brominated diphenyl ethers (BDEs) would be persistent, bioaccumulative in food webs and subject to long-range transport. However, there are several recent reports of natural organohalogen compounds which bioaccumulate in the marine environment. The most thoroughly studied has been the halogenated 1,1′-dimethyl-2,2′- bipyrroles (HDBPs), which are probably of marine bacterial origin. Four congeners are in found in marine seabirds and mammals (Tittlemier et al. 1999). All available ring carbons are substituted with halogens, ranging from Br_3Cl_3 to Br_4, and the two aromatic nitrogens are bonded to methyl groups. These compounds have been shown to biomagnify in an Arctic marine food web up to seabirds (but not seals) to nearly the same extent as persistent PCBs, and to have similar physical–chemical properties. This is the first report of a biomagnifying natural compound. The structure of these compounds fits well within the rules for biomagnification in terrestrial endotherms that were developed for anthropogenic organohalogen compounds.

An issue that has received increasing attention during the last decades is the effect of organic pollutants to the first steps of the trophic web, phytoplankton, bacteria and zooplankton. This is relevant because in terms of fluxes of carbon, these are the major vectors for carbon fluxes and cycling in the marine environment. A small effect of organic pollutants in phytoplankton or bacteria can induce a high effect in terms of perturbation of the carbon fluxes. In addition, there is modeling work that shows that indirect effects of pollutants can be found at high levels of the trophic web even though the pollutant is only toxic at lower trophic levels (Bacelar et al. 2009).

The previous work on phytoplankton sensitivity to organic pollutants has being made studying the effects of herbicides in coastal regions and the influence on PAHs on phytoplankton including the role of phototoxicity (DeLorenzo and Serrano 2003; Grote et al. 2005; Pelletier et al. 2006; Petersen and Dahllöf 2007). These studies show that indeed organic pollutants can affect the photosynthesis system and decrease the abundance of phytoplankton communities in the marine environment. The work done so far, shows that the effects are observed at concentrations higher than those measured in open ocean waters. However, these studies have been done for a single chemical or a simple mixture of chemicals, which in the marine environment there are thousands of chemicals that can have synergistic, or just additive effects (Dachs and Méjanelle 2010). In addition, the effects are not observed at the same concentrations for all phytoplankton species. Recently, Echeveste et al. have shown that the concentration at which the effect is observed depends on the cell size, being the small organisms, *Prochlorococcus* sp. and *Synechococcus* sp., mainly, the more sensible to organic pollutants such as PAHs (Echeveste et al. 2010). These pioneering studies show that there is need for a more comprehensive assessment of the effects of real mixtures of organic pollutants to phytoplankton, bacteria and zooplankton in order to determine whether there is a significant coupling between POP occurrence in the ocean and the major vectors of organic matter in oceanic waters.

8.8 Oceanic Sinks of Organic Pollutants

In addition to covering a major fraction of the earth's surface, the oceans can be deep, with well developed vertical structures due to physical barriers of stratification, or incomplete mixing or biological activity mainly concentrated at the top 100 m. Vertical transport of pollutants in the marine environment can occur as associated to particulate matter and due to physical mixing. For hydrophobic POPs, the biological pump mediates the oceanic sink of POPs. Indeed, pollutants sorb to phytoplankton and other organic matter pools, a fraction of this organic matter settles to the deep ocean and carries the organic matter-bound POPs (Dachs et al. 1996, 2002; Fowler and Knauer 1986). In addition, the biological pump plays also an important role be decreasing the dissolved concentrations, thus modifying the air–water gradient in concentrations which leads to enhanced air–water fluxes of POPs. Dachs et al. assessed the role of the biological pump at the global scale. They reached the conclusion that increased fluxes were found at high latitudes and in other regions with high primary productivity such as upwelling regions. The role of the biological pump is more important for the more hydrophobic compounds. Jurado and Dachs (2008) have also shown that the biological pump can considerably reduce the atmospheric residence times of hydrophobic POPs. The mechanisms currently taken into account when estimating the role of the biological pump are in fact a simplification of the complex nature of the processes driving the vertical fluxes of POPs, but it provides a reasonable estimation of the magnitude of the biological pump. Figure 8.5 shows the comparison of the measured fluxes measured in the north Atlantic (Gustafsson et al. 1997), the Mediterranean sea

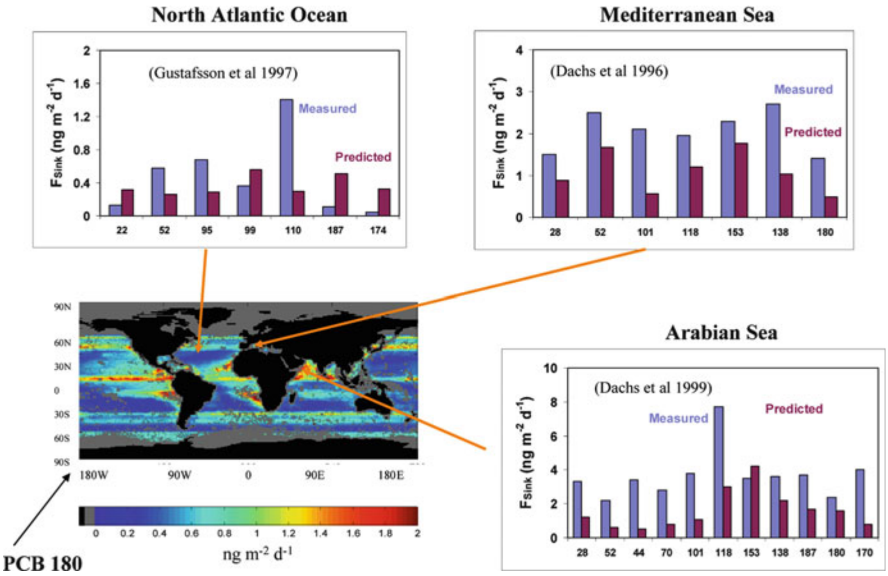

Fig. 8.5 Comparison of measured settling fluxes of PCBs and predicted fluxes (From Dachs et al. 2002) for the Mediterranean Sea, the Arabian Sea and the north Atlantic Ocean

(Dachs et al. 1996), and the Arabian sea (Dachs et al. 1999) with the predictions from current models of the role of the biological pump. It shows that predictions of settling fluxes are usually within a factor of three of predictions, and this gives an idea of the uncertainty associated with current models of the marine POPs. In order to improve these predictions, a better knowledge of processes driving the fluxes of organic matter and associated pollutants should be obtained. Jurado et al. (2004 and 2005) have provided for example the overall magnitude of the Atlantic ocean sink of PCBs and PCDDFs, and Lohmann et al. (2006) have shown that this is the main global sink for the more hydrophobic chemicals, while the atmosphere (due to reaction with OH radicals) may be the dominating sink for the less hydrophobic POPs.

Recently, Lohmann et al. (2006) estimated the magnitude of the physical pump for PCBs. The physical pump is due to the subduction of large masses of water in the Ross Sea, the Weddell Sea, the Greenland current and Labrador Sea. They showed that the physical pump is more important in magnitude regionally than the biological pump, but when integrated at the global scale, the biological pump is still the main oceanic sink of hydrophobic POPs.

The biological pump will also be the major sink for other hydrophobic POPs such as polybrominated biphenyl ethers, even though this has not been quantified so far. However, some emerging POPs such as perfluorinated compounds have different physical–chemical properties and can be considered as “swimmers” because they do not adsorb much to organic matter and are found mainly in the dissolved phase. Yamashita et al. (2008) has suggested that they behave as passive tracers, thus following marine currents and turbulent mixing. However, the magnitude of the oceanic sink for these chemicals has not yet being estimated.

8.9 Major Unknowns, Conclusions, and the Challenges for Future Research

Even though the study of the oceanic POPs has been active since the early days of the research on the environmental chemistry of POPs (Bidleman and Olney 1974), the field has been limited by the methods available for the measurement of oceanic POPs. However, during the last decade, the amount of research on oceanic POPs has increased considerably and the role of oceanic sinks and cycling has been recognized as key for understanding the global dynamics of POPs. However, the field still needs of the development of new techniques to better estimate the different pools of POPs in oceanic waters, to estimate the coupling of the cycle of POPs with the cycle of organic matter, and the oceanic sinks. In addition, the field would benefit from techniques that could allow increases in the number and frequency of samples analyzed, if not of continuous measurements, so that processes can be better understood.

One of the major unknowns is the vertical distribution of POPs in the ocean. There is not a single vertical profile of POPs in the dissolved phase, and this lack of knowledge introduces a huge uncertainty in current global mass balances and assessment of global sinks of POPs. Other issues that will receive much attention during the coming years are the effects that complex mixtures of POPs and other compounds play as environmental stressors of phytoplankton, zooplankton, the microbial loop and rest of oceanic biota.

Because of the fast development during the last decades of the global economy, the use of resources has increased exponentially, and presumably the number of organic chemicals that have entered the environment has also being increasing. Even though not all these chemicals will be persistent, a fraction of them may persist in the environment for decades, in fact, every year there are new pollutants that are "discovered" in the environment. Their introduction should be viewed as another vector of current global change which represents an additional stressor for organisms, communities and ecosystems that is largely not understood.

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Chapter 9
Chemistry of POPs in the Atmosphere

Wolf-Ulrich Palm

9.1 Introduction

The discovery of the insecticidal properties of DDT by Paul Müller (Läuger et al. 1944; DDT was synthesized more than 50 years ago (Zeidler 1874) can be deemed as one of the starting points of intensive search of organic compounds to be used as pesticides. These organic compounds were – and are – used and applied deliberately especially in the environment due to their properties as poisons against plants, fungi or insects. However, already in the beginning of the 1950s of the last century the persistence (i.e., high lifetime) of these compounds in the environment was realized and culminated 1962 in the publication of 'Silent Spring' by Carson (2000; Marco et al. 1987). Besides these highly chlorinated pesticides of the first generation, high amounts of chemically bad characterized mixtures such as polychlorinated biphenyls (PCB) were often used. Although these substances and further byproducts, such as chlorinated dibenzodioxins and dibenzofurans (as far as we know never used commercially), are from a chemical point of view not a homogenous group, besides other general properties, they are man-made and known to be at least persistent in the environment. As a consequence, these organic compounds were termed Persistent Organic Pollutants (POP).

Besides persistence, POPs can be characterized as organic compounds that (Ritter et al. 1995),

- To a varying degree resist photolytic, biological and chemical degradation.
- Have low water solubility and high lipid solubility, leading to their bioaccumulation in fatty tissues.
- POPs are also semi-volatile, enabling them to travel long distances in the atmosphere before deposition occurs.
- Exposure to POPs, either acute or chronic, can be associated with a wide range of adverse health effects, including illness and death.

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9.2 Which Compounds Are POPs?

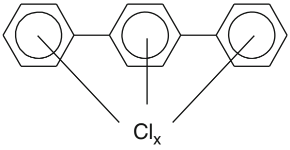
A first attempt to provide a detailed identification of compounds with properties already defined in the last section was the “dirty dozen” list, at least in part initiated by the United Nations Environmental Programme (UNEP). After several years of negotiations and based on this list, the Stockholm Convention was adopted on May 22, 2001 in Stockholm, Sweden (Stockholm Convention 2001).

The Stockholm Convention is a global legally binding agreement outlawing the production, use and release of the 12 compounds and groups of compounds of the “dirty dozen” list, respectively (summarized in Table 9.1).

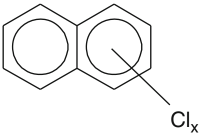
The definition of POPs in the Stockholm Convention is comparable as mentioned above:

“The Parties to this Convention [recognize] that persistent organic pollutants possess toxic properties, resist degradation, bioaccumulate and are transported, through air, water and migratory species, across international boundaries and deposited far from their place of release, where they accumulate in terrestrial and aquatic ecosystems [...]”. In addition, the Stockholm Convention is not restricted to the 12 compounds (groups) summarized in Table 9.1 and explicitly states in Article 3: “Each Party that has one or more regulatory and assessment schemes for new pesticides or new industrial chemicals shall take measures to regulate with the aim of preventing the production and use of new pesticides or new industrial chemicals which, taking into consideration the criteria [which] exhibit the characteristics of persistent organic pollutants.” Hence, besides the 12 compounds shown in Table 9.1, numerous chemicals are under review as candidates to be included in the Stockholm Convention, summarized also in Table 9.1.

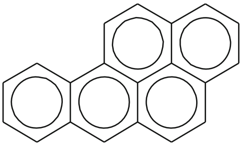
Nevertheless, besides the compounds already defined in Table 9.1, many other substances are considered as POPs. Examples are Polycyclic Aromatic Hydrocarbons (PAH) and especially benzo[a]pyrene (within the Convention on Long-range Transboundary Air Pollution (UNECE 1998; van der Gon et al. 2006) or candidates of the former protocol such as polychlorinated naphthalenes, pentachlorophenol, hexachlorobutadiene or polychlorinated terphenyls (PCTs) and persistent pesticides in general and especially atrazine as an example of an triazine derivative (see the project MEPOP within the EUROTRAC-2 project, Munthe and Palm 2003).



polychlorinated terphenyls (PCTs; here para-terphenyls only)



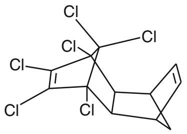
polychlorinated naphthalenes



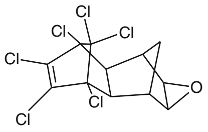
benzo[a]pyrene

Table 9.1 POPs of the Stockholm Convention (for chlordane: only the trans-isomer is shown) and chemicals under review as candidates to be included in the convention (for endosulfane: only the β-isomer is shown)

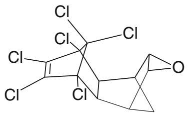
POPs of the Stockholm Convention



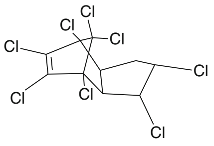
Aldrin



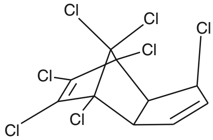
Endrin



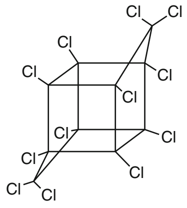
Dieldrin



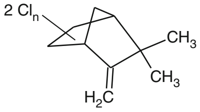
Chlordan



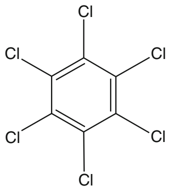
Heptachlor



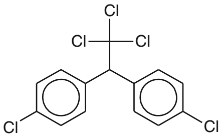
Mirex



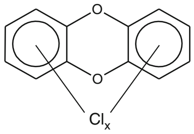
Toxaphene



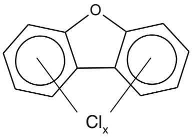
Hexachlorbenzene



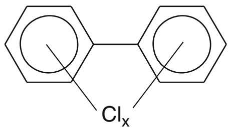
DDT



Cl_x-
Dibenzodioxins



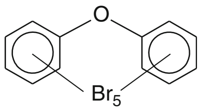
Cl_x-
Dibenzofurans



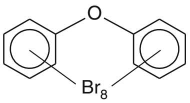
PCBs

POPs under review as candidates of the Stockholm Convention

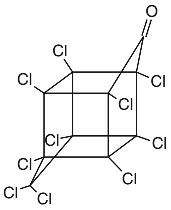
$C_xH_{(2x-y+2)}Cl_y$
x = 10–13
y = 1–13
Chlorinated paraffins



Penta-BDE



Octa-BDE

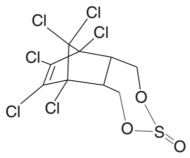


Chlordecone

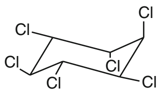
(*continued*)

Table 9.1 (continued)

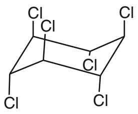
POPs of the Stockholm Convention



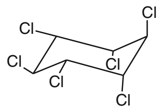
Endosulfane



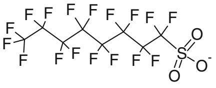
α-HCH



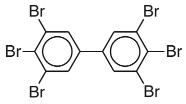
β-HCH



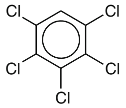
γ-HCH



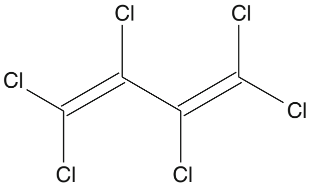
PFOS



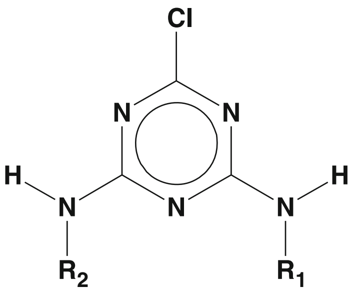
Hexabromo-Biphenyl



Pentachlorben-zene



hexachlorobutadiene



atrazine ($R_1 = C_2H_5$; $R_2 = CH(CH_3)_2$)
simazine ($R_1 = C_2H_5$; $R_2 = C_2H_5$

9.2.1 Some Chemical Remarks

Obviously most of the persistent compounds discussed so far as POPs possess chlorine and bromine in the molecule. As will be discussed in Sect. 3.3 in more detail, some of the compounds described above have a short lifetime in the gas phase or the aqueous phase (which would reject these compounds as POP candidates). However, the situation with respect to reactivity complicates due to the (temperature-dependent) low vapour pressure, leading to variable amounts adsorbed on (particle) surfaces or due a high octanol–water partitioning coefficient absorbed into particles. Unfortunately, the reactivity of ad- or absorbed compounds is to a large extent at least uncertain, if not even unknown.

Furthermore, many of the POPs represent not a single structure, but are often complicated mixtures. The family of polychlorinated biphenyls (PCB) and polybrominated diphenylether (PBDE) consists of 209 different congeners (Faroon et al. 2003; and by far not all PBDE congeners were synthesized up to now). The family of polychlorinated dibenzodioxins, as well as the family of polychlorinated naphthalenes (Howe et al. 2001; Kucklick and Helm 2006), consists of 75 congeners and the family of polychlorinated dibenzofurans is made up of 135 congeners (Al-Alawi 2008). For all polychlorinated terphenyls the tremendous number of 8,557 different chlorinated congeners is possible (Remberg et al. 1998). However, the most complicated is toxaphene, a mixture consisting primarily of chlorinated bornanes with lesser amounts of chlorinated camphenes, dihydrocamphenes, bornenes and bornadienes. The addition of 1–18 chlorine atoms for bornanes only leads to 32,768 different congeners with 16,128 pairs of enantiomers (Kucklick and Helm 2006).

As an example the assignment of congeners in two technical mixtures of pentabrominated diphenylethers and octabrominated diphenylethers is shown in Fig. 9.1.

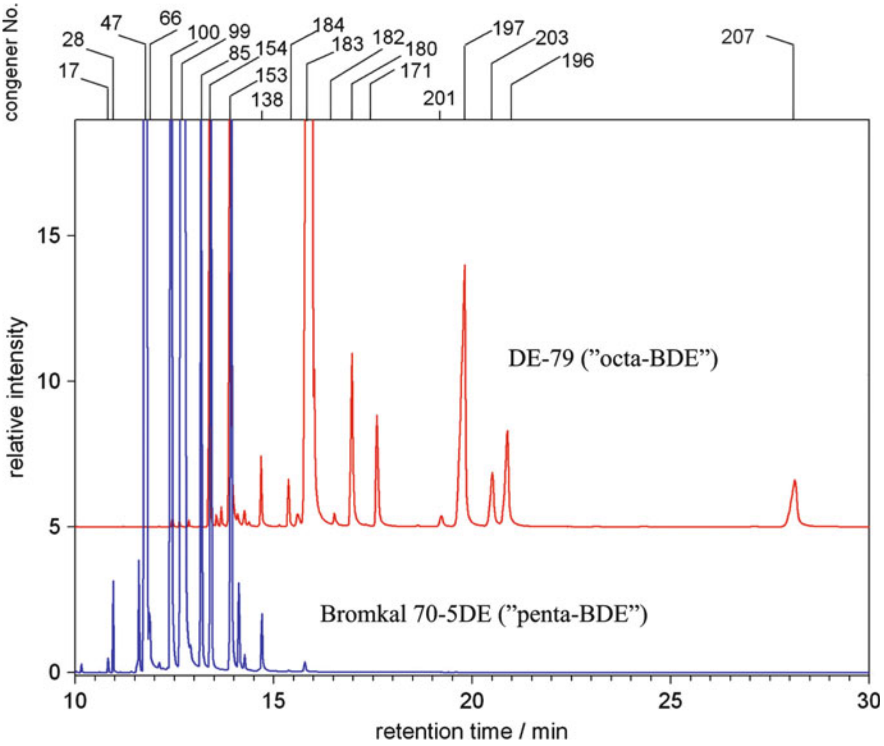


Fig. 9.1 Assignment of congeners in the technical mixtures of PBDE. DE-79 = octa BDE and Bromcal 70-5DE = penta BDE. Assignment performed by reference compounds and from information in Sondack et al. (1993), Sjödin et al. (1998), Rayne and Ikonomou (2003), Bezares-Cruz et al. (2004), and Wellington (2005)

Table 9.2 Possible number of isomers in the families of polychlorinated biphenyls (PCB) and polybrominated diphenylethers (PBDE)

Number of Cl or Br	Number of isomers
Mono	3
Di	12
Tri	24
Tetra	42
Penta	46
Hexa	42
Hepta	24
Octa	12
Nona	3
Deca	1
Sum	209

In addition, the chemistry and analysis of POPs is even more complicated due to the presence of isomers. A simple example is DDT (p,p′-DDT, exact name 1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane), one of the possible three isomers besides o,o′-DDT and o,p′-DDT. Technical endosulfane is a mixture of two isomers, termed as α-endosulfane and β-endosulfane and chlordane is a mixture of a cis/trans isomer pair. As already discussed above, numerous mixtures of POPs are always mixtures of isomers. The number of isomers of the PCBs and PBDEs are summarized in Table 9.2.

The synthesis of hexachlorocyclohexane (HCH) by chlorination of benzene leads to eight different configurational isomers. Seven of these isomers are meso-compounds and only α-HCH (see Fig. 9.2) exists as a pair of enantiomers which can be resolved and analyzed in environmental samples using chiral high-resolution gas chromatography (Müller et al. 1992).

9.3 Abiotic Degradation Reactions of POPs

9.3.1 Theory

Direct photolysis and the reaction with reactive molecules (as the OH-radical) are the main abiotic degradation reactions of organic molecules in general and of POPs in particular. Hydrolysis plays a minor role in the degradation of POPs.

The general equation of the abiotic loss of a POP with concentration c (mol L^{-1}) is shown in (9.1).[1]

$$-\frac{dc}{dt} = \Phi \cdot I_A + c \cdot \sum_i k_i \cdot c_i \tag{9.1}$$

---

[1] Equations are given with units common in solution chemistry. For the gas phase concentrations units are different (cm^{-3} instead of mol L^{-1}) and cross sections (logarithm base e) are used instead of molar decadic absorption coefficients (logarithm base 10).

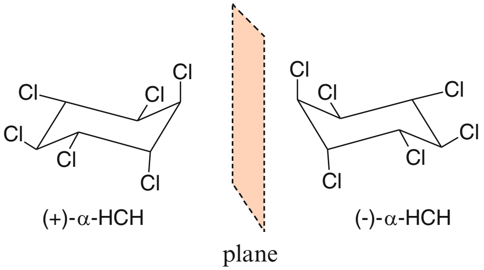


Fig. 9.2 Enantiomers of α-HCH

Besides the quantum yield Φ (mol/mol) and the absorbed moles of photons I_A (mol L^{-1} s^{-1}) the bimolecular rate constant k_i (L mol^{-1} s^{-1}) of the reactive species i with concentration c_i (mol L^{-1}) has to be known. Using (9.2), I_A is transformed for low concentrations of the POP into the product of (solar) irradiance I_0' (mol cm^{-2} s^{-1}), concentration c, molar decadic absorption coefficient ε (L mol^{-1} cm^{-1}) and optical path-length l (cm).

$$I_A = I_0 \cdot \left(1 - 10^{-\mathrm{cel}}\right) = I_0 \cdot 2.303 \cdot c \cdot \varepsilon \cdot l = I_0' \cdot 2303 \cdot c \cdot \varepsilon \tag{9.2}$$

Combination of (9.1) and (9.2) leads to (9.3), a monoexponential reaction of the POP,

$$-\frac{dc}{dt} = (2303 \cdot \Phi \cdot I_0' \cdot \varepsilon + \sum_i k_i \cdot c_i) \cdot c, \tag{9.3}$$

with the corresponding rate constant k (s^{-1}) of the monoexponential reaction shown in 9.4 assuming a constant concentration c_i of reactive species i.

$$k = 2303 \cdot \Phi \cdot I_0' \cdot \varepsilon + \sum_i k_i \cdot c_i \tag{9.4}$$

Hence, four parameters have to be known to assess the abiotic degradation of a POP:

Intrinsic parameters of the POP:

- The molar decadic absorption coefficient ε
- The bimolecular rate constants k_i with reactive species i

Environmental parameters:

- The solar irradiance I_0
- The concentration of reactive species c_i

If the spatial resolution and the resolution in time of the parameters given in (9.4) for all compartments are known, the abiotic degradation of a POP is defined.

9.3.2 Experimental Methods

Unfortunately, the optimistic picture outlined in the former section is by far not fulfilled in practice. POPs are usually low volatile compounds with low reactivities. Both properties considerably complicate the experimental determination of degradation reactions. Nevertheless, the low reactivity justifies the use of mean values and the assumption of constant concentrations of reactive species, at least on a regional scale. However, numerous parameters are not known and often estimations have to be used:

- Molar decadic absorption coefficients are often known for organic solvents but, due to low solubility, not for water.
- Cross sections in the gas phase are often not known and data obtained in non polar solvents are used as a rough estimation.
- Solar irradiances in the gas phase are well known. However, corresponding values necessary to even predict the photolysis of a compound adsorbed on surfaces are not defined.
- Numerous models to predict the adsorbed (or absorbed) fraction of a compound were developed. However, interactions between compound and surface (and the different types of surfaces present in the environment) are complicated and especially the more simple models do not represent this interaction.
- Rate constants are determined at temperatures around 293 K or even at elevated temperatures. However, temperatures in the environment are highly variable and certainly often below the temperatures used in laboratory experiments (important especially for a global transport). Unfortunately, the temperature dependence is often poorly defined. This holds for rate constants in general, absorption coefficients and for the fraction adsorbed.
- Some rate constants for the reaction of OH-radicals with a POP are known for the gas phase, the reactivity with respect to other species is often not known and assumed to be low (i.e., negligible).
- The reactivity of compounds in the aerosol-borne state is usually not known. Due to the lack of data, the adsorbed fraction of a compound is assumed to be not reactive. The situation is more complicated due to the strong temperature dependence of the vapour pressure, leading to increasing adsorption (or absorption) with decreasing temperature.

A representative compilation of quantum yields (usually in solution) and rate constants of complex organic molecules especially with respect to OH-radicals in solution and in the gas phase is given in the Appendix in Tables 9.4–9.10.

Quantum yield measurements are usually obtained using polychromatic light sources in a merry-go-round apparatus or (less common) wavelength resolved on an optical bench. Techniques, experimental set ups and necessary actinometric measurements (Dulin and Mill 1982; Kuhn et al. 2004) are described in Mill and Mabey (1985), Zepp (1978, 1982), Harris (1982), Mill et al. (1981a, b), Zepp and Cline (1977), Mill (1999), Ruzo et al. (1974), Leifer (1988), Klecka et al. (2000), Murov et al. (1993), in the references given in Tables 9.4 and 9.5 in the Appendix and in available guidelines (EPA 1998; ASTM 1987; UBA 1992; DOE 1993; ECETOC 1984; Lemaire et al. 1985; OECD 1997). Rate constants of the usually low volatile POPs using a relative method are determined in smog chambers in the gas-phase (Biermann et al. 1985; Atkinson and Aschmann 1985) or in the aerosol-borne state (Behnke et al. 1987, 1988; Behnke and Zetzsch 1989; Palm et al. 1997a, b; Zetzsch 1991a, b; Liu et al. 2005; Zetzsch et al., 2004), and at elevated temperatures in the gas phase (Anderson and Hites 1996; Brubaker and Hites 1998a, b). In addition, the fluorescence of the OH-radical is used for gas-phase measurements by laser-induced fluorescence (LIF) techniques (Witte and Zetzsch 1990; Kwok et al. 1994).

For the relative method always a reference compound with a well known rate constant is always used. For the reaction by OH-radicals (9.5–9.8) hold for the POP and the reference compound (REF), respectively.

$$-\frac{dc_{POP}}{dt} = k_{OH,POP} \cdot c_{POP} \cdot c_{OH} \tag{9.5}$$

$$-\frac{dc_{REF}}{dt} = k_{OH,REF} \cdot c_{REF} \cdot c_{OH} \tag{9.6}$$

$$\ln\left(\frac{c_{POP,0}}{c_{POP,1}}\right) = k_{OH,POP} \cdot \int_0^t c_{OH} dt \tag{9.7}$$

$$\ln\left(\frac{c_{REF,0}}{c_{REF,1}}\right) = k_{OH,REF} \cdot \int_0^t c_{OH} dt \tag{9.8}$$

Combination of (9.7) and(9.8) leads to (9.9). With time-dependent concentrations of the POP and reference compound and the known OH-rate constant of the reference compound, the OH-rate constant of the POP can be calculated.

$$\ln\left(\frac{c_{POP,0}}{c_{POP,t}}\right) = \frac{k_{OH,POP}}{k_{OH,REF}} \cdot \ln\left(\frac{c_{REF,0}}{c_{REF,t}}\right) \tag{9.9}$$

Equation (9.9) holds for the gas-phase and the aqueous phase and was used extensively especially for the reaction of OH-radicals (see literature in Tables 9.7–9.9).

Due to problems with the low vapour pressure only a few OH-rate constants of POPs are known in the gas phase and the aqueous phase (see Tables 9.7–9.9 in the Appendix). However, for aromatic molecules in solution a value of k_{OH}(solution) $\approx 5 \times 10^9$ L mol^{-1} s^{-1} (diffusion limit) can be used as a rough estimate. Hence, the well known correlation of k_{OH} in the gas phase for the electrophilic OH-radical with the minimum sum of Hammett's substitution parameters (introduced by Zetzsch 1982 and used in estimation methods) is not valid in the aqueous phase. A plot of OH-rate constants of aromatic molecules in solution (taken from Ross et al. 1992) versus corresponding values of $\sum \sigma_i^+$ (taken from Hansch et al. 1991;

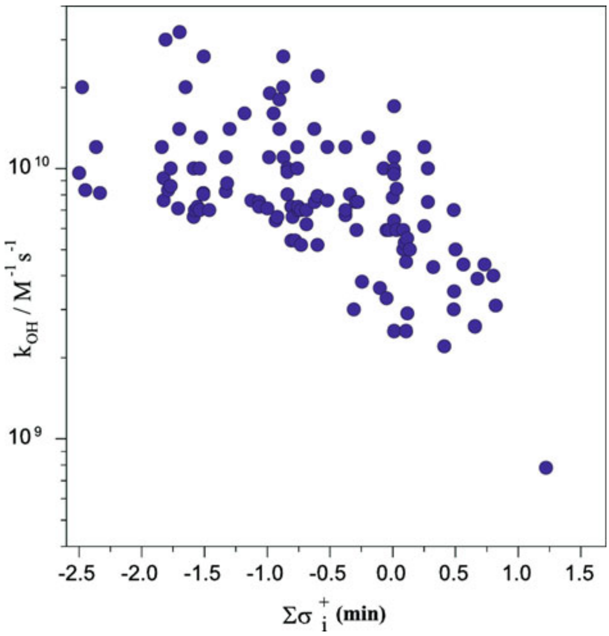


Fig. 9.3 Dependence of OH-rate constants of aromatic molecules in solution on the minimum sum of Hammett's substitution parameters $\sum\sigma_i^+$. Experimental data for k_{OH} are from Ross et al. (1992), $\sum\sigma_i^+$ values from Hansch et al. (1991) and Taylor (1990)

Taylor 1990) is shown in Fig. 9.3. Apart from the high scatter, only a slight trend of decreasing OH-rate constants with increasing values of substitution parameters for $\sum\sigma_i^+ > 0$ is found.

The knowledge of OH-radical reactivities at elevated temperatures plays an important role in measurements of semi-volatile compounds (and thereby for POPs) in the gas phase. Temperature-dependent OH-rate constants in the gas phase are shown in Fig. 9.4. Obviously activation energies are highly different. Dependent on the mechanism (abstraction or addition), activation energies can even be negative. Hence, an estimation of activation energies could lead to completely false results and a measurement of temperature dependent rate constants is always recommended.

Nevertheless, using the many rate constants determined for the reaction of ozone (Atkinson and Carter 1984), nitrate radical (Wayne et al. 1991) and OH-radical (Atkinson 1986b; Atkinson 1989; Atkinson et al. 1997; NIST 2005) in the gas phase, estimation methods based on a description of the molecule by fragments are available, especially for the reaction of the OH-radical (Atkinson 1986a, 1987, 1988, 1989; Zetzsch 1982; Kwok and Atkinson 1995) at room temperature (298 K). An implementation of the estimation system developed by Atkinson as a user friendly computer programme (Meylan and Howard 1992) and a free database (EPI-Suite) provided by the EPA is available (EPA 2007).

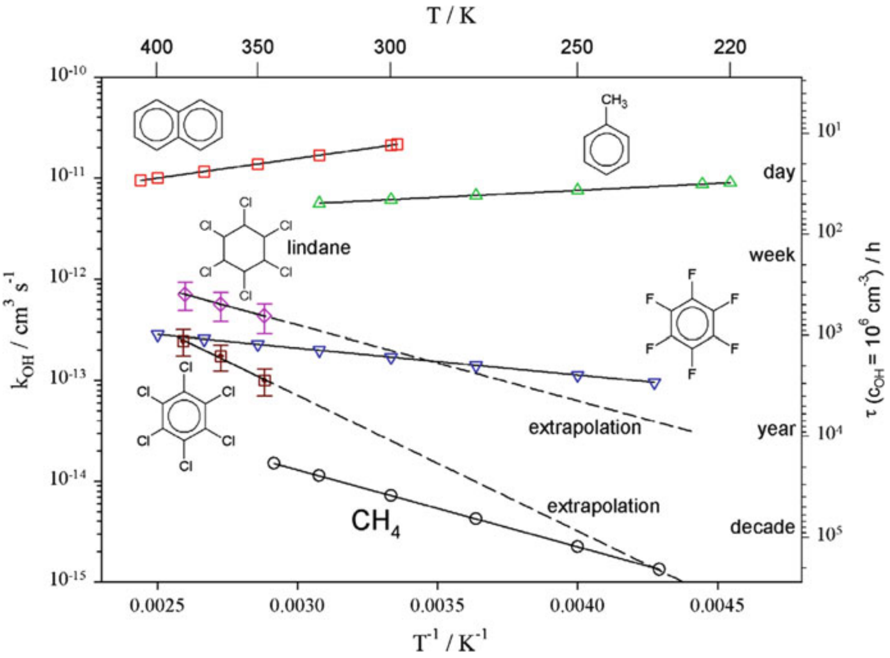


Fig. 9.4 Temperature dependence of the OH-rate constant of hexachlorobenzene (HCB) and γ-HCH (Brubaker and Hites 1998a) and for comparison of three aromatic molecules (naphthalene, toluene and hexafluorobenzene) and methane (Atkinson, 1986b)

As long as the estimated OH-rate constant is within the range of rate constants used to define the database (interpolation) and no unknown fragments are present in the molecule, the uncertainty of estimated OH-rate constants can be assumed within a range of a factor of 2. A much worse estimation of rate constants for the nitrate radical and for ozone is assumed.

A comparison of measured and estimated OH-rate constants of pesticides and other complex organic compounds using the data summarized in Tables 9.7 and 9.8 is shown in Fig. 9.5. A sufficient agreement of estimated OH-rate constants with experimental data is found (however, obviously for polycyclic aromatic compounds the estimation method is ill-defined). Rate constants for HCH isomers differ by about a factor of 4. However, estimation methods cannot distinguish between various configurational isomers. In addition, besides other compounds experimental rate constants for isomers of HCH were obtained by extrapolation from high temperatures to room temperature. Hence, the discrepancy of measured and estimated OH-rate constants is understandable.

Taken together, these results indicate that in practice for POPs even the well defined, extensively measured and thereby best known reactivity of organic compounds by OH-radicals in the gas phase is often not known (i.e., not measurable). An instructive example is the corresponding, very recently available assessment of

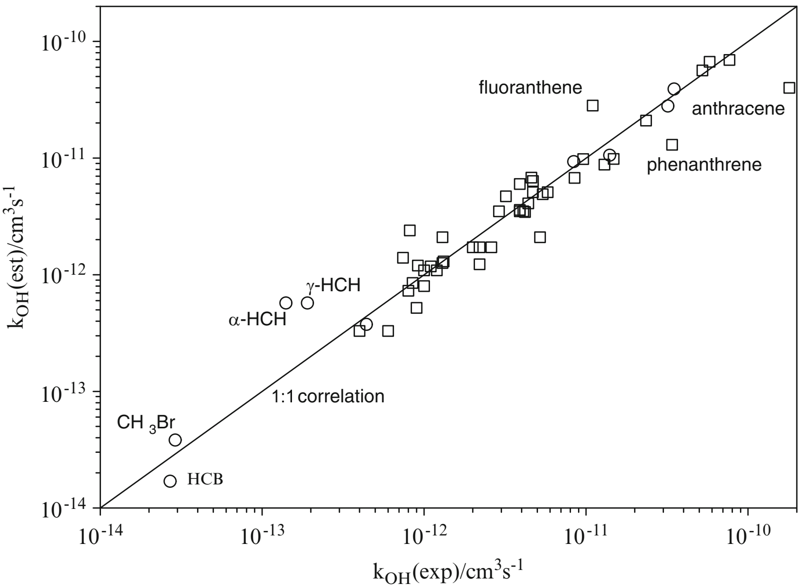


Fig. 9.5 Comparison of measured and estimated OH-rate constants of pesticides (*circles*, experimental data from Table 9.8 with the exception of phosphine) and other complex organic molecules (*squares*, experimental data from Table 9.7). Estimated data were calculated from the EPI-Suite Programme (EPA 2007). The line is the 1:1 correlation between experimental and estimated rate constants

alpha- and β-endosulfane (German Federal Environment Agency (UBA) 2007), based on measurements (in numerous cases not published in the open literature) only at elevated temperatures or in halogenated solvents, or on estimation methods. Rate constants with an uncertainty by a factor of about 10 have to be used in the assessment leading to corresponding uncertain lifetimes in the atmosphere. Furthermore, it has to be emphasized that low rate constants especially of semi-volatile compounds always hold the problem of additional loss reactions superimposing the OH-radical reactivity (or other processes), even in well defined experimental setups.

9.3.3 The Problem of Adsorption

The influence of particles on the transport of POPs is far beyond the scope of this contribution. However, the more a compound is ad- or absorbed on or in surfaces, the lesser is our knowledge of the reactivity of the compound. Several models are available in the literature: the Junge model, the Mackay model and the KOA model proposed by Bidleman. Detailed descriptions of the Junge model can be found in Bidleman (1988) and for the other models in Boethling et al. (2004), Bidleman and Harner (2000). All three models are implemented in the newest version of the programme EPI-Suite (EPA 2007) with a detailed description of the parameters used.

All models describe the dependence of the fraction of a compound ($0 \leq \Theta \leq 1$) adsorbed or absorbed from vapour pressure (Junge model), particle–gas partition coefficient (Mackay) or octanol–air partition coefficient (K_{OA}-model) and concentrations of aerosols (some properties of selected POPs can be found in the Appendix in Table 9.11). However, these models possess fundamental weaknesses:

- No interaction exists between aerosol and compound, i.e., no difference of polar and non-polar compounds with the same vapour pressure.
- The type of aerosol is not included in the model, i.e., no dependence on soot, sea salt, silicon dioxide or other aerosol types.

Nevertheless, the models are very easy to handle and for the moment there is no practical substitute. For more sophisticated models and detailed discussions see Goss and Schwarzenbach (1999); Roth et al. (2002).

A comparison of adsorbed fractions Θ of selected POPs for three models (see data in Table 9.12) for T = 298 K is shown in Fig. 9.6. For most of the compounds

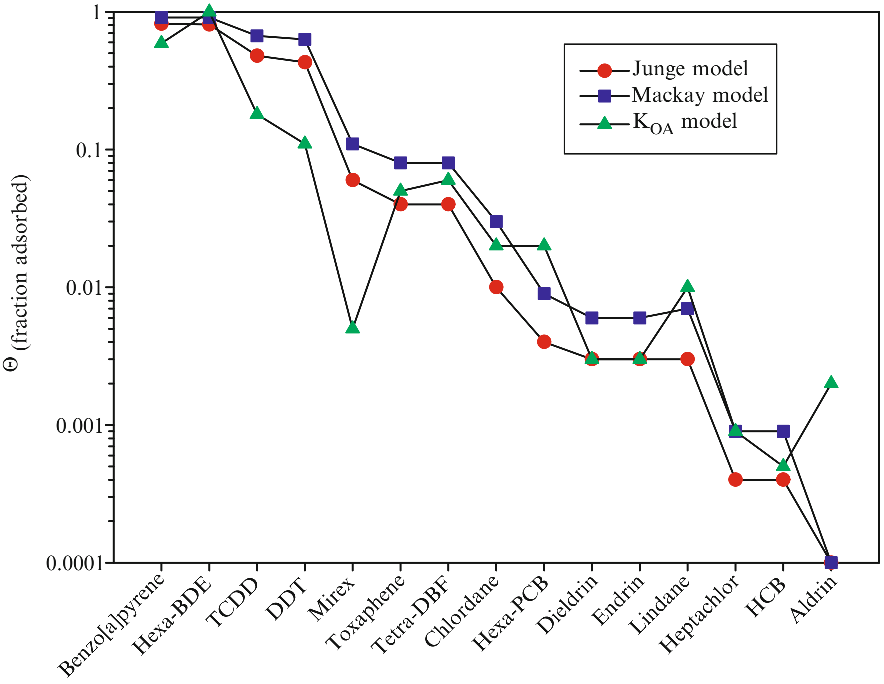


Fig. 9.6 Comparison of adsorbed fractions Θ of selected POPs for three models (see data in Table 9.12). *HCB* hexachlorbenzol, *Hexa-PCB* 2,2′,4,4′,6,6′-hexachlorobiphenyl, *Hexa-BDE* 2,2′,4,4′,6,6′-hexabromodiphenylether, *Tetra-DBF* 1,2,6,7-tetrachlorodibenzofuran, *TCDD* tetrachlordibenzodioxin

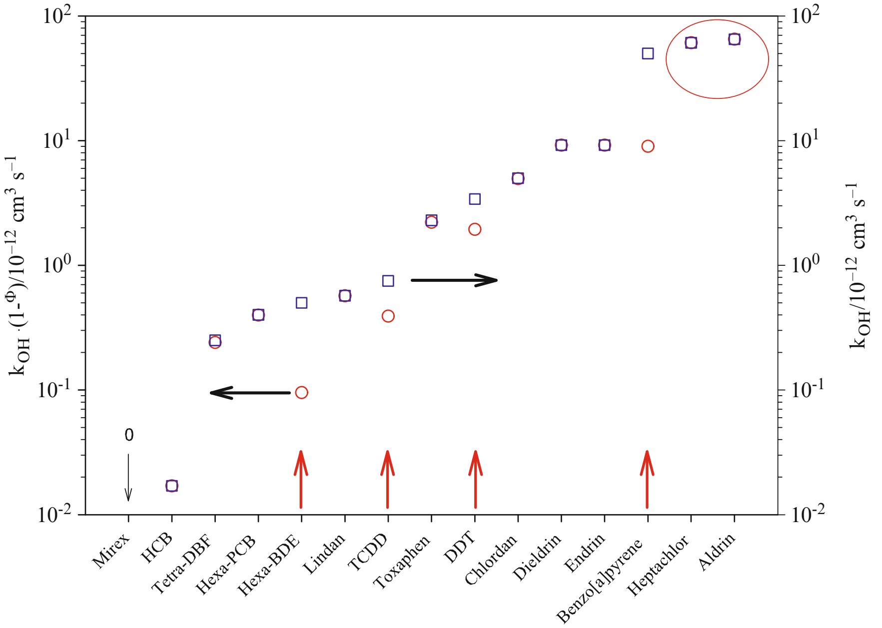


Fig. 9.7 Influence of the adsorbed fraction on the OH-rate constant of selected POPs for T = 298 K. *Squares* = OH-rate constant (*right scale*); *circles* = reduced OH-rate constant by the fraction adsorbed (*left scale*). *Arrows* on the x-axis indicate compounds with a strong influence of adsorption on OH-reactivity. The OH-radical rate constant of the *circled* compounds heptachlor and aldrin is at the collision limit and not influenced by adsorption. *Arrow* for mirex indicates no reactivity for this POP. *HCB* hexachlorbenzol, *Hexa-PCB* 2,2′,4,4′,6,6′-hexachlorobiphenyl, *Hexa-BDE* 2,2′,4,4′,6,6′-hexabromodiphenylether, *Tetra-DBF* 1,2,6,7-tetrachlorodibenzofuran, *TCDD* tetrachlordibenzodioxin

the KOA-model (which describes an absorption in a volume) and the Junge- and Mackay model (which describe an adsorption on a surface) leads to comparable values. However, for TCDD, mirex, DDT, and aldrin, differences of more than a factor of 10 are found.

The influence of the adsorbed fraction on the OH-rate constant of selected POPs for T = 298 K is shown in Fig. 9.7. Therefore the estimated OH-rate constant (data Table 9.12) is reduced by the factor 1- Θ, with Θ as the adsorbed fraction calculated from the Junge model (vapour pressures are given in Table 9.11). Only for a few compounds (2,2′,4,4′,6,6′-hexachlorobiphenyl, tetrachlordibenzodioxin, DDT, benzo[a]pyrene) the OH-radical reactivity is influenced due to adsorption processes at 298 K. The reactivity of mirex is practically zero in the gas phase.

However, the estimated OH-radical rate constant of aldrin and heptachlor is extremely high at 298 K (see Table 9.12) and from the Junge-model for both compounds the adsorption on surfaces is negligible. Hence, on the basis of these criteria, both compounds are, with respect to reactivity and adsorption, not POPs.

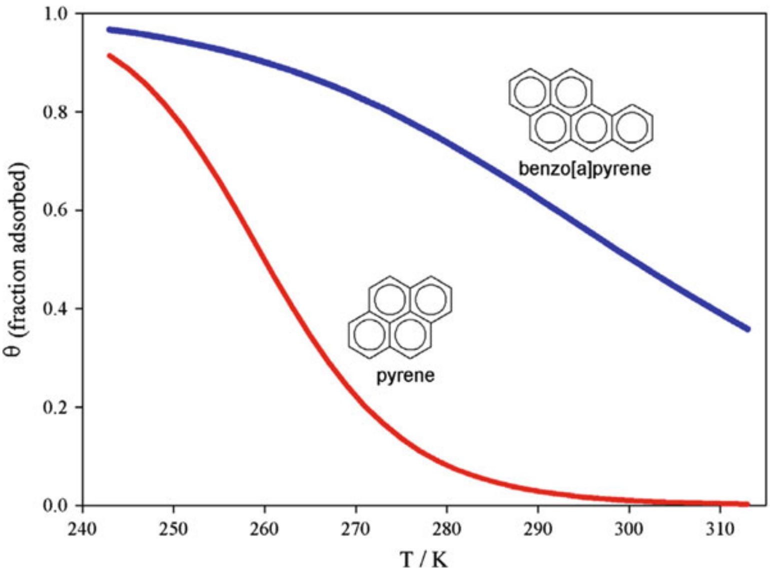


Fig. 9.8 Temperature dependent adsorbed fraction of benzo[a]pyrene and pyrene calculated from the K_{OA}-model. Temperature dependent KOA-data were taken from (Harner and Bidleman 1998)

The assessment of aldrin using these simple criteria is in accord with model calculations (ELPOS-model) (Beyer and Matthies 2001).

However, using temperature-dependent parameters such as the KOA the corresponding calculated absorbed fraction (using KOA absorption in a volume will be calculated) strongly increases with decreasing temperature. A comparison of the absorbed fraction of benzo[a]pyrene and pyrene from KOA data published in (Harner and Bidleman 1998) is shown in Fig. 9.8. Using this model, about 50% of benzo[a]pyrene is adsorbed even at room temperature in aerosols, whereas pyrene is almost completely in the gas phase. However, at −20°C benzo[a]pyrene is almost completely absorbed and pyrene is absorbed by about 80%.

9.3.4 Lifetimes of POP in the Atmosphere

Regarding the problems concerning reactivity and adsorbed or absorbed fractions as outlined above the lifetimes of POPs in the atmosphere are highly uncertain. Reactivities of POPs have to be compared with persistence criteria defined from threshold values (i.e., half-lives) in the Stockholm Convention of $t_{½} > 2$ months in water, $t_{½} > 6$ months in soil and sediment and $t_{½} > 2$ days in air. For rough estimations of half-lives of POPs from a gas-phase reaction with OH radicals a single, global mean OH-radical concentration of $c_{OH} = 1 \times 10^{6}\ \text{cm}^{-3}$ can be used (general discussion in Prinn et al. 1987; Spivakovsky et al. 1990; Lu and

Table 9.3 Rate constants of POPs in soil (k_S), water (k_W) and air (k_A) (Scheringer 2002) and the corresponding half-lives (in days) for the compartment air (From Scheringer 2002)

Compound	k_S (soil) (10^{-8} s^{-1})	k_W (water) (10^{-8} s^{-1})	k_A (air) (10^{-8} s^{-1})	$t_{½}$ (air) (days)	$T_{½}$ (air)[a] (days)
Aldrin	5.18	7.20	6,730	0.12	0.12
Chlordane	1.12	0.998	1,170	0.69	1.6
DDT	0.573	4.16	344	2.3	2.4
DDE	0.495	29.1	344	2.3	1.1
Dieldrin	1.29	1.85	1,510	0.53	0.87
Endrin	2.42	0.295	13,300	0.06	0.87
HCB	0.564	0.564	1.62	495	472
Heptachlor	3.80	192	6,150	0.13	0.13
α-HCH	13.4	13.7	282	2.8	14.1
γ-HCH	3.85	36.5	308	2.6	14.1
Mirex	0.129	5.36	0.0176	45,600	∞
PCB-8	1.13	3,50	88.3	9.1	4.7
PCB-101	0.35	0.35	10.4	77	27
PCB-194	0.35	0.35	1.13	710	134
TCDD	0.664	8.33	524	1.5	11

Rate constants based on estimated OH-rate constants. Influence of aerosols is not considered. For mirex the rate constant describes not a chemical reaction but the transfer into the stratosphere

[a]For comparison, half-lives in air were calculated from data in Table 9.8 and additional data as discussed in the text

Khalil 1991, an overview of global values and the problems in the definition of such a value is given in Lawrence et al. 2001).

Representative values of monoexponential rate constants of POPs in soil, water and air (with corresponding half-lives for reactions in the air), taken from Scheringer (2002) and for comparison rate-constants in air calculated from the estimated OH-rate constants summarized in Table 9.12 are shown in Table 9.3. Besides OH-rate constants of compounds already given in Table 9.12 additional OH-rate constants for PCB-8 = 2,4′-dichlorobiphenyl ($k_{OH} = 1.7 \times 10^{-12}$ cm^{-3}), PCB-101 = 2,2′,4,5,5′-pentachlorobiphenyl ($k_{OH} = 3 \times 10^{-13}$ cm^{-3}), PCB-194 = 2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl ($k_{OH} = 6 \times 10^{-14}$ cm^{-3}) and DDE ($k_{OH} = 7.4 \times 10^{-12}$ cm^{-3}) and a mean OH-concentration of $c_{OH} = 1 \times 10^{-6}$ cm^{-3} for the calculation of k_A was used. OH-rate constants were estimated from the EPI-Suite programme EPA (2007).

Comparison of rate constants k_A given in Table 9.3 from Scheringer (2002) and calculated from Table 9.12 should serve as an example of obvious differences due to at least different OH-concentrations and different estimated (!) rate constants for otherwise comparable data sets. It has to be emphasized that the author of the data summarized in Table 9.3 explicitly states an uncertainty of at least a factor of 10 and data “should not be cited as a reference for POPs properties” Scheringer (2002).

However, the aspect of adsorption (or absorption) and the influence of the aqueous phase (as an integral part of aerosols) are totally disregarded for the data given in Table 9.3. Thus, considering the unknown impact of surfaces in general and of aerosols in particular, especially under environmental conditions, lifetimes of POPs in the atmosphere are still highly uncertain or even unknown.

9.4 Conclusions

- POPs are compounds with low water solubility, low vapour pressure and high K_{OW}. Up to now, these properties significantly complicate measurements and prevent the assessment of degradation reactions of POPs.
- Our knowledge of degradation reactions on surfaces (i.e., aerosols or suspended particles) in particular is limited.
- Nevertheless, different experimental setups are available to investigate degradation reactions of POPs.
- However, to transfer results to the environment, care has to be taken to use suitable conditions in the laboratory (e.g., organic solvents are bad models).

Appendix

This appendix summarizes quantum yields and rate constants for complex organic molecules. The compilation should serve as an overview of the dynamics in both parameters and makes no claim to completeness. For complex organic compounds with low vapour pressure, only a very few quantum yields are known in the gas phase, most values were therefore determined in solution. Rate constants are given for the reaction with OH-radicals, nitrate radicals and ozone in solution (predominantly in the aqueous phase), in the gas phase and adsorbed on aerosols.

Quantum Yields

See Tables 9.4 and 9.5

Photolysis-Rate Constants of Pesticides in the Gas Phase

See Table 9.6

Rate Constants for the Reaction with OH- and Nitrate Radicals and Ozone

See Tables 9.7–9.10

Properties of Selected POPs

See Table 9.11

Rate Constants of OH-Radicals and of Ozone and Adsorbed Fractions of Selected POPs

See Table 9.12

Table 9.4 Quantum yields Φ of complex organic molecules

Compound	Wavelength (nm)	Solvent	Φ	Reference
Acenaphthene	Poly	Water	0.009	Fasnacht and Blough (2003)
Acridine	Sun	Water	3.93×10^{-5}	Wiegman et al. (1999)
Acridine	300/350	Water	139.9/ 0.20×10^{-5}	Wiegman et al. (1999)
Anthracene	313	Water	0.003	Schwarzenbach et al. (1993)
Anthracene	Poly	Water	0.0042	Fasnacht and Blough (2003)
Anthracene	366	Water	0.0042	Zepp and Schlotzhauer (1997)
Benzo[a]acridine	300/350	Water	3.32/ 0.07×10^{-5}	Wiegman et al. (1999)
Benzo[c]acridine	300/350	Water	4.46/ 0.1×10^{-5}	Wiegman et al. (1999)
Benzo[a]anthracene	313/366	Water	0.0032/0.0034	Mill et al. (1981b)
1,2-Benzanthracene	313,366, sun	1% CH_3CN	0.0032	Schwarzenbach et al. (1993)
Benzo[b]fluoranthene	Poly	Water	0.00013	Fasnacht and Blough (2003)
Benzo[k]fluoranthene	Poly	Water	0.00014	Fasnacht and Blough (2003)
Benzo[a]pyrene	Poly	Water	0.0054	Fasnacht and Blough (2003)
Benzo[a]pyrene	313/366	Water	0.00089/ 0.00054	Mill et al. (1981)
Benzo(a)pyrene	313, 366, sun	1–20% CH_3CN	0.00089	Schwarzenbach et al. (1993)
BDE-3	Poly	THF	0.35	Palm et al. (2004)
BDE-15	Poly	THF	0.30	Palm et al. (2004)
BDE-28	Poly	THF	0.47	Palm et al. (2004)
BDE-47	Poly	THF	0.49	Palm et al. (2004)
BDE-99	Poly	THF	0.49	Palm et al. (2004)

(*continued*)

Table 9.4 (continued)

Compound	Wavelength (nm)	Solvent	Φ	Reference
BDE-153	Poly	THF	0.50	Palm et al. (2004)
hepta-BDE	Poly	THF	0.21	Palm et al. (2004)
octa-BDE	Poly	THF	0.29	Palm et al. (2004)
nona-BDE	Poly	THF	0.31	Palm et al. (2004)
BDE-209	Poly	THF	0.38	Palm et al. (2004)
BDE-209	Poly	THF	0.29	Palm et al. (2004)
BDE-209	Sun	Hexane	0.47	Bezares-Cruz et al. (2004)
Bromiodomethane	Sun	Water	0.17	Jones and Carpenter (2005)
Chloral (CH_3CHO)	Sun	Air	1.00	Wenger et al. (2004)
Chlorobenzene	Sun	Water	0.09–0.29	Mansour et al. (1989)
2-Chlorobiphenyl	Sun	Water	0.021	Mansour et al. (1989)
4-Chlorobiphenyl	Sun	Water	0.00025	Mansour et al. (1989)
Chloroiodomethane	Sun	Water	0.26	Jones and Carpenter (2005)
p-Chlorophenole	Sun	Water	0.0042	Mansour et al. (1989)
3-Cresole	254	Water	0.057	Wan et al. (1994)
Chrysene	Poly	Water	0.0025	Fasnacht and Blough (2003)
Chrysene	313	Water	0.0028	Zepp and Schlotzhauer (1997)
DDE	Sun	Water	0.75	Mansour et al. (1989)
p,p′-DDE	313	Water	0.3	Zepp et al. (1977)
p,p′-DDE	Poly	Water	0.14	Draper (1985)
Dibenzo[a,i]acridine	300	Water	0.00117	Wiegman et al. (1999)
Dibenzo[c,h]acridine	300/350	Water	$48.59/1.51 \times 10^{-5}$	Wiegman et al. (1999)
3,4-Dichloraniline	313, poly	pH 7–10	0.044	Schwarzenbach et al. (1993)
3,4-Dichloraniline	290	Buffer pH = 7	0.052	Skurlatov et al. (1983)
3,5-Dichloraniline	313, sun	pH 4–10	0.052	Schwarzenbach et al. (1993)
1,4-Dichlorobenzene	Sun	Water	0.017	Mansour et al. (1989)
Diiodomethane	Sun	Water	0.61	Jones and Carpenter (2005)
4,6-Dinitro-o-cresole	254	Water	0.00048	Wan et al. (1994)
2,4-Dinitrotoluene	313		0.0020	Schwarzenbach et al. (1993)
DMDE	313	Water	0.3	Zepp et al. (1977)
Fluoranthene	Poly	Water	3.2×10^{-5}	Fasnacht and Blough (2003)
Fluoranthene	313/366	Water	$5.7/0.1 \times 10^{-5}$	Zepp and Schlotzhauer (1997)
Fluoranthene	Sun	Water	1.33×10^{-5}	Wiegman et al. (1999)
Fluoranthene	300/350	Water	$12/0.2 \times 10^{-5}$	Wiegman et al. (1999)
Fluorene	Poly	Water	0.0033	Fasnacht and Blough (2003)
1-Hydroxypyrene	Poly	Water (+oxygen)	0.00277	Sigman et al. (1998)

(*continued*)

Table 9.4 (continued)

Compound	Wavelength (nm)	Solvent	Φ	Reference
Isoquinoline	300/350	Water	196.1/ 5.95×10^{-5}	Wiegman et al. (1999)
Naphthalene	313	Water	0.015	Schwarzenbach et al. (1993)
p-Nitroanisole	366	Water	0.00039	Dulin and Mill (1982)
p-Nitroanisole	Poly	On Kaolinit	$1.4–1.8 \times 10^{-4}$	Ciani et al. (2005)
p-Nitroanisole	355	On Kaolinit	$6.8–9 \times 10^{-4}$	Ciani et al. (2005)
Nitrobenzene	313	Water	2.9×10^{-5}	Schwarzenbach et al. (1993)
2-Nitrophenole	254	Water	0.002	Wan et al. (1994)
3-Nitrophenole	254	Water	0.00019	Wan et al. (1994)
4-Nitrophenole	313, poly	pH 2–4	0.00011	Schwarzenbach et al. (1993)
4-Nitrophenolate	365, poly	pH 9–10	8.1×10^{-6}	Schwarzenbach et al. (1993)
Nitrotoluene	366	Water	0.0052	Schwarzenbach et al. (1993)
PCB-40	300	Cyclohexane	0.007	Ruzo et al. (1974)
PCB-47	300	Cyclohexane	0.1	Ruzo et al. (1974)
PCB-52	300	Cyclohexane	0.01	Ruzo et al. (1974)
PCB-54	300	Cyclohexane	0.006	Ruzo et al. (1974)
PCB-77	300	Cyclohexane	0.005	Ruzo et al. (1974)
PCB-80	300	Cyclohexane	0.002	Ruzo et al. (1974)
1,2,3,7-PCDD	313	Water/ acetonitrile	0.000542	Choudhry and Webster (1989)
1,3,6,8-PCDD	313	Water/ acetonitrile	0.00217	Choudry and Webster (1989)
2,3,7,8-PCDD	313	Water/ acetonitrile	0.0022	Choudry and Webster (1989)
1,2,3,4,7-PCDD	313	Water/ acetonitrile	9.78×10^{-5}	Choudry and Webster (1989)
1,2,3,4,7,8-PCDD	313	Water/ acetonitrile	0.00011	Choudry and Webster (1989)
1,2,3,4,6,7,8-PCDD	313	Water/ acetonitrile	1.53×10^{-5}	Choudry and Webster (1989)
Octachloro-PCDD	313	Water/ acetonitrile	2.26×10^{-5}	Choudry and Webster (1989)
Pentachlorophenolate	313, poly	pH 8–10	0.013	Schwarzenbach et al. (1993)
Perylene	Poly	Water	0.00054	Fasnacht and Blough (2003)
Phenanthrene	Poly	Water	0.0035	Fasnacht and Blough (2003)
Phenanthrene	313	Water	0.010	Zepp and Schlotzhauer (1997)
Phenanthrene	313	Water	0.01	Schwarzenbach et al. (1993)
Phenanthridine	300/350	Water	112.3/ 3.46×10^{-4}	Wiegman et al. (1999)
Phenole	254	Water	0.021	Wan et al. (1994)
Pyrene	Poly	Water	0.009	Fasnacht and Blough (2003)

(*continued*)

Table 9.4 (continued)

Compound	Wavelength (nm)	Solvent	Φ	Reference
Pyrene	313/366	Water	0.002/0.0022	Zepp and Schlotzhauer (1997)
Pyrene	Poly	Water (+oxygen)	0.00211	Sigman et al. (1998)
Pyrene	Poly	Water (−oxygen)	0.000519	Sigman et al. (1998)
Pyridine	Sun	Water	$6.7–13 \times 10^{-4}$	Mansour et al. (1989)
Quinoline	300/350	Water	$211.8/0.33 \times 10^{-5}$	Wiegman et al. (1999)
2,4,6-Trinitrotoluene	313,366, sun		0.0021	Schwarzenbach et al. (1993)
Triphenyl phosphate	254	Water	0.29	Wan et al. (1994)

Sun polychromatic irradiation by sun light, *poly* polychromatic irradiation in the lab with $\lambda > 290$ nm

Temperatures are in the range of 298 K (±5°C)

Table 9.5 Quantum yields Φ of pesticides

Compound	λ (nm)	Solvent	Φ	Reference
Ametryne	Poly	Water 5% CH_3CN	0.043	Palm and Zetzsch (1996)
Atratone	Poly	Water	<0.002	Palm and Zetzsch (1996)
Atrazine	254	Water	0.05	Nick et al. (1992)
Atrazine	254	Water	0.051	Tace et al. (1992)
Atrazine	254	Water	0.038	Hessler et al. (1993)
Atrazine	Poly	pH 9	0.061	Palm and Zetzsch (1996)
Atrazine	Poly	Acetonitrile	0.026	Palm and Zetzsch (1996)
Carbaryl	313	Water	0.006	Zepp (1978)
Carbomethoxyfenitrothione	254	Water	0.00084	Wan et al. (1994)
Chlorthalonile	Poly	Acetonitrile	7×10^{-5}	Hüskes and Palm (1995)
Bromoxynil	Poly	Water + 0.5% CH_3CN	0.0093	Millet et al. (1998a)
Carbaryl	313	Water	0.006	Roof (1982)
Chloronyxil	Poly	pH 3.5,7,9, water + 0.5% CH_3CN	0.0026–0.006	Millet et al. (1998a)
Chloropyrifos	254/313	Water	0.016/0.052	Wan et al. (1994)
Chloropyrifos-methyl	254/313	Water	0.013/0.040	Wan et al. (1994)
Chlorthalonil	Poly	Water + 7% CH_3CN	0.00011	Millet et al. (1998a)
Chlortolurone	Poly	Acetonitrile	0.045	Millet et al. (1998b)
Chlortolurone	Poly	Hexane	0.41	Millet et al. (1998b)

(*continued*)

Table 9.5 (continued)

Compound	λ (nm)	Solvent	Φ	Reference
Chlortolurone	Poly	pH 4,7,9 + 0.5% CH_3CN	0.055–0.092	Millet et al. (1998b)
Coumaphos	254	Water	0.0027	Wan et al. (1994)
Cyanazine	Poly	Water	0.051	Palm (2010)
2,4-D, Methylester			0.13	Zepp et al. (1975)
2,4-D, Methylester	313	pH 6.6	0.031	Zepp et al. (1975)
2,4-D, Buthoxyethylester	313	pH 6	0.054	Zepp et al. (1975)
DDT	254	Hexane	0.16	Mosier and Miller (1969)
Diazinon	254/313	Water	0.082/0.012	Wan et al. (1994)
EPN	254/313	Water	0.0081/0.0070	Wan et al. (1994)
Fenchlorfos	254	Water	0.71	Wan et al. (1994)
Fenitrothion	254/313	Water	0.0091/0.0031	Wan et al. (1994)
Fenpyroximate	poly	Water	0.075	Swanson et al. (1995)
Fensulfothion	254	Water	0.049	Wan et al. (1994)
Fenthion	254	Water	0.092	Wan et al. (1994)
Imazethapyr	Poly	Water	0.023	Avila et al. (2006)
Ioxynil	Poly	pH 3.5, 7, 9, water + 0.5% CH_3CN	0.0024	Millet et al. (1998a)
Isofenphos	254	Water	0.068	Wan et al. (1994)
Isoproturone	Poly	pH 4, 7, 9 + 0.5% CH_3CN	0.004	Millet et al. (1998b)
MCPA	254	Water	0.53	Saborit (1986); Soley et al. (1986)
Metamitron	Poly	pH 4, 9, water	0.018	Palm et al. (1997b)
Metam-Sodium	Poly	Water	0.36	Draper and Wakehamt (1993)
Mefenpyrdiethyl	Poly	Water	8.8×10^{-5}	Palm et al. (2007)
Metolachlor	313	pH 7	3.0×10^{-5}	Kochany and Maguire (1994)
Metoxychlor	Poly	Water	0.28	Draper (1985)
Metoxychlor	Poly	Water	0.3	Zepp et al. (1976)
Parathion	300	pH 6.4	0.0015	Draper (1985)
Parathion-methyl	Poly	Water	0.00067	Draper (1985)
Parathion-methyl	254/313	Water	0.00043/0.00017	Wan et al. (1994)
Parathion-ethyl	254	pH 4.6–9.6	0.0016–0.007	Gal et al. (1992)
Phenmedipham	263	Water	0.014	Mansour et al. (1989)
Picloram	Sun	Buffer pH = 7	0.066	Skurlatov et al. (1983)
Pirimicarb	Sun	Water	0.075	Pirisi et al. (1996)
Prometryn	Poly	Water	0.040	Palm (2010)
Propazine	254	Water	0.099	Nick et al. (1992)
Propazine	Poly	Water + 5% CH_3CN	0.048	Palm and Zetzsch (1996)
Prothiofos	254	Water	1.1	Wan et al. (1994)
Pyridaphenthion	254/313	Water	0.00032/0.00010	Wan et al. (1994)
Simazine	254	Water	0.083	Nick et al. (1992)

(*continued*)

Table 9.5 (continued)

Compound	λ (nm)	Solvent	Φ	Reference
Simazine	Poly	pH 9 + 5% CH_3CN	0.060	Palm and Zetzsch (1996)
2,4,5-T	290	Buffer pH = 7	0.015	Skurlatov et al. (1983)
Terbuthylazine	254	Water	0.094	Nick et al. (1992)
Terbuthylazine	Poly	pH 7, 1% CH_3CN	0.062	Palm and Zetzsch (1996)
Terbuthylazine	Poly	Acetonitrile	0.033	Palm and Zetzsch (1996)
Terbuthylazine	poly	Hexane	0.027	Palm and Zetzsch (1996)
Tolclofos	254	Water	0.017	Wan et al. (1994)
Trifluralin	366	Water	0.002	Zepp and Cline (1977)
Trifluralin	Poly	On Kaolinit	0.00019–0.00022	Ciani et al. (2005)
Trifluralin	420–460	On Kaolinit	7–16 × 10^{-5}	Ciani et al. (2005)
Trifluralin	Poly	Water	0.002	Draper (1985)
Triphenyltin hydroxide	Poly	Water	1.25	Palm et al. (2003)
Trinexapac	Poly	pH 7	0.00037	Palm (2010)

λ – excitation wavelength, *poly* polychromatic irradiation with $\lambda > 290$ nm
Temperatures in the range of 298 K (±5°C)

Table 9.6 Rate constants of direct photolysis of pesticides in the gas phase (Data from Atkinson et al. 1999)

Compound	k/s^{-1}
Trifluralin	≈3–6 × 10^{-4}
Phorate	≈2 × 10^{-3}
Parathion	≈2 × 10^{-3}
Chloropicrin	≈5.7 × 10^{-5}
Methyl isothiocyanate	≈6.7 × 10^{-6}

In some cases (e.g., trifluralin) OH-radical reactivity could not be excluded. Rate constants are valid for summer months around midday at latitudes of about 40°. Temperatures in the range of room temperature

Table 9.7 Rate constants of complex molecules with OH– and nitrate radicals and with ozone in the gas phase

Compound	k_{OH}	k_{NO3} ($cm^3\ s^{-1}$)	k_{O3}	Reference
Acenaphthene	5.8 × 10^{-11}	–		Brubaker and Hites (1998a)
Anthracene	11 × 10^{-11} (325 K)	–	–	Biermann et al. (1985)
Anthracene	19 × 10^{-11}	–		Brubaker and Hites (1998b)
Anthracene	18 × 10^{-11}	–		Ananthula and Taylor, (2006)
Biphenyl	8.5 × 10^{-12}	–	–	Atkinson and Aschmann (1985)
Bromobenzene	9.15 × 10^{-13}	–		Wallington et al. (1987)
Chlorobenzene	7.41 × 10^{-13}	–		Wallington et al. (1987)
Diphenylether	9.6 × 10^{-12}	–	–	Kwok et al. (1995)
Diphenylether	7.45 × 10^{-12}	–	–	Raff and Hites (2006)

(*continued*)

Table 9.7 (continued)

Compound	k_{OH}	k_{NO3} ($cm^3\ s^{-1}$)	k_{O3}	Reference
Dibenzofuran	3.9×10^{-12}	$<1.6 \times 10^{-15}$	$<8 \times 10^{-20}$	Kwok et al. (1994)
Dibenzofuran	3.5×10^{-12}	–	–	Brubaker and Hites (1998b)
Fluoranthene	1.1×10^{-11}	–		Brubaker and Hites (1998b)
Fluorene	1.3×10^{-11}	–		Brubaker and Hites (1998b)
Fluorobenzene	6.31×10^{-13}	–		Wallington et al. (1987)
Fluorobenzene	8.17×10^{-13}	–		Ohta and Ohyama (1985)
Iodobenzene	1.32×10^{-12}	–		Wallington et al. (1987)
Naphthalene	2.35×10^{-11}	–	$<3 \times 10^{-19}$	Biermann et al. (1985) Atkinson and Aschmann (1986)
Naphthalene	2.3×10^{-11}	–		Brubaker and Hites (1998b)
2-Methylnaphthalene	5.23×10^{-11}	–	$<4 \times 10^{-19}$	Atkinson and Aschmann (1986)
2,3-Dimethylnaphthalene	7.68×10^{-11}	–	$<4 \times 10^{-19}$	Atkinson and Aschmann (1986)
Phenanthrene	3.4×10^{-11}	–	–	Biermann et al. (1985)
Phenanthrene	2.7×10^{-11}	–		Brubaker and Hites (1998b)
2-PCB	2.9×10^{-12}	–	–	Atkinson and Aschmann (1985)
2-PCB	2.7×10^{-12}	–	–	Anderson and Hites (1996)
3-PCB	5.4×10^{-12}	–	–	Atkinson and Aschmann (1985)
3-PCB	5.0×10^{-12}	–	–	Anderson and Hites (1996)
4-PCB	3.9×10^{-12}	–	–	Atkinson and Aschmann (1985)
4-PCB	3.4×10^{-12}	–	–	Anderson and Hites (1996)
2,2′-PCB	2.2×10^{-12}	–	–	Anderson and Hites (1996)
2,2′-PCB	2.0×10^{-12}	$<8 \times 10^{-12}$	$<2 \times 10^{-20}$	Kwok et al. (1995)
3,3′-PCB	4.1×10^{-12}	–	–	Kwok et al. (1995)
3,5-PCB	4.2×10^{-12}	–	–	Kwok et al. (1995)
4,4′-PCB	2.0×10^{-12}	–	–	Anderson and Hites (1996)
2,4-PCB	2.6×10^{-12}	–	–	Anderson and Hites (1996)
2,4,4′-PCB	1.1×10^{-12}	–	–	Anderson and Hites (1996)
2,4,5-PCB	1.3×10^{-12}	–	–	Anderson and Hites (1996)
2,4′,5-PCB	1.2×10^{-12}	–	–	Anderson and Hites (1996)
2′,3,4-PCB	1.0×10^{-12}	–	–	Anderson and Hites (1996)
2,2′,3,5′-PCB	8×10^{-13}	–	–	Anderson and Hites (1996)

(*continued*)

Table 9.7 (continued)

Compound	k_{OH}	k_{NO3} ($cm^3\ s^{-1}$)	k_{O3}	Reference
2,2′,4,4′-PCB	1.0×10^{-12}	–	–	Anderson and Hites (1996)
2,2′,3,5′,6-PCB	4×10^{-13}	–	–	Anderson and Hites (1996)
2,3,3′,4′,6-PCB	6×10^{-13}	–	–	Anderson and Hites (1996)
2,3,4,5,6-PCB	9×10^{-13}	–	–	Anderson and Hites (1996)
2-Bromodiphenyl ether	4.7×10^{-12}	–	–	Raff and Hites (2006)
3-Bromodiphenyl ether	4.6×10^{-12}	–	–	Raff and Hites (2006)
4-Dromodiphenyl ether	5.8×10^{-12}	–	–	Raff and Hites (2006)
2,4-Dibromodiphenyl ether	3.9×10^{-12}	–	–	Raff and Hites (2006)
3,3′-Dibromodiphenyl ether	3.2×10^{-12}	–	–	Raff and Hites (2006)
2,2′-Dibromodiphenyl ether	1.3×10^{-12}	–	–	Raff and Hites (2006)
4,4′-Dibromodiphenyl ether	5.2×10^{-12}	–	–	Raff and Hites (2006)
Dibenzo-p-dioxin	1.48×10^{-11}	$<8 \times 10^{-15}$	$<5 \times 10^{-20}$	Kwok et al. (1994)
Dibenzo-p-dioxin	1.2×10^{-11}	–		Brubaker and Hites (1998b)
2,8-Dichlorodibenzofuran	2.2×10^{-12}	–	–	Brubaker and Hites (1998b)
1-Chlorodibenzo-p-dioxin	4.7×10^{-12}	$<1.6 \times 10^{-14}$	$<7 \times 10^{-20}$	Kwok et al. (1995)
2,7-Dichlorodibenzo-p-dioxin	4.4×10^{-12}	–	–	Brubaker and Hites (1998b)
1,2,3,4-Tetrachloro-dibenzo-p-dioxin	8.5×10^{-13}	–	–	Brubaker and Hites (1997)

Temperatures are in the range of 298 K (±2°C)

Table 9.8 Rate constants of pesticides with OH- and nitrate radicals and with ozone in the gas phase (Discussion see Atkinson et al. 1999)

Compound	k_{OH}	k_{NO3} ($cm^{-3}\ s^{-1}$)	k_{O3}	Reference
Methyl bromide	2.9×10^{-14}	–	–	Atkinson et al. (1997)
1,2-Dibromo-3-chloropropane	4.4×10^{-13}	–	$<3 \times 10^{-20}$	Tuazon et al. (1986)
cis-1,3-Dichloropropane	8.4×10^{-12}	–	1.5×10^{-19}	Tuazon et al. (1984)
trans-1,3-Dichloropropane	1.4×10^{-11}	–	6.7×10^{-19}	Tuazon et al. (1984)
EPTC	3.2×10^{-11}	9.2×10^{-15}	$<1.3 \times 10^{-19}$	Kwok et al. (1992)
Cycloate	3.5×10^{-11}	3.3×10^{-14}	$<3 \times 10^{-19}$	Kwok et al. (1992)
α-HCH	1.4×10^{-13}	–	–	Brubaker and Hites (1998a)
γ-HCH	1.9×10^{-13}	–	–	Brubaker and Hites (1998a)
HCB	2.7×10^{-14}	–	–	Brubaker and Hites (1998a)
Phosphine	1.6×10^{-11}	–	–	Fritz et al. (1982)

Temperatures are in the range of 298 K (±5°C)

Table 9.9 OH-rate constants of pesticides in water (and some additional selected organic compounds, more data can be found in NIST 2007)

Compound	k_{OH}/ $10^9\ M^{-1}\ s^{-1}$	Method	Reference
2,4-D	1.6	Hydrogen peroxide	Mabury and Crosby (1996)
Alachlor	7	Estimation using ¾-values	Haag and Yao (1992)
Aldicarb	8.1	Fenton	Haag and Yao (1992)
Ametryn	26	Fenton + ozone	NDRL (2002)
Atrazine	2.6	Photo-Fenton	Haag and Yao (1992)
Atrazine	0.82	Hydrogen peroxide	Mabury and Crosby (1996)
Atraton	3.3	Fenton + ozone	NDRL (2002)
Carbaryl	5.0	Photo-Fenton	NDRL (2002)
Carbaryl	3.4	Hydrogen peroxide	Mabury and Crosby (1996)
Carbofuran	7	Estimation using ¾-values	Haag and Yao (1992)
Carbofuran	2.2	Hydrogen peroxide	Mabury and Crosby (1996)
Chlordane	0.06–17	Photo-Fenton	Haag and Yao (1992)
Cyanazine	1.9	Fenton + ozone	NDRL (2002)
2,4-D	1.6	Hydrogen peroxide	Mabury and Crosby (1996)
2,4-D	5	Estimation using ¾-values	Haag and Yao (1992)
Dalopon	0.073	Photo-Fenton	Haag and Yao (1992)
Dinoseb	4	Estimation using ¾-values	Haag and Yao (1992)
Diquat	0.8	Fenton	Haag and Yao (1992)
Endrin	0.27–1.3	Fenton and photo-Fenton	Haag and Yao (1992)
Glyphosate	0.18	Photo-Fenton	Haag and Yao (1992)
Hexazinon	0.62	Hydrogen peroxide	Mabury and Crosby (1996)
Imazethapyr	7.8	Hydrogen peroxide	Avila et al. (2006)
Lindane	5.2–1.1	Fenton	Haag and Yao (1992)
MCPA	1.7	Hydrogen peroxide	Mabury and Crosby (1996)
Mefenpyrdiethyl	7.6	Sodium nitrate	Palm et al. (2007)
Methoxychlor	2	Estimation using ¾-values	Haag and Yao (1992)
Molinat	0.85	Hydrogen peroxide	Mabury and Crosby (1996)
Naphthalene	5–12	Pulse radiolysis	NDRL (2002)
PAHs	10	Estimation using ¾-values	Haag and Yao (1992)
Penta-PCB (2,3,3,′,5,6)	5	Estimation using ¾-values	Haag and Yao (1992)
Hexa-PCB (2,2′,4,4,′,5,5′)	6	Estimation using ¾-values	Haag and Yao (1992)
Pentachlorophenol	4	Estimation using ¾-values	Haag and Yao (1992)
Pentachlorophenoxy anion	1.1–3.7	Pulse radiolysis	NDRL (2002)
Picloram	3.4	Fenton	Haag and Yao (1992)
Picloram	1.3	Hydrogen peroxide	Mabury and Crosby (1996)
Propanil	1.6	Hydrogen peroxide	Mabury and Crosby (1996)
Propazine	1.8	Fenton + ozone	NDRL (2002)
Quinclorac	0.36	Hydrogen peroxide	Mabury and Crosby (1996)
Simazine	2.8	Photo-Fenton	Haag and Yao (1992)
2,4,5-T	4	Estimation using ¾-values	Haag and Yao (1992)
2,3,7,8-TCDD	4	Estimation using ¾-values	Haag and Yao (1992)
Toxaphene	0.012–0.81	Fenton	Haag and Yao (1992)
Triphenyltin hydroxide	9.4	Sodium nitrate	Palm et al. (2003)

Temperatures in the range of 298 K (±5°C)

Table 9.10 Rate constants of pesticides with OH-radicals and with ozone in the adsorbed state

Compound	k_{OH}	k_{O3} (cm $^{-3}$ s^{-1})	Comment	Reference
Aldrin	In progress	–	$T < 279.5$ K, remark A	Palm et al. (2004)
DDT	$(0.5–5) \times 10^{-12}$	–	$T = 280.5$ K, remark A	Liu et al. (2005)
BDE-153	$\approx 1.8 \times 10^{-12}$	–	$T = 280.5$ K, remark A	Zetzsch et al. (2004)
Dicofol	2×10^{-12}	–	$T = 280.5$ K, remark A	Liu et al. (2005)
Isoproturone	1.2×10^{-11}	–	$T = 298$ K, remark B	Palm et al. (1998)
Lindane	6.0×10^{-13}	–	$T = 298$ K, remark A	Zetzsch (1991a)
Pyrifenox	1.8×10^{-11}	$<5 \times 10^{-19}$	$T = 298$ K, remark A	Palm et al. (1999)
Simazine	1.1×10^{-11}	–	$T = 298$ K, remark B	Palm et al. (1998)
Terbuthylazine	1.1×10^{-11}	$<5 \times 10^{-19}$	$T = 298$ K, remark A	Palm et al. (1997a)
Terbuthylazine	5.3×10^{-12}	–	$T = 279.5$ K, remark A	Palm et al. (2004)

Remarks: *A* silicon dioxide, aerosol; *B* silicon dioxide, filter samples

Table 9.11 Physical properties of some POPs

Compound	Mol.mass (g mol^{-1})	Log k_{OW}	K_H (Pa m^3 mol^{-1})	L (water) (g L^{-1})	p (Pa)
Aldrin	364.92	6.50	5.03×10^1	$17–180 \times 10^{-6}$	5.0×10^{-3}
Chlordane	409.78	5.54	4.91	65×10^{-6}	1.1×10^{-3}
DDT	354.49	5.98	2.77	$1.2–5.5 \times 10^{-6}$	1.3×10^{-5}
Dieldrin	380.91	4.32	5.88	140×10^{-6}	5.0×10^{-4}
Endrin	380.92	4.56	7.74×10^{-1}	$220–260 \times 10^{-6}$	4.0×10^{-4}
HCB	284.78	5.31	1.32×10^2	40×10^{-6}	2.5×10^{-3}
Heptachlor	373.32	5.27	1.55	180×10^{-6}	5.3×10^{-2}
Lindane	291.0	3.61	2.96×10^{-1}	7×10^{-3}	7.4×10^{-3}
Mirex	545.5	6.89	7.10×10^1	3×10^{-6}	1.3×10^{-4}
Hexa-PCB	360.9	6.80	3.00×10^1	$0.4–0.7 \times 10^{-6}$	1.0×10^{-4}
TCDD	322.0	6.50	1.00	0.06×10^{-6}	2.0×10^{-7}
Toxaphene	413.82	4.80	6.10×10^{-1}	550×10^{-6}	8.9×10^{-4}

Log K_{OW} = octanol–water coefficient, K_H = Henry's Law constant and p = vapour pressure from Scheringer (2002)

L (water) = solubility in water from Ritter et al. (1995)

Solubilities of TCDD and Mirex were calculated from the Henry's Law constant; solubility of Lindane from Industrieverband Agar (1990). All data are valid for T = 20–25°C

HCB hexachlorobenzene, *Hexa – PCB* 2,2′,4,4′,6,6′- Hexachloro – biphenyl, *TCDD* Tetrachlorodibenzodioxin

Table 9.12 Rate constants estimated by the EPI-Suite programme (EPA 2007) for the reaction by OH-radicals (k_{OH}) and by ozone (k_{O3}) for selected POPs

Compound	k_{OH} (10–12 cm^3 s^{-1})	k_{O3} (10^{-17} cm^3 s^{-1})	Φ (Junge)	Φ (Mackay)	Φ (KOA)
Aldrin	65	20	0.0001	0.0001	0.002
Chlordane	5.0	0.0036	0.01	0.03	0.02
Dieldrin	9.2	0.0036	0.003	0.006	0.003
Endrin	9.2	0.0036	0.003	0.006	0.003

(*continued*)

Table 9.12 (continued)

Compound	k_{OH} (10–12 cm^3 s^{-1})	k_{O3} (10^{-17} cm^3 s^{-1})	Φ (Junge)	Φ (Mackay)	Φ (KOA)
Heptachlor	61	20	0.0004	0.0009	0.0009
Toxaphene	2.3	Neg.	0.04	0.08	0.05
Mirex	0.0	Neg.	0.06	0.11	0.005
DDT	3.4	Neg.	0.43	0.63	0.11
HCB	0.017	Neg.	0.0004	0.0009	0.0005
Hexa-PCB	0.40	Neg.	0.004	0.009	0.02
TCDD	0.75	Neg.	0.48	0.67	0.18
Tetra-DBF	0.25	Neg.	0.04	0.08	0.06
Hexa-BDE	0.50	Neg.	0.81	0.91	1.00
Lindane	0.57	Neg.	0.003	0.007	0.01
Benzo[a]pyrene	50	Neg.	0.82	0.91	0.59

Rate constants are valid for T = 25°C. Adsorbed (or absorbed) fractions using three models (Φ (Junge), Φ (Mackay), Φ (K_{OA})) are valid for T = 20–25°C and taken from the EPI-Suite programme (EPA 2007)

HCB hexachlorbenzol, *Hexa-PCB* 2,2′,4,4′,6,6′-hexachlorobiphenyl, *Hexa – BDE* 2,2′,4,4′,6,6′ – hexabromodiphenylether, *Tetra-DBF* 1,2,6,7 – tetrachlorodibenzofuran, *TCDD* Tetrachlordibenzodioxin

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Chapter 10
Determination of Atmospheric Volatile and Semi-volatile Compounds

Ravindra Khaiwal

10.1 Introduction

Volatile organic compounds (VOCs) are normally present in the vapor phase at room temperature (vapor pressure greater than 0.1 mmHg [0.0133 kPa] at 25°C). Compounds less volatile are known as semi-volatile organic compounds (SVOCs). SVOCs may be present in the atmosphere in the vapor phase, but are more normally associated with aerosol, either as dusts or liquid droplets (Lodge 1991; Kouimtzis and Samara 1995; Harper 2000). There is growing concern over the VOCs/SVOCs present in the atmosphere. Some of them play a major role in defining atmospheric chemistry and processes. Several short chain hydrocarbons affect the formation of ozone and other photochemical oxidants. Other VOCs/SVOCs play a role in stratospheric ozone depletion, tropospheric photochemical ozone formation and enhancement of the "greenhouse effect." Further, many of VOCs/SVOCs are known for their carcinogenic and mutagenic properties (Ravindra et al. 2001, 2008a). The World Health Organization has estimated that urban air pollution contributes each year to approximately 800,000 death and 4.6 million lost life-years worldwide (World Health Organization 2002). These consequences require a priority to identify and chemically characterize the atmospheric pollutants and especially those attached to the fine and ultra fine fraction of airborne particles (Ravindra et al. 2008b). This will help us to understand their possible implications for human health and also their environmental distribution and fate.

Volatile and semi-volatile species are ubiquitous in the atmosphere and to understand their role in various atmospheric processes, it is important to identify and quantify their actual levels and trends. Measurement of atmospheric VOCs/SVOCs is a difficult task as the concentration of VOCs/SVOCs in air fluctuates in both time and space. The measurement techniques must be designed to accommodate these fluctuations and to provide a result which can be used for the intended

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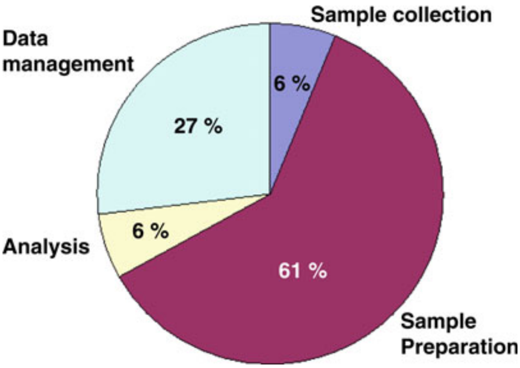


Fig. 10.1 Relative error of different steps for analytical procedure for organic compounds (Major 1995)

purpose. This requires several scientific and analytical skills to avoid, or at least compensate for, the errors in monitoring and/or during measurement.

Major (1995) describes the relative errors that can be introduced during various analytical steps (Fig. 10.1). The figure indicates that samples preparation is a critical step where chances of significant error may occur. Sample preparation includes extraction and purification steps, hence it is important to follow these steps with extra care. Furthermore, other steps should also be processed with full precaution and attention.

In this article, some of the basic concepts of sampling in order to monitor atmospheric VOCs/SVOCs are covered. Further, several sample preparation steps and extraction methods are described to give a choice for targeted organic compounds. Although special attention has been paid to a fast and robust extraction technique called pressurized liquid extraction (PLE), the article also covers some approaches towards cleanup and enrichment steps. Finally, the article focuses on the chromatographic analysis of targeted organic compounds and especially highlights some recent techniques such as low pressure-gas chromatography (LP-GC); proposed for fast screening of various organic compounds.

10.2 Site Selection

The first requirement of sampling is the site selection, which must be representative of an area under study. One should also identify the environmental population and area of interest. The sampling site for air pollutants must be located in such a way that the collected samples represent air actually breathed by the exposed population or for required modeling purposes. In the former case, the sampling site would therefor be ideally located at the breathing level height. Further, to get a representative sample, the sampler must not be positioned near a wall or other obstruction that would prevent the free air flow. Historical meteorological data is required to assess the prevailing wind direction and speed, temperature, relative humidity, rainfall, etc. A representative sampling site should also have availability of 24 h power supply and the facilities to protect the instrumentation.

10.3 Sampling

Sampling is an important step of any analytical procedure. The sample is the source of information about the environment. If it is not collected properly and if it does not represent the system accurately (we are trying to analyze); then all careful laboratory work will be useless (Kebbekus and Mitra 1998). Unlike water and soil samples, air is compressible and probably the most difficult matrix to sample. A liter of air does not fully describe the amount of air sampled and a complete description of the volume of air sampled includes the sample pressure, temperature, and volume. Each sampling methodology includes the following steps:

- The sampling plan
- Selection and preparation of sampling media
- Definite sampling process
- Transport and storage of the collected samples

The selection of optimal sampling method for target compounds depends on the physico-chemical nature of the targeted compounds and their expected concentrations in air. Sampling volume must be compatible with the sensitivity of the analysis method, and the expected behavior of the targeted compounds during each step of the sampling process must be carefully considered. Whole air sampling, collection in a solvent or on impregnated surfaces and chemisorption are the most common sampling method for volatile and semi-volatile organic compounds. These sampling techniques are defined briefly below and for more details reader are encouraged to read the detailed reviews on these topics by Camel and Caude (1995), Harper (2000), and Kumar and Víden (2007).

10.3.1 Whole Air Sampling

The simplest way to collect air samples is to use special pre-cleaned evacuated containers. The most widely used sampling vessels are flexible polymer bags, glass bulbs and stainless steels containers. The polymer bag usually made from Teflon, Tedlar or Aluminum Tedlar. The sample volume can range from 0.10 to 100 L of air. During the recurring use these bag may show memory effect and hence one should make sure that these bags are cleaned by repeated filling with pure nitrogen or ultra pure zero air and evacuating it under small pressure.

Glass bulbs and steel containers are normally use for low volume, except in the cases where samples are pressurized to allow larger volume of air to be collected

Fig. 10.2 Examples of whole air sampling canisters

Table 10.1 Common sorbents, their properties and applications

Sorbent	Surface area ($m^2 g^{-1}$)	Means size (Å)	Temperature limit (°C)	Application
Activated charcoal	800–1,000	15–20	200–400	Low to medium boiling polar and nonpolar organics
Silica gel	300–800	20–40	–	Amines and polar organics
Graphitized carbon	–	–	–	C_4–C_{12} hydrocarbons, PCBs
Carbon molecular sieve	800–910	15–40	400	C_2–C_5 hydrocarbons
Tenax (polyphenylene oxide)	19–35	720	300–450	Nonpolar VOCs
XAD-2 resin	300	–	200	SVOCs, PAHs
Polyurethane foam				VOCs/SVOCs
Propak	100–600	75–150	190–250	Low chain hydrocarbons
Hayesep	165–795	–	165–275	

(Fig. 10.2). This sampling method is especially useful for the most volatile species, e.g., propane, butane.

10.3.2 *Sorbent Sampling*

Volatile and semi-volatile species are normally collected on suitable adsorbent as this allows larger volume to be collected than canisters. However, selection of suitable adsorbents is very critical as it depends on the sample matrix and on the compound to be collected. Table 10.1 lists some of the common sorbent and their applications. For non-volatile and strongly adsorbed compounds sample recovery remains the limiting step while on the other hand very volatile solutes may cause breakthrough problems (may pass through adsorbent without being trapped). Also, the adsorbent must avoid inconsistent results as well as contamination. The quantity of the substance which can be captured on the adsorbent depends on the amount of sorbent, sampling speed and ambient conditions such as pressure, temperature, concentration, humidity.

10.3.3 Chemisorption

Chemisorption process is normally used to collect high boiling, reactive and polar substances. Normally the volume of air is passed through impingers and/or through bubblers containing liquid to dissolve the analyte. During this process the substances to be measured are absorbed irreversibly in liquid phase and then they are altered by a chemical reaction with other components present. Typical applications of bubblers and impingers include the determination of reactive gases such as hydrogen sulfide and sulfur dioxide, acidic or basic organic vapors of low volatility such as amines, carboxylic acids and phenols and chemically unstable compounds such as aldehydes and chloroacetyl chloride after conversion to a more stable product with favorable detection characteristics.

10.3.4 Cryogenic Concentration

Cryogenic concentration also known as cryotrapping, provides an option to trap air samples. In general no adsorbents are used in cryogenic concentration and this allows desorption at moderate temperatures i.e., 40–70°C. This procedure helps to avoid interferences arising from solutes thermal degradation. During the analysis, an addition of a second cryotrap, just at the entry of the chromatographic column, is necessary to give narrow chromatographic bands, compatible with a capillary analytical column. The cryogenic concentration has been successfully applied for the hydrocarbon (C2–C10) and volatile sulfur compounds.

10.3.5 Collection onto Filters

10.3.5.1 Glass Fiber Filters or Quartz Fiber Filters

High- or low-volume samplers (HVS, LVS) are generally used of VOCs/ SVOCs sampling (Cheremisinoff 1981; Ravindra et al. 2008a). In HVS or LVS the particulate phase is first trapped on a filter and the gaseous phase is trapped on a solid adsorbent (e.g., polyurethane foam) located downstream from the filter (Fig. 10.3). Glass fiber filters or quartz fiber filters (GFF or QFF) are use to collect high-molecular- weight organics associated with atmospheric particles or aerosol

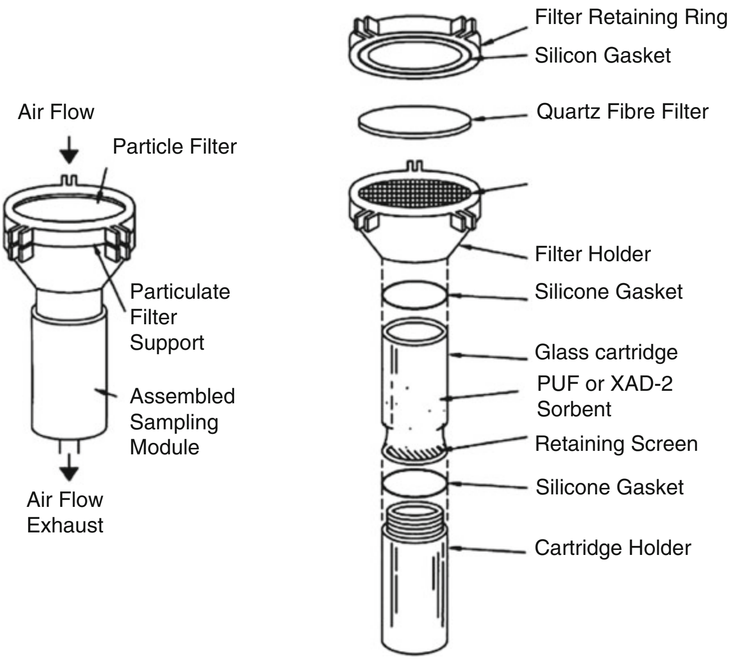


Fig. 10.3 Typical absorbent cartridge assembly for sampling PAHs (TO-13A)

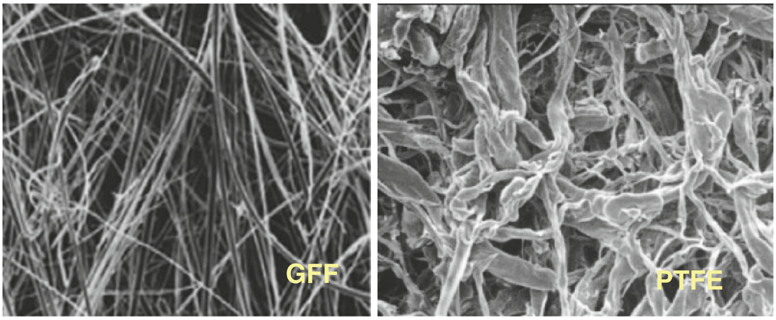


Fig. 10.4 Scanning electron microscopic image of GFF and PTFE filters

(Figs. 10.3 and 10.4). These filters may also be used in conjunction with other trapping materials such as solid sorbents.

Hence, a sampling apparatus combines a quartz-fiber filter and polyurethane foam plugs (PUFPs) or XAD resin. The retained analytes on these filters are generally recovered by Soxhlet extraction, ultrasonic treatment or pressurized liquid extraction as discussed in details in Sect. 10.7. Several application of GFF or QFF includes the measurement of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), organotin compounds, chlorophenols and polycyclic aromatic hydrocarbons (PAHs).

10.3.5.2 PTFE Filters

Poly tetrafluoroethylene (PTFE) filters are very effective in sampling atmospheric aerosols (Fig. 10.4). Using X-ray fluorescence, the elemental composition of the sample could be determined, while ion chromatography allowed the characterization of the chemical form of the compounds (Camel and Caude 1995).

10.3.5.3 Coated Filters

Reactive organic compounds can also be collected on a diffusive sampler. It primarily consists of a reagent-coated filter and other part includes sliding cover, screen (with holes) and badge housing. The filter part under the holes is used as a sampling filter, the other half as a reference filter. There are several application of this type of sampler including measurement of formaldehyde with a 2,4-DNPH-coated filter, diethylamine with a 1-naphthyl isothio cyanate-impregnated filter and amines (methylamine, isopropylamine, n-butylamine, alkylamine and dimethylamine) with the latter reagent.

10.3.6 Collection onto Fibers

Solid-phase microextraction (SPME) is a very useful technique for air sampling. SPME is a fiber coated with a liquid (polymer), a solid (sorbent), or a combination of both. The fiber coating extracts different kinds of analytes (volatile or non-volatile), which can be in liquid or gas phase. The quantity of analyte extracted by the fiber is proportional to its concentration in the sample, as long as equilibrium is reached or, in case of short time pre-equilibrium, with help of convection or agitation (Pawliszyn 1997). After extraction of the SPME fiber the extract is transferred directly into to gas chromatograph for desorption and analysis. It is portable, inexpensive, requires no solvent, and can be used with any type of gas chromatograph.

10.4 Sampling Artifact

During canisters sampling, high or low water vapor content in the canister may result in VOCs/SVOCs losses. Further, vapor pressure, polarity, water solubility, and aqueous reactivity of the compounds may also influence the stability of the targeted organic species. While performing sorbent sampling the degradation of adsorbent may cause sampling artifacts. In comparison to Tenax TA and Tenax GC; Carbotrap B, Carbotrap C and Carbosieve SIII are more resistant adsorbents to degradation. Precautions must be taken during whole air sampling to avoid memory effect. Further some VOCs/SVOCs may also be lost during prolonged storage.

If sampling is performed using HVS, LVS; there are chances for reactive breakdown of VOCs/SVOCs species between the gas and particulate phases (Ravindra et al. 2008a and reference therein). In the particulate phase, positive artifacts (over estimation of the particle phase concentrations) are mainly due to sorption of gaseous compounds on the filter, while negative artifacts (under estimation of the particle phase concentrations) result from the volatilization of particulate PAH from the filter (Goriaux et al. 2006). Moreover, chemical degradations of PAHs by oxidizing compounds such as nitrogen oxides ($NO_x = NO + NO_2$), hydroxyl radical (OH), halogens, nitric acid (HNO_3), hydrogen peroxide (H_2O_2) and ozone (O_3) may also occur during sampling (Tsapakis and Stephanou 2003; Schauer et al. 2003). Very recently Goriaux et al. (2006) reported that the atmospheric PAH concentrations measured using conventional samplers not equipped with an ozone trap can affect the PAH concentration drastically. This was especially relevant when the samples were collected in the vicinity of a point source of particulate PAHs and also for highly reactive compounds such as Benzo[a]pyrene (Fig. 10.5).

The importance of the sampling artifacts depends mainly on sampling conditions such as temperature, humidity including atmospheric concentrations of VOCs/SVOCs species and oxidants (Goriaux et al. 2006). To reduce artifacts induced by conventional samplers, denuder sampling devices were developed (Coutant et al. 1988, 1989, 1992; Lane and Gundel 1996). The denuder sampler systems were designed to trap the gas phase on a solid sorbent coated on the surface of the trap prior to collecting the particulate phase on a filter. This methodology avoids the phenomenon of adsorption of the gas phase on the filter and reduces the desorption artifact by collecting the volatilized fraction on a sorbent cartridge placed downstream from the filter. Finally, the chemical degradation of particulate VOCs/SVOCs species may be reduced as the sorbent coated on the denuder tubes can remove the oxidizing species included in the gas phase (Tsapakis and Stephanou 2003; Ravindra et al. 2008a).

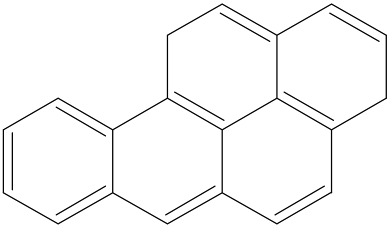


Fig. 10.5 Benzo[a]pyrene (B[a]P)

10.5 Precautions During Sampling

As discussed, sampling is a most important step and errors committed during this stage cannot be corrected later during any other step. Hence, one should plan the sampling procedure carefully in advance according to targeted organic compounds. Following is list of some precaution to be followed during and after the sampling

- The canisters must be cleaned and evacuated to avoid contamination. If, HVS and LVS are used, switch off the pumps after the designated sampling period and note that the start and stop time including flow rate are recorded.
- Teflon Polymer bags must be checked for leaks.
- Breakthrough volumes of the VOCs/SVOCs must be measured before the final samplings.
- During chemisorptions the best reagent must be chosen for a particular application.
- The particle phase PAHs can be lost from particle filter during sampling due to desorption and volatilization, especially during summer months at ambient temperature of 30°C and above.
- Glassware should be properly cleaned by acid-wash and followed by solvent rising prior to any use.
- Matrix interference may be caused by contaminates, i.e., hydrocarbon and other organics that are co-extracted from sample. In this case clean up by column chromatography will be required prior to quantification and confirmation of individual compounds by mass-spectrometer.
- Contaminations in low grade filter, solvents, reagents on glassware and other sampling processing devices may also cause interference in the method used for analysis.

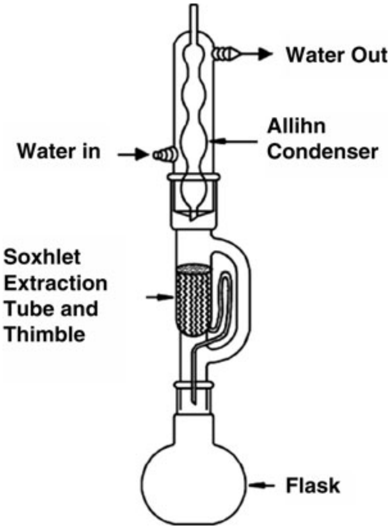
10.6 Sample Preservation

The way samples should be preserved depends on the sampling method. Such as, in case of filter sampling, samples are wrapped in an aluminum foil and should be stored in a refrigerator at below 4°C in a dark and dry place to avoid photo-oxidation of the targeted compounds. As a good lab practice a sample should processed for analysis as soon as possible, however, in exceptional cases they can be stored up to a period of 2 month or so under the correct conditions. It is generally suggested that where extracted samples have to be stored for a long period, it should be in deep freeze.

10.7 Sample Extraction

Extraction is a separation procedure in which specific components are dissolved from solid or liquid mixtures using suitable inert solvents (extracting agent). There are solid–liquid and liquid–liquid extractions. There are also cold and hot

Fig. 10.6 Soxhlet extraction apparatus (TO-13A)



extractions, continuous and discontinuous procedures. The extraction procedure is a significant step as it quantitatively recovers the collected organic compounds. Extraction of different analytes depends on nature of the sample, type of sample matrix and on choice of solvent. Soxhlet, ultrasonic and microwave are the most common choice of extraction. Recently, microwave assisted extraction (MAE), supercritical fluid extraction (SFE) and pressurized liquid extraction (PLE) have also gained popularity due to fast extraction and equal or better analytical results (Dean 1998). A detailed description of these extraction methods is presented in Fig. 10.6.

10.7.1 Soxhlet

The soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. The sample is mixed with anhydrous sodium sulfate and placed in an extraction ceramic thimble or between two plugs of glass wool (extractor). This unit is connected to a flask containing the extraction solvent, and a reflux condenser is connected above the extractor (Fig. 10.6).

Several extraction solvents of low to medium polarity (e.g., cyclohexane, toluene, methylene chloride, tetrahydrofuran, benzene, methanol, and acetone) have been used individually and in combination (in case of azeotrope). The solvent is boiled and, in the standard extractor, the vapor passes through a bypass arm to reach the condenser, where it condenses and drips onto the sample in the thimble. Once the solvent level reaches the top of the siphon arm, the solvent and extract are siphoned back into the lower flask. The solvent re-boils, and the cycle is repeated until the sample is completely extracted, and the extract is in the lower flask. Extraction time may vary range from 1 to 48 h.

10.7.2 Ultrasonic

The ultrasonic process, sonication, is simpler than the above extraction method in that there is close contact between sample matrix and a large volume of the extraction solvent. The approach can be varied depending on the expected concentration of organics in the samples. The low concentration method (individual organic components of less than or equal to 20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (lower concentrations are more difficult to extract). The medium/high concentration method (individual organic components of greater than 20 mg/kg) is much simpler and therefore faster. Normally 20–30 g sample is mixed with anhydrous sodium sulfate to form a free-flowing powder. This solvent is extracted one to three times (depending on low or high concentration) using ultrasonic extraction. The extract is separated from the sample by vacuum filtration or centrifugation and is ready for cleanup and/or for analysis.

10.7.3 Microwave Assisted Extraction

The above discussed traditional extraction methods such as Soxhlet and ultrasonic are time- and labor-consuming. Further they also required large amounts of organic solvents. Therefore, new extraction methods such as MAE, SFE and PLE [or commercially known as accelerated solvent extractor (ASE)] have been developed. Several research studies have shown that these methods can be equally or even more efficient than Soxhlet extraction (David and Seiber 1996; Heemken et al. 1997; Schantz et al. 1997; Bautz et al. 1998; Brumley et al. 1998; Berset et al. 1999; Godoi et al. 2004; Ravindra 2006; Ravindra et al. 2008c, d).

MAE significantly reduces the extraction time (15–30 min) and consumption of toxic solvents. MAE applies the energy of microwave radiation to heat solvents quickly. Hence, MAE suited well to thermolabile compounds and offers an efficient extraction. The recoveries were noticeably much higher as the temperature remains low (Letellier and Budzinski 1999; Mandal et al. 2007). MAE can also be performed at higher temperatures in a closed system and this further reduces the extraction time. MAE can be performed by

- Using one single solvent, i.e., having optimum microwave adsorption
- Using a mixture of solvents such as a combination of solvent with low adsorption and solvent with high adsorption
- Using a solvent with low microwave adsorption together with a heating element

The rate at which the solvent is heated depends on three factors, i.e., ionic conduction, viscosity, and dielectric loss factor. The important physical parameters such as solubility, dielectric constant, and the dissipation factor should also be considered prior to MAE. A selection of solvent having high dielectric constant as well as a high dissipation factor support maximum heat distribution through the matrix. During MAE, a polar solvent with a high dielectric constant surrounds the matrix. Hence, if using a mixture of solvents, there must be sufficient polar solvents in the mixture. The dominate factors that govern the extraction of an analyte from a matrix by MAE are the solubility of the analyte in the solvent, the mass transfer kinetics of the analyte from the matrix to the solution phase, and the strength of analyte/matrix interactions.

Microwave heating has been applied to the extraction of organic contaminants such as PAHs, polychlorobiphenyls, pesticides, herbicides, phenols, neutral and basic priority pollutants in various matrices such as sediments, soils or atmospheric particles. Srogi (2006) shows several application of MAE in environmental sciences but there seems limited application to atmospheric samples. Hence this approach still needs to be elaborated for atmospheric sciences.

10.7.4 Supercritical Fluid Extraction

Since the last decades, SFE has become an established extraction method (Fig. 10.7). A supercritical fluid is a substance above its critical temperature and pressure. Supercritical fluids possess several useful characteristics for the rapid extraction of organics from matrices such as.

- Solvent strengths that approach those of liquid solvents
- Lower viscosities and higher diffusion coefficients

These properties results in a rapid mass transfer in supercritical fluids and hence extraction time is reduced. The leading factors that govern the SFE of an analyte from a matrix are the solubility of the analyte in the supercritical fluid, the mass transfer kinetics of the analyte from the matrix to the solution phase, and interactions between the supercritical fluid and the matrix.

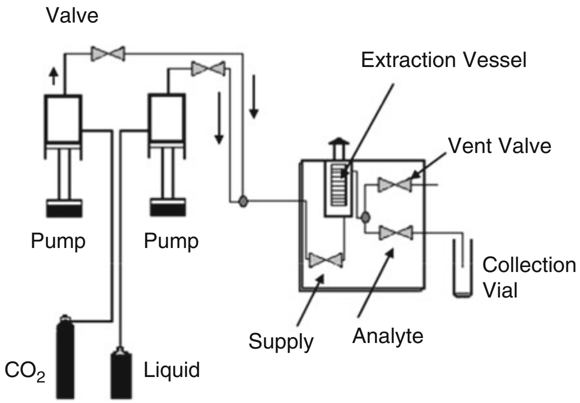


Fig. 10.7 Schematic instrumentation setup of SFE and PLE

Supercritical carbon dioxide (CO_2) is the most widely used solvent in SFE (Bøwadt and Hawthorne 1995; Dean 1996). CO_2 is non-polar, non-toxic, and economical. The selectivity of the solvent can be easily altered in order to increase the solubility of polar compounds by adding a modifier, such as methanol, acetone and acetonitrile. Extraction efficiency can also be enhanced by changing extraction temperature, solvent density, matrix exposure time, and the composition of solvent. The solvating power of supercritical fluid increases with increasing density. This can be accomplished by either lowering the temperature of the extraction or increasing the pressure. Hence, analyte trapping is an important feature in SFE. There are two main approaches for analyte trapping using SFE, i.e.,

- Liquid solvent collection
- Solid-phase trapping

Liquid-trapping has proven to be a reliable recovery technique for SFE because of the lower temperatures produced by Joule–Thompson cooling when the pressure on CO_2 is released. This results in enhanced trapping of VOCs/SVOCs. Solid phase trapping involves collection of the analytes from the gas phase onto solid sorbents. The trapped analytes are thermally desorbed from the sorbent material and then transported directly to the GC column. On-line coupling of SFE to GC increases analyte detectability because sample losses via intermediate preparation steps are avoided, this allows the effective measurement of the total extract. SFE is a reasonable technique for the extraction of SVOCs and pesticides from various matrices. Further, thermally labile compounds can be extracted with minimal damage. However, the time required to complete the extractions is longer than microwave assisted extraction for comparable recovery data.

10.7.5 Pressurized Liquid Extraction

The PLE is a new extraction method that significantly streamlines sample preparation (Fig. 10.8). PLE uses the similar principles to MAE but replaces microwave energy with oven heating. The PLE instrumentation is the same as a SFE but whereas the SFE use carbon dioxide (CO_2) (sometimes modified with organic solvents), the PLE uses organic solvents (Fig. 10.7). CO_2 does not possess the solvent strength needed to efficiently extract polar analytes from complex matrices and the use of modifiers only moderately increases the solvent strength; this limits the applicability of SFE. Solvent strength is not a limitation when employing PLE.

PLE combines elevated temperature and pressure with liquid solvents to achieve fast and efficient removal of analytes from various matrices. The solvent is pumped into the extraction cell containing the sample, which is than brought to a high temperature (20–200°C) and pressure. Minutes later, the extract is transferred from the cell to a standard collection vial for cleanup or analysis. The entire extraction process is fully automated and performed in minutes for fast and easy extraction with low solvent consumption.

Fig. 10.8 Accelerated solvent extractor

Table 10.2 PLE parameters used for PAHs extraction

Parameters	Values
System pressure	2,000 psi
Oven temperature	100°C
Oven heat-up time	5 min
Static time	5 min
Solvent	Dichloromethane/acetone (1:1, v/v)
Flush volume	60% of extraction cell volume
Nitrogen purge	150 psi for 60 s

Application of PLE has been shown for the recovery of PAHs from various environmental matrices such as contaminated soils (Lundstedt et al. 2000), solid waste (Popp et al. 1997), water samples (Doong et al. 2000), fly ash and lignite coal (Arditsoglou et al. 2003), mussels (Martinez et al. 2004) and airborne particles (Alexandrou et al. 2001; Godoi et al. 2004; Ravindra 2006; Ravindra et al. 2008c). PLE thus provides a very fast procedure with a relatively small consumption of toxic solvents and hence environmental burden, nowadays two crucial parameters in the choice of the extraction technique. Table 10.2 summarizes the optimized parameter for PAHs extraction from Ravindra (2006); where as a details description of selection of PLE parameters for atmospheric samples is given below.

10.7.5.1 Sample Clean Up

Sample preparation is an essential part of every solvent-based extraction procedure. However, QFFs or GFFs and PUFs can be efficiently extracted without any pretreatment; other samples may require some manipulation for an efficient extraction to occur. In general, the same sample preparation that is done prior to Soxhlet or Sonication extraction should be done prior to extraction by PLE (Richter et al. 1996, 1997).

Many environmental samples contain water that can prevent nonpolar organic solvents from reaching the target analytes. The use of more polar solvents (e.g., acetone, methanol) or solvent mixtures (e.g., hexane/acetone, methylene chloride/acetone) can assist in the extraction of wet samples. Sample drying prior to extraction is normally accomplished by direct addition of a drying agent such as diatomaceous earth. The choice of drying agent depends on the sample type. Cellulose may be used for very wet, soft matrices such as fruits and vegetables. The use of magnesium sulfate is not recommended with PLE due to the potential for melting at higher temperature. Sodium sulfate should also not be used because it can solubilize in the extraction process and may then be deposited in the exit lines (Dionex 1998).

10.7.5.2 Practical Selection of PLE Parameters

Solvent: For an efficient extraction, the solvent must be able to solubilize the target analytes. The polarity of the extraction solvent should closely match that of the target compounds. Mixing solvents of differing polarities can be used to extract a broad range of compound classes. Generally, if a particular solvent has been shown to work well in a conventional procedure, it will also work well in PLE (Dionex 1998). Solvents that exhibit marginal results at ambient conditions may perform adequately under PLE conditions. Most liquid solvents, including water and buffered aqueous mixtures, can be used in PLE. Strong acids (HCl, HNO_3, and H_2SO_4) are not recommended, as they react with the stainless steel in the system. When required, weak acids such as acetic or phosphoric can be used. These should be added to aqueous or polar solvents in the 1–10% (v/v) range.

Temperature: Temperature is the most important parameter used in PLE extraction. High temperatures increase the viscosity of the solvent and thereby increase its ability to wet the matrix and solubilize the target analytes. Thermal energy also assists in breaking of analyte–matrix bonds and encourages analyte diffusion to the matrix surface. Most PLE applications operate in the 75–125°C range, with 100°C the standard temperature for environmental applications except dioxins. If the sample has a tendency to melt in the extraction cell, a cellulose Soxhlet thimble can be used to facilitate extraction and sample removal. The temperature not only increases the analyte recovery but also the reproducibility (Dionex 1998).

Pressure: The effect of pressure is to maintain the solvents as liquids above their atmospheric boiling points, and to rapidly move the fluids through the system. The pressure used in PLE are well above the thresholds required to maintain the solvents in their liquid states, so pressure adjustments for changing solvents are not required. Changing the pressure will have very little impact on analyte recovery, and it is not considered a critical experimental parameter. Most PLE extractions are performed between 1,000 psi (7 MPa) and 2,000 psi (14 MPa), with 1,500 psi (10 MPa) the standard operating pressure.

Cycles: The use of static cycles was developed to introduce fresh solvent during the extraction process, which helps to maintained favorable extraction equilibrium.

This effectively approximates dynamic extraction conditions without the need for troublesome flow restrictors to maintain pressure. When more than one cycle is used in a method, the flush volume is divided by that number and no additional solvent is used for the extraction. When the first static cycle is complete, the divided portion of the flush volume is delivered to the cell, with the “used” solvent directed to the collection vial. The system then holds the sample and solvent for a second static period. The nitrogen purge step is initiated only after the final static cycle. Static cycles have proven to be useful for sample types with a very high concentration of analyte, or samples with matrices that are difficult to penetrate. The static time can be adjusted to minimize the total extraction time. For example, three 3-min static cycles can be used in place of 9-min static step. When low temperature extractions are desired (<75°C), multiple static cycles should be used to compensate for the lack of fresh solvent normally introduced during the heatup step, as the static valve pulses to regulate the pressure.

Time: Certain sample matrices can retain analytes within the pores or other structures. Increasing the static time and temperature can facilitate the diffusion of these compounds into the extraction solvent. The effect of static time should always be explored in conjunction with static cycles, in order to produce a complete extraction in the most efficient way possible.

10.7.6 Comparative Assessment Including Others Extraction Methods

Table 10.3 provides a comparative overview of extraction methods. In addition to the methods discussed above, several other extraction methods such as liquid–liquid extraction (for SVOCs), abbreviated solvent extraction (for SVOCs), solid phase micro extraction, i.e., SPME (for VOCs and SVOCs), thermal desorption (for PAHs, PCBs, etc.) are also applied for the extraction of targeted organics species from atmospheric and environmental samples.

10.8 Cleanup and Enrichment

Cleanup, i.e., the removal of non-relevant materials, is an important step to separate the targeted compounds from the complex arrays of organic compounds present in the extracts. The cleanup and fractionation involves several steps and is generally performed using liquid-liquid chromatography, column chromatography and thin layer chromatography. Several adsorbents such as silica gel, alumina are used for open column chromatography. Figure 10.9 depicts a silica column used of the cleanup and enrichment of PAHs.

In addition to the cleanup, column chromatography can also be used for the separation of the extracted organic fraction into sub fractions containing compounds of similar molecular weight or properties. Further the samples can also be

Table 10.3 Comparative assessment of extraction methods

	Soxhlet	Ultrasonic	MAE	SFE	PLE
Sample weight[a] (g)	5–10	5–30	0.5–1	1–10	1–10
Solvent	Dichloromethane, acetone, hexane, cyclohexane, toluene, etc.	Dichloromethane, acetone, hexane, cyclohexane, toluene, etc.	Hexane/ethanol	CO_2	Dichloromethane, acetone, hexane, cyclohexane, toluene, etc.
Solvent volume (mL)	>300	300	10–20	5–25	15–30
Vessel volume (mL)	200–1,000	500	<100	5–25	40–100
Temperature (°C)	Boiling point	Room temperature	40–100	50, 200	50, 200
Time	16 h	30 min	30–45 s	30–60 min	15–30 min
Pressure	Ambient	Ambient	1–5 atm	15–650 atm	Up to 136 atm
Analytes	SVOCs	SVOCs	TPH, PAHs, PCBs, pesticides	SVOCs	PAHs, PCBs, pesticides
Standard methods	3,540C, 3,541	3,550B	–	3,560, 3,561	3,545

atm atmospheric unit (standard)

[a] Depends on the concentration and type of samples

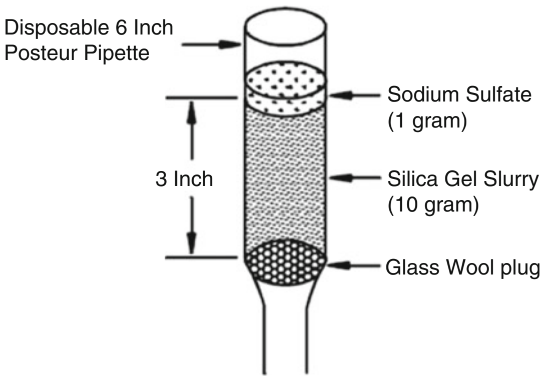


Fig. 10.9 Silica gel cleanup column for PAHs (TO-13A)

divided into nonpolar and polar fractions such as aliphatic (e.g., n-alkanes) and aromatic compounds (e.g., PAHs).

10.9 Analytical Methods

Several techniques have been developed to identify, chemically characterize and quantify the atmospheric organic compounds. However, most of the applications are focused on the chromatographic methods for quantitative as well as qualitative analysis of VOCs/SVOCs (Table 10.4).

Various chromatographic systems such as gas chromatography (GC), high performance liquid chromatography (HPLC), and ion chromatography (IC) follows the same basic principles but they have different analytical characteristics. The important parameters for the chromatographic analysis are:

- Type of stationary and mobile phase
- Composition of the sample and the analytes
- Sample injection technique and injector systems (particularly in GC)
- Temperature, pressure, flow velocity of the mobile phase
- Detector selection, sensitivity
- Data processing, chromatograms

GC is an analytical technique for separating compounds based primarily on their volatilities, it provides both qualitative and quantitative information for individual compounds present in a sample. Compounds move through a GC column as gases, either because the compounds are normally gases or they have been heated and vaporized into a gaseous state. The compounds partition between a stationary phase, which can be either solid or liquid, and a mobile phase (gas).

The differential partitioning into the stationary phase allows the individual compounds to be separated in elution time and quantified by detector response.

Table 10.4 Selected standard methods for the determination of VOCs/SVOCs in atmosphere

Method	Focus	Brief detail	Instrumentation
TO-13A	PAHs	Compendium of methods for the determination of toxic organic compounds in ambient air – second edition	GC/MS
TO-15A	VOCs	Compendium of methods for the determination of toxic organic compounds in ambient air	GC/MS
8100	PAHs	Polynuclear aromatic hydrocarbons	By GC[a]
8310	PAHs	Polynuclear aromatic hydrocarbons	By HPLC[a]
8270A	PAHs/PCBs	Test methods for evaluating solid waste, physical/chemical methods	Thermal extraction followed by GC-MS[a]
8270C	SVOCs	Test methods for evaluating solid waste, physical/chemical methods	GC/MS
ISO 11338-1:2003	PAHs	Stationary source emissions – determination of gas and particle-phase PAHs – Part 1: sampling	
ISO 11338-2:2003	PAHs	Stationary source emissions – determination of gas and particle-phase PAHs – Part 2: sample preparation, clean-up, and determination	HPLC-UV and GC/MS
ISO 12884:2000 (E)	PAHs	Ambient air – determination of total (gas and particlephase) PAHs – collection on sorbent-backed filters with gas chromatographic–mass spectrometric analyses	GC/MS
ISO16362:2005	PAHs	Ambient air – determination of particle-PAHs by HPLC	HPLC-FL and HPLC-DAD
ASTM D 6209-98 (2005)	PAHs	Standard test method for determination of gaseous and particulate PAHs in ambient air (collection on sorbent – backed filters with GC/MS analysis)	GC/MS

[a]Methods focus on solid samples but the approach can also be used for atmospheric samples

10.9.1 Components of a GC

As shown in Fig. 10.10, a GC system includes the five basic components, i.e., carrier gas unit, sample injection port, columns, detectors and a data recorder. The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. The sample injector port is a hollow, heated, glass-lined cylinder where the sample is introduced into the GC. The temperature of the injector is controlled such that all the components in the sample will be vaporized. The glass liner is about 4 in. long and 4 mm internal diameter. The injector can introduce the sample in either split or splitless mode.

The GC column is the heart of the system. It is coated or packed with a stationary phase which greatly influences the separation of the compounds. The structure of the stationary phase affects the amount of time the compounds take to move

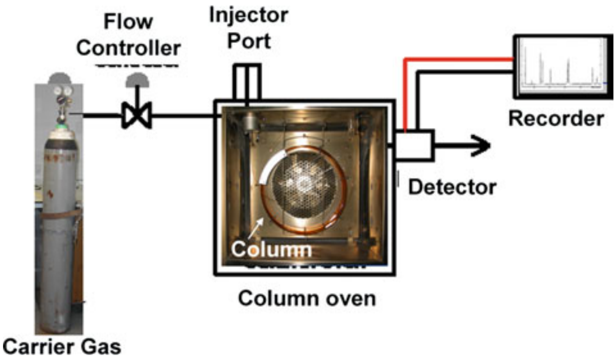
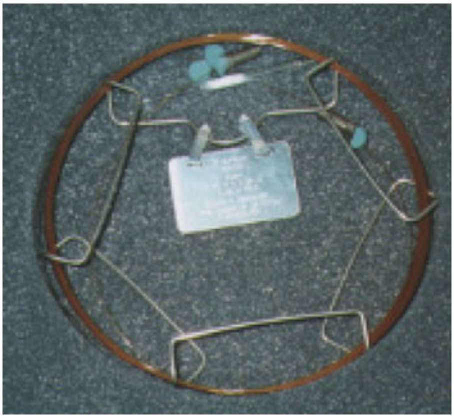


Fig. 10.10 Schematic representation of gas chromatography

Fig. 10.11 Capillary GC column



through the column (in general the longer the time the better the separation but also the broader the peaks). Typical stationary phases are large molecular weight polysiloxane, polyethylene glycol, or polyester polymers with a 0.1–2.5 μm film thickness. Columns are available in many stationary phases' sizes. A typical capillary column is 15–60 m in length and 0.25–0.32 mm i.d. (Fig. 10.11). A typical packed column is 2–6 m long and 2.2 mm i.d.

The column is placed in an oven where the temperature can be controlled very accurately over a wide range of temperatures. Typically, GC oven temperatures range from room temperature to 300°C, but cryogenic conditions can be used to operate at temperatures from about −20°C to 20°C.

There are many detectors which can be used in gas chromatography. Different detectors will give different types of selectivity (Table 10.5). A *non-selective* detector responds to all compounds except the carrier gas, a *selective detector* responds to a range of compounds with a common physical or chemical property and a *specific detector* responds to a single chemical compound. Detectors can also be grouped into *concentration dependant detectors* and *mass flow dependant*

Table 10.5 Selected detectors and their applications

Detector	Type	Support gases	Selectivity	Detectability	Dynamic range
Flame ionization (FID)	Mass flow	Hydrogen and air	Most organic compounds	100 pg	10^7
Thermal conductivity (TCD)	Concentration	Reference	Universal	1 ng	10^7
Electron capture (ECD)	Concentration	Make-up	Halides, nitrates, nitriles, peroxides, anhydrides, organometallics	50 fg	10^5
Nitrogen–phosphorus	Mass flow	Hydrogen and air	Nitrogen, phosphorus	10 pg	10^6
Photo-ionization (PID)	Concentration	Make-up	Aliphatics, aromatics, ketones, esters, aldehydes, amines, heterocyclics, organosulphurs, some organometallics	2 pg	10^7

http://teaching.shu.ac.uk/hwb/chemistry/tutorials/chrom/gaschrm.htm

detectors. The signal from a concentration dependant detector is related to the concentration of solute in the detector, and does not usually destroy the sample Dilution of with make-up gas will lower the detectors response. Mass flow dependant detectors usually destroy the sample, and the signal is related to the rate at which solute molecules enter the detector. The response of a mass flow dependant detector is unaffected by make-up gas. Have a look at the tabular summary of common GC detectors in Table 10.5.

The data recorder plots the signal from the detector over time. This plot is called a chromatogram. The retention time, which is when the component elutes from the GC system, is qualitatively indicative of the type of compound. The data recorder also has an integrator component to calculate the area under the peaks or the height of the peak. The area or height is indicative of the amount of each component.

10.9.2 Hyphenated Chromatographic Methods

10.9.2.1 Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC-MS) is becoming the tool of choice for tracking organic pollutants in the environment. GC-MS combines the application of gas–liquid chromatography and mass spectrometry to separate

Fig. 10.12 Gas chromatography-mass spectrometry (GC-MS)

and identify different substances in an extract or sample (Fig. 10.12). (The gas chromatograph uses the difference in the chemical properties between different molecules in a compound to separate the molecules. The molecules take different amounts of time [called the retention time] to come out of the gas chromatograph, and this allows) the mass spectrometer downstream to evaluates the molecules separately in order to identify them. The mass spectrometer does this by adding a charge to each molecule, which may subsequently break into ionized fragments, and detecting the parent ion and the charged fragments using their charge to mass ratio. Each molecule has a specific fragment spectrum which allows for its identification.

These two components, used together, allow a much finer degree of substance identification than either unit used separately. It is possible to make an accurate identification of a particular molecule by gas chromatography or mass spectrometry alone. The mass spectrometry process normally requires a very pure sample while gas chromatography can be confused by different molecular types that both happen to take about the same amount of time to travel through the unit (i.e., have the same retention time). Sometimes two different molecules can also have a similar pattern of ionized fragments in a mass spectrometer (mass spectrum). Combining the two processes makes it extremely unlikely that two different molecules will behave in the same way in both a gas chromatograph and a mass spectrometer. So when an identifying mass spectrum appears at a characteristic retention time in a GC-MS analysis, it is usually taken as proof of the presence of that particular molecule in the sample.

10.9.2.2 Low Pressure-Gas Chromatography

In GC, the application of vacuum column-outlet condition is an attractive way to increase the speed of analysis. However, very little attention has been paid to evaluating the possibilities of operating columns at reduced pressure, so-called vacuum outlet capillary GC or vacuum GC (Fig. 10.13). A considerable gain, of up to a factor 3–5 in speed, is possible, especially for short and or wide bore columns (Ravindra et al. 2008d and reference therein). Moreover, in contrast to other methods for fast gas chromatography GC, the vacuum outlet route has significantly increased sample loadability.

Despite the attractive speed and loadability characteristics of wide-bore columns operated under vacuum outlet conditions, this approach is hampered by associated experimental difficulties. Vacuum outlet conditions are most readily obtained by using a mass spectrometer (MS) as the detection device. Direct coupling of a short and/or wide-bore column to an MS however, give problems. First, the carrier-gas inlet and the injection system have to be operated at sub-ambient pressures. Second, the high column outlet flow might increase the pressure in the ion source of the mass spectrometer to a level exceeding the tolerable limit.

A vacuum in the analytical column can be realized by coupling a capillary with a large diameter (0.53 mm) to a deactivated restriction capillary, which is positioned at the inlet section. Such a restriction can vary, depending upon whether a very short capillary of 20 mm i.d. or a longer capillary of 0.1–0.15 mm i.d. is used. The column configuration is shown in Fig. 10.13. In this work with a 0.1 mm i.d. capillary of 50–60 cm was connected by quick-seal as well as single ferrule column connectors. As a result the 0.53 mm column is operated for a large part under a lower pressure than would be achieved with a 0.25 mm column.

The optimal linear velocity for a given capillary directly depends on the pressure in the column. Practically the optimal velocity of 0.53 mm columns operated at low pressure is ten times higher than under normal pressure. An optimal velocity was found around 90–100 cm/s for helium using a 10 m × 0.53 mm CP-Sil 5 CB with a restriction at the inlet. It is obvious that high velocities will result in very short analysis time. It can be a factor 3–5 higher and up to ten times higher for temperature programmed and for isothermal elution, respectively. Further this allows

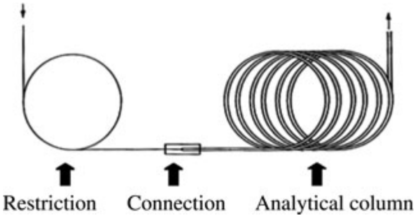


Fig. 10.13 Vacuum separation by applying a restriction column at the injection side of the system (Ravindra et al. 2008d)

components to elute at lower temperatures which can be beneficial for sensitive components.

LPGC-ITMS also features:

- Higher sensitivity: typically the signal-to-noise ratio will increase by at least a factor of 3
- It is compatible with existing injection techniques and ion trap detection technology
- Less bleeding is found due to low elution temperature and the loadability is higher
- For a column with film thickness from 0.1 to 1 μm and 0.53 mm i.d. capillaries can take more stress than the smaller bore columns

A further advantage of the method was that the low elution temperature significantly reduced the background, due to column bleeding. Figure 10.14 shows a comparison of LP-GC and conventional CP Sil-8 column separation of PAHs for 128–202 molecular weight analogs. For a detailed evaluation of the chromatographic separation obtained on conventional and LPGC-ITMS columns, the readers are encouraged to read a recent review by Ravindra et al. (2008d). This review explores recent developments and application of LP-GC for pesticides, PAHs, VOCs, plant and flower oils, organotin compounds, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs) and SVOCs. Further the review also focuses on the use of various column systems and analyzers and covers the prospects and limitation of LP-GC.

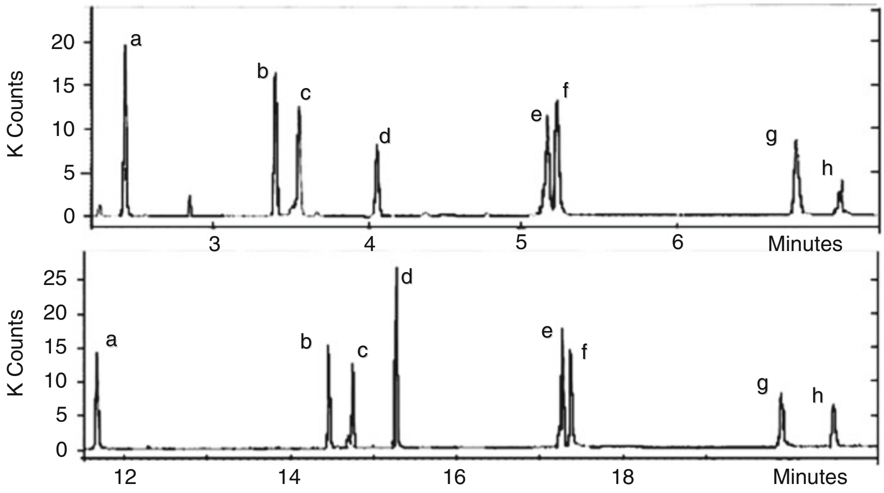


Fig. 10.14 Comparison of the mass chromatogram for PAHs with molecular weight of 128–202 using LPGC-ITMS (*top*) and CP Sil –8 conventional column GC-MS (*bottom*). [Naphthalene (a), acenaphthene (b), acenapthylene (c), fluorene (d), phenanthrene (e), anthracene (f), fluoranthene (g), pyrene (h)]

10.9.2.3 High Performance-Liquid Chromatography

HPLC is widely used in the analysis of organic compounds. It offers useful separation of nonpolar as well as polar substances. Normal phase HPLC is sometimes used as initial step before subsequent separation by reversed phase. This mode of chromatography can separate polar organics from the PAHs, and even separate the PAHs by the number of bonds (Vo-Dinh 1998). Following is a brief description of PAHs analyzed by HPLC from Ravindra (2006).

The filers or PUFs samples were extracted as per procedure defined in Section 10.7.5. After the cleanup and enrichment steps the extract are introduced to HPLC having programmed fluorescence detection and UV-detection (for acenaphtylene). Separation of the PAHs can be obtained on a Vydac 201TP (250 mm × 4.6 mm) column, having a gradient elution ranging from a 50% (v/v) acetonitrile-water mixture to 100% acetonitrile in 20 min. The fluorescence of PAHs is monitored with automatic selector of the wavelengths for each compound according to its retention time. The excitation wavelengths ranged between 260 and 300 nm, while the emission wavelengths lay between 380 and 465 nm. These details for individual PAHs are shown in Table 10.6. The wavelength of the UV-detector was 325 nm. Linear calibration graphs should also be obtained for all the studied PAHs. The method offers quantification of less than 1 ng/m^3 of PAHs in the air.

10.9.3 Other Techniques

There are several other wide ranges of techniques for the measurement of VOCs/SVOCs species at trace levels. Examples of other techniques include DOAS

Table 10.6 Selected wavelengths for fluorimetric analysis of PAHs with HPLC (Ravindra 2006)

Compounds	Times (s)	Excitation (nm)	Emission (nm)
Naphthalene	0	290	320
Acenapthylene			
Acenaphthene		290	320
Fluorene		290	320
Phenanthrene	700	250	358
Anthracene		250	385
Fluoranthene	840	260	420
Pyrene		260	420
Benzo[a]anthracene	980	265	380
Chrycene		265	380
Benzo[b]fluoranthene	1,200	290	430
Benzo[k]fluoranthene		290	430
Benzo[a]pyrene		290	430
Dibenz[a,h]anthracene	1,380	300	465
Benzo[ghi]perylene	1,440	300	465
Indeno[1,2,3,cd]pyrene		300	465

(differential optical absorption spectroscopy) for gaseous BTEX (benzene, toluene, ethyl benzene and xylene) and formaldehyde, and MIMS (membrane introduction mass spectrometry) for gaseous and liquid samples (Dewulf et al. 2002). These techniques are quite sensitive and selective. Further they have the advantage that they can also perform a real time measurement of these species.

10.10 Quality Assurance and Quality Control

The purpose of quality assurance (QA) and quality control (QC) is to identify, measure, and keep these errors under control. QA/QC measures are necessary during field sampling as well as in laboratory procedure. One should always determine the accuracy and precision of a method. Accuracy is determined by comparing the measured values to the known concentration; where as precision involves replicate measurements. In a book by Prichard (1997) all these concern are covered in details. Further, Lodge (1991), Swartz and Krull (1997) and Kebbekus and Mitra (1998) also discuss QA/QC issues in analytical method development and validation.

The organic chemistry laboratories are potentially one of the more dangerous laboratories. As the procedures outlined utilize toxic and inflammable solvents, high temperatures and the usage of electrical apparatus one should always follow precautions and be aware of the safety guidelines. Readers are encouraged to read Zubrick (1997) for further details on chemical, analytical and instrumentation safety issues, if they are about to handle the environmental samples for organic analysis.

10.11 Conclusions

This book contribution summarized some of the basic concepts of atmospheric VOCs and SVOCs measurement. The site selection criteria and various sampling methods were also discussed to achieve sampling objectives and to capture targeted atmospheric organic pollutants. Several extraction methods were described in brief with special emphasis on PLE applications. Further, a comparative assessment of extraction methods was given to have a choice of extraction and for maximum recovery of targeted organic species from collected samples. Cleanup and enrichment step are important steps to enhance the selectivity and sensitivity of any instrumental methods. Application of GC and hyphenated techniques were discussed for qualitative and quantitative analysis of various organic compounds. Further, several standard methods are listed to have a choice for particular application. The QA, QC and safety are important issues in any environmental analysis and should not be ignored.

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Chapter 11
Polyfluorinated Compounds in the Coastal and Marine Atmosphere

Annika Jahnke and Ralf Ebinghaus

11.1 Introduction

Per- and polyfluorinated compounds (PFCs) comprise a large group of chemicals, consisting of a hydrophobic alkyl chain and usually possessing a hydrophilic functional group. The alkyl chain is partly or fully fluorinated and typically contains between 4 and 18 carbon atoms (De Voogt and Saez 2006). Therefore, PFCs are both oleophobic and hydrophobic and form strong surfactants. PFCs comprise ionic compounds like perfluoroalkyl sulfonates (including perfluorooctane sulfonate, PFOS) and perfluoroalkyl carboxylates (PFCAs including perfluorooctanoate, PFOA, Table 11.1) as well as neutral, volatile PFCs like fluorotelomer alcohols (FTOHs), N-alkylated fluorooctane sulfonamides (FOSAs) and sulfonamidoethanols (FOSEs, Table 11.2).

Due to the high-energy C–F bond, ionic PFCs are extraordinarily persistent as they resist hydrolysis, photolysis, microbial degradation and metabolism. They also show certain bioaccumulative and toxic properties. PFOS, PFOA and a suite of additional PFCs have been found in biota of remote locations, such as the Canadian and European Arctic (Martin et al. 2004; Smithwick et al. 2005a, b) and the Southern Ocean (Tao et al. 2006). Since these compounds are non-volatile and moderately water soluble, the question came up how they reach remote ecosystems.

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Table 11.1 Ionic PFCs, acronyms and structures

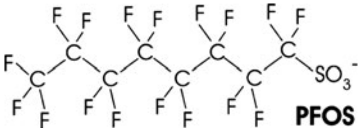
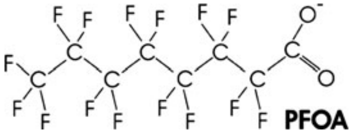
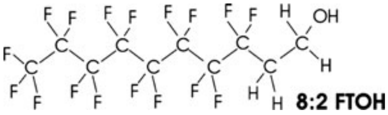
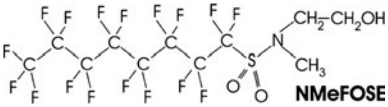
Analytes	Acronyms	Example structures
Perfluoroalkyl sulfonates	PFSAs	
C_4: Perfluorobutane sulfonate	PFBS	
C_6: Perfluorohexane sulfonate	PFHxS	
C_8: Perfluorooctane sulfonate	PFOS	
C_{10}: Perfluorodecane sulfonate	PFDS	
Perfluoroalkyl carboxylates	PFCAs	
C_5: Perfluoropentanoate	PFPeA	
C_6: Perfluorohexanoate	PFHxA	
C_7: Perfluoroheptanoate	PFHpA	
C_8: Perfluorooctanoate	PFOA	
C_9: Perfluorononanoate	PFNA	
C_{10}: Perfluorodecanoate	PFDA	
C_{11}: Perfluoroundecanoate	PFUnA	
C_{12}: Perfluorododecanoate	PFDoA	
C_{13}: Perfluorotridecanoate	PFTrA	
C_{14}: Perfluorotetradecanoate	PFTA	
C_{15}: Perfluoropentadecanoate	PFPDA	

Table 11.2 Neutral PFCs, acronyms and structures

Analytes	Acronyms	Example structures
Fluorotelomer alcohols	FTOHs	
C_6: 4:2 fluorotelomer alcohol	4:2 FTOH	
C_8: 6:2 fluorotelomer alcohol	6:2 FTOH	
C_{10}: 8:2 fluorotelomer alcohol	8:2 FTOH	
C_{12}: 10:2 fluorotelomer alcohol	10:2 FTOH	
Fluorooctane sulfonamides/ sulfonamidoethanols	FOSAs/ FOSEs	
Fluorooctane sulfonamide	FOSA	
N-methyl fluoroctane sulfonamide	NMeFOSA	
N-ethyl fluorooctane sulfonamide	NEtFOSA	
N-methyl fluorooctane sulfonamidoethanol	NMeFOSE	
N-ethyl fluorooctane sulfonamidoethanol	NEtFOSE	

One potential explanation was that neutral precursors of PFOS and PFOA are volatile and thus prone to long-range atmospheric transport (LRAT). In combination with the above mentioned persistent, bioaccumulative and toxic properties of ionic PFCs, they can therefore be classified as persistent organic pollutants (POPs). PFOS and other PFCs have already been declared ‘candidate’ POPs (Kaiser and Enserink 2000, www.unep.org).

In December 2005, the European Commission presented a proposal for restriction measures for PFOS. Since the end of 2006, the placing on the market and use of

PFOS as well as PFOS containing products is, with a few exceptions, prohibited. Concerning PFOA, hazard assessments are ongoing in order to evaluate the need for potential legal actions.

All PFCs with carbon chain lengths >2 are anthropogenic and are produced almost exclusively by one of two major manufacturing processes:

1. Electrochemical fluorination (ECF) was used since the 1950s and produced mixtures of linear and branched isomers of approx. 70% and 30%, respectively (Giesy and Kannan 2002).
2. Telomerisation is in use since the 1970s for the production of PFCAs and FTOHs, yielding exclusively linear compounds. FTOHs contain an even number of fully fluorinated and two non-fluorinated carbon atoms adjacent to the hydroxyl function. Their general structure is CF_3–$(CF_2)_n$–CH_2–CH_2OH, where $n = 3, 5, 7, 9$ and they are named based on the ratio of fluorinated to non-fluorinated carbon atoms, e.g., 8:2 FTOH for $n = 7$ (Schultz et al. 2003).

The application spectrum of PFCs is very broad. FOSAs and FOSEs were used in a variety of products inducing water- and stain-repelling properties on carpets, leather, upholstery and textiles, as paper protectors and performance chemicals (e.g., in aqueous film forming fire-fighting foams (AFFFs); De Voogt and Saez 2006) or as an insecticide (N-ethyl fluorooctane sulfonamide (NEtFOSA): Sulfluramid®). FTOHs are used in similar applications as FOSAs and FOSEs, such as precursor compounds in the production of fluorinated polymers used in paper and carpet treatments, moreover in the production of paints, coatings, adhesives etc. (Ellis et al. 2003; Dinglasan et al. 2004).

In 1999, the U.S. Environmental Protection Agency (EPA) was alerted by data on PFOS showing that it was persistent, unexpectedly toxic, bioaccumulative, and found in the blood of the general population and in wildlife around the world (www.epa.gov). Since then, numerous studies have been performed to investigate levels in organisms at different trophic levels. Furthermore, PFC concentrations in various matrices such as humans, the aqueous phase (surface water, sewage treatment plant (STP) influents/effluents, precipitation), the solid phase (food, dust, sediment/soil, STP sludge), consumer products as well as indoor and outdoor air have been under intensive investigation.

As pointed out above, PFOS, PFOA and a suite of additional PFCs have been found in organisms from remote locations, although they are non-volatile with relatively low vapour pressures and only moderately water soluble. Two major transport hypotheses have been proposed to explain their large-scale distribution:

1. Direct transport of ionic PFCs via oceanic currents and/or sea spray could occur as described by Prevedouros et al. (2006) and Armitage et al. (2006).
2. Neutral, volatile precursors could undergo LRAT and be degraded (biotically/abiotically) to the persistent ionic compounds at remote sites (Ellis et al. 2004). Airborne precursor compounds of PFOS and PFCAs include FTOHs as well as N-alkylated FOSAs and FOSEs.

Recently, Kim and Kannan (2007) and McMurdo et al. (2008) additionally suggested that PFOA and further PFCAs in their protonated form may volatilise from water surfaces into the gas phase via aerosol formation. They may then undergo atmospheric transport.

The two major suggested transport pathways are illustrated in Fig. 11.1. Both of them have recently received some supporting evidence. On the one hand, a number of ionic PFCs were detected in Arctic water samples as described by Theobald et al. (2007). Furthermore, recent modelling results support the theory of long-range oceanic transport of PFOA to the Arctic (Prevedouros et al. 2006; Armitage et al. 2006).

On the other hand, the second hypothesis was supported by the ubiquitous detection of a suite of neutral, volatile precursors in North American (Martin et al. 2002; Stock et al. 2004; Shoeib et al. 2004, 2005; Piekarz et al. 2007; Loewen et al. 2008; Primbs et al. 2008), European (Barber et al. 2007; Jahnke et al. 2007b, d, Dreyer et al. 2008) and Asian environmental air (Piekarz et al. 2007; Oono et al. 2008). They have additionally been determined in air from remote locations such as the Arctic (Shoeib et al. 2006; Stock et al. 2007; Jahnke 2007) and from the Atlantic Ocean along the African West Coast (Jahnke et al. 2007c). Furthermore, biodegradation (Dinglasan et al. 2004; Tomy et al. 2004; Wang et al. 2005a, b) as well as smog chamber degradation studies (Ellis et al. 2003; Martin et al. 2006; D'Eon et al. 2006) indicated the plausibility of the LRAT theory. Finally, recent results from modelling studies seem to further substantiate the LRAT hypothesis (Wallington et al. 2006).

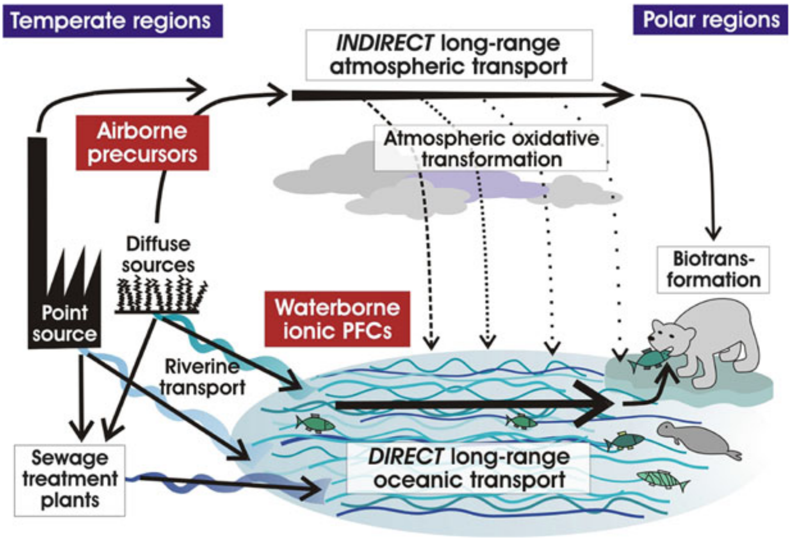


Fig. 11.1 Two possible global transport routes for PFCs to remote, polar regions

This article tries to summarise our understanding of the occurrence, distribution pattern, concentration gradients and transport mechanisms of neutral, volatile PFCs between source regions and remote, marine locations.

11.2 Sampling and Analysis of Polyfluorinated Compounds in Environmental Air Samples

For this work, the trace-analytical protocol for the identification and quantification of a suite of neutral, volatile PFCs in environmental air samples as published by Martin et al. 2002 was optimised and fully validated (Jahnke et al. 2007a). This included numerous experiments like recovery tests, the evaluation of analyte breakthrough, matrix effects, and two interlaboratory comparison tests of instrumental quantification as well as quantification methods, respectively. Special emphasis was set on the evaluation of several isotope-labelled compounds to be used as internal standards (IS).

The following analytes were investigated: four FTOHs (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, 10:2 FTOH), further two FOSAs (NEtFOSA, NMeFOSA) and FOSEs (NMeFOSE, NEtFOSE) each. Two additional compounds were included in the analytical protocol, but not determined above their method quantitation limits (MQLs) in any of the environmental samples (fluorooctane sulfonamide, FOSA and 1H,1H,2H,2H-perfluorooctyl ethylacrylate, 6:2 FTA).

The sampling procedure included the enrichment of the analytes on glass fibre filters (GFFs, providing an estimate of the proportion associated with the particle phase) and glass columns filled with XAD-2 resin sandwiched between two polyurethane foam slices (PUF/XAD, representing the fraction associated with the gaseous phase). PUF/XAD columns or GFFs were spiked with five isotope-labelled IS before sampling or sample extraction, respectively. High-volume air samples of $>1{,}000\ m^3$ were collected in duplicates over 3.5 days to investigate the repeatability of the method. Sample extraction was done by cold column elution with ethyl acetate (EtOAc). Two recovery internal standards (RIS) were spiked to final extracts before analyses to investigate recoveries of the IS.

For quantification of the analytes, gas chromatography coupled to mass spectrometry using positive chemical ionisation (GC/PCI-MS) with confirmation of some compounds in the negative chemical ionisation mode (NCI) was used. MQLs between 0.2 pg/m^3 (NMeFOSA) and 2.5 pg/m^3 (6:2 FTA) were achieved. As part of the method validation, absolute analyte recoveries revealed significant signal enhancement of FOSEs in the specific PUF/XAD-derived matrix resulting from elution with EtOAc (see also Barber et al. 2007; Dreyer et al. 2008) as well as considerable losses of the most volatile FTOHs during sampling, sample extraction and extract concentration. This lack of accuracy could be remediated by application of the suite of isotope-labelled IS, so that IS-corrected relative recoveries were around 100% for most compounds.

11.3 Airborne PFCs at Two Sites in Germany

In order to assess the concentrations of airborne PFCs in Northern Germany, two sampling locations were chosen (Jahnke et al. 2007b): Hamburg in order to cover an urban area with a presumably relatively high contaminant load and Waldhof, a rural site without potential sources in the direct neighbourhood. Waldhof is a background monitoring site of the German Federal Environmental Agency (UBA) and European Monitoring and Evaluation Program (EMEP) station. Sampling was conducted at the Max Planck Institute (MPI) for Meteorology in the Hamburg city center (sample abbreviation HH1–HH7) and at the UBA site in Waldhof (located approx. 100 km south-east of Hamburg, sample abbreviation W1–W4).

The sampling campaign was carried out between April and June, 2005, and provided first concentration data of neutral, volatile PFCs outside North America. Duplicate sets of air samples of 850–1,570 m^3 with a mean volume of 1,160 m^3 were collected. For each sample, field blanks were taken by attaching open PUF/XAD columns close to the sampling sites during the sampling time (individual blanks). Furthermore, field blanks were taken for the whole sampling period in Hamburg and Waldhof, respectively (overall blanks).

Quantitative analysis of the samples revealed a wide distribution of FTOHs as well as FOSAs and FOSEs in German environmental air. Except for 6:2 FTA and FOSA, all analytes could be determined in the gaseous phase of German air samples. NMeFOSE and NEtFOSE could additionally be quantified in the particulate phase of all samples. 8:2 FTOH (<MQL), NMeFOSA (not detected (n.d.) < MQL) and 10:2 FTOH could be detected on GFFs, but quantification was possible only sporadically. 6:2 FTA, FOSA, 4:2 FTOH, 6:2 FTOH and NEtFOSA were not detected on any of the GFFs. The particulate phase concentrations as determined on the GFFs are possibly underestimated, due to the known drawback of high-volume air sampling whereby revolatilization of particle-bound analytes from the filter and diffusion into the PUF/XAD columns may occur, especially at higher temperatures (Gundel et al. 1995).

Duplicate samples were in good agreement, illustrating the precision of the method. Despite the complex analytical protocol, only 13% of the gaseous phase concentration data obtained from duplicate samples deviated by more than ± 30%, reflecting the excellent repeatability, as described in more detail in Jahnke et al. (2007a). The most volatile IS, 2H2,13C2-6:2 FTOH showed low recoveries in some samples, probably attributable to high temperatures at the time the IS were spiked. Therefore, IS-corrected concentrations of 4:2 FTOH and 6:2 FTOH may be overestimated for these samples.

Box-whisker plots of concentrations for individual analytes determined in Hamburg and Waldhof are given in Fig. 11.2, including means and medians for the gaseous (a) and particulate (b) phase.

Concentrations of ΣFTOHs were almost one order of magnitude higher than ΣFOSAs + FOSEs. 8:2 FTOH was the predominant compound, followed by 6:2 FTOH. This distribution pattern was the same at both sampling sites. Of the FOSAs

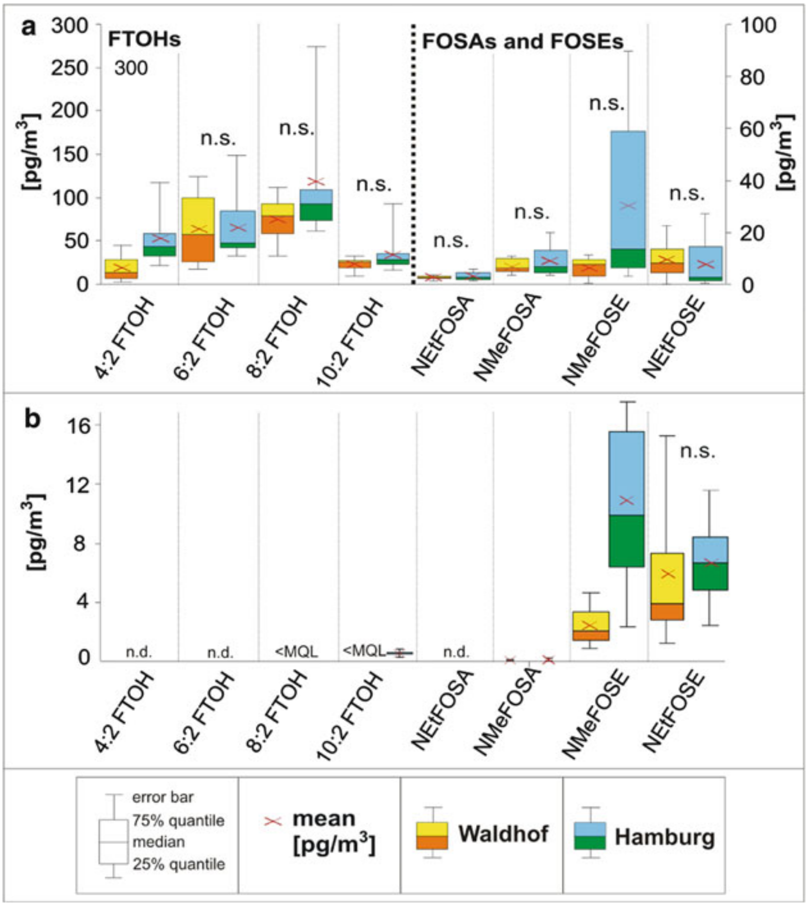


Fig. 11.2 Box-whisker plots showing concentrations (pg m^{-3}) of volatile PFCs in (**a**) the gaseous (PUF/XAD) and (**b**) the particulate phase (GFF) of German air samples. Note different scales for FTOHs as well as FOSAs and FOSEs in the gaseous phase (**a**). Mean concentrations are indicated as a cross, while the boxes show medians as well as 25 and 75 percentiles. Concentration differences between Hamburg and Waldhof, which are not significant (Mann–Whitney U-test [$p < 0.01$]), are indicated by 'n.s.'

and FOSEs, NMeFOSE was the prevailing compound in Hamburg, while NEtFOSE showed highest concentrations in Waldhof. PFC levels at the rural site were in most cases not significantly lower than in metropolitan Hamburg, underlining the widespread distribution of PFCs in Northern Germany.

The following airborne PFC concentrations were significantly higher in samples from the urban sampling site in Hamburg compared to the background site at Waldhof (Mann–Whitney U-test [$p < 0.01$]): 4:2 FTOH (gaseous phase) and NMeFOSE (particulate phase). This observation indicates the influence of possible point and diffuse sources at the urban site for these two compounds. Prior to application of the Mann–Whitney U-test, concentrations were divided by the mean temperatures (in K) during the respective sampling periods for each site.

Two samples from Hamburg showed very high concentrations for all PFCs investigated in this study. This phenomenon might be related to the prevailing wind direction, possibly passing a point source. However, due to frequently changing wind conditions within the long sampling times of 3.5 days, no correlation could be found between the predominant wind directions and analyte levels. Further studies are required to establish a relationship between PFC concentrations and air mass back trajectories.

A significant positive correlation was found between the ambient air temperatures and concentration levels of neutral, volatile PFCs (Fig. 11.3). This observation may be attributable to temporary deposition of PFCs at lower temperatures and revolatilisation when temperatures are higher. Furthermore, the study showed that FOSEs were distributed between the gaseous and particulate phase in dependence of ambient air temperatures, while FTOHs and FOSAs were found almost exclusively in the gaseous phase (Fig. 11.3). The observed correlation of the gas/particle distribution of FOSEs in dependence of ambient air temperatures has implications on their long-range transport potential. Being mainly associated with airborne particles at lower temperatures, they undergo wet or dry deposition relatively quickly.

11.3.1 Comparison of Airborne PFC Levels with 'Classical' POPs in Waldhof

A comparison of PFC concentrations with levels of several 'classical' and further 'new and emerging' POPs from a study conducted in Waldhof in 2002 was performed (see Table 11.3). Jaward et al. 2004 presented data of polychlorinated biphenyls (PCBs), selected organochlorine pesticides (hexachlorobenzene, HCB, α- and γ-hexachlorocyclohexanes, HCH, pp-dichlorodiphenyltrichloroethane, DDT) and polybrominated diphenylethers (PBDEs) from 22 countries across Europe. The German sampling sites included Waldhof.

The comparison revealed that 8:2 FTOH and 6:2 FTOH were present at higher levels than γ-HCH, the prevailing POP from the former study, thus underlining that PFCs are an important contaminant group. Further locations in Germany (one rural site in Southern Germany and one urban location in Western Germany) showed similar levels as Waldhof in the study by Jaward et al. 2004. This is in line with our findings concerning most airborne PFCs, which showed similar concentration levels in Waldhof and Hamburg, respectively. However, the insufficient amount of data available for classical POPs in Waldhof impeded further use of statistical tests.

Considering individual compounds, concentrations of γ-HCH reported for Waldhof were between 40 and 52 pg m^{-3}, depending on the sampling rate used for calculations (3–4 m^3 day^{-1}). The second highest concentrations were determined for HCB (32–42 pg m^{-3}), while levels of individual PCBs were highest for PCB 149 (6.7–8.8 pg m^{-3}). By comparison with volatile PFC data, mean 6:2 FTOH and

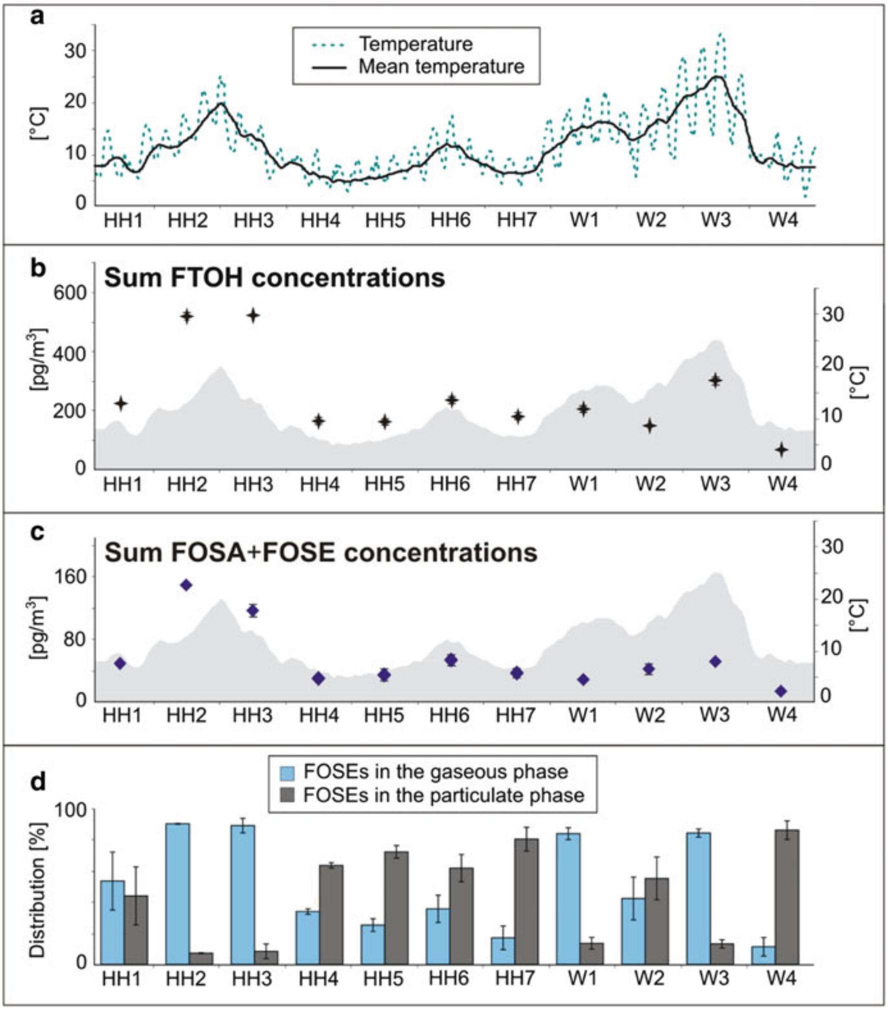


Fig. 11.3 Ambient temperatures (**a**), ΣFTOH (**b**) and ΣFOSA + FOSE (**c**) concentrations as well as the distribution of FOSEs between the gaseous and particulate phase (**d**) during the sampling campaign at Hamburg and Waldhof. FTOHs and FOSAs are almost exclusively found in the gaseous phase, while the distribution of FOSEs is correlated with ambient temperatures. Higher percentages are found in the gaseous phase at higher temperatures

8:2 FTOH concentrations were slightly higher than γ-HCH concentrations. Maximum values of the predominant FTOHs were by a factor of 2–3 higher, making 6:2 FTOH and 8:2 FTOH the prevailing POPs investigated in Waldhof air so far.

Sum concentrations of 29 PCBs and eight PBDEs in Waldhof were lower than for the sum of four FTOHs, underlining that FTOHs are the predominant POP group in Waldhof determined so far. Mean concentrations of ΣFOSAs + FOSEs were

Table 11.3 Comparison of air concentrations of neutral, volatile PFCs with those of 'classical' and further 'new and emerging' POPs (Jaward et al. 2004) determined at the Waldhof site

	Concentration (pg/m^3)	Reference
6:2 FTOH	17–125 (mean 64)	Jahnke et al. (2007b)
8:2 FTOH	33–112 (mean 75)	
ΣFTOHs	64–311 (mean 181)	
ΣFOSAs + FOSEs	14–52 (mean 34)	
γ-HCH	40–52	Jaward et al. (2004)[a]
HCB	32–42	
pp-DDT	5.5–7.2	
PCB 149	6.7–8.8	
Σ29 PCBs	73–96	
Σ8 PBDEs	9.7–13	

[a] Values were derived from passive samplers (ng analyte/sampler) and the minimum/maximum air volume sampled (130/170 m^3, respectively). The sampling was done from June 15 to July 30, 2002 (6 weeks)

slightly higher than ΣPBDEs. As Jaward et al. 2004 described relatively low levels of airborne POPs in Germany compared to other European regions, even higher FTOH concentrations are assumed to occur elsewhere. This was supported by first data from the U.K. (Barber et al. 2007).

11.3.2 Additional Sampling in Hamburg

An additional sampling event was carried out at the MPI in Hamburg in April, 2006 (Jahnke et al. 2007d). Concentrations of neutral, volatile PFCs were lower than during sampling in 2005, probably due to lower ambient air temperatures (average temperatures of 6.5°C vs. 10.9°C). PFC levels determined at the Hamburg site in 2006 were even lower than those observed at Waldhof in 2005 (average temperature during sampling 16.4°C).

High proportions of FOSEs were found in the particulate phase, corresponding to relatively low ambient air temperatures (Jahnke et al. 2007b). Regarding NMeFOSE, 88%, 54% and 82% were found on GFFs. NEtFOSE was detected just above a signal-to-noise ratio (S/N) of 10 in all particulate phase samples extracted from GFFs. A ratio could only be calculated for one sample, where 91% of the total NEtFOSE were found on the GFF.

11.4 Airborne PFCs at the European Background Site at Mace Head (Ireland)

Furthermore, one sampling campaign was performed at Mace Head, which is an EMEP and Global Atmospheric Watch (GAW) station located on the West coast of Ireland (Jahnke et al. 2009). Since the major wind direction brings air masses from the open Atlantic Ocean, the region is ideally suited to investigate European background levels of contaminants. Sampling took place during 2 weeks in March, 2006, generating four consecutive sets of duplicate samples (abbreviated as MH1@MH4). However, in the beginning of the sampling period, the prevailing wind direction was from the east and turned to the west during collection of sample MH3.

Generally, concentrations of neutral, volatile PFCs observed at the European background site were low. ΣFTOH levels were comparable with those observed in Arctir air, whereas ΣFOSA + FOSE concentrations at Mace Head were even lower (see below). Within the samples MH1-MH4, relatively high concentrations of neutral, volatile PFCs were found in sample MH3. This is possibly attributable to air masses having travelled over the U.K. and Northern France which was shown in air mass back trajectories (Jahnke et al. 2009). However, PFC concentrations analysed in sample MH4 can be considered as European background levels since the sampled air masses mainly came over the open Atlantic Ocean. Even though ambient air temperatures were the highest observed during the 2 weeks of sampling at Mace Head, concentrations in sample MH4 were lowest, underlining that the collected air masses were relatively ‘clean’.

11.5 Airborne PFCs in the European Arctic

First ship-based concentration data of neutral, volatile PFCs were obtained by sampling during scientific expedition ARKXX-1/2 of the German research vessel POLARSTERN of the Alfred-Wegener-Institute (AWI), Bremerhaven. The sampling campaign was carried out in the European Arctic between June and August, 2004 (Jahnke 2007). Although the analytical protocol used in this work had not been fully optimised and validated and several drawbacks have therefore to be taken into account (no duplicate sampling, only one isotope-labelled IS available), concentrations at relatively low levels could be reported. During the expedition, seven single samples were collected (sample abbreviation ARK1–ARK7).

NMeFOSE was n.d. except for one sample, while NEtFOSE was not detected at all. The determination of 6:2 FTOH, NEtFOSA and NMeFOSA was frequently possible, although often close to a S/N of 10. 8:2 FTOH and 10:2 FTOH were determined in most samples at relatively constant levels throughout the sampling period. No clearly decreasing trend was observed between Bremerhaven, Germany, and Arctic regions. However, the ship moved rapidly towards the North and air mass back trajectories revealed that the air which was sampled while passing by Norway came from the polar region without having travelled over land. Surprisingly, sample ARK5 collected close to Longyearbyen, Svalbard, showed highest levels of most target analytes, underlining the importance of possible diffuse sources.

11.6 Airborne PFCs Along the African West Coast

An additional ship-based sampling campaign applying the optimised analytical protocol took place on board of the German research vessel POLARSTERN (Jahnke et al. 2007c). The Atlantic transfer of the ice-breaker between Bremerhaven, Germany, and Capetown, Republic of South Africa, was used to collect eight sets of duplicate air samples along a latitudinal gradient from locations in Central Europe with supposedly many point and diffuse sources towards a less industrialised region. The scientific expedition ANTXXIII-1 was undertaken in October/November, 2005, providing first concentration data of neutral, volatile PFCs from the Southern Hemisphere. The samples obtained on this ship expedition are abbreviated as ANT1 to ANT8.

Sample ANT1 collected in the North Sea and channel between the European continent and the U.K. confirmed the former results from Hamburg, as concentration levels were in the same range. In addition to field blanks taken on the ship, this comparison underlined that the ship was a negligible contamination source for the investigated compounds. In sample ANT2 from the Biscay region, levels of neutral, volatile PFCs were already about one order of magnitude lower than in sample ANT1.

Between Spain and the equator (ANT3-ANT5), increasing PFC concentrations were found. This could be explained by higher ambient air temperatures towards the equator. After crossing of the innertropical convergence (ITC) zone at 3°N, PFC levels dropped, in some cases below the method detection limit (MDL) (ANT6-ANT8). 6:2 FTOH and NEtFOSE were n.d. and NMeFOSE was only detected once, while 8:2 FTOH, 10:2 FTOH and NMeFOSA could still be determined in all samples from the Southern Hemisphere. Those results demonstrated that neutral, volatile PFCs are mainly restricted to the Northern Hemisphere due to their atmospheric lifetimes between 2 and >20 days. However, trace amounts of several analytes could still be quantified south of the ITC.

11.6.1 Comparison of Ship-Based Measurements of Airborne PFCs

Concentrations of neutral, volatile PFCs as determined during the scientific cruises on the POLARSTERN could be set into context with data from another ship-based campaign in the Arctic as published by Shoeib et al. 2006. Their research group analysed air samples from the Atlantic Ocean taken on board of the Swedish ice-breaker ODEN between Gothenburg, Sweden and Barrow, Alaska. The ship-based data from ARKXX-1/2 and ANTXXIII-1 as well as those available from literature are summarised in Table 11.4.

Shoeib et al. 2006 found FTOHs, FOSAs and FOSEs in the particulate phase, while during the POLARSTERN expeditions, none of the target analytes was

Table 11.4 Ship-based measurements of neutral, volatile PFCs (pg m^{-3})

	Ship	ΣFTOHs	ΣFOSAs + FOSEs
ARKXX-1/2	POLARSTERN, North Atlantic	24.5[a]	10.6[a]
Shoeib et al. (2006)	ODEN, gaseous phase	20.4[b]	10.2[b,c]
	ODEN, particulate phase	4.3	4.6
ANTXXIII-1, Jahnke et al. (2007c)	POLARSTERN, English channel	379	33.4
	POLARSTERN, remote (Northern Hemisphere)	48.4	7.4
	POLARSTERN, remote (Southern Hemisphere)	7.7	1.1

[a] Mean of individual sum concentrations for each sample
[b] Sum of mean values for each analyte over all samples
[c] Analysis of NMeFOSE and NEtFOSE only

detected on GFFs. Mean ΣFTOH levels of Shoeib et al. 2006 and sampled during ARKXX-1/2 are comparable. As to expedition ARKXX-1/2, ΣFOSA + FOSE levels were represented mainly by NMeFOSA, while FOSEs were n.d. in most samples. However, Shoeib et al. 2006 only investigated FOSEs, so that the reported sum concentrations did not include FOSAs.

Regarding expedition ANTXXIII-1, sample ANT1 from the English channel was comparable to land-based measurements from central Europe. Samples ANT2 to ANT5 taken on the Northern Hemisphere were characterised by relatively high concentrations in comparison to ARKXX-1/2 and Shoeib et al. 2006, probably attributable to the crossing of temperate and tropical zones. In samples ANT6 to ANT8 from the Southern Hemisphere, FOSEs were mainly n.d., according to their relatively short atmospheric lifetimes (~2 days, D'Eon et al. 2006). NEtFOSA was only detected in some cases. However, 8:2 FTOH, 10:2 FTOH and NMeFOSA could be quantified in all samples with decreasing levels from tropical to temperate regions (Jahnke et al. 2007c).

11.7 Comparison of PFC Concentrations in Environmental Air

All data given in Jahnke 2007 are summarised in Fig. 11.4. Generally, 8:2 FTOH was the prevailing neutral, volatile PFC determined in our studies, followed by 6:2 FTOH and 10:2 FTOH, whereas FOSA and FOSE levels were much lower. This pattern in European environmental air samples has also been observed elsewhere (Barber et al. 2007; Dreyer et al. 2008).

Concentrations of neutral, volatile PFCs were highest in metropolitan Hamburg during the sampling period in spring, 2005, at relatively high ambient air temperatures. Levels observed in the ship-based sample ANT1 collected in the channel between the European mainland and the U.K. agreed well with these urban samples. PFC concentrations at the rural site in Waldhof were slightly lower. During sampling in Hamburg in spring, 2006, lower concentrations were determined. This may be due to the lower ambient air temperatures, since a positive correlation

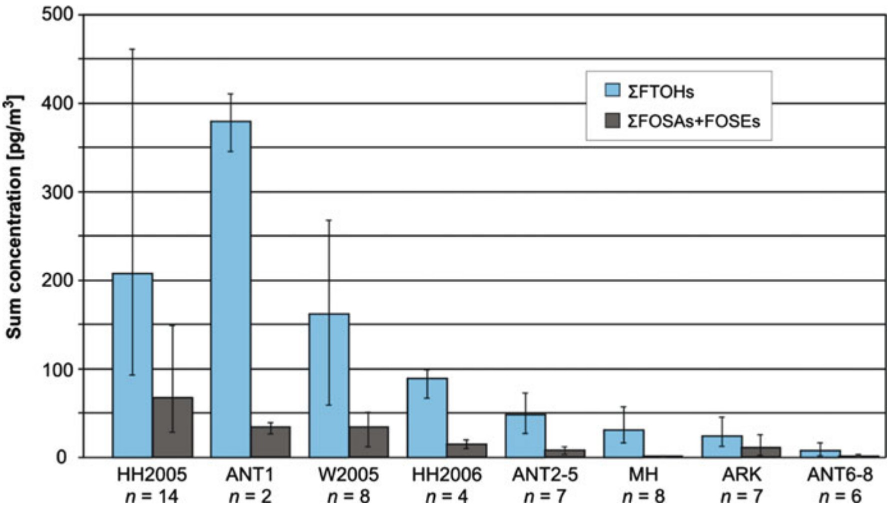


Fig. 11.4 Sum concentrations of neutral, volatile PFCs in environmental air from urban and rural locations in Europe as well as from remote marine locations. The following studies are included in Jahnke (2007) and Jahnke et al. (2007a, b, c, d, 2009). Σ6:2 FTOH + 8:2 FTOH + 10:2 FTOH and ΣNEtFOSA + NMeFOSA + NMeFOSE + NEtFOSE concentrations are given. Error bars represent the maximum and minimum sum concentrations observed, respectively

was shown between ambient air temperatures and levels of neutral, volatile PFCs in environmental air samples (Jahnke et al. 2007b).

PFC concentrations declined further in the ship-based samples ANT2–ANT5 from the Northern Hemisphere, at the European background site Mace Head and in the ship-based samples from the European Arctic, and were lowest on the Southern Hemisphere (samples ANT6–ANT8), where only three of the analytes were above their respective MDLs.

If comparing our results with the first data reported from North America (Martin et al. 2002; Stock et al. 2004), European FTOH levels were comparable or slightly higher, while concentrations of FOSAs and FOSEs in Europe seemed to be lower than in the U.S. However, if a single IS (e.g., 7:1 or 9:1 fluorinated alcohol) is applied for correction of the calculated concentrations of all analytes, FOSAs and especially FOSEs may be significantly overestimated due to matrix-effects (Jahnke et al. 2007a, 2009; Barber et al. 2007; Dreyer et al. 2008). Higher FOSA and FOSE than FTOH concentrations were also observed in Japanese air (Piekarz et al. 2007). Very high FTOH data in air samples collected in Japan were reported by Oono et al. 2008.

More recent data showed that FOSA and FOSE levels in North America have declined (Shoeib et al. 2006; Piekarz et al. 2007), probably partly due to the phase-out of perfluorooctane sulfonylfluoride (PFOSF)-based products by the major manufacturer by the end of 2002.

Arctic data obtained for FTOHs by Shoeib et al. 2006 were in the same range as observed during our sampling campaign (Jahnke 2007), whereas FOSA and FOSE concentrations were elevated in the studies reported by Shoeib et al. 2006 and Stock et al. 2007. However, when comparing data from different studies, it has to be kept in mind that in addition to analytical details, non-use based factors like meteorological conditions, seasonality and specific sampling locations may contribute to the observed differences.

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Part IV
Transport and Modelling

Chapter 12
Chemical Transport Modelling

Armin Aulinger

12.1 Introduction

A model in the here discussed form is first of all a description of complex processes in nature. This starts with a description by words or graphics (conceptual model) and goes up to complex mathematical or numerical simulation models that run on supercomputers. The complexity of a model is determined by several factors. It can be simply limited by computational resources which involves the questions if enough computer power or storage media for the data output is available or if there are appropriate tools available to make sure the data can be evaluated in a reasonable way. Developing a model can be seen as an interactive and iterative process. You can use a model to reproduce and understand experimental findings whereas at the same time experimental results are used to refine models. The most important point to consider before you build or acquire a model is the purpose the model should serve. Conceptual models e.g., could be used to describe physical or chemical processes in the atmosphere be it in lectures or for scientific discussions of processes. Mathematical models allow a more profound investigation of physical and chemical processes. Ultimately, models that are used to simulate the dispersion of substances over e.g., the European continent or to predict ambient air concentrations and deposition rates in a high spatial and temporal resolution can be very comprehensive. They often require a lot of input variables (e.g., meteorology, emissions) and parameters (e.g., physical–chemical constants). Insufficient knowledge of these inputs may lead to erroneous results or misleading interpretation of the results. The repertory of numerical simulation models ranges from simple box models that can e.g., represent a closed system and contain only one substance in one compartment and thus require little computer power to elaborate three-dimensional grid models containing plenty of substances involved in a number of physical and chemical processes. A scientist who develops or applies a model has to

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balance the complexity and expense of the model with the available input variables and parameters, the available computational resources and the demanded precision of the model results (Jacobson 2005).

An example for a simple mathematical model is the description of the degradation of a certain substance by the equation for first order reactions (I will explain this later in the text). Whenever possible the applicability of a particular mathematical formula to describe a process should be confirmed by laboratory experiments. This means in the above mentioned example that one would plot the concentration of the substance over the reaction time and determine the formula that describes the yielded curve best. Advanced numerical models consist of large sets of mathematical formulas to describe physical and chemical processes which are usually interconnected by linear and often non-linear relations (Jacobson et al. 1996; Liang and Jacobson 2000). Thus, the complexity of numerical models rises very quickly with each chemical reaction included. It is impossible to describe every single process a substance undergoes in the environment by detailed formulas because many processes are not yet fully understood and, further, representing everything in detail would be very costly in terms of computer power. To circumvent this, a lot of processes are simplified and described by parameters rather than using complex sets of mathematical formulas. A prominent example for parameterization is the description of turbulent movement in the atmosphere by the so called stability parameters (Stull 1988). An example for the simplification of chemical processes is "lumping" (see later in the text). As models have to be simplified for practical reasons they contain – depending on the degree of complexity – a number of assumptions. So it is obvious that model results like simulated ground level concentrations are only more or less uncertain estimations of real values. As a consequence, before a model can be used for scientific investigations or for operational purposes such as the forecast of aerosol concentrations in cities it has to be evaluated, most commonly by comparing the simulated concentrations with values measured in ambient air.

In the following I will explain basic modelling concepts and introduce some important model types that extend the basic concepts to comprehensive modelling systems. I will briefly present some popular models that are used for environmental modeling. Finally, by means of a benzo(a)pyrene (B(a)P) case study with the Eulerian grid model CMAQ I will illustrate in detail a concrete modeling application.

12.2 Basic Concepts

12.2.1 Box Model

The most basic element of all types of atmospheric chemistry transport models presented here is a volume element in the shape of a box. This box has in the simplest case a fixed size and is filled with a fluid, i.e., air, and a chemical substance

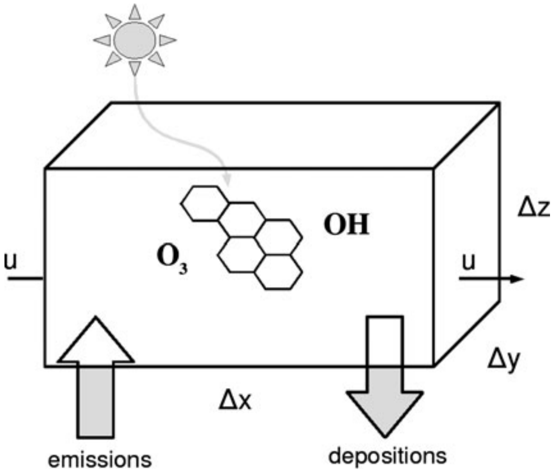

Fig. 12.1 Simple scheme of a box model

whose atmospheric fate is the subject of the investigation (Fig. 12.1). The concentration of the substance is everywhere in the box the same. This means the concentration has no dimensions in space, for which reason the box model is called a zero dimensional model – although the box itself has spatial dimensions. The concentration of the substance at model start (time = 0) is the initial concentration. If the simulated fluid is intended to be more realistic the box contains also water – as vapour or liquid – and a variety of chemicals in the gas phase, dissolved in water or adsorbed to particles. If the box is not closed, air from inside the box can be exchanged with air from outside the box by horizontal fluxes of air. This process is called horizontal advection and can lead to dilution or accumulation of substances depending on the concentration gradient between the inside and the medium outside the box (Jin and Demerjian 1993). In this way, a box is the smallest module of a atmospheric transport model.

12.2.2 Emissions and Deposition

Emissions from the bottom of the box represent a source and increase the concentration of substances. In the zero-dimensional box model it does not play a role whether the emissions come from an area or a point source or at which altitude they are emitted. Of importance is whether they are constant in or dependent on time and above all the source strength, i.e., how many molecules are emitted per time unit. Usually we discriminate between anthropogenic and natural emissions. Anthropogenic emissions emanate from combustion (e.g., heating, energy production, traffic), deliberate or accidental release into the environment (e.g., pesticides, fertilizers, oil spills) or product use (e.g., tire abrasion, solvents, lubricants) (Donahue et al. 2009; Dai and Rocke 2000). Natural sources involve volcanism, biogenic gases (e.g., terpenes) and wind blown dust. Most natural and some anthropogenic sources are dependent on the ambient temperature and the season or show diurnal variations (Marr and Harley 2002; Kuhlwein et al. 2002; Houyoux et al. 2000).

One sink for substances in air are depositions to the bottom of the box – the ground. These are distinguished by dry and wet deposition fluxes. Dry deposition fluxes are proportional to the concentrations in air with the constant of proportionality being the dry deposition velocity. For practical reasons in most models the inverse of the deposition velocity is calculated as the integral of the inverse vertical diffusivity over the planetary boundary layer height. This formulation is called the aerodynamic resistance concept. In analogy to electricity, resistances can be in series or parallel. The dry deposition velocity is in the end the inverse of the overall resistance. For gas phase species the overall resistance consists of three main in-series resistances: The aerodynamic resistance that is a function of turbulent transfer, the quasi-laminar layer resistance describing the laminar transport near the ground and the canopy resistance that characterizes the direct uptake of substances by soil or plants (Baer and Nester 1992). The canopy resistance itself consists of further sub-components which I do not want to explain in detail here (Gao et al. 1993). Chemicals can occur not only in the gas phase but also in particulate form. In that case the settling velocity comes into play. It depends on the size or mass distribution of the particles and is connected in-parallel with the aerodynamic, quasi-laminar and canopy resistance.

The wet deposition is an even more effective sink for many gaseous and particulate compounds than dry deposition. The loss of a substance through washout, the washout ratio, depends on the precipitation rate and the concentration of the substance dissolved in cloud water (Huret et al. 1994; Struyf and Vangrieken 1993).

In the case of gaseous species the quotient of dissolved and gaseous concentration is described by their Henry's Law constant. However, if the compounds participate in aqueous phase chemistry the effective Henry's Law constant depends also on the reactivity, the presence of other chemicals and the pH value. Concerning aerosols, it is often assumed that the major mass fraction of the aerosols is completely scavenged by cloud and rain water. Only for ultra fine particles (< 0.1 μm), it has to be taken into account that they are slowly absorbed into the cloud water (Binkowski and Roselle 2003; Binkowski and Shankar 1995) and thus the scavenging rate is smaller than for accumulation (< 2.5 μm) and coarse mode (< 10 μm) particles.

12.2.3 Chemical Degradation

Not only input and output processes determine the fate of substances in the atmosphere. A number of compounds emerge or disappear by means of chemical reactions where the vast majority of chemical reactions in the atmosphere are triggered by electro-magnetic radiation, i.e., sunlight. If a substance is degraded by radiation directly then the process is called direct photolysis. These reactions are usually first order reactions which means that the degradation rate depends only on the concentration of the degraded substance. Frequently photolytic reactions produce highly reactive radicals which then react with other substances in air. These reactions are called photochemical reactions that are normally of second or higher order. In practice the modelers try to avoid to formulate reactions of high orders in their models – by assuming the concentrations of the photo reactants being constant – because both the computational effort and the error of predicted degradations increase quickly due to the fact that the concentration of each reactant contains inevitable uncertainties and the relation between interdependent chemical reactions are non linear. In reality multiple reactions occur in the atmosphere in parallel and the degradation rates for the reactions are interconnected through highly non-linear relations. In Finlayson-Pitts and Pitts (2000), the most important reactions in the atmosphere and how they are dealt with in models are very well described. A necessary simplification of reaction schemes in addition to the above described reduction of reaction orders is the combination of various similar reactions to reaction types, the so called lumping (Makar et al. 1996). Thereby chemicals which are similar in their chemical structure and reactivity are lumped into one species. In the carbon-bond mechanism e.g., hydrocarbons are combined according to their bonds and functional groups: single bond (alkanes), double bond (alkenes), alcohols, and so on (Kuhn et al. 1998; Gery et al. 1989). In spite of these simplifications a chemical mechanism as used in comprehensive models consists of an extensive system of non-linear equations that has to be solved which is an ambitious mathematical challenge and requires powerful computers (Dabdub and Seinfeld 1994).

12.3 Model Types

12.3.1 Multi-compartment Box Model

In a multi-compartment box model the exchange of a substance between different compartments and sometimes between different phases within the compartments is simulated. There are three main compartments – atmosphere, water and soil – that can contain further subdivisions. The atmosphere could be subdivided into troposphere and stratosphere for example, the soil could consist of arable land, forest and urban area and the water could be distinguished by fresh and sea water, and so on. Within each compartment the model could have a solid, aqueous and a gaseous phase. The chemical species are then equilibrated between the different compartments and phases. The equilibration processes can operate on different time scales and depend on physical features of the substances and meteorological conditions like temperature, humidity, wind, and so on. The degradation scheme I explained for the atmosphere in the previous section applies in principle also to the other compartments. In soil and water, however, also biological degradation plays an important role (Klasmeier et al. 2006; Stroebe et al. 2004).

A zero-dimensional box model has by definition no spatial resolution. One defines a domain that is represented by the box, e.g., Europe, and the compartments that are contained in this domain. Then the model calculates average concentrations in each of the compartments and fluxes – defined by the model time steps – between the compartments and phases (Hollander et al. 2007). At certine time steps concentrations and fluxes are written to files. Boxes can be nested within one another. Then they are often not strictly zerodimensional any longer. Frequently, these models are also called multimedia fate models. As an example, one could define Germany as the innermost box. This may be surrounded by a box for the European continent that exchanges masses with the inner box according to defined time steps e.g., by advection and diffusion. The European box could then be surrounded by a hemispheric and a global box (Fig. 12.2). Thereby, model time steps and compartments can be different in each nest. Degradation processes and interactions between compartments and phases do not necessarily have to be exactly the same in all nests. Especially the temporal and spatial resolution is often higher in the inner nests. The outer nests serve to derive the boundary conditions for the inner nests.

12.3.2 Trajectory Model

A trajectory model takes as input the initial box location and the magnitude and direction of the winds (known as wind field analyses) and uses this information to determine whence the air parcels originated and where they are going to go (Fig. 12.3). The initial location of the box could be an emission source like

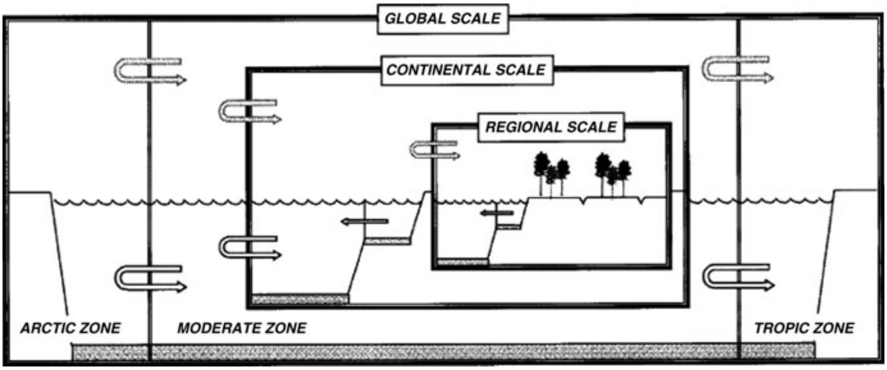

Fig. 12.2 Multimedia fate model SimpleBox2.0 (From Brandes et al. 1996)

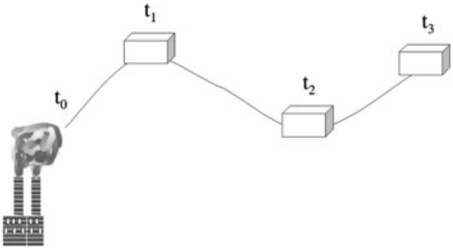

Fig. 12.3 Box moving along a trajectory starting at time t_0

a stack. While the box is hauled along a trajectory by the movement of air, i.e., advection, convection and turbulence, the same processes can apply as in the non-moving box. The chemicals can undergo reactions, adhere to particles and be dissolved in cloud water. In the simplest case, the model consists of one single moving cell assuming that the integrity of the air parcel is maintained throughout its travel along its projected path. In more advanced models an arbitrary number of boxes can be defined having permeable walls that can exchange masses with the surrounding air or other boxes if two trajectories meet. Of course, the computational effort increases the more boxes are involved in the simulation. A frequent application of trajectory models is the tracking of a plume of hazardous chemicals after an accident. It is also possible to let the box move along a trajectory backwards in time. This is then called a back-trajectory model. It means that the box starts at a certain location – e.g., a measurement site – with the measured concentration as initial concentration and moves back to the source with all the processes running backwards in time. Such a model is used for source apportionment i.e., estimating the contribution of different sources to the concentration levels at or the deposition fluxes into certain regions, the so called receptor regions (Stohl 1998; Rao et al. 1983).

12.3.3 Eulerian Grid Model

In the Eulerian formulation a fixed coordinate system or grid is laid out over the entire region of interest, the model domain (Russell and Dennis 2000; Peters et al. 1995). It has already been explained that one single box represents zero-dimensions in space. If several boxes of equal base area are stacked to a pile and the boxes can model exchange of matter amongst each other the concentration distribution along an axis can be modelled (Fig. 12.4a). Such a model has one dimension. Frequently

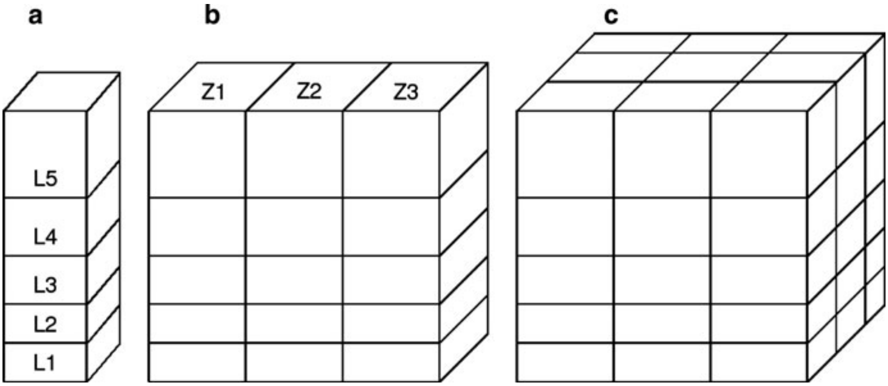

Fig. 12.4 single column model (**a**), zonal model (**b**) and 3D-Eulerian model (**c**)

the axis represents the height (z-axis) and the model is called a column model that simulates the vertical distribution of substances. A second dimension is introduced if more such columns are placed in a row (Fig. 12.4b). This concept can be applied for example in a zonal model. In zonal models each column represents a particular zone like the tropical, subtropical, moderate and polar zone or any other zone defined by the model designer.

A three-dimensional Eulerian model consists in that way of many stationary boxes – the grid cells – of base areas ($\Delta x \times \Delta y$) which are spanned in the horizontal plane (Fig. 12.4c). Along the z-axis (height) a defined number of layers of boxes are stacked. It is important to note that Δx and Δy is fixed and the same for all boxes in the grid while delta z is variable between the layers and usually increases with height. The most important reason why the vertical resolution has to be higher near the ground is the determination of the planetary boundary layer (PBL) which should be as exact as possible. The PBL defines a layer from the ground to a height up to which the atmosphere is well mixed due to permanent convection and turbulence. There, the density of air pollutants and photo-oxidants is relatively high. Thus, the processes determining the fate of pollutants are usually more complex within the PBL. Also the emission and deposition takes almost exclusively place in the PBL. The top of the PBL is a barrier for chemicals and aerosols. Its height depends mostly on the ground temperature and wind speed which drives the convection and is thus variable in time. When the height decreases like during night time the air masses near the PBL top are detrained and with them substances and particles which are then hardly available to deposition and can be transported over large distances by air being advected by geostrophic winds. If the temperature increases during sunny days the PBL top rises. Then substances and aerosols are entrained in the PBL and easier available for deposition.

The faces of the grid cells are permeable so that matter, heat, humidity, and so on, is exchanged between the cells in every model time step. Thereby it must be ensured that the masses of all substances remain constant in the model domain except for losses and gains. This constraint is reflected by the mass balance equation [see (12.1)]. It contains first of all terms for large scale movement (advection in horizontal and convection in vertical direction) that is dependent on the wind speed u in x-, y- and z-direction as well as small scale movements (turbulence) of air described by the turbulent diffusivity K. The concentration of pollutant i in each cell (x,y,z) of the grid at time t is then calculated by explicitly solving the mass balance equation, using numerical methods and the help of a computer, over a series of short time intervals. In cells which contain emission sources, a source term E is added to the right side of the equation. The loss of the substance by deposition is reflected by the loss term S. To complete the system for non-inert species the mass balance equation requires also a term that accounts for gains and losses by photolytic and photochemical reactions R which can cause either loss (degradation) or gain (production) of substances. The Eulerian grid model approach is most useful for situations in which multiple sources are located or if concentrations need to be predicted for an entire region (Zlatev et al. 1992).

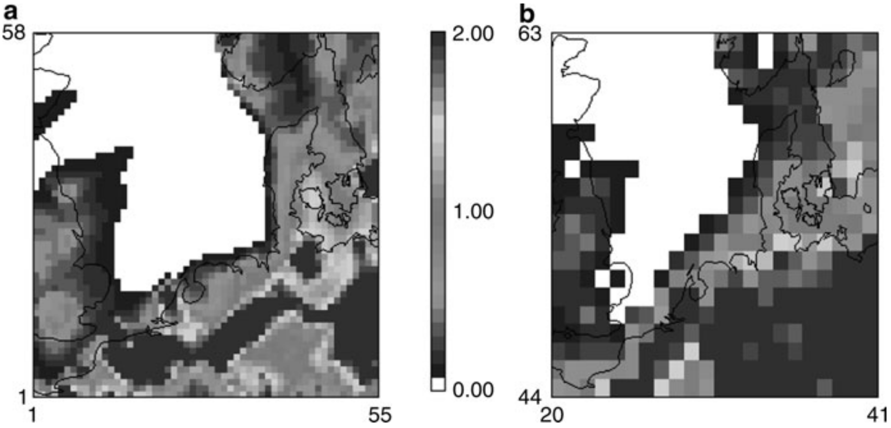

Fig. 12.5 Depositions of B(a)P simulated on a 18 × 18 km^2 (**a**) and a cut-out of the 54 × 54 km^2 (**b**) grid

$$\frac{\partial c_i}{\partial t} + u_x \frac{\partial c_i}{\partial x} + u_y \frac{\partial c_i}{\partial y} + u_z \frac{\partial c_i}{\partial z} = \frac{\partial}{\partial x}\left(K_{xx}\frac{\partial c_i}{\partial x}\right) + \frac{\partial}{\partial y}\left(K_{yy}\frac{\partial c_i}{\partial y}\right) + \frac{\partial}{\partial z}\left(K_{zz}\frac{\partial c_i}{\partial z}\right) + R_i(c) + E_i(x,y,z,t) + S_i(x,y,t) \tag{12.1}$$

Like box models also many Eulerian grid models can be run in nested mode. Then, a model covering a larger domain in coarse resolution – which means larger grid cells – is run first to determine the boundary conditions for the nest or inner domain (Fig. 12.5). The inner domain covering usually a region of major interest has a finer resolution or smaller grid cells allowing a better representation of e.g., convective clouds or a profiled terrain and the processes involved. As the computational effort rises quickly with the resolution it can be reasonable to zoom only into that part of a model domain where it appears advisable, for example if the terrain is complex like in mountain or coastal regions or where many different sources are located.

12.3.4 Examples of Models Used for POPs

Very popular for simulating the fate of POPs are multi-compartment box models (or multimedia fate models) because most POPs are exposed to various chemical, biological and physical processes in the atmosphere as well as in the aquasphere and in soil and vegetation. With the box model concept it is feasible to consider these manifold processes because they are simulated – usually – with only a few boxes which reduces the computational costs. The drawback is that the spatial resolution is low. However, many multi-compartment box models combine boxes that represent different regions. This is, for example, applied in the SimpleBox2.0

model (Fig. 12.2). SimpleBox is a nested multi-media fate model of the "Mackay type". Mackay proposed to calculate fugacities do describe the flux of a compound from one compartment into another (Mackay 1991). The environment is modelled as consisting of a set of well-mixed, homogeneous compartments (air, two water compartments, sediments, three soil compartments and two vegetation compartments) in regional, continental and global scales. The model takes emission rates and rate constants for transport and transformation of micropollutants as input and computes steady-state concentrations as output. SimpleBox is a generic model in the sense that it can be customized to represent specific environmental situations which includes to define the number, size and location of the boxes. As air masses are exchanged between boxes at different locations the model has one dimension in terms of concentrations (Brandes et al. 1996).

Another example of such a one-dimensional multi-compartment box model is CliMoChem. It contains a flexible number (typically 20–30) of latitudinal zones with different temperatures and compartment volumes. CliMoChem does not have a spatial resolution in east–west direction while in north–south direction, the spatial resolution is given by the number of zones. Compartments included are soil, oceanic surface water and tropospheric air as well as vegetation and vegetation soil (Scheringer et al. 2000). More examples of multi-compartment box models used in modelling the environmental fate of POPs are ELPOS (Beyer and Matthies 2001) and EVN-BETR (Hansen et al. 2006).

An example for a two-dimensional zonal model is Globo-POP (Wania and Mackay 1995). This model is a zonally averaged global multimedia fate and transport model formulated in fugacity notation (Mackay 1991). Ten climate zones are distinguished based on a climatic classification of the world. The atmosphere is divided into four vertical layers. Vertical and horizontal atmospheric advective transport velocities and macro-diffusivities are defined with a monthly resolution, as are temperatures and the concentrations of OH radicals. Within each latitudinal zone, the Earth's surface is represented by two soil (agricultural and non-cultivated soil), a fresh water, a fresh water sediment and a surface ocean compartment. Chemical fate processes considered include: equilibrium phase partitioning between subcompartments, advective and diffusive transport between compartments (including meridional transport in the atmosphere and ocean), first order degradation in each compartment (second order in atmosphere between vapour phase chemical and OH radical), transfer to the deep sea and fresh water sediment burial.

To model concentration the transport of a pollutant in all three dimensions in space one could use a trajectory model. One trajectory model that is applied in modelling the environmental fate of POPs in the atmosphere is HYSPLIT. This is a three-dimensional Lagrangian model developed at the National Oceanic and Atmospheric Administration (NOAA). When simulated puffs enter new grids, they are split and follow their own trajectory. Meteorological data is interpolated between date time periods. The HYSPLIT is able to preserve source-to-receptor identity while simulating atmospheric transport, destruction and deposition of hypothetical emission puffs, from each source point to target receptor areas. The source-to-receptor relationship can be represented, as an output of HYSPLIT, by the ratio deposited to the receptor from one unit emission from the source, the atmospheric transport coefficient (ATC). When ATCs are mapped, the effect of weather patterns and pollutant chemical properties on transport can be evaluated (Draxler and Hess 1998; Cohen 1997).

Three-dimensional Eulerian grid models are designed to model three-dimensional concentration gradients. The MSCE-POP model combines the principle of a 3D Eulerian grid model with the multi-compartment approach. It describes processes in and exchange between the atmosphere, soil, seawater and vegetation. The spatial resolution of the model is 150 × 150 km. In particular, apart from atmospheric transport the model takes into account the transport of pollutants by sea currents. Further, transport from vegetation to soil is considered, in which forest litter was introduced as an intermediate media between vegetation and soil. The atmosphere, soil, and sea are separated vertically into a number of layers to describe the vertical transport of pollutants. To describe variability of soil and vegetation properties in the horizontal direction the corresponding land-use and leaf area index information is taken into account (Shatalov et al. 2000).

The DEHM-POP is a 3D atmospheric transport model initially developed to describe the long-range transport of sulphur into the Arctic (Christensen 1997). It has recently been further developed by adding a scheme with 54 chemical species (e.g., O_3, NH_3, and NO_x) involved in 110 reactions. Also, mercury and persistent organic pollutants (POPs) were considered in the expanded model. This included also a description of the exchange processes between the land/ocean surfaces and the atmosphere in order to account for the multi-hop transport of POPs (i.e., repeated deposition and reemission). The environmental parameters for the surface compartments and the parameterization of the air/surface exchange processes have been adapted from a multimedia box model (Strand and Hov 1996). The processes described by DEHM-POP are atmospheric advection, diffusion and wet deposition, air/surface gas exchange and degradation in the three media. The model has a horizontal resolution of 150 × 150 km and 20 unevenly distributed vertical layers in terrain-following sigma-coordinates extending to about 18 km height.

12.4 A B(a)P Case Study with the CMAQ Model

12.4.1 Model Description

The Models-3 Community Multiscale Air Quality (CMAQ) modelling system (Byun and Ching 1999) has been developed under the leadership of the Atmospheric Modelling Division of the EPA National Exposure Research Laboratory in Research Triangle Park, NC. The modelling system and its source codes are freely available for use by air quality regulators, policy makers, industry, and scientists to address multiscale, multi-pollutant air quality concerns. It includes a three-dimensional Eulerian chemistry transport model that currently allows simulating concentrations and deposition of the major air pollutants, particulate matter and Hg. Because of its generalized coordinate system and its advanced nesting features CMAQ can be used to study the behavior of air pollutants from local to regional scales. It can be investigated where pollutants that can travel over long distances originate from and how they behave within smaller domains that are driven by particular meteorological conditions like the coastal zones. At the Institute for Coastal Research of the Helmholtz-Zentrum Geesthacht, a version of CMAQ has been developed that can be used to study the trans-boundary transport of PAHs and PCBs and their deposition into coastal regions (Aulinger et al. 2007; Matthias et al. 2009). CMAQ is a 3D Eulerian regional model that was in our case configured for the European continent. The entire model domain is split into an outer domain that covers Europe from the Mediterranean Sea to the North Polar Sea and from Iceland to Western Russia with a grid cell size of $54 \times 54\ \text{km}^2$ and a nest covering the North Sea with a cell size of $18 \times 18\ \text{km}^2$. It has 30 vertical layers that reach 100 hPa.

The CMAQ chemistry transport model (CCTM) was mainly designed for classical air pollutants like SO_2, NO_x, O_3, and particulate matter (PM). In our model version the CBIV chemical mechanism (Gery et al. 1989) was applied – combined with aqueous and aerosol chemistry routines – that takes into account the atmospheric reactions of the main pollutants including the production of photooxidants as well as the formation of secondary organic and inorganic aerosols both of which are crucial for the fate of B(a)P in the atmosphere. At the Helmholtz-Zentrum Geesthacht, the CCTM was extended to cope with the transport of B(a)P in the gas phase and adsorbed to particles (Aulinger et al. 2007). Thereby, special emphasis was laid on considering the mass transfer of B(a)P between the gaseous and the particulate phase. The partition of the compound between the gas and the particle phase as well as its distribution between particles of different size modes is dependent on temperature and particle surface, mass of organic aerosols and aerosol water content in each mode. The physical–chemical properties of B(a)P which determine the partition are hence its liquid vapour pressure, octanolair partitioning coefficient and Henry's Law constant. In the current version of our B(a)P module gaseous B(a)P is degraded by photolysis and by reactions with OH and ozone radicals. However, at temperatures prevailing in middle Europe B(a)P occurs mainly bound to aerosols. Even though the degradation reactions of particle bound B(a)P is orders of magnitude slower than those of the gaseous form (Esteve et al. 2006) heterogeneous reactions, i.e., reactions of gaseous chemicals with particulate B(a)P are relevant to simulate the atmospheric fate of B(a)P. According to Kwamena et al. (2007) the decisive reaction is the reaction with gaseous ozone which has been implemented in the CCTM.

12.4.2 Required Input

To drive the transport and deposition mechanisms of the CCTM several meteorological parameters are required which are calculated with the meteorology chemistry interface processor (MCIP) from prognostic variables provided by a meteorological model. To calculate the meteorological variables we used NCARs fifth generation mesoscale atmospheric model (MM5) which is widely used within the scientific community and whose applicability for use with CMAQ for the European model domain has been tested (Matthias et al. 2008; Grell et al. 1995). Other input data needed to run the model are boundary conditions, i.e., concentrations of substances at the borders of the model domain, and initial conditions, i.e., concentrations when the model is started. For the simulations presented here the boundary conditions of the main pollutants were taken from MOZART (Horowitz et al. 2003) model results. The data have a spatial resolution of 1°x1° and a temporal resolution of 1 day. They include the gas phase species O_3, O, O^1D, CO, NO, NO_2, SO_4, HO_2, OH, PAN, HCOH, isoprene, terpenes and HNO_3. The modelled concentrations of these species were interpolated to the boundary of the outer CMAQ domain. However, as the MOZART data vary only day by day and the model input frequency is 1 h, the data had also to be temporally interpolated. Intercontinental transport of aerosol particles was not considered. Further, we had no knowledge of B(a)P concentrations outside the model domain why the boundary concentrations for B(a)P were set in a way that avoids a concentration gradient through the border. Boundary conditions of all substances for the inner domain are derived from results of model runs in the outer domain. Initial conditions are set once to average winter concentrations found on 25 December the year before run started. By this spinup time of 7 days, the influence of the initial conditions is kept very low. For a detailed description of how to set up and run CMAQ refer to Byun and Ching (1999).

Next to the correct representation of the meteorological conditions that drive the transport of air in the model simulations the emission of substances into the model domain are crucial to obtain precise predictions of substance concentrations and depositions. Thus, much research is carried out about emissions to provide detailed emission inventories for modellers.

For the here presented simulations an emission inventory of the gaseous species NO_x, SO_2, CO, NH_3 and 35 non methane volatile organic compounds as well as PM10 and PM2.5 was purchased from the Institute for Energy Economics and the Rational Use of Energy (IER), Stuttgart, Germany. The inventory contains gridded data for the inner and outer CMAQ domain in hourly resolution for the year 2000. The annual country emissions from the EMEP data base and the European Pollutant Emission Register (EPER) were taken as a basis. Experts at IER interpolated these data to our model domain under consideration of population density, roads and industrial plants and took also care of the temporal disaggregation of the emissions. Details on the emissions model of IER are described in Friedrich and Reis (2004).

Emissions of the biogenic chemicals isoprene and terpenes that are the most important precursors of secondary organic aerosols were taken from the POET data base while emissions of particulate organic matter and elemental carbon was derived from the Global Fire Emissions data base. Dust was considered using the Aerocom emission data sets for the year 2000. These data sets are usually used for global models and are typically given as monthly averages on a 1°× 1° grid.

For our purposes we interpolated them spatially first to the outer and subsequently to the inner domain and temporally down to daily varying emissions.

For B(a)P we used an emission inventory developed by TNO. They provided an emission inventory for Europe containing yearly bulk emissions for the year 2000 (van der Gon et al. 2005). The base for this inventory was officially reported country emissions. In addition, the authors of the study created a reference data base derived from emission activities and emission factors which they used to complete and correct the official data where this appeared advisable to them. The resulting emission inventory was kindly provided to us in a gridded version projected on the $50 \times 50\,\mathrm{km}^2$ polar stereographic EMEP grid. Because the emissions from residential heating (wood and coal burning) are highly dependent on season, we introduced a temporal cycle that depends on ambient temperature for this source category. Weekly and diurnal cycles of the B(a)P emissions were also considered. They were chosen to follow the NO cycle for traffic emissions and the CO cycle for heating processes (Bewersdorff et al. 2009).

12.4.3 Simulations

The input files with meteorological variables and emissions must be in the same grid format, involving projection type and spacial resolution, as the model is intended to run on. If this is not the case the input data must be interpolated so that they are consistent with the model grid. The temporal resolution of the input variables is 1 h like the output time step – when simulated values are written to a file. In this test case we ran the model for the entire year 2000. CMAQ is configured to write output to files every hour of simulation time containing concentrations and deposition fluxes of substances and particulate matter. Thus, the model yields values representing hourly concentrations for every grid cell for more than 80 substances as well as fluxes for each cell in the lowest layer of the model domain which sums up to more than 2 Gbyte of data for every day simulated. To evaluate and interpret this huge amount of data several graphical and statistical methods can be applied.

Generally, it is evident that the highest B(a)P concentrations and deposition fluxes occur in regions where also high emission rates can be observed (Fig. 12.6). The reason is that B(a)P is mostly bound to particles and the larger part of it is therefore deposited before it can reach higher levels and be transported over large distances. However, a small fraction of B(a)P is indeed available for long range transport and can be found far away from the sources. The highest concentrations occur in densely populated areas like the Rhine–Ruhr area in Germany, and especially in regions where coal and oil are burned without efficient purification of the exhaust gases like the greater Moscow area. At the same time, the deposition rates are also determined by precipitation rates because wet deposition is a very important sink for atmospheric B(a)P and other PAHs. The total B(a)P emissions in the Rhine-Ruhr area were in 2000 about 10 t. This resulted in a deposition rate of

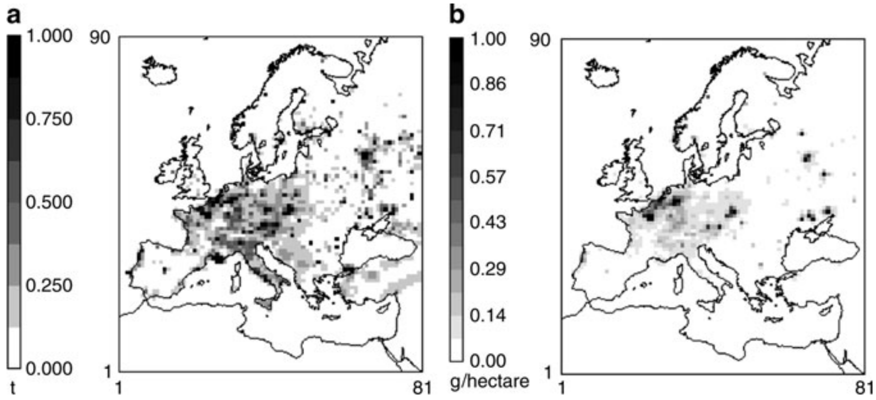

Fig. 12.6 Total emissions (**a**) and depositions (**b**) of B(a)P in 2000 in Europe

0.29 g/ha for the year 2000 averaged over this area and the total deposition into this region was 203 kg. Over the Baltic Sea without any emissions – ship emissions are not considered so far – the average deposition rate for 2000 was 0.02 g/ha (Fig. 12.6) which sums up to 701 kg direct atmospheric input of B(a)P into the Baltic Sea. The reason is that B(a)P is transported mainly from middle and eastern European regions in northern direction towards the Baltic Sea where it is scavenged by rain water. The dominating influence of rain events on the deposition pattern can be seen from the fact that the highest deposition fluxes occurred in October and November, the months with the highest precipitation rates, and not in December and January, when emissions were at its maximum.

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Chapter 13
Assessment of Source–Receptor Relations by Inverse Modelling and Chemical Data Assimilation

Hendrik Elbern, Achim Strunk, Elmar Friese, and Lars Nieradzik

13.1 Introduction: Objectives of Data Assimilation and Inverse Methods

Data assimilation and Inverse Modelling may serve various purposes by use of manifold techniques. A reasonable definition reads as follows:

> The objective of atmospheric data assimilation is to produce a regular, physically consistent four dimensional representation of the state of the atmosphere from a heterogeneous array of in situ and remote instruments which sample imperfectly and irregularly in space and time. The regular, physically consistent aspect of the procedure comes from the use of models, and thus data assimilation is a discipline which naturally integrates theory (via models) with sampled reality (via instruments). . . .
>
> Data Assimilation
>
> - extracts the signal from noisy observations (filtering)
> - interpolates in space and time (interpolation) and
> - reconstructs state variables that are not sampled by the observation network (completeness).
>
> (Daley 1991)

Typically, the parameter to be estimated is a prognostic variable of a model, which changes continuously. In contrast, inverse modelling is likely to focus on more stable parameters, given a data set of a short time span.

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The Objectives of Inversion:

1. Estimates of dynamic fields by sparse observations, physical laws, and statistical knowledge, to analyse consistent data sets and optimal initial and boundary values (Data assimilation)
2. parameter estimates and parameter optimisation of models and algorithms
3. sensitivity studies and solutions of ill–posed numerical problems
4. optimisation of observation systems
5. test of scientific hypotheses

(Bennet 1992)

Given K observations $y_0 = ((y_0)_i, \ldots, (y_0)_K)^T$ and a regular grid with N gridpoints $x = (x_1, \ldots, x_N)^T$, said the analysis or model grid. Usually, $K \ll N$. We seek to identify or reconstruct or "analyse" the field of the observed quantity on the analysis grid by observations, that is we try to find an estimate of the most probable, or the least flawed state in terms of all available information.

In tropospheric chemistry data assimilation a variety of aspects are to be considered, which differ considerably from traditional atmospheric data assimilation. As always in atmospheric chemistry, the number of parameters per grid point is much higher than in meteorology. A state of the art air quality model prognoses more than 50 constituents in gas phase only. If aerosol dynamics and chemistry are included, this number is easily doubled.

In addition, the underlying chemistry models are only an approximation to the presumably most important constituents. Especially hydrocarbons, referred to as volatile organic compounds (VOC) occur in a variety of components, which cannot be accounted for in a complete way. Further, aerosol particles are even more different in size, shape, chemical composition and complexity of reactions, engendering even more deficits of required knowledge.

While the focus of tropospheric chemistry analysis is usually placed on the surface, smaller scales of time and space gain increasing importance. Local air quality is forced by local emissions, with background values controlled by transport processes of larger scales. As a consequence, a sequence of scales should be covered from simulating long range, even intercontinental transport of pollutants, down to a proper representation of emissions effectuated by point and line sources like stacks and streets. In practice, different chemical regimes prevail on short spatial scales. Sinks are acting by surface uptake from soil and vegetation, again imposing a much finer pattern as mesoscale meteorological features typically show.

In atmospheric chemistry data assimilation, as is in meteorology, initial state variables of the model are typically the parameters to be optimized. Hence, these initial values are implicitly assumed to be the least well known parameters and, at the same time, the critical factor for an improved analysis or forecast skill. As tropospheric chemistry transport models solve an initial–boundary value problem with strong dependencies on surface parameters, the restriction to initial value optimization only is no longer justified. Moreover, it is well known that, under favourable conditions, freshly emitted surface pollutants can easily enter the free and upper troposphere. Therefore, better knowledge of the emission strength and meteorological stability conditions appear to be at least as important as of initial values.

More precisely, emissions are not only a problem of scale, but also an issue of both impact on model results and paucity of knowledge. Especially in areas exposed to air quality problems, the errors in the emission rate estimates can be considered as among the primary causes for prediction deficiencies of pollution levels. Consequently, emission rates must be considered as optimisation parameter.

To demonstrate the feature of joint emission rate – initial value inversion, the semi-rural observation site Eggegebirge, Germany, is presented, where both parameter types are of like importance for a 2 day forecast: the site has minor emission sources in its vicinity, but polluted air can be advected from within some 100 km distance. Figure 13.1 displays an unsatisfying skill of a prediction without assimilation, while pure initial value optimisation exhibits a good performance during the time of the assimilation window, the ensuing forecast on the second day relaxes toward the forecast without assimilation, clearly demonstrating a short "chemical memory" of the system. On the other hand, pure emission rate optimisation exhibits a clear positive impact at the second day, without significant improvements during the assimilation interval. This is due to the fact that the local emission rates are low, but also due to the delay caused by the oxidation time from precursors for ozone production. A joint emission rate – initial value inversion combines both positive impacts and clearly leads to the desired effect of forecast skill improvement.

As an optimal choice in this case, a combined and balanced initial value/emission rate optimisation appears to be advisable. By the like arguments, deposition velocities could also be considered as optimisation quantity, if they are poorly known.

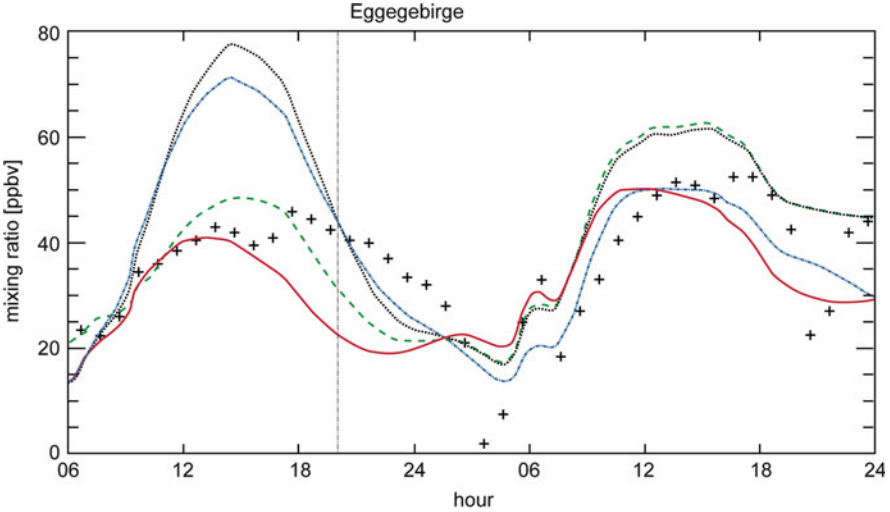

Fig. 13.1 Assimilation results and performance at the ozone measurement site Eggegebirge for August 7 and 8, 1997. *Black crosses*: observations, *left* of *vertical line* at August 7, 20:00 taken for assimilation, later observations for forecast verification only. Reference forecast: *black dotted line*, initial value optimisation only: *green dashed line*, emission rate optimisation: *blue dash-dotted line*, joint emission rate/initial value optimisation: *red bold line*

An estimate of uncertainties and sensitivities of ozone prediction due to uncertainties of various input parameters has been provided by various studies, e.g., Hanna et al. (1998), Hanna et al. (2001) or Schmidt and Martin (2003). While parameters like photolysis rates and meteorological conditions are of importance, emissions still figure prominently as control parameters.

At the beginning of chemical data assimilation, techniques to analyse tracer fields were based on mono-variate kriging techniques of surface concentrations (see e.g., Fedorov 1998 for a review). Attempting to combine observations of different times, intermittently applied spatial data assimilation procedures cannot make use of the known physical and chemical laws as a most useful constraint. Ability to do so, would not only enlarge the observational data base per assimilation procedure by measurements over a full time interval, but also enforce some chemical consistency, dependent on the model design.

A first real world application with a full fledges chemistry–transport model (CTM), the EURAD model, is given in Elbern and Schmidt (2001). By including all emitted species at each surface grid points, the typical optimisation space of initial values by atmospheric chemical state constituents is replaced by a scaled emission rate space in Elbern et al. (2007). An example on assimilation of satellite data in tropospheric chemistry models is given by a dedicated section in Lahoz et al. (2007).

A practical application on the microscale has been presented by Quélo et al. (2005) for NO_x emissions and their diurnal profile, using the Polair3D model. Another regional tropospheric 4D-var assimilation system exists with the STEM–2K1 (Chai et al. 2006).

Adopting the variational inversion technique on the global scale, Muller and Stavrakou (2005) assimilated tropospheric column retrievals of CO and NO_2, to assess emission rates of continental scales.

In the Netherlands two CTMs were furnished with sophisticated implementations of complexity reduced Kalman filters. These include the reduced rank square root Kalman filter of the Long Term Ozone Simulation (LOTOS) model (van Loon et al. 2000) and the EUROS model (Hanea et al. 2004). The reduced rank square root approach was selected to factorize covariance matrices by a few principal components (Verlaan and Heemink 1995). Further elaboration on this technique by combination with an ensemble Kalman filter method resulted in additional skill (Hanea et al. 2004). Optimisation parameters include emission rates, photolysis rates, and deposition rates, the correction quantities of which are formally introduced as "noise" parameters in the Kalman filter formulation.

Model based chemistry data assimilation and complex aerosol modelling in full fledged air quality models are emerging issues of only recent years. In Collins et al. (2001) the authors applied the MATCH model, in which sulphate, black carbon, organic carbon and mineral dust are predicted while sea salt aerosols are diagnosed. Optimal interpolation is applied as assimilation scheme. The assimilation parameter is the aerosol optical depth (AOD) retrieved from NOAA AVHRR over oceans. By contrast, van Loon et al. (2000) used a Reduced Rank Square Root Kalman filter (RRSRKF) to assimilate AOD gained from ATSR-2 into the LOTOS model, which crudely estimates the model AOD by doubling the value resulting from modelled $SO_4{}^{2-}$, $NO_3{}^{-}$, and $NH_4{}^{+}$. A variational approach for aerosol dynamics in a box model is presented by Sander et al. (2005) with sectional discretisation and adjoint formulation of the integro-differential equation of coagulation, growth, and nucleation processes. While in Collins et al. (2001) emphasis is placed on modelling of a more sophisticated aerosol optical depth by state of the art modules, the OI assimilation scheme applied here provides for the BLUE property only as a purely spatial algorithm.

Data assimilation has also been extended to inverse modelling of biomass burning emissions. Zhang et al. (2005) applied a Bayesian inversion technique to find special sensitivity of the results to a priori emissions and to the altitude of the aerosol layer. In a 4D-var context Benedetti and Fisher (2007) introduced the NMC method to assess the background error statistics of global aerosol distribution for earth system monitoring, using satellite aerosol retrievals and in situ data. With similar intentions, an operational variational AOD data assimilation system is described by Zhang et al. (2008). Recently, Yumimoto et al. (2008) applied a 4D-var data assimilation system for a regional dust model RAMS/CFORS-4DVAR to an adjoint inversion of a heavy dust event over eastern Asia, where the vertical profiles of the dust extinction coefficients derived from a Lidar network are directly ingested. The authors could demonstrate significant improvements for dust emission inversion.

A broad synthesized overview on the emerging field of advanced chemical data assimilation can be further gained from Carmichael et al. (2007). In Benedetti et al. (2009) the global ECMWF aerosol assimilation system is presented, where all aerosols are treated as tracers. The assimilated data include MODIS, with MISR, AERONET data for independent comparison.

13.2 Formulation of the Inversion Problem

Given a vector space $\mathrm{XcR^N}$ suitable to describe system states $x \in X$ of a fluid with sufficient accuracy. Further, a vector space Y for observations $\mathrm{y_0} \in \mathrm{YcR^M}$. Finally, an operator H (forward interpolation, smoothing, filter, or integration operator)

$$\mathrm{H : R^N -> R^M}$$

$$\mathrm{x -> y = H(x)}$$

As we are interested in x: is there an operator $\mathrm{H^*}$, with $\mathrm{H^*(y_0) = x}$?
(Associated phrases:

“Given the answer, what was the question?” (Foffonov)

“Can you hear the shape of the drum?” (Wunsch)

We consider the probability of a fluid to have the state x, that is $p(x)dx := P(x_0 \leq x < x_0 + dx)$. The Bayesian rule reads here:

$$p(x|y_0) = \frac{p(y_0|x)p(x)}{\int_X p(y_0|x)p(x)dx} \tag{13.1}$$

Here, the denominator is a statistical convolution integral, as with varying fluid state x the conditional probability of its observations y_0 changes.

Interpretation:

- $p(y_0)$ denotes the probability that for observations as realisations of the random variables Y_i holds $(Y_1, \ldots, Y_M)^T = y_0$.
- p(x) contains our statistical knowledge on the probability of the system to take state x prior to the observations y_0 (first guess, background information, a priori knowledge), usually taken from climatologies or a preceding forecast.
- The *likelyhood function* $p(y_0|x)$ denotes the probability to observe y_0, if the system state is x.
- We seek the probability of the most probable system state x, that is the a posteriori distribution $p(x|y_0)$, given observations y_0.

Example:

Observation and background error follow Gaussian error distribution:

Let us assume the probability p(x) of the true state x deviates from a forecasted state or climatology x_b (a priori knowledge, first guess, background) is described by the normal distribution (Gaussian) (see Fig. 13.2)

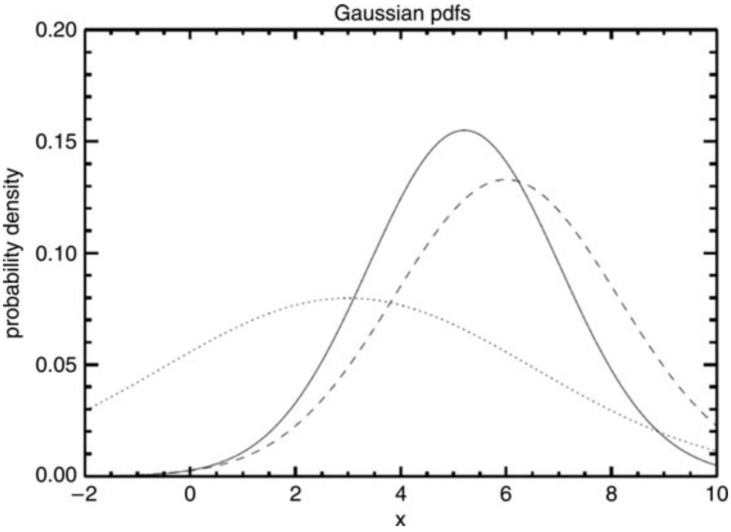

Fig. 13.2 Gaussian PDFs for, say, the a priori distribution (12.2) with $x_b = 3$, $\sigma_b = 5$ (*dotted*), the observation (12.3) with $y_0 = 6$, $\sigma_b = 3$ (*dashed*), and the resulting analysis (13.4) with x_a and σ_a following (9.7) (*solid*)

$$p(x) =: N(x|x_b, \sigma_b^2) := \frac{1}{\sqrt{2\pi}\sigma_b} \exp\left(-\frac{(x - x_b)^2}{2\sigma_b^2}\right) \tag{13.2}$$

(This also includes the assumption of unbiased model results.) Likewise, for the observations, we describe

$$p(y_0|x) =: N(y_0|x, \sigma_0^2) := \frac{1}{\sqrt{2\pi}\sigma_0} \exp\left(-\frac{(y_0 - x)^2}{2\sigma_0^2}\right) \tag{13.3}$$

We finally need the denominator of the Bayesian rule

$$p(y_0) = \int_X p(y_0|x)p(x)dx \tag{13.4}$$

With the convolution theorem for the normal distribution

$$N(\mu_1, \sigma_1^2) * N(\mu_2, \sigma_2^2) = N(\mu_1 + \mu_2, \sigma_1^2 + \sigma_2^2) \tag{13.5}$$

(see for example Pfanzagl), we obtain

$$p(y_o) =: N(y_0|x, \sigma_0^2 + \sigma_b^2) := \frac{1}{\sqrt{2\pi(\sigma_0^2 + \sigma_b^2)}} \exp\left(-\frac{(y_0 - x_b)^2}{2(\sigma_0^2 + \sigma_b^2)}\right) \tag{13.6}$$

If we set $\frac{x_a}{\sigma_a^2} = \frac{y_0}{\sigma_0^2} + \frac{x_b}{\sigma_b^2}$ and again with $\frac{1}{\sigma_a^2} = \frac{1}{\sigma_0^2} + \frac{1}{\sigma_b^2}$, we arrive at

$$p(y|y_0) =: N(x|x_a, \sigma_a^2). \tag{13.7}$$

The most probable state is the maximum of p(x|y$_0$), which as it is a Gaussian distribution, is also the state with minimal variance. For convenience, we apply the negative logarithm, to obtain a simpler expression, the minimum of which is identical to the maximum of p(x|y$_0$):

$$\begin{aligned} -\ln(p(x|y_0)) &= -\ln(p(y_0|x) - \ln(p(x)) + const \\ &= \frac{(x - x_b)^2}{2\sigma_b^2} + \frac{(x - y_0)^2}{2\sigma_0^2} + const \\ &= \frac{(x - x_a)^2}{2\sigma_a^2} + const \end{aligned} \tag{13.8}$$

13.3 Theory of Spatio-Temporal Techniques in Tropospheric Chemistry Data Assimilation

The specific objective of tropospheric chemistry data assimilation given above has clear implications for the data assimilation methodology to be selected. Chemistry-transport models (CTMs) do not passively accept external 3-dimensional state analyses, where no care is taken of chemical balance or naturally forced imbalances. The detrimental effects are given by the generation of spurious relaxations toward some other chemical state, which is not any more subject to the control of an objective quality criterion. As a solution, models can, as integrated part of the assimilation algorithm, contribute with their chemical kinetics as constraint to estimate both balanced and most probable chemical states or parameter values, thereby at least potentially providing for the BLUE property. However, data assimilation algorithms with the BLUE property allow for hypothesis testing.

There are two families of algorithms with this property in a spatio–temporal context: the four-dimensional variational data assimilation, and Kalman filtering. In both cases, the underlying device is the extension of the state vector to include the critical sources on uncertainties.

Kalman filter equations. The basis form are the Kalman filter equations. The forecast equation propagating the model state x^f from time $i - 1$ to i by the model resolvent or integration operator $M(t_i, t_{i-1})$ reads

$$x^f(t_i) = M(t_i, t_{i-1})x^a(t_{i-1}) + \eta, \tag{13.9}$$

where superscripts a and f indicate analysis and forecast, respectively. The observation error is η.

Adopting traditional notation, the forecast error covariance matrix P_i^f at time step i is inferred by

$$P_i^f = M(t_i, t_{i-1})P_i^a M^T(t_i, t_{i-1}) + Q, \tag{13.10}$$

involving the analysis error covariance matrix P_i^a and model error covariance matrix Q. Given the vector of observations y_i, and the forecasted model equivalent obtained by the observation operator H applied to the forecasted state $x^f(t_i)$, the optimally estimated state

$$x^a(t_i) = x^f(t_i) + K_i(y_i - H\,x^f(t_i)), \tag{13.11}$$

is found by the Kalman gain matrix

$$K_i := P_i^b H_i^T (H_i P_i^b H_i^T + R_i)^{-1} \ \in \mathbf{R}^{n\times pi} \tag{13.12}$$

The analysis error covariance matrix P_i^a is given by

$$P_i^a = (I - K_i H)P_i^b. \tag{13.13}$$

As the Kalman filter equations given above are computationally too costly, in particular (12.1), it is the Ensemble Kalman Filter (EnKF) and the Reduced Rank Square Root Kalman filter (RRSRKF) which allow for a feasible spatio–temporal data assimilation approach, while approximating the BLUE property. Hanea et al. (2004) successfully implemented both methods for tropospheric chemistry data assimilation, and Constantinescu et al. (2007a, b) the former.

Ensemble Kalman filter. The practical realisation of the EnKF is for example described in Hamill (2006) and given here for completeness. An ensemble matrix X^f is composed by ensemble members

$$X^f := (x_1^b, \ldots, x_m^b), \tag{13.14}$$

with the ensemble mean

$$\bar{x}^f := \frac{1}{m} \sum_{i=1}^{m} x_i^b. \tag{13.15}$$

With the perturbation of the ith member $x_i' b := x_i^b - \bar{x}^f$, the matrix of the ensemble perturbations then reads

$$X'^f := (x_1' b, \ldots, x_m' b). \tag{13.16}$$

Let $\tilde{P}^f$ denote the ensemble estimate of the forecast error covariance matrix P^f. Then this is calculated by

$$\tilde{P}^f = \frac{1}{m-1} X'^f X'^{bT}. \tag{13.17}$$

For the stochastic update algorithm

$$x_i^a = x_i^b + K_i(y_i - H(x_i^b)) \tag{13.18}$$

we generate m sets of “perturbed observations”

$$y_i = y + y_i', \quad i = 1, \ldots, m, \tag{13.19}$$

where $y_i' \propto N(0, R)$ have a Gaussian error distribution.

The elements of the Kalman gain matrix with the mean observation operator and the forecast error covariance matrices, partial and full in observation space, can then be calculated as follows:

$$\overline{H(x^f)} := \frac{1}{m}\sum_{i=1}^{m} H(x_i^b) \tag{13.20}$$

$$\tilde{P}^f H^T := \frac{1}{m-1}\sum_{i=1}^{m}\left(x_i^b - \bar{x}^f\right)\left(H(x_i^b) - \overline{H(x^f)}\right)^T \tag{13.21}$$

and

$$H\tilde{P}^f H^T := \frac{1}{m-1}\sum_{i=1}^{m}\left(H(x_i^b - \overline{H(x^f)}\right)\left(H(x_i^b - \overline{H(x^f)}\right)^T \tag{13.22}$$

We obtain for the analysis mean

$$\bar{x}^a(t_{i+1}) = \bar{x}^f(t_{i+1}) + K_{i+1}(y - H(\bar{x}_i^b), \tag{13.23}$$

and for the individual perturbations

$$x'^a{}_{(t+1)} = x'^b{}_{(t+1)} + K_{i+1}H(x'_i b), \tag{13.24}$$

from which the analysis error covariance matrix P^a can be calculated analogue to (13.14).

In the case of 4D-var, examples for spatio–temporal BLUEs applied in tropospheric chemistry include Elbern et al. (2007), with the EURAD–IM (EURopean Air pollution Dispersion–Inverse Model).

The particular component in this implementation is the additional inversion for emission rate optimisation, also of not observed species. Here, deviations of the background chemical state $x(t_0) - x_b = \delta x(t_0)$and the emission inventory $e(t_0) - e_b = \delta e(t_0)$ may be combined to define an incremental formulation of a cost function, objective function or distance function J as follows (see for example Elbern et al. (2000) for a more detailed description):

$$\begin{aligned} J(\delta x(t_0), \delta e) = {} & \frac{1}{2}(\delta x)^T B^{-1} \delta dx + \frac{1}{2}\int_{t_0}^{t_N} (\delta e)^T K^{-1} \delta e \, dt \\ & + \frac{1}{2}\int_{t_0}^{t_N} (d(t) - H(t)\delta x(t))^T R^{-1}(d(t) - H(t)\delta x(t))dt \end{aligned} \tag{13.25}$$

where J is a scalar functional defined on the time interval $t_0 \leq t \leq t_N$ dependent on the vector valued state variable $\mathbf{x}(t)$. $d(t) := y(t) - H(t)\ \delta x_b(t)$ is the observation minus model discrepancy at time t, when first guess initial values and emission inventory values are taken. The error covariance matrices are defined as follows: for the first guess or background values $B \in R^{N \times N}$ with N number of model variables, for the emission factors $K \in R^{E \times E}$ with E number of emitting grid points times emitted species, and of observation errors are denoted $R \in R^{M(t) \times M(t)}$, with M(t) the number of available observations at time t. Operator H(t) calculates the model equivalent to each observation.

The gradient of *J* with respect to the joint chemical state and emission rate variable z = $(\delta x,\delta e)^T$, and find as gradient $\partial J/\partial(\delta x,\delta e)^T$ is to be determined for minimisation. The gradient J then reads

$$\partial J/\partial(\delta x,\delta e)^T = -B^{-1}(\delta x(t)) - \sum_{t_0}^{t_N} M^T(t_0,t)H^T(t)R^{-1}(d - H(t)\delta x(t)) - \sum_{t_0}^{t_N} K^{-1}(e_b(t) - e(t)), \tag{13.26}$$

where M^T (t_0, t) denotes the adjoint (= transposed T) model operator, formally integrating from time t backward in time to the initial time t_0.

With square root factorisations $B = B^{1/2}B^{T/2}$ and $K = K^{1/2}K^{T/2}$ we define new variables v and w by

$$v := B - 1/2\ \delta x, w := K - 1/2\ \delta u, \tag{13.27}$$

leading to a minimisation problem equivalent to (13.13).

The cost function then reads

$$J(v,w) = \frac{1}{2}v^Tv + \frac{1}{2}w^Tw + \frac{1}{2}\sum_{i=0}^{T}(d_i - H\delta x_i)^T R^{-1}(d_i - H\delta x_i). \tag{13.28}$$

The gradient of J with respect to $(v,w)^T$ can be shown to be

$$\nabla_{(v,w)^T}J = -\begin{pmatrix} v \\ w \end{pmatrix} - \begin{pmatrix} B^{1/2} & 0 \\ 0 & K^{1/2} \end{pmatrix} \times \sum_{m=0}^{T} M^T(t_0,t_m)H^T R^{-1}(d(t_m - H\delta x(t_m)). \tag{13.29}$$

This optimisation problem can be solved by some quasi–Newton minimisation procedure, like L–BFGS.

13.4 Available Observations

Ground–based in situ observations of chemical constituents are the backbone of the observation suite, usually provided by regional national or European environmental protection agencies. Typically, ozone, nitrogen dioxide, sulfur, carbon monoxide and particulate matter integrated up to 10 μm (PM_{10}) or 2.5 μm ($PM_{2.5}$) are observed. While these measurement sites operate on a regular basis (sometimes the data can be provided in near real time), the deployment strategy of site locations is not adapted to data assimilation needs, unlike in meteorological data assimilation. In particular, locations are often not spatially representativity for model grid sizes larger than 10 km resolution, and the density of measurement sites is biased toward densely populated areas. While these facts are comprehensible, they must be considered when interpreting chemical data assimilation results. As a critical consequence of the different scales and chemical regimes, legacy surface in situ observations are not only sparse, but also hampered by this spatial representativity problem in populated areas. The available ozone radiosonde network is even much sparser.

Satellite data are a highly welcomed complement. Remote sensing data from orbiting earth observation platforms are scattered in space and time. Prerequisite for a full exploitation of these sensors is therefore the integration of some application of numerical models for spatio–temporal interpolation. Tropospheric satellite data are limited to very few species and often only given in terms of tropospheric columns. Available are nitrogen dioxide, elevated levels of sulphur dioxide and formaldehyde, mostly retrieved from GOME (ERS2 platform) or SCIAMACHY (ENVISAT) (e.g., Eskes and Boersma 2003; Heue et al. 2005). Recently, further tropospheric column data became available through OMI and GOME-2 sensors on-board of AURA and METOP, respectively.

Also carbon monoxide soundings from MOPITT sensors (Deeter et al. 2003) as well as neural network retrieved ozone profiles are available (Müller et al. 2003). Finally, in situ observations made on board of commercial aircraft, in the frame of the MOZAIC (Measurement of Ozone and Water Vapor by Airbus In-Service Aircraft) activity (Thouret et al. 2000) can be assimilated. The MOZAIC initiative (Marenco et al. 1998) consists of automatic and regular measurements by some long range passenger airliners flying all over the world. A special value of this observing system is obtained by vertical profiles of observations obtained during take–off and landing phases. Target species are O_3, water vapour, CO and total reactive nitrogen NO_y measurements. The next generation of aircraft data is provided by IAGOS (Integration of routine Aircraft measurements into a Global Observing System).

13.5 Results

A careful estimation of the error of (spatial) representativity, which is to be defined for each grid resolution separately, is prerequisite for success. Specifically, model grid resolutions of about 50 km, widely used for continental scale integration domains, admit only for a limited number of species to be assimilated by point measurements. For coarse grids, data from quickly oxidizing point and line source emitted $NO_x \in \{NO, NO_2\}$ should only be assimilated by observation sites situated at background locations, which are rarely available. In practice, gaseous constituent assimilation in coarse grid models mostly rests on ozone observations. A nesting technique is implemented for adjoint modelling and applied to the 1998 urban plume campaign BERLIOZ (Volz-Thomas et al. 2003) species around the metropolitan area of Berlin, Germany. Assimilated species are O_3, NO, NO_2, CO and SO_2 within an assimilation window of 14 h, from 06 UTC to 20 UTC on July 20, 1998. The nesting procedure included a coarse grid simulation with horizontal grid size of 54 km and three recursively nested grids with a nesting ratio of three. Hence, there is a 2 km final resolution. Figure 13.3 demonstrates the assimilation performance for three measurement stations mostly within the greater Berlin area, as achieved by the 6 km resolution grid (nest 2) using different analyses by joint emission rate and initial value optimisation (see next section). When using an analysis achieved by application of nested 4D-var, a significantly improved performance of the forecast can be seen beyond the assimilation interval. It can be concluded, that, under conditions given, a 6 km horizontal resolution allows for a satisfying exploitation of the suburban NO_x observation sites.

Figure 13.4 demonstrates the statistical progress attained through a longer-running (10 days) 4D-var nesting application for a suite of observed species, here for the VERTIKO campaign in June 2003 (Bernhofer and Köstner 2005). Simulation setup implies three domain levels with a coarse grid resolution of 125 km and a nesting ratio of 5. Improvements are given in cost function values normalised by the control run values on each nest level, averaged over the complete simulation period. Ozone, carbon and nitrogen oxide exhibit different optimisation success on the different nesting levels. Ozone analyses are already quite reasonable on coarser grids (25 km), reflecting the smoother distribution pattern of a secondary pollutant. The contrary is the case for NO, showing increasing success from coarser to finer grid resolution. Even for a grid resolution of 5 km, the source distribution and short lifetime cannot yet be completely reflected (see previous section),

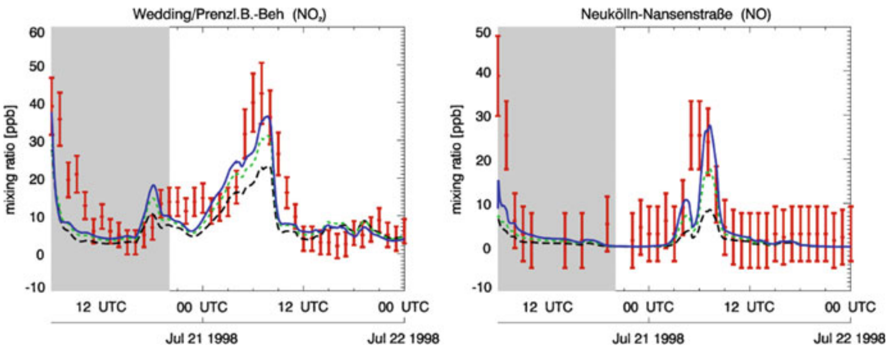

Fig. 13.3 Assimilation results for stations in the Berlin area obtained with a grid resolution of 6 km. *Green line*: first guess run, using analysis obtained on 18 km grid. *Blue line*: assimilation result based on analysis on 6 km grid. Black line: no data assimilation. Observations and their error estimates: red bars. Only grey shaded time interval has been used for assimilation, other observations are for quality control only

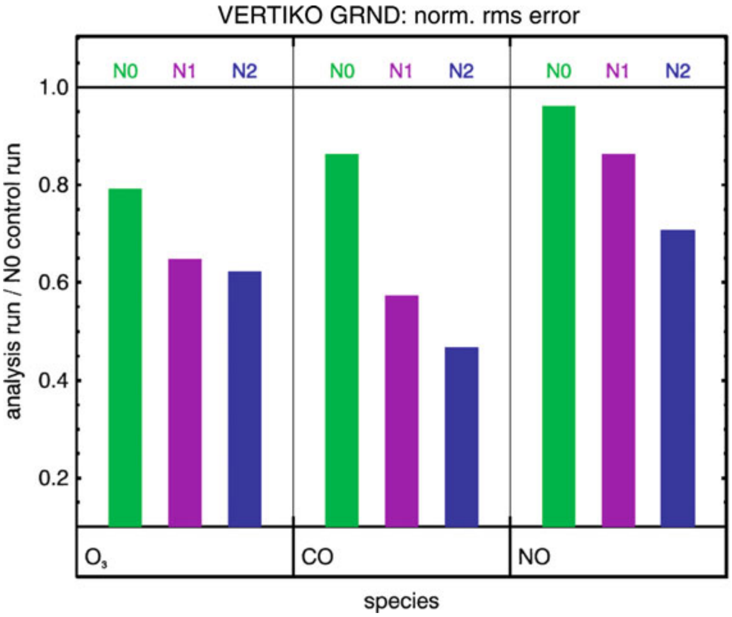

Fig. 13.4 Relative reduction of root mean square errors for ozone, carbon monoxide and nitrogen oxide due to nested grids (N_0 to N_2) with increasing horizontal resolution (from 125 to 5 km). Normalisation value 1 is given for coarse grid (125 km) simulations without data assimilation

requiring additional nesting levels. Carbon monoxide exhibits a mixture of this described behaviour, reflecting a primary emitted constituent with a longer lifetime in the troposphere (compared to NO).

As a unique feature, the adjoint calculus has the potential to optimise initial values as well as emission rates. The impact of emission rate optimisation is demonstrated by Fig. 13.5, which shows SO_2, CO, NO_2, and xylene optimisation factors over the integration domain of the finest BERLIOZ grid (2 km resolution). The inversion process at each grid level hands over the result to the next finer grid, allowing for an increasingly better resolved emission estimate, provided the necessary observational density is given. Since Berlin is mostly a large urban island within a rural environment, sulfur emissions are confined to the greater metropolitan area. The upper left panel of Fig. 13.5 clearly indicates a nearly overall reduced emission rate over the densely populated area. In the case of CO similar effects can only be claimed for the area east of Berlin.

The effects vary moderately for NO_2, while xylene appears to be underestimated by the emission inventory, with an amplification factor of about 1.2. In all exhibited cases, the inversion results remain well within the error limits of the inventory. Emission rate optimisation of SO_2 and CO is mainly based on concentration observations of these species. In the case of other emissions, which are rarely observed,

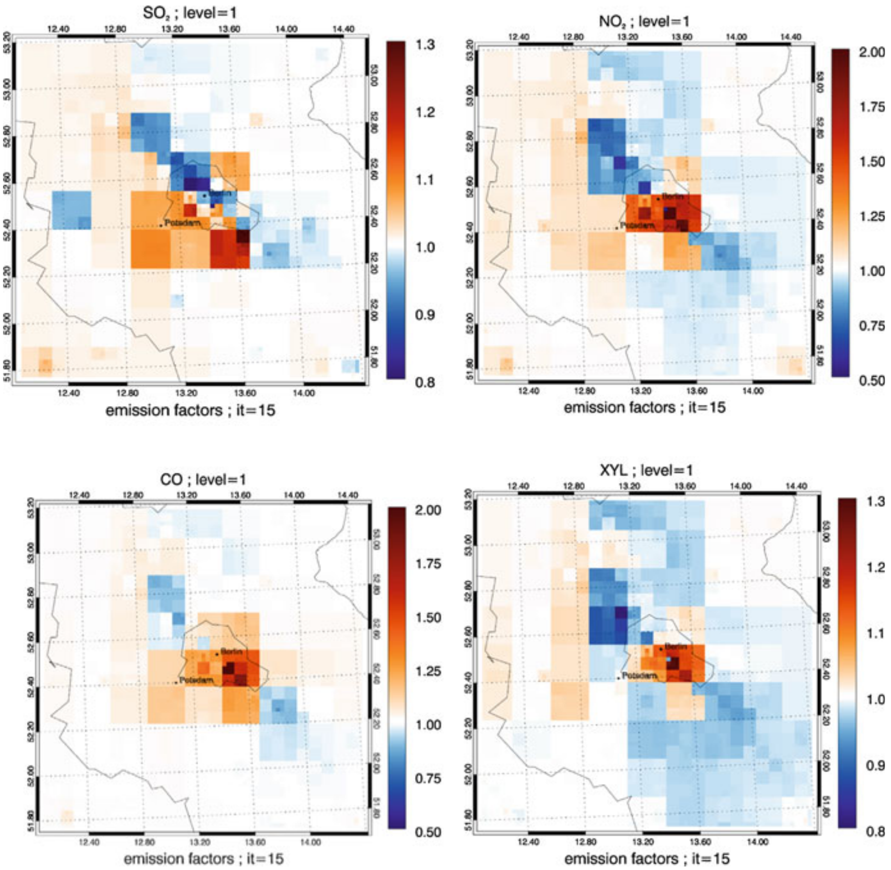

Fig. 13.5 SO_2, CO, NO_2, and xylene optimisation factors over the integration domain of the finest grid (2 km resolution) over the greater Berlin area for the surface layer. Coloured squares indicate the impact areas of the individual nests, ranging from 54 to 2 km resolution, involving four nest levels

inference can only rest on measured product constituents, most prominently ozone. This capability is another prominent feature of the 4D-var technique (see Fig. 13.6).

The 4D-var approach is computationally very expensive. For operational forecasts, a 3D-var approach is chosen in most cases. Within the framework of the European project PROMOTE an operational 3D-var data assimilation setup is chosen to produce daily analyses and high-quality forecasts on various European domains. Starting with a coarse European domain with a horizontal grid spacing of $45 \times 45\ km^2$ and using one intermediate nest level with $15 \times 15\ km^2$ grid spacing, target domains include Switzerland, Austria, Ireland, Mecklenburg-Western Pomerania and Northrhine-Westfalia in Germany at a horizontal resolution of $5 \times 5\ km^2$. A special nest is prepared for the Rhine-Ruhr area with a grid spacing of $1 \times 1\ km^2$. Due to the numerical demands of the 4D-var technique, only a spatial

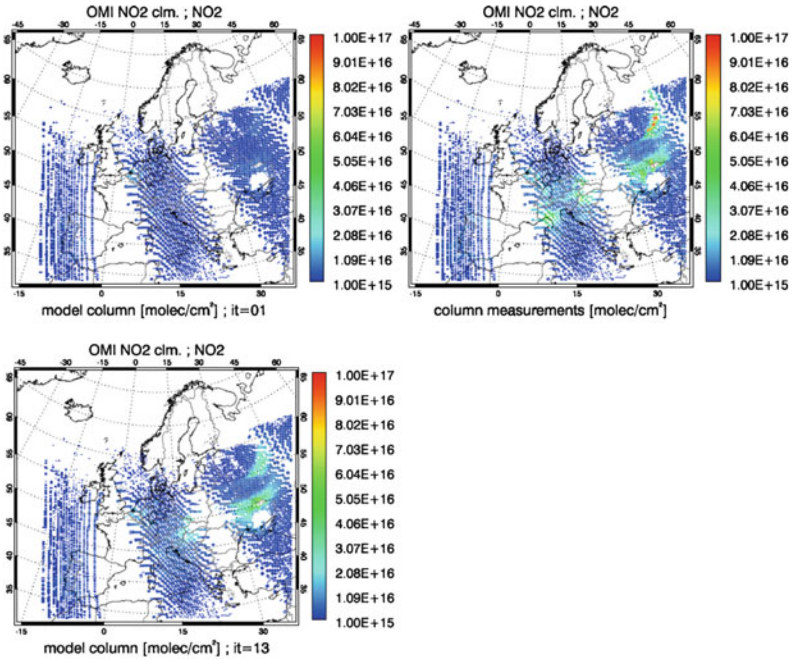

Fig. 13.6 NO_2 tropospheric column assimilation of OMI by averaging kernels for November 11, 2007. Upper panel shows first guess (*left*) and retrieved tropospheric columns by KNMI (*right*), lower left panel gives the model equivalent after 4D-var assimilation. Unit are given in terms of 10^{15} molecules/cm^2

analysis algorithm has been chosen allowing for activation of the aerosol module MADE (Ackermann et al. 1998) in EURAD-IM. Figure 13.7 shows scatter plots for O_3 on the European domain and PM10 on the Northrhine-Westfalian grid, emphasising the benefits of the data assimilation system for the forecast skill. Four model realisations are given, basing on different meteorological and chemical analyses: The simulations *forecast day-1* and *control day-0* base on the same chemical analysis, but *control day-1* uses a more recent meteorological analysis (by 12 h). The difference in model performance is thus given by different meteorological conditions only. In comparison, *forecast day-0* uses the same meteorology like *control day-0*, but an updated chemical analysis inferred by available observations from the day before. The lower bias and rmse values are therefore due to the chemical data assimilation procedure only. A significantly lower bias and rmse can be stated both for ozone at coarse resolution as well as for particulate matter in the nested domain. The fourth model simulation statistics *analysis day-0* is given for the sake of completeness, showing the results after performing 3D-var assimilation of the given observations on November 27 with *forecast d-0* as model background.

Satellite retrievals from tropospheric height levels are increasingly abundant and important in earth observation, although there is a limited number of species like

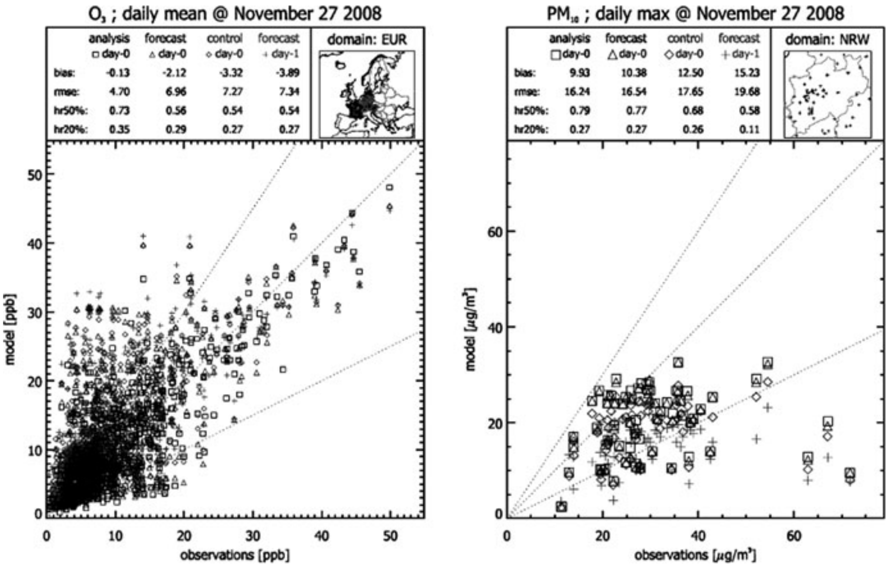

Fig. 13.7 Scatter plots of O_3 at the European domain and PM10 at the nested Northrhine-Westfalian grid, showing the benefit of the operational analysis procedure for the forecast skill on November 27, 2008, as given by bias and root mean square errors (rmse) for several model realisations. Locations of measuring stations are given by crosses in the upper right corner of the plot areas. See text for further explanations

SO_2, NO_2 and formaldehyde, which is presently amenable for retrieval. Moreover, in these cases data are presented in terms of tropospheric columns.

The flexibility of the variational technique in taking into account various types of observations like temporally and spatially dense earth observations will be emphasised in the following. This is of even more importance, since satellite retrievals for tropospheric height levels is a strongly emerging issue in earth observation with focus on air quality monitoring. The results of assimilating nitrogen dioxide tropospheric column retrievals (provided by KNMI; Boersma et al. 2004) of GOME observations – which come along with averaging kernel and footprint information – are shown in Fig. 13.8. The observations show features with elevated NO_2 column densities coincidently with higher expected NO_2 surface concentrations, namely the area from London over the Channel and Netherlands/Belgium to the German Rhine-Ruhr area as well as Paris and the Spanish north-coast. Although underestimated, the higher NO_2 column densities over the Channel and the adjacent areas already become apparent in the model equivalents by the background model simulation.

The structures in the observed NO_2 column densities can be reproduced by the analysis run in a remarkable manner. The remaining discrepancies coincide with very low observed values, which the model does not reproduce. To emphasise the kind of information contained in the observed column densities including footprint

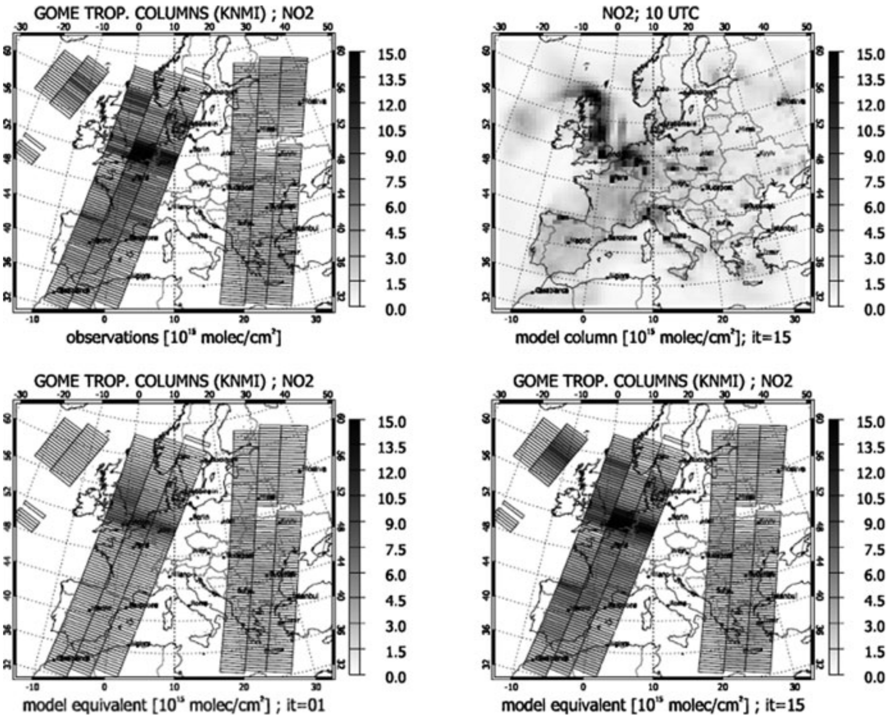

Fig. 13.8 Assimilation results on the European grid for GOME tropospheric NO_2 columns on July 20, 1998. *Upper left*: retrievals; *upper right*: total model column (analysis); *lower left*: model equivalents (*background*); *lower right*: model equivalents (*analysis*). Column densities are in 10^{15} molecules/cm^2

information, the total tropospheric model columns as produced by the analysis run is given, too. Here, the locations with high NO_2 surface concentrations also push through in the tropospheric column density, but remain concentrated ashore. The higher NO_2 column densities over Scotland and the Atlantic Ocean are linked to a cyclonic low, transporting polluted air masses – originating from surface levels – over long distances.

The aerosol component of the EURAD model system includes inorganic and secondary organic aerosol modules. The Modal Aerosol Dynamics model for Europe (MADE) has been developed for the EURAD model as an extension to the EURAD chemistry transport model to allow for a detailed treatment of aerosol effects in the model. In MADE the particle size distribution of the aerosol is represented by three overlapping lognormal modes, delineating the Aitken mode, accumulation mode and coarse mode, with variable mean values. Due to the complexity of the aerosol model, no full adjoint is available yet. Therefore, a 3D-var algorithm has been implemented, which only involves the adjoint of the observation operator (Nieradzik and Elbern 2006).

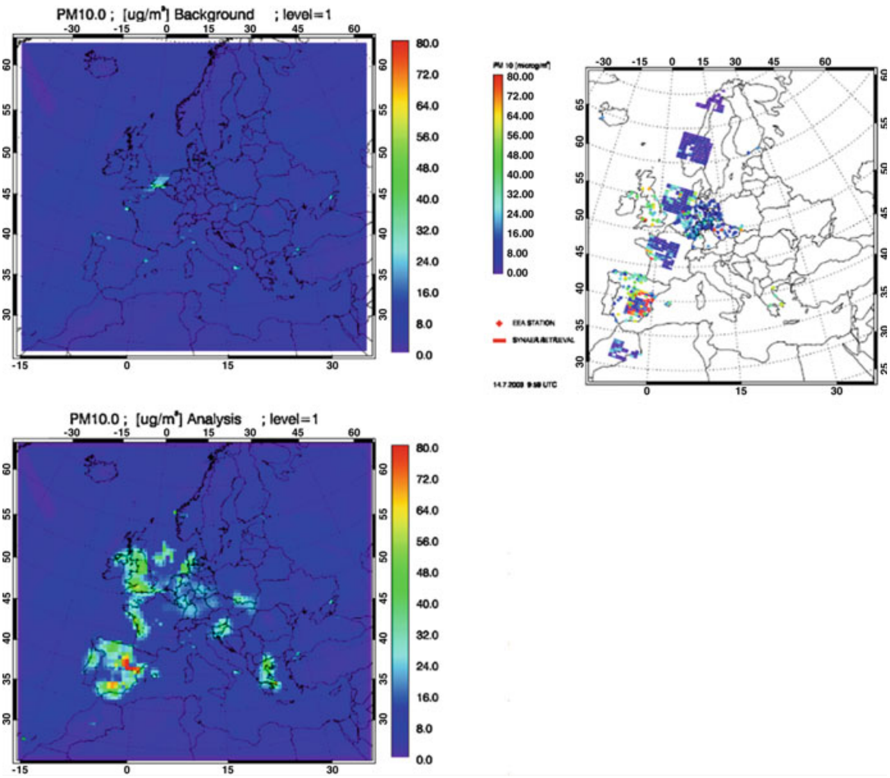

Fig. 13.9 PM10 concentrations (μg/m^3) at July 14, 2003, 11:00 UTC, as forecasted without assimilation (*upper left*). Available observations, both in situ and SYNAER retrievals (*upper right*), assimilation results based on all observations (*lower left*)

The presented analysis makes use of SYNAER retrievals (Holzer-Popp et al. 2002), providing for a two ENVISAT sensor based particulate matter retrievals, which allows for freely adjustable integrated aerosol sizes, and results in size distributed aerosol mass information. The assimilation of aerosol data is particularly useful in case of irregular events like biomass burning. On July 14, 2003, this was the case over the Iberian Peninsula. The assimilation procedure has been conducted with available ground based in situ data, only with satellite data, and with both observational sets combined. Figure 13.9 reveals that the pure forecast is shown to give too low aerosol loads. Both satellite and in situ data enforce significantly higher values in the analyses.

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Chapter 14
Aerosols as Transport Vehicles of Persistent Pollutants

Volker Matthias

14.1 Introduction

Aerosol particles belong to the most important constituents of the Earth's atmosphere. Cloud formation and cloud properties strongly depend on the amount and the type of atmospheric aerosol particles. By scattering and absorbing solar radiation they have a large impact on the global radiation budget and locally on the visibility. Finally, they consist of various chemical compounds including harmful or even toxic substances. The atmospheric lifetime of aerosols strongly depends on meteorological conditions. On the one hand, they are efficiently washed out during rain events. On the other hand they accumulate in the atmosphere under dry conditions and they can be transported over long distances, particularly if they have been mixed into higher altitudes before. Furthermore persistent pollutants like lead and other heavy metals, polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) are often bound to these particles and are transported with them. Their regional distribution and deposition can only be understood together with the knowledge about atmospheric aerosol particles.

14.2 Characterisation of Aerosols

Aerosol is defined as a mixture of a gas (which is air for atmospheric aerosol) with particles that are suspended in this gas. However, if we say "aerosol" we mostly refer to the particles within the mixture and in the following the terms "aerosol" and "aerosol particles" both mean aerosol particles. These particles have a typical size in the range of 1 nm to approximately 100 μm in diameter. Although aerosol particles may almost completely consist of water, they have to be distinguished

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from cloud droplets. The latter can be described as “activated” cloud condensation nuclei (CCN, which again are aerosols) and they are typically larger than aerosols (10 μm–3 mm).

Aerosols can be very complex particles; they have very different shapes and consist of one or more different chemical components. Depending on this they may be hydrophilic or hydrophobic, but this is subject to change over time since the aerosol particle’s chemical composition may change. This happens by chemical reactions inside the particle and on the surface of the particle. Aerosol particles collide with each other and form new, larger ones with a different chemical composition. If they serve as CCN they become part of a cloud droplet and undergo aqueous chemical reactions. Cloud droplets become larger by collecting other smaller droplets and this again changes the chemical composition of the cloud droplet. If this droplet then evaporates again (which is the case for all non-precipitating clouds) a new particle with different size, shape and chemical composition is formed.

Since aerosol particles are so manifold there are several ways to characterize them and to make the attempt to describe the properties of a large number of aerosol particles. First of all, they can be distinguished by the source they originate from and whether they are directly emitted or formed out of precursor gases in the atmosphere. Then, we can look at their size or their size distribution, respectively, and how it changes with time. This is a physical approach to describe aerosols and the temporal evolution of their number, surface and volume density in the atmosphere. As already mentioned, the chemical composition of the aerosol particles plays an important role for their behaviour and also for their possible health effects, and this is another way to gather information about atmospheric aerosols. Finally, the optical properties of aerosol particles determine their effect on global radiation, visibility and optical depth. Because many measurements rely on optical methods (including satellite observations) it is also of great importance to describe the optical properties of aerosols.

14.3 Aerosol Sources

First, we distinguish between sources of primary aerosols, i.e., directly emitted particles, and sources of secondary aerosols, which means that precursor gases are emitted and the aerosols are then formed in the atmosphere. For both source types natural and anthropogenic sources exist. Tables 14.1 and 14.2 give an overview of the estimates of aerosol emissions. On the global scale, natural emissions are much larger than anthropogenic emissions, although the source strengths of the largest sources, sea salt from the oceans and desert dust, are still very uncertain. The variability of natural emissions is higher than the total amount of anthropogenic emissions, but in some highly industrialized regions on Earth anthropogenic emissions can be the main source for aerosol particles. This holds in particular for secondary sulfate, nitrate and ammonium aerosols formed out of the precursor

Table 14.1 Global source strengths of primary aerosols

Primary aerosol particles					
Source	Aerosol component	Source strength			Reference
		Best estimate	Range	Unit	
Natural origin					
Deserts	Dust	1,678	1,000–2,150	Tg/year	Dentener et al. (2006), Zender (2004)
Oceans	Sea salt	7,925	1,000–10,000	Tg/year	Dentener et al. (2006), Gong et al. (2002), Penner et al. (2001)
Anthropogenic origin					
Industry	Dust	110	11–120	Tg C/year	Wolf and Hidy (1997)
Fossil fuel	Organics, soot	27	16–28	Tg C/year	Liousse et al. (1996), Bond et al. (2004), Haywood and Boucher (2000)
Biomass burning	Organics, soot		14–67	Tg C/year	Dentener et al. (2006), Bond et al. (2004), Liousse et al. (1996)

Table 14.2 Global source strengths of secondary aerosol precursors. Note that only a fraction of the emitted precursor gases forms aerosols and that the formation rate is highly variable

Precursors of secondary aerosol particles					
Source	Aerosol component	Source strength			Reference
		Best estimate	Range	Unit	
Natural origin					
Volcanoes	SO_2	12.6	3.4–14	Tg S/year	Dentener et al. (2006), Haywood and Boucher (2000)
Oceans	DMS	18.2		Tg S/year	Dentener et al. (2006)
Biomass burning	NO_x	11		Tg N/year	Wang et al. (1998), Benkovitz et al. (1996)
Soil, lightning	NO_x	7.5		Tg N/year	Wang et al. (1998), Benkovitz et al. (1996)
Oceans	NH_3	8	3–16	Tg N/year	Bouwman et al. (1997)
Vegetation	Isoprene		250–750	Tg C/year	Wiedinmyer et al. (2004)
Vegetation	Terpenes		60–310	Tg C/year	Wiedinmyer et al. (2004)
Anthropogenic origin					
Combustion	SO_2		65–99	Tg S/year	Dentener et al. (2006), Haywood and Boucher (2000)
Combustion	NO_x	20		Tg N/year	Wang et al. (1998), Benkovitz et al. (1996)
Agriculture, animals	NH_3	37	17–52	Tg N/year	Bouwman et al. (1997)
Combustion, solvents	Terpenes	127		Tg/year	Bond et al. (2004)
Combustion, solvents	ORVOC	261		Tg/year	Kanakidou et al. (2005)

gases sulfur dioxide (SO_2), nitric oxides (NO, NO_2) and ammonia (NH_3) in the Eastern US, Europe and Southeast Asia.

Concerning the global distribution of aerosol sources, sea salt emissions are connected to the oceans and are particularly high in regions of high wind speeds like the whole region around 50°S and the North Atlantic. Desert dust emissions are high in the Sahara desert and central Asia, the western US, Australia, Southwest Africa and Chile. Biogenic emissions (natural organic carbon) but also emissions of anthropogenic black carbon and organic carbon, the latter caused by biomass burning, dominate in tropical forests. Depending on season, biomass burning is also quite frequent in North America, Russia and some south European regions. Here, biomass burning is regarded as an anthropogenic source of aerosols and it includes open forest and agricultural fires as well as wood burning for heating and cooking. Many forest fires are of natural origin but it is difficult to discriminate them from man made fires.

The sources of organic aerosols are also highly uncertain und much research is currently conducted around organic aerosols (see e.g., Kanakidou et al. 2005; Fuzzi et al. 2006; Wiedinmyer et al. 2004). This is related to the role of organics in the formation of secondary organic aerosol (SOA) particles (see Sect. 14.4.1) and to the precursor gases themselves. Here, biogenic emissions of volatile organic compounds (VOCs), in particular terpenes, are the most important VOCs to form SOA. The amount of emitted terpenes depends on the leaf area, the photosynthetically available solar radiation (PAR) and the temperature, on the type of vegetation and on its condition, e.g., in terms of water stress or disease. Significant amounts of terpenes and other reactive VOCs (ORVOC) may be of anthropogenic origin, too.

14.4 Aerosol Dynamics

Aerosols underly various modification processes, mainly in terms of their chemical composition and their size distribution. In this section, the physical state of a large number of aerosol particles in a defined air volume will be investigated by describing the dependence of their number, surface and volume on their radius or diameter. This implies that aerosol particles can be regarded as spherical. For many biogenic particles, dust particles and black carbon this is not true. However, under ambient conditions most aerosol particles contain a lot of water and their shape comes close to sphericity.

The temporal development of the number (or surface or volume) density distribution of an aerosol population is called aerosol dynamics. It depends on three major processes:

1. Nucleation (the formation of new particles)
2. Condensation/deposition (the growing of particles from molecules in the gas phase)
3. Coagulation (the growing of particles by collection of other particles)

Measured aerosol size distributions usually show three or four peaks where a high number of particles can be found around a certain particle diameter. In most cases, each peak can be approximated by a log-normal distribution and the whole size distribution can be regarded as a superposition of three or four log-normal distributions (Fig. 14.1 top and middle). Each of these peaks, and the distribution of

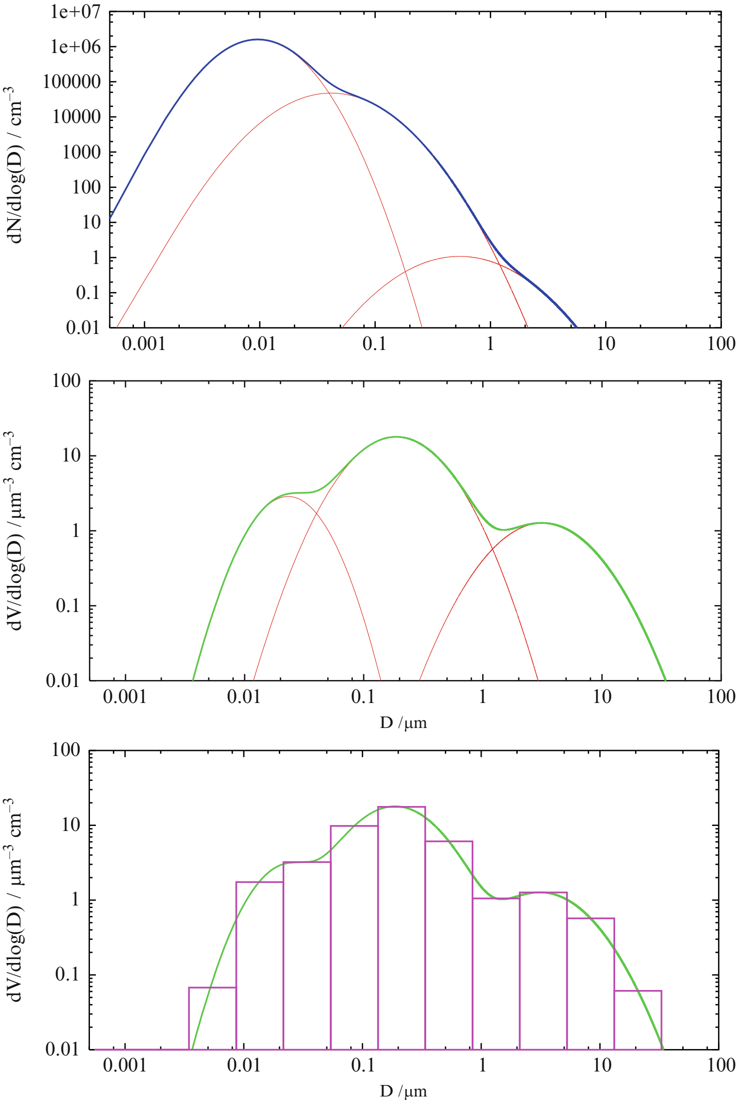

Fig. 14.1 Example for an aerosol size distribution combined out of three lognormal modes (Aitken mode, accumulation mode, coarse mode). Number distribution (*top*), volume distribution (*middle*) and discretized volume distribution (sectional approach, *bottom*)

aerosol particles around it, is called a “mode” and we distinguish between four main modes belonging to different size classes.

1. Nucleation mode (3–20 nm, freshly nucleated particles)
2. Aitken mode (20–100 nm, ultrafine particles)
3. Accumulation mode (100 nm–2.5 µm, fine particles)
4. Coarse mode (>2.5 µm, coarse particles)

Particles in the nucleation mode can only be found directly after a nucleation event, when a large number of new particles is formed out of precursor gases. Particles in the Aitken mode are rapidly formed out of the freshly nucleated particles, usually by coagulation and condensation. Because larger particles can very efficiently collect smaller particles the larger particles grow at the expense of the smaller ones, leading to an aerosol size distribution where the largest part of the aerosol mass is in the accumulation mode. Both Aitken mode and accumulation mode particles also grow by condensation of gases with low volatility on their surface. Often, these gases are emitted by combustion processes in high temperature exhausts. Under ambient temperatures they condense quickly on existing surfaces and the aerosol surface distribution is dominated by accumulation mode particles. Particles in the accumulation mode have the longest life time of all aerosol particles. They are too slow to collide frequently with larger particles and their mass is not big enough to let them sediment to ground. Their typical lifetime in the atmosphere is about 1 week. Their main sink is wet deposition because they efficiently serve as CCN. During precipitation events they are washed out by rain and also the aerosol particles that did not act as CCN (the so called interstitial aerosol) but are within or below the precipitating cloud are collected by scavenging and then deposited. However, most rain and cloud droplets do not reach the ground, they evaporate again and the non-water substances within the droplet form a new aerosol. This is one of the most important ways how particles are transformed, as well chemically (see Sect. 14.6) as in size. This process leads to deviations of the above described size distribution function in the accumulation mode. Here, two modes may form, one being developed by coagulation and condensation and one resulting from evaporated cloud droplets.

The particles in the coarse mode usually have different sources than those in the smaller modes. They are frequently formed by mechanical processes like wind and erosion or by bursting bubbles of sea water and subsequent evaporation of the water. Due to their weight coarse particles undergo a sedimentation process but they can also be washed out by precipitation. Although they contribute significantly to the total aerosol mass, their number density is too small to efficiently collect other particles by coagulation (see Sect. 14.4.3).

In numeric atmospheric models or in dynamical aerosol models the aerosol size distribution is represented by two main approaches, the sectional approach and the modal approach (see Fig. 14.1 bottom). In the sectional approach the size range is divided into typically 3–20 size classes. The aerosol number, surface and volume in each size class may change during the simulation. This allows the simulation of arbitrary size distributions but it may become inexact if only a low number of size classes is available and on the other hand computationally expensive if a high number of size classes is chosen.

The modal approach assumes that the size distribution in each mode is log-normal. By this only two parameters, the mean diameter and the width of the distribution function are necessary to describe each mode and no more than eight parameters are necessary to describe a complete aerosol size distribution. However, size distributions that differ significantly from the log-normal distribution cannot be described adequately.

14.4.1 Nucleation

The generation of new particles out of precursor gases in the atmosphere is called nucleation. There is still a lot of research under way to determine precisely the conditions for nucleation. It is somehow photochemically induced (because it usually happens during daytime) and it requires the presence of at least sulfuric acid and water vapour. Investigations by Kulmala (2003) and co-workers showed that in polluted areas also the presence of ammonia and of organics might be important for the generation of new particles.

The nucleation processes are subdivided into homogeneous and heterogeneous nucleation. The former happens without the aid of another surface, i.e., an existing particle while in the latter case the existing surface of another particle serves as substrate for the nucleation process. A homogeneous nucleation process is very similar to the formation of cloud droplets in the atmosphere which follows the Koehler theory (see e.g., Pruppacher and Klett 1997). It depends on the surface tension of the resulting droplet (that might consist of sulfuric acid), the radius of an initial cluster of molecules, the temperature and the supersaturation of the gaseous components of the nucleating substance. If only water and sulfuric acid participate in the nucleation process we call it a binary homogeneous nucleation. This happens mainly in clean atmospheres like the free troposphere. In the more polluted planetary boundary layer, the ternary homogeneous nucleation with additional participation of ammonia is believed to dominate the nucleation process (Kulmala 2003). Ion induced nucleation in the upper troposphere and the lower stratosphere and homogeneous nucleation involving iodide in coastal environments are two additional homogeneous nucleation processes of importance. Which of these processes really dominates is still under discussion and it seems to depend on the individual location and the presence of the necessary gases.

The Koehler theory predicts that a small droplet can only be formed if a critical radius is reached; otherwise the surface tension inhibits the formation of a small droplet. The particle generation can be described by three stages, see Fig. 14.2 (Kulmala 2003). First, a thermodynamically stable cluster out of a few molecules is formed by ternary or ion induced nucleation. This cluster has a diameter of about 1 nm. Then other gases, mainly of organic origin, start to stick to this cluster and make it grow to a certain size of about 3 nm. Afterwards the particle can grow further because it is now large enough to overcome the counteracting surface tension.

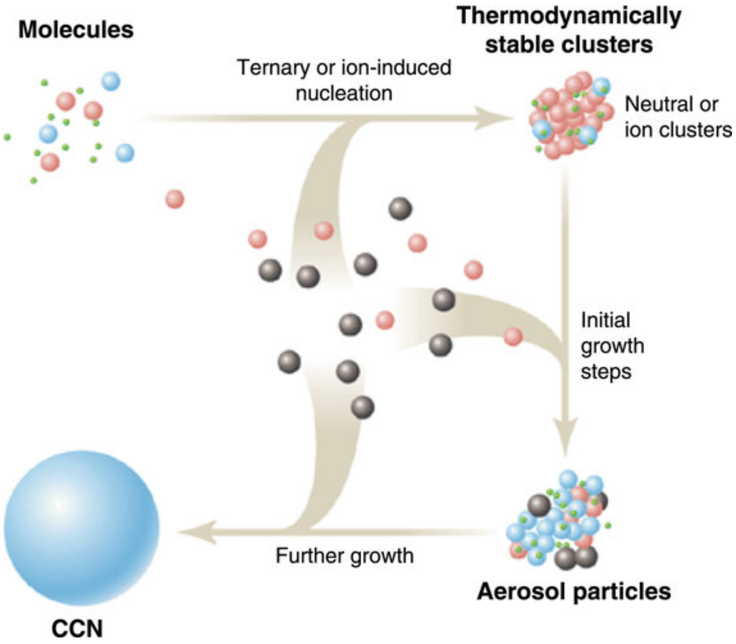

Fig. 14.2 Model of the particle nucleation process with cloud condensation nuclei (CCN) as final step (After Kulmala 2003)

The heterogeneous nucleation on existing particles is only of minor importance. Its efficiency depends on the type of surface that is available, whether it is hydrophilic or hydrophobic, on the radius of the cluster and the substrate and again on temperature and supersaturation. The binary nucleation of sulfuric acid and water vapour on an existing particle surface is the dominant heterogeneous process in the atmosphere.

14.4.2 Condensation and Deposition

Two major processes that determine the growth of an aerosol particle are condensation and deposition. Condensation means that atmospheric gases get into the liquid phase of an existing aerosol particle while deposition means that it gets into the solid phase. Both processes are reversible, particles can also become smaller or even vanish if they evaporate or sublimate. Whether condensation or deposition, respectively, happens or not depends on the vapour density and the temperature, the particle radius and its composition. As mentioned in Sect. 14.4.1, condensation on a particle occurs only if the particle is big enough or the supersaturation is high enough. Freshly nucleated particles preferably grow by condensation. Typical growth rates are in the order of 1–20 nm/h, depending on the amount of condensable vapours in the atmosphere. In the Arctic for example the growth rate will be much lower while it will be significantly higher in a polluted boundary layer or in coastal areas.

Hygroscopic particles grow also by water uptake. Sea salt particles start to grow at relative humidities around 75%, ammonium sulfate and ammonium nitrate particles at approx. 80% relative humidity. If the relative humidity approaches 100%, the particle mass has typically grown by a factor of 5 or more, this means that these particles consist of more than 80% water. When the relative humidity decreases again the water evaporates and the particle becomes smaller, however it will not be totally dry again at 75 or 80% relative humidity. Chamber experiments have shown that it needs relative humidities as low as 30–40% until wet particles have lost all their water (Tang et al. 1981). This effect results in a hysteresis of the function describing the aerosol particle mass dependence on relative humidity. It means that the same particle at the same relative humidity can contain different amounts of water. Figure 14.3 illustrates the modifications of the size distribution if condensation or water uptake takes place in an exemplary calculation. It can be seen that large changes in the volume distribution (lower panel) are connected with a low number of particles in the larger size bins (top panel).

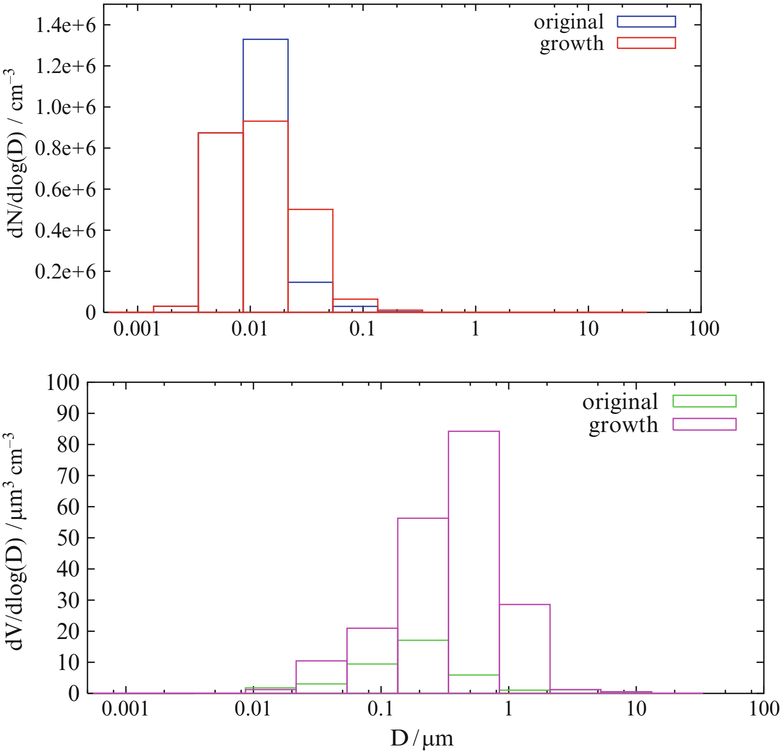

Fig. 14.3 Particle growth by condensation. In this exemplary calculation a typical size distribution was prescribed ("original") and it has then been assumed that particles with 10 nm $< D <$ 1 µm grow by mass uptake ("growth"). Thirty percent of the particles in each size bin move to the next higher bin. Number distribution (*top*) and volume distribution (*bottom*)

14.4.3 Coagulation

Coagulation is a process during which particles collide and stick together. The coagulation rate is given by the product of the number concentration and the coagulation efficiency. The latter is also called coagulation kernel and it depends mainly on the sizes of the interacting particles. To describe the coagulation kernels, first two size dependent flow regimes are distinguished. One is called the continuum regime with many particle collisions; the other is the free molecular regime with infrequent particle collisions. Both flow regimes can be characterized by the so called Knudsen number Kn, which is the quotient of the mean free path of air molecules λ_a and the radius of the particle r_i:

$$\mathrm{Kn} = \lambda_a / r_i$$

The mean free path of air is defined as $\lambda_a = 2\eta_a/(\rho_a v_a)$ where η_a is the dynamic viscosity of air, ρ_a is the density of air and v_a is the thermal velocity of air. At standard conditions at ground (T = 15°C and p = 1,013 hPa) $\lambda_a = 0.063$ μm. Small particles have large Knudsen numbers and belong to the free molecular regime. Large particles have small Knudsen numbers and belong to the continuum regime. Between these extreme regimes is the transition regime.

The coagulation kernels can now be written as follows:

$$\beta = \pi\left(r_i + r_j\right)^2 \sqrt{v_{p,i}^2 + v_{p,j}^2}$$

for the free molecular regime and

$$\beta = 4\pi\left(r_i + r_j\right)\left(D_{p,i} + D_{p,j}\right)$$

for the continuum regime. In both equations r_i and r_j denote the radii of the particles participating in the collision process, $v_{p,i} = \sqrt{(8k_BT)/(\pi M_{p,i})}$ is their thermal velocity and $D_{p,i} = (k_BT)/(6\pi r_i \eta_a)$ the diffusion coefficient. The symbols k_B and $M_{p,i}$ denote the Boltzmann constant (1.38×10^{-23} J/K) and the mass of the particle i in kg, respectively. In the transition regime the coagulation kernel can be described by an interpolation formula (Jacobson 1999) that simplifies to the expressions in the free molecular and the continuous regime if $\mathrm{Kn} \gg 1$ and $\mathrm{Kn} \ll 1$, respectively.

In Fig. 14.4, the coagulation kernels that follow the equations above are given for different regimes and different radii of the first particle. Obviously, the coagulation efficiency increases rapidly with the size of the second particle. In the free molecular regime small particles are more efficiently collected than larger ones. The coagulation efficiency has a minimum when both particles have the same radius.

This general dependence holds even if correction terms, which shouldn't be explained in more detail here, are applied considering the effects of convection, gravitation and turbulence in the atmosphere. For a given particle size distribution

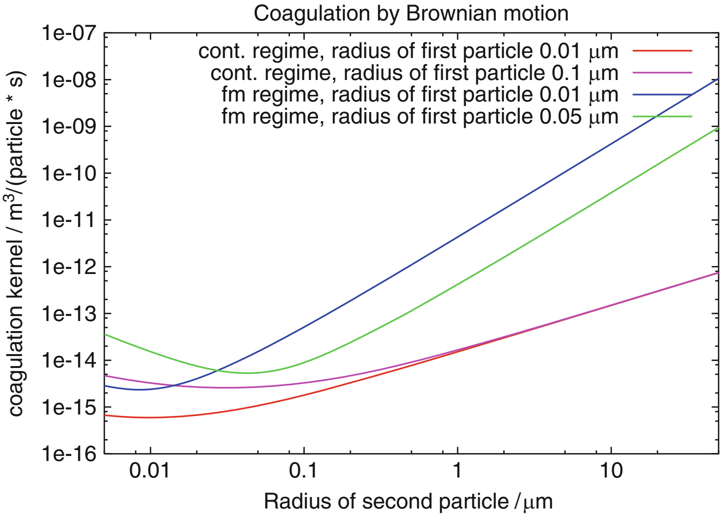

Fig. 14.4 Coagulation kernels caused by Brownian motion for particles of given size in the free molecular regime and the continuum regime in dependence of the size of the second particle

the coagulation process reduces the total number of particles because these particles are collected by the larger ones and shifts the size distribution towards larger particles while the total mass remains unchanged (see Fig. 14.5). It should be noted that even if the coagulation kernel is large, changes in the particle concentration might be low because the concentrations themselves are low.

14.5 Aerosol Mass Concentrations

The most frequent aerosol measurements that are available are those of the aerosol mass in air close to ground. Often, these measurements distinguish only between two different size regimes, one that comprises all particles with diameter below 2.5 μm (called PM2.5) and one that comprises all particles with diameter below 10 μm (called PM10). PM10 includes almost the entire size spectrum of the particles, only some of the very large particles are not taken into account, while PM2.5 neglects coarse particles and contains only the accumulation and Aitken mode particles. In Europe and the United States, aerosol mass measurements are mainly done because of the health impact of high particle concentrations. High concentrations are responsible for a number of diseases including asthma, pulmonary diseases, bronchial carcinoma and cardiovascular diseases. In the US measurements concentrate on PM2.5 because these particles are more easily respirable than the coarse particles. Additionally, the coarse particles consist mainly of aerosols of

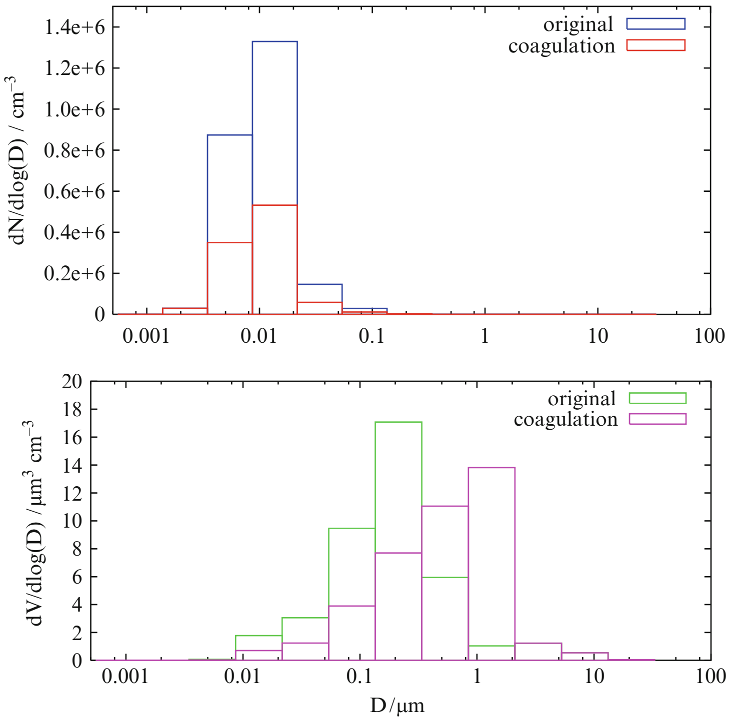

Fig. 14.5 Particle growth by coagulation. In this exemplary calculation a typical size distribution was prescribed ("original") and it has then been assumed that 60% of the particles with 5 nm $< D <$ 0.5 μm are collected by larger ones ("coagulation"). The mass is redistributed proportional to D to all size bins <2 μm. Number distribution (*top*) and volume distribution (*bottom*)

natural origin like crustal materials and sea salt while a large fraction of the smaller particles (both primary and secondary) is of anthropogenic origin. In Europe the focus is still on PM10 because the EU legislation defines threshold values for PM10 and the measurement techniques were more easily available.

The daily mean aerosol mass in air varies considerably from day to day and throughout the year and it depends strongly on the location. Aerosol mass concentrations are much higher inside big cities and in highly industrialized regions than in remote areas (Fig. 14.6). In Europe typical annual average PM10 values in polluted regions are on the order of 40–50 μg/m^3 with individual daily averages reaching 100 μg/m^3 (van Dingenen et al. 2004). Background values in remote areas are typically around 10 μg/m^3. Somewhat lower PM2.5 values for polluted regions are observed in the Eastern US (Malm et al. 2004). The highest aerosol mass concentrations are nowadays found in Southeast Asia, particularly China, where a combination of natural (from deserts) and anthropogenic aerosols can lead to PM10 values as high as 300–400 μg/m^3 (e.g., Zhang et al. 2008).

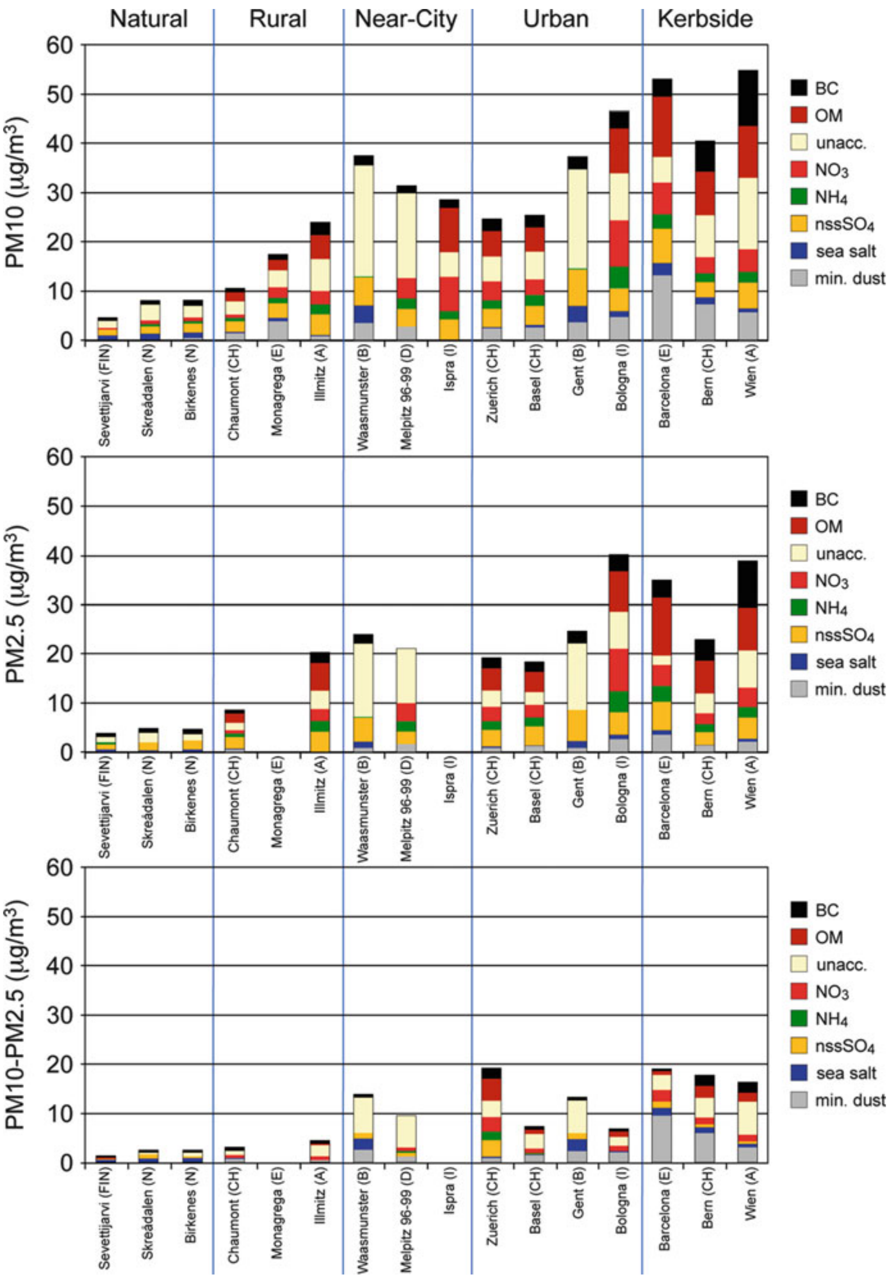

Fig. 14.6 Measured aerosol chemical compositions in Europe (After Putaud et al. 2004)

14.6 Chemical Composition

14.6.1 Measured Composition

The atmospheric aerosol mass density is determined by collecting the particles on glass fibre, quartz fibre or teflon filters that are placed into a well determined air flow. The total aerosol mass is determined by weighing the filters before and after the measurements period of typically 24 h. Before a weighing of the sampling filters takes place they are dried to reach equilibrium with the surrounding air at a predefined relative humidity (RH) value of 50%. The chemical analysis of the filters is subsequently done with species dependent methods (e.g., ion chromatography and mass spectrometry).

The different origin of aerosol particles in a given sample is reflected by their chemical composition. In polluted regions like in large parts of Europe the main components are sulfate (SO_4), nitrate (NO_3), ammonium (NH_4), sea salt (Na, Cl), dust (or soil), elemental carbon (EC, soot) and organic matter (OM). Some of these components include numerous other species. Dust for example consists of iron, magnesium, calcium, aluminium and other species. Organic matter may include biological particles like pollen and secondary formed hydrocarbons. Water is one additional important fraction of the total aerosol mass. It is usually excluded when the chemical composition is measured but it may still be a significant fraction of the total aerosol mass when the filters are weighed at 50% RH.

Like the aerosol mass, also the average compositions of aerosol particles depend strongly on the location where they are observed. In polluted environments that are dominated by anthropogenic emissions, about half of the aerosol mass is secondary inorganic aerosol of the components sulfate, nitrate and ammonium. Typically another third is organic material and elemental carbon. Sea salt and mineral dust are only included in considerable amounts in some regions in Europe (Putaud et al. 2004). Another fraction of the measured aerosol mass, which may be 20–50% of the total mass, remains chemically unspecified. It is believed that this fraction consists of organic material that could not be further analyzed by the methods that are available today but it may also be water that is not fully evaporated during the drying procedure of the filter (Putaud et al. 2000, 2004).

14.6.2 Persistent Pollutants Connected to Aerosol Particles

Besides the main chemical components that dominate the composition of the aerosol particles, some very small fractions may also be of significant importance due to the great threat they put to human health and to certain ecosystems. Some of these pollutants are of organic origin and very long-lived, they are called persistent organic pollutants (POPs). The group of polychlorinated biphenyls (PCBs) and some insecticides (e.g., DDT) belong to them. One other group of long-lived organic pollutants are polyaromatic hydrocarbons (PAHs). They are combustion products of organic material like oil, wood and coal and consist of more than one (typically 2–6) benzene rings in different configurations and sometimes with H atoms replaced by other atoms or functional groups. The larger these molecules are the lower is their volatility. PAHs with two rings are semi-volatile and can be found both connected to aerosol particles and in the gas phase while 5-ring and larger PAHs can be found almost completely connected to particles at ambient atmospheric conditions (Richter and Howard 2000). Some of the PAHs are known to be highly carcinogenic, like the 5-ring PAHs benzo(a)pyrene (B(a)P), benzo(k) fluoranthene (B(k)F) and benzo(b)fluoranthene (B(b)F) (Committee on Pyrene and Selected Analogues, 1983.). Very heavy PAHs are precursors of soot particles, but all PAHs can also stick to other particles present in the combustion exhaust. A sketch of the PAH formation in combustion exhausts can be seen in Fig. 14.7.

Measurements by Allen et al. (1996) have shown that the heavier 5-ring PAHs are mainly connected to accumulation mode particles, which means that they are transported together with them and have similar lifetimes of several days in the atmosphere. If they are lifted in regions above the planetary boundary layer (PBL) they might be transported over thousands of kilometers. In contrast, the lower weight PAHs are also found in significant amounts in the coarse mode which indicates that they were first in the gas phase before they were adsorbed to other particles. Together with the coarse particles they are more quickly deposited by sedimentation than the heavier PAHs in the accumulation mode.

14.7 Optical Effects

Aerosol particles scatter and absorb solar radiation, by this they determine visibility and they have a large influence on the radiative balance of the Earth. The aerosol distribution can be measured with optical techniques that give important information about the optical depth and about the vertical distribution of aerosols. The optical depth is the product of the extinction coefficient σ and the path length l in which this extinction happens. The largest part of the light extinction of aerosols is caused by scattering (typically around 90–95%), but depending on the chemical composition also absorption might play a role. If the extinction coefficient varies within a given volume (here: the atmosphere) the optical depth (OD) between the surface (height 0) and some other height or some distance l can be written as

$$OD = \int_{0}^{l} \sigma(z)dz$$

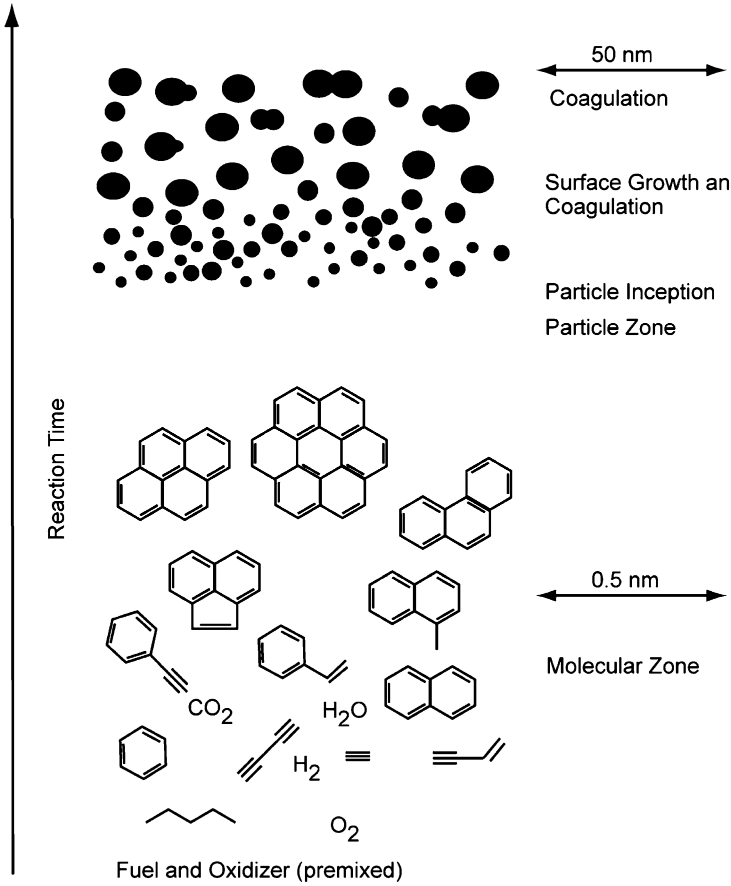

Fig. 14.7 Schematic of PAH formation in the atmosphere (After Richter and Howard 2000)

Following Lambert's law a portion of incoming solar radiation is attenuated by aerosols by a factor proportional to exp (−OD):

$$\mathrm{I} = I_0 \exp(-OD).$$

In the visible spectrum, the aerosol extinction is usually larger than the extinction caused by Rayleigh scattering of the air molecules, so the aerosol optical depth (AOD) is usually larger than the optical depth caused by Rayleigh scattering. Additionally the aerosol extinction is highly variable in time and therefore the aerosols determine the changes in visibility.

If AOD is used in the scientific literature, it means the vertically integrated aerosol extinction coefficient between ground level and the top of the atmosphere. At daytime under cloud free conditions, the AOD can be measured by sun photometers. Since the late 1990s a worldwide sun photometer network, the Aeronet

(Holben et al. 1998), has been built up to monitor the aerosol optical depth (and other aerosol parameters) at more than 200 locations distributed over the whole globe. A global annual average AOD in the mid visible (550 nm) of 0.135 measured by Aeronet was reported by Kinne et al. (2006). From satellite data a slightly higher value of 0.15 was given in the same publication. Globally, natural aerosols dominate the AOD. Highest values are found over the Sahara desert and the Atlantic Ocean west of the Sahara (AOD $\approx$ 1), lowest values are observed in marine environments of the southern hemisphere (AOD $\approx$ 0.05). Very high optical depths connected with anthropogenic activities are also observed in South-, Southeast- and East-Asia.

Regular lidar observations can deliver information about the vertical aerosol distribution. In Europe, such measurements were performed in the framework of the EARLINET project (Bösenberg et al. 2003), statistical results about the vertical aerosol distribution in Europe are given by Matthias et al. (2004), and aerosol transport over Europe has been studied with the help of back trajectories by Wandinger et al. (2004). It was found that the AOD over Europe is lower in winter than in summer although aerosol mass measurements at ground level are lower in summer. The stronger vertical transport in summer leads to a larger depth of the aerosol layer and consequently to a higher integrated value over the entire air column. Long range transport, e.g., of Saharan dust and of fire generated aerosol particles in elevated layers above the PBL is also much more frequent in summer than in winter. This additionally enhances the AOD in South- and Southeast-Europe.

14.8 Summary

Aerosol particles are very different in shape, size, and chemical composition. They are directly emitted into the atmosphere or generated by gas–particle conversion. Globally most aerosol particles are of natural origin (sea salt and dust) but regionally, in highly industrialized regions, particles of anthropogenic origin can dominate the atmospheric aerosol composition. Aerosol size distributions can be approximated by three or four log-normal size modes. Measurements of the aerosol mass in air often distinguish between fine particles (PM2.5) smaller than 2.5 μm and particles smaller than 10 μm (PM10). The aerosol size distribution undergoes a continuous change. New particles are emitted or generated by gas to particle conversion. The particles grow by condensation, deposition and water uptake, they shrink by evaporation, sublimation and loss of water. Coagulation leads to the growing of larger particles at the expense of smaller ones. Finally, wash out by precipitation and sedimentation of large particles removes the particles out of the atmosphere.

The chemical composition of aerosol particles can be as diverse as their sources. Most particles are mixed out of several chemical components. This may include very harmful or toxic substances like POPs that are transported together with the aerosols. PAHs are generated during combustion processes and they may be adsorbed to numerous other particles that are also emitted along with this. Many aerosol particles are water soluble or at least hydrophilic and they take up water when the relative humidity reaches approx. 80% or more. Then, chemical reactions in the aqueous phase may modify the particle and its properties.

Scattering and absorption of sunlight by aerosol particles determine the horizontal visibility. The direct and indirect radiative effects of aerosol particles are responsible for a large part of the uncertainties connected with climate projections by general circulation models. Therefore, their spatial distribution, chemical composition and optical properties are of highest interest to the scientific community.

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Chapter 15
The Global Distribution of Aerosols

Hartmut Graßl

15.1 Introduction

The radiation budget of planet Earth, given the solar irradiance at the top of the atmosphere, is to a large extent determined by minor constituents of the atmosphere. Less than three thousandths of its mass – including water vapour, cloud water and cloud ice – regulate how much solar radiation reaches the surface and from where in the atmosphere or on the surface the same amount of energy as absorbed globally from solar irradiance is radiated back to space in the thermal infrared. The least understood part of the Earth's radiation budget and its changes is related to an extremely small fraction of the minor constituents, the aerosol particles, liquid or solid particles suspended in air in the size range from about a nanometer to a few micrometers. At a typical mass mixing ratio of 10 $\mu g/m^3$ in the free troposphere aerosol particles constitute only about 10^{-10} of the mass or 10^{-13} of the volume fraction of tropospheric air.

Why are these particles so important? Firstly, because their size is equal to or slightly less than the visible wavelength of solar radiation leading to an effective scattering cross section up to a factor 4 and in parts also to a considerable absorption cross section for solar radiation, and secondly because each cloud droplet and nearly each ice crystal in clouds must have had at least one of these particles as condensation or freezing nucleus, allowing massive growth at low super-saturation with respect to a plane water or ice surface.

The first characteristic makes these particles strong scatterers and partly also absorbers from the ultraviolet to the near infrared, also causing for our eyes air turbidity. However, scattering and less so absorption are comparably small in the thermal infrared radiation range, thus leading to a strong asymmetry of the particles'

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influence between the solar and terrestrial radiation ranges. Hence, while higher turbidity lowers solar irradiance at the surface it does not change as much emission of thermal radiation to space. Depending on their capacity to absorb in the visible and near infrared aerosol particles can lead to both enhanced or decreased local planetary albedo of the cloudfree atmosphere/surface system as already found in the early 1970s (Yamamoto and Tanaka 1972; Eschelbach 1973). For example, aerosol particle populations with an above average black carbon content over a highly reflecting snow surface would certainly lower local planetary albedo, while the same aerosol particle population would probably – depending on black carbon content – increase it over the dark ocean surface. In addition the planetary albedo change can change sign with solar zenith angle.

Present estimates favour an increase of planetary albedo by aerosol particles; however, the error bars are still nearly as large as the given mean global negative radiative forcing of about -0.3 W/m^2 (IPCC 2007). A major reason for the large remaining uncertainty lies in the scarcity of the observations of the amount of black carbon or soot contained in tropospheric aerosol particles.

The second of the above reasons for a strong aerosol particle influence on the Earth's radiation budget is probably part of one of the key feedbacks in the earth system. The number, the size and to a lesser degree the chemical composition of aerosol particles determines besides circulation parameters the cloud droplet size distribution and thus optical depth of a water cloud and hence its albedo. In addition, the initiation of precipitation (warm rain) also depends on the aerosol particle number and size distribution entering at cloud base. But also the initiation of precipitation via freezing nuclei is mainly depending on the number density of deposition or contact freezing nuclei in tropospheric aerosol.

Over millions of years the mean surface temperature of the Earth varied by only about ±5 K compared to present day values, despite major changes in atmospheric composition, solar irradiance variation, continental drift, volcanism etc. Therefore, a negative feedback must exist keeping the Earth a hospitable planet or, in other words, not allowing too much global planetary albedo variation. A potential candidate for this regulation by a negative feedback are tropospheric aerosol particles as they depend via biotic emissions on life and via re-suspension of terrigenous particles on atmospheric circulation. Research to find this stabilizing negative feedback is still in its infancy. Firstly, it needs clarification of anthropogenic cloud property changes as demonstrated in first steps by Kaufman (2006), Rosenfeld (2006) as well as Krüger and Graßl (2002, 2004).

A forerunner of this type of research on the overarching negative feedback in the climate system are the attempts to understand human influence on optical cloud properties and precipitation formation. The workshop on "Solar Variability and Terrestrial Climates" organized by the International Space Science Institute in Berne, Switzerland, in 2006 was in parts such an attempt (Calisesi et al. 2007). This text is in parts influenced by that workshop. The following small sections called "Brown Haze" (Sect.15.2), "Clouds in a polluted environment" (Sect. 15.3) and "Radiation Budget Changes" (Sect. 15.4) integrate results from the workshop and add recent findings from research, also in my own group.

15.2 Brown Haze

The typical urban and metropolitan pollution plumes, which have in parts already reached continent-wide proportions, repeatedly termed "brown clouds" by, e.g., Ramanathan et al. (2005) after the evaluation of the Indian Ocean Experiment (INDOEX), are a mix of directly injected absorbing organic aerosol particles, including black carbon or soot, and particles formed from or enlarged by supersaturated vapours in the atmosphere. The latter are mainly due to emissions of so-called precursor gases like sulphur dioxide (SO_2), dominantly from coal-fired power plants, refineries and vegetation fires, nitrogen oxides ($NO_x = NO + NO_2$), mainly from road traffic and all power plants using fossil fuels, and – if intense animal husbandry exists – ammonia (NH_3). Here the term "brown haze" is preferred as no activation of these aerosol particles as cloud condensation nuclei must be involved, and the particles cause radiative forcing also in cloudless parts of the atmosphere.

Satellite sensors, like MODIS on the NASA satellites Aqua and Terra or MERIS on ESA's Envisat, have helped to separate the anthropogenic contribution from the natural for optical depth of tropospheric aerosol particles (Fig. 15.1). As demonstrated by Kaufman (2006), the average contribution to the optical depth of aerosol particles is about 0.03, roughly a quarter of total natural optical depth and the modelling of the anthropogenic component comes to similar values and regional distribution.

The agreement between modelling and satellite-derived observations for the "natural" component of the tropospheric aerosol particles is not yet satisfactory, because the models strongly underestimate it. Because most of the optical depth of this aerosol component is related to desert dust, i.e., suspended minerals, and human influence on desert dust originating from semi-arid areas can by no means be neglected, the word natural above is put in quotas. Because the sub-grid scale wind speed variability (e.g.,

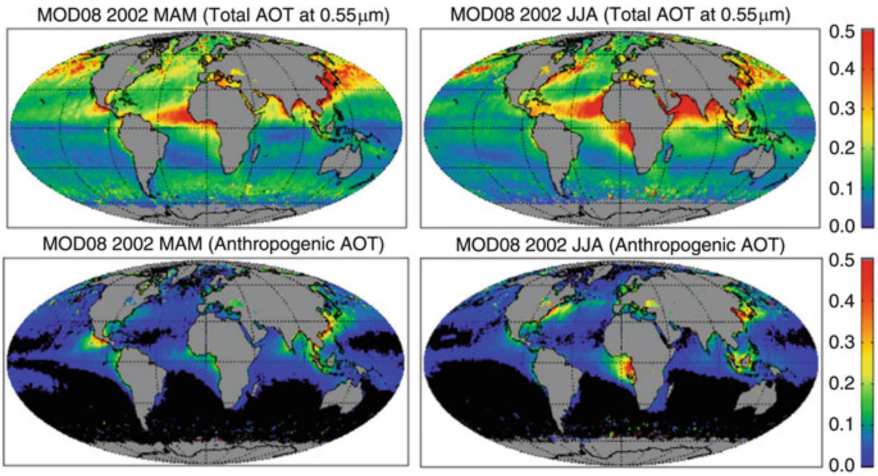

Fig. 15.1 Global distribution over the oceans of (*top*) the total aerosol optical thickness and (*bottom*) the anthropogenic component derived from MODIS data : (*left*) March–May, (*right*) June–August 2002 (From Kaufman et al. 2005; Kaufman 2006; see also Kaufman et al. 2006)

the one caused by dust devils and local orography) is not yet represented in numerical models; the source strength of desert dust is probably severely underestimated.

A first summary of this small section could be: There is a strong anthropogenic contribution to total optical depth of tropospheric aerosol particles both from urban air pollution and vegetation fires. The anthropogenic aerosol particle plumes have reached the size of continents and are also clearly visible over large ocean areas (see also Figs. 15.2–15.5). However, the main contribution to optical depth stems from mineral dust particles originating from arid and semi-arid climate zones. But also the vegetation fires in the dry seasons of many semi-arid zones but also humid climates are a considerable part of aerosol loading in the lower and mid-troposphere. Natural aerosol particles from deserts are coloured, hence they absorb solar radiation as can easily be seen in Fig. 15.3, which, however, also points to eastern China as a major source of aerosol absorption caused by black carbon or soot. In areas with a strong soot component local planetary albedo may even decrease with increasing aerosol optical depth (see also Krüger and Graßl 2004). As an indication for the in situ and the remote sensing networks existing, Fig. 15.5 displays for a short period in 2001 values of aerosol optical depth, retrieved from MODIS data, together with the Aeronet stations (upper part) and the Lidar stations.

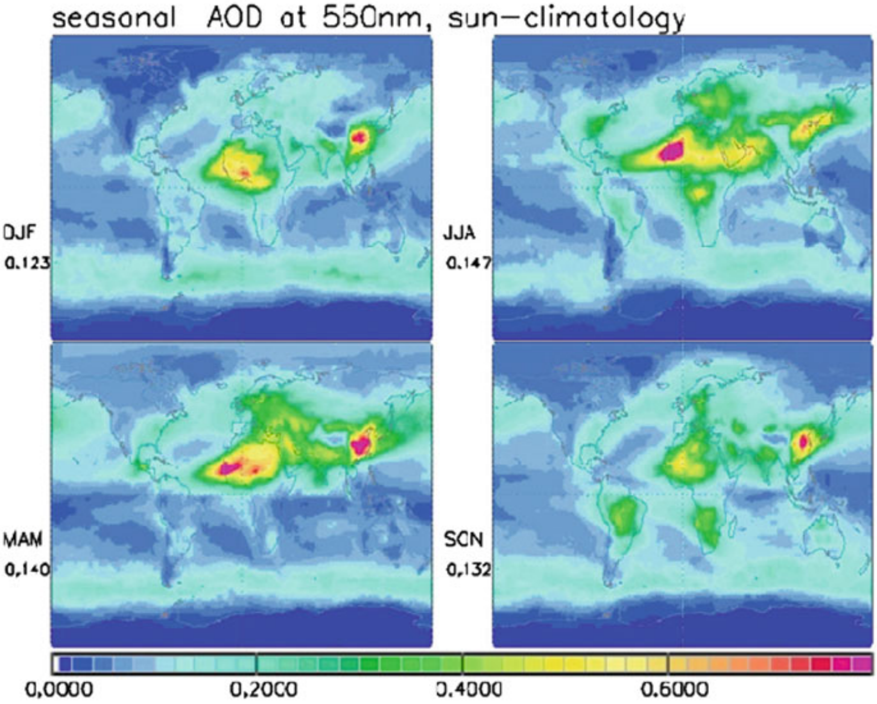

Fig. 15.2 Global distribution of aerosol optical depth at 550 nm wavelength for the different seasons derived from multi-year ground-based Aeronet observations and global aerosol modelling (multi-model average). Please note the main contribution from desert dust and a few strongly urbanized areas like eastern China (Courtesy of Stefan Kinne)

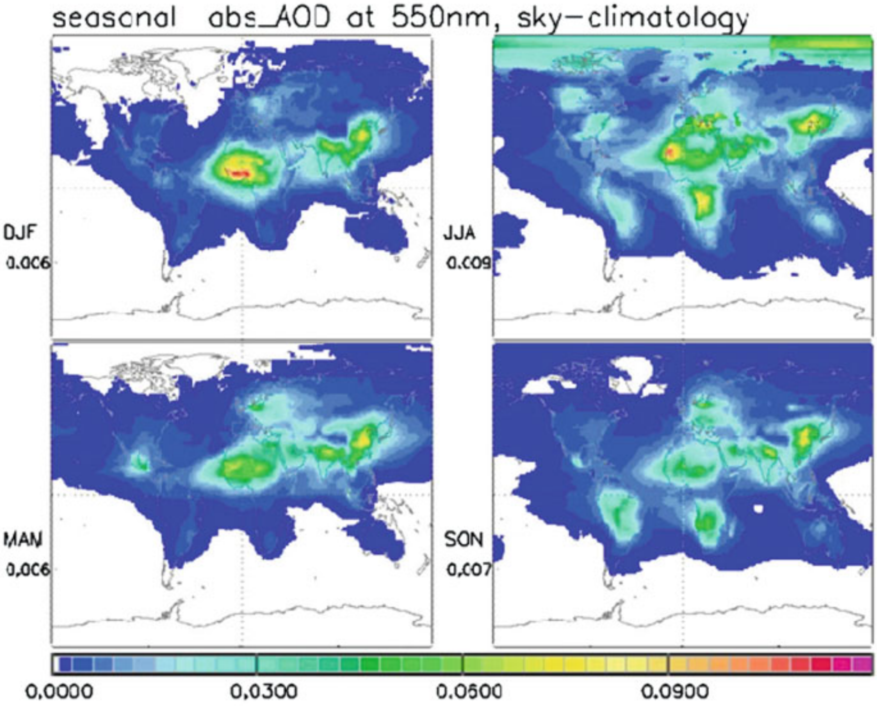

Fig. 15.3 Global distribution of optical depth of tropospheric aerosols due to absorption for all four seasons derived from Aeronet data and global aerosol modelling. Please note the high values over eastern China throughout the year and the comparably high values over deserts and areas with vegetation fires (Courtesy of Stefan Kinne)

15.3 Clouds in a Polluted Environment

Each cloud droplet and nearly all ice crystals in cirrus clouds or mixed phase clouds have been formed using at least one aerosol particle in the radius range above about 0.02 μm in order to overcome the high super-saturation barrier otherwise needed for so-called homogeneous nucleation of droplets or ice crystals. Therefore all clouds must react to the aerosol particle population in which they form. Since clouds have a very strong influence on both backscattered solar radiation and terrestrial radiation emitted to space, aerosol particles get a potentially very big climate-lever via clouds. This influence on the Earth's radiation budget could easily override the particles' climate effect in the cloud-free parts of the atmosphere.

However, no reliable global radiative forcing of clouds caused by aerosol particles existed in 2001 when the third assessment report of IPCC has been published. In IPCC (2001) no global estimate with error bars could be given, but a large potential range reaching a negative radiative forcing of -1.9 W/m^2 was indicated. Hence only rough estimates were available.

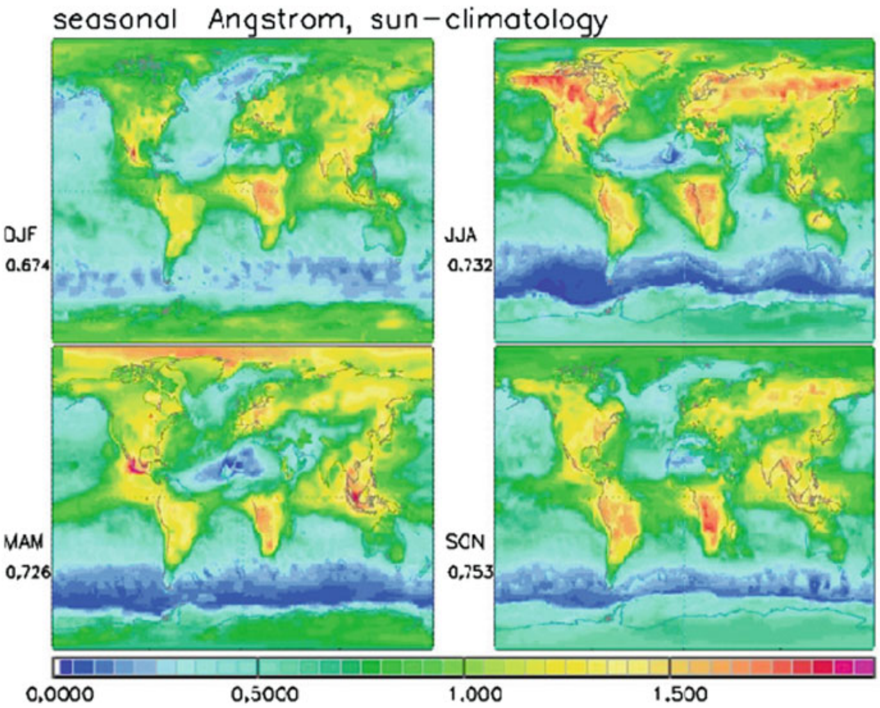

Fig. 15.4 Angström coefficient (ratio of 0.44 and 0.87 μm values of optical depth) of tropospheric aerosol particles as a measure for the aerosol size distribution for all four seasons (data and modelling as in Figs. 15.2 and 15.3). Please note the low values over the southern ocean and in desert dust plumes, where the large particle sizes lead to low or negligible wavelength dependence (Courtesy of Stefan Kinne)

In the fourth assessment report of IPCC (2007) the scientific community could lower the uncertainty and was able to give wide error bars from -1.3 to -0.2 W/m^2 for the indirect aerosol effect on clouds. In this estimate the potential influence on terrestrial radiation was not taken into account. Would anthropogenic aerosol particles lead to a slightly higher cloud top level at slightly lower cloud top temperatures, as indicated in a regional study on the potential influences of ship emissions on cloud properties (Devasthale et al. 2006), the radiative forcing of aerosol particles via changed cloud properties would shrink further and may regionally even change the sign of the forcing (see Fig. 15.6). This would have major consequences for the anthropogenic climate-change debate, because the masking of mean global warming by aerosol influences (on average cooling) would be less. Hence, climate system sensitivity to the enhanced greenhouse effect would be lower than estimated today.

For some regions with major changes in air pollution first changes in cloud albedo could be derived by using long-term satellite observations. As shown by Krüger and Graßl (2002) and repeated in Fig. 15.7 for a considerable part of Europe,

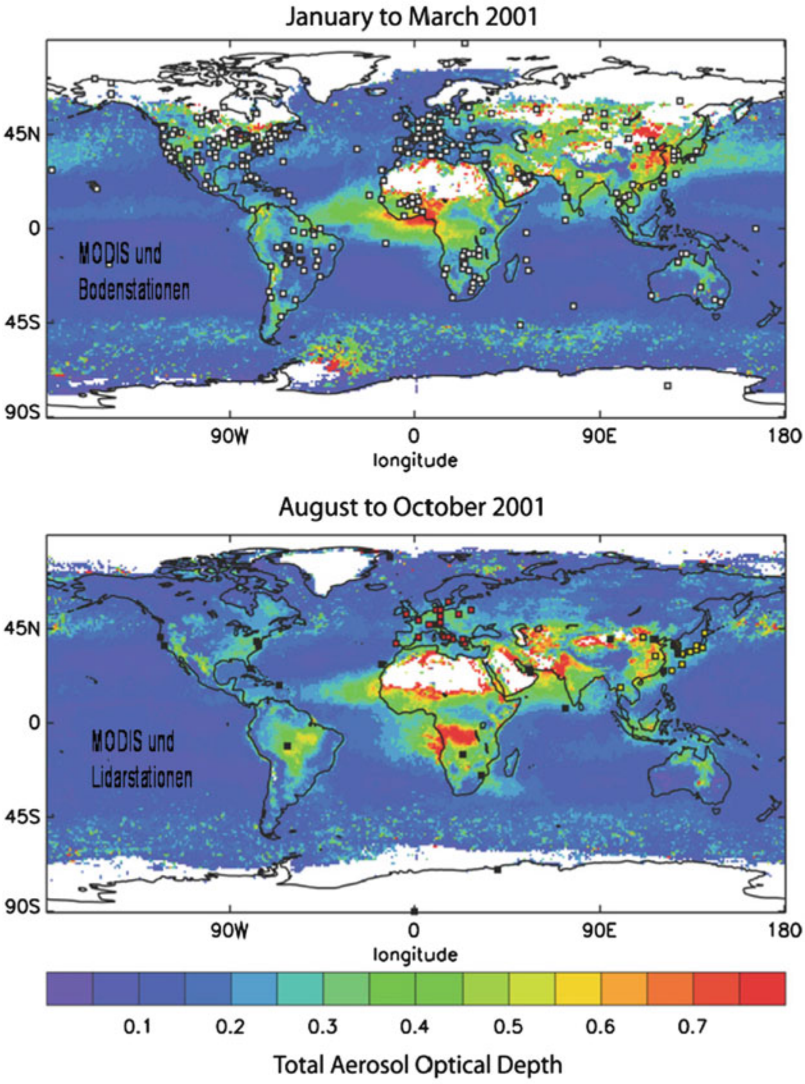

Fig. 15.5 Aerosol optical depth derived from MODIS data and Aeronet stations (*upper part*) as well as Lidar stations for a 3 months period in 2001 (Courtesy of Stefan Kinne)

the effects of a pollution decrease after the late 1980s (collapse of the East Block and clean air acts in Western Europe) were consistent with two influences of aerosol particles on clouds. Firstly, enhanced apparent cloud albedo by air pollution with particles of comparably low absorption capability (called Twomey effect, Twomey 1972, 1977), and secondly, reduced albedo for optically thick clouds close to the emission sources, where soot has a stronger influence because the transformation of a considerable part of SO_2 emissions into sulfate aerosol particles is not yet

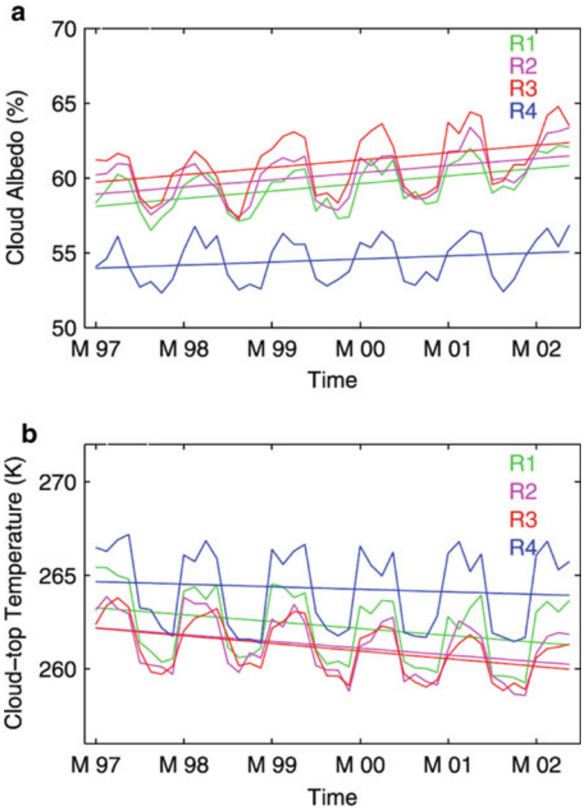

Fig. 15.6 Time series of apparent cloud albedo (ratio of *upward* and *downward* radiance; *top*) and cloud top temperature (CTT; *bottom*) derived from AVHRR channels over European coastal waters or harbour areas (Devasthale et al. 2006)

finished. Averaged over the entire region, the reduction of cloud albedo via the reduced pollution level, i.e., the Twomey effect, dominated for the period from 1985 to 1999, as clearly visible in Fig. 15.7. For example, the apparent albedo of clouds, i.e., the ratio of satellite reflectances or satellite radiances, in the reflectance range from 60 to 62 % during the 1986–1989 period was lower by 32,000 or 3.2% in the 1996–1999 period. In addition, it also became clear that in the May to August period a strong apparent albedo reduction for optically thick clouds occurred; probably because of the much larger part of SO_2 transformation into sulfate particles at high photochemical activity due to much higher solar elevation angles in this part of the year.

15.4 Radiation Budget Changes

As assessed by IPCC (2007), four out of eight anthropogenic influences on global climate are due to tropospheric aerosol particles, namely the direct aerosol particle effect, the indirect aerosol particle effects on optical cloud properties, soot

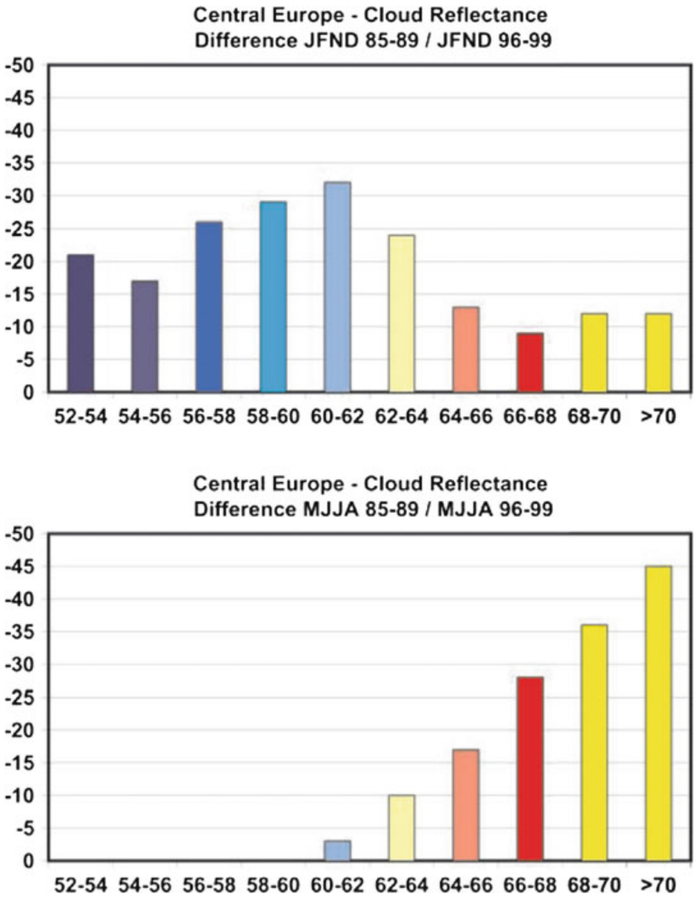

Fig. 15.7 Decrease of cloud reflectance in thousandths from 1985–1989 to 1996–1999 for different mean reflectance classes (unit: %) as derived from AVHRR channel 2 satellite measurements over parts of Europe (Central Europe and parts of Western and eastern Europe) for four winter (*top*) and summer half year (*bottom*) months. This is interpreted as a net reaction to less aerosol and soot emission after the breakdown of parts of the eastern European industry production around 1990 and implementation of clean air acts in the European Communities

deposition lowering snow albedo, and formation of longer lasting linear condensation trails (contrails) caused by aircraft, when they fly through air masses with super-saturation with respect to a plane ice surface and circumvent ice nucleation by condensation of cloud droplets in the hot exhaust plume of an aircraft containing aerosol particles and water vapour from the burning of kerosene. As displayed in Fig. 15.8 the first two are the largest cooling influences (hence with a negative radiative forcing), off-setting to a considerable part the positive radiative forcing caused by the increased concentration of the long-lived greenhouse gases carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and the halogenated

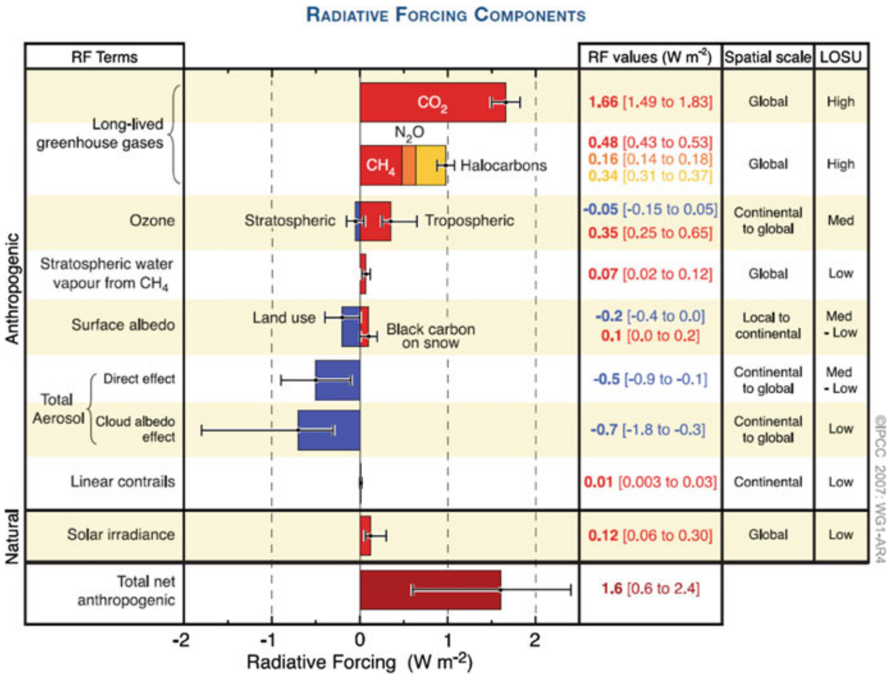

Fig. 15.8 Radiative Forcing of climate change due to anthropogenic activities as given by IPCC (2007a). Also the forcing caused by solar radiation changes is given

hydrocarbons (including chlorfluorocarbons (CFCs)). However, it must be repeated here that the particles' influence on cloud top height and thus emission of longwave radiation is not yet taken into account.

15.5 Concluding Remarks

Both the anthropogenic influences on global climate and the long-term natural climate system feedbacks involve in many ways tropospheric aerosols. We are far from being able to give reliable estimates for the first topic and have not yet begun to study the latter. The following research topics need more attention besides all the other ongoing research activities:

1. Is there an influence of air pollution on cloud top height? An answer to it would have strong repercussions for the climate change debate. Lower clouds would give a negative feedback adding to the solar radiation range influence of aerosol particles, which is estimated to cause negative radiation forcing. Therefore, on average lowered cloud tops and therefore higher cloud top temperatures would enhance the masking of the enhanced greenhouse effect by aerosol particles'

influence. Should cloud top height increase and thus cloud top temperature decrease, as indicated by first studies in small regions, the radiative forcing in the solar radiation range by tropospheric aerosol particles would be less negative or even negligible and would lead to a strong change in the anthropogenic climate change debate, because climate system sensitivity to an enhanced greenhouse effect would be lower than estimated up to now.

2. Do anthropogenic activities change freezing nuclei populations inadvertently? There is no other trace substance class with such a high specific influence on properties of the earth system. Depending on their chemical composition and their surface properties they may initiate the Bergeron-Findeisen process of precipitation formation at temperatures ranging from a few degrees below 0°C to less than −30°C. On average, freezing nuclei constitute only a tiny fraction of tropospheric aerosol particles. Therefore, cloud properties, cloud height, cloud cover, precipitation occurrence and rate, relative humidity, water vapour column content, local planetary albedo and other parameters depend on this tiny mass fraction of about 10^{-13}. In recent years, cloud seeding, i.e., the artificial enhancement of freezing nuclei close to cloud tops, has become a major activity in some countries like China. We need to know how air pollution enhances or inhibits the freezing nuclei populations.
3. Is there a feedback between global mean warming and gas to particle conversion from precursor gases? The chemical transformation of organic compounds emitted by vegetation and of dimethyl sulfide from the ocean is temperature dependent as well as the emissions. Hence aerosol load might increase establishing a negative feedback.

All these questions are also related to the question on the fundamental negative feedback stabilizing the Earth's climate to such an extent that a runaway greenhouse effect has never occurred. However, answers to the above questions are a prerequisite for the discussion of this feedback. Because the changes to be expected in the twenty-first century are so rapid a major new question comes up: Will the negative feedback work under present day conditions with a very rapid global warming.

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Chapter 16
The Role of Clouds in Atmospheric Transport and Chemistry

Markus Quante

16.1 Introduction

Clouds are ubiquitous in the Earth's atmosphere. They are important for a multitude of reasons. By intervening with the radiation and energy budget of our planet clouds play a major role in climate and global change (Kiehl and Trenberth 1997; Quante 2004). Furthermore, they possess a key role in the global and regional water cycles (Quante and Matthias 2006). Besides these prominent influences on weather, climate and water availability, clouds are involved in several ways in the distribution and transformation of pollutants in the atmosphere. That clouds play an active role in the processing and cycling of atmospheric substances has long been recognized.

Pollutants which entered cloud particles by one of several possible processes can be transported horizontally as well as vertically in the atmosphere. Gases and aerosol particles may enter cloud droplets through absorption/condensation (of soluble gases) and activation and impact scavenging (of aerosol particles) (Pruppacher and Klett 1997).

Clouds can particularly influence atmospheric chemistry and the fate of pollutants by transporting boundary layer constituents to the free troposphere. Here, updrafts and downdrafts in convective clouds are efficient ways of redistributing atmospheric tracers in the vertical (cloud venting). Clouds also act as an important sink for pollutants in the atmosphere through the production of precipitation. Precipitation particles may contain pollutants via the collected cloud particles (rain out) or they can take up pollutants during their journey below the cloud (wash out). If the precipitation with its freight reaches the ground the overall process is called wet deposition. However, not all of the precipitation reaches the Earth's surface; in that case precipitation evaporation can play an important role in redistributing tracer mass in the vertical.

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Clouds are providing a medium for aqueous chemistry in cloud and rain drops. A large portion of cloud-processed gases and particles, often physically and chemically altered, will be released back to the atmosphere upon cloud dissipation and evaporation as a large fraction of clouds globally is non-precipitating.

Clouds also effectively alter photochemistry inside, above and below the cloud layer by altering the photo-dissociation frequencies of several species through their profound influence on solar radiation and thus on the actinic flux. The influence on photochemical reactions leads to changes in the oxidation capacity of the atmosphere, which in turn will have an effect on the degradation of several persistent pollutants.

To summarize, the important cloud effects on pollutants are via (see also sketch in Fig. 16.1):

- An influence on transport of atmospheric constituents (i.e., cloud venting)
- Liquid and solid phase chemistry in cloud and precipitation particles
- Wet deposition
- An influence on photochemistry

This overview will start with some introductory remarks on clouds and their spatial distribution. From several ways clouds transport pollutants the important and effective cloud venting has been selected for a more detailed description in Sect. 16.3. Wet deposition processes are presented in Sect. 16.4 and the influence of

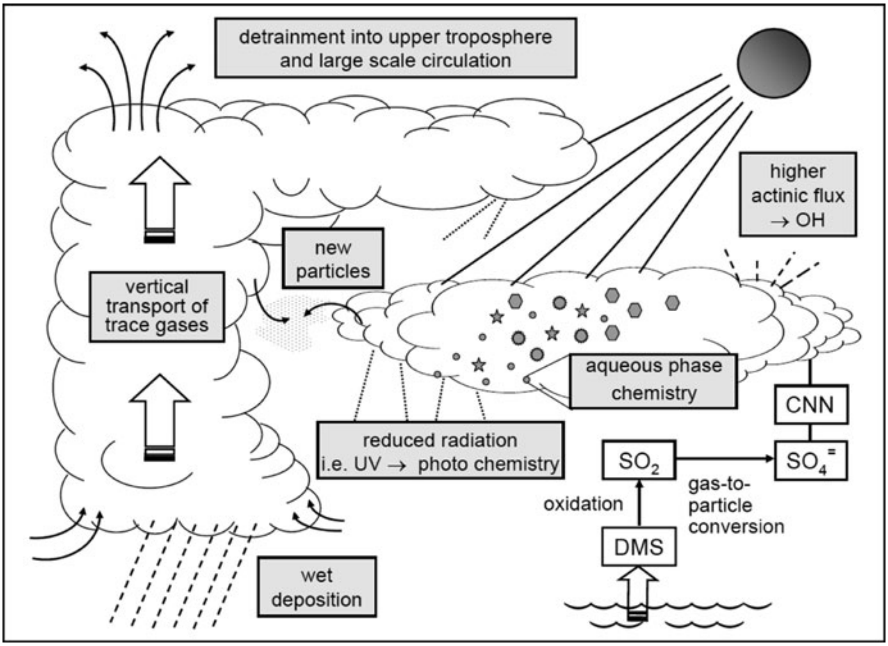

Fig. 16.1 Schematic of important aspects of the influence clouds have on atmospheric transport and chemistry

cloud decks on photochemistry is described in Sect. 16.5. The article concludes with some general remarks.

Chemistry in the atmospheric liquid and ice phase is an extremely broad field; it cannot be adequately addressed in this overview. Some initial information highlighting different research areas may be found e.g., in Warneck (1991), Liang and Jacob (1997), Sander (1999), Lin and Pekhonen (1999), and Seinfeld and Pandis (2006). Certainly, liquid phase chemistry has the potential to influence the oxidation capacity of the troposphere and, hence, the degradation of several persistent pollutants.

16.2 Some Remarks on Clouds

16.2.1 Cloud Types

Clouds are an integral component of the earth system. At any given time clouds cover between 60% and 70% of the globe. According to the World Meteorological Organization (WMO), a cloud is an aggregate of minute, suspended particles of water or ice, or both, above the Earth's surface that are in sufficient concentrations to be visible. Many different types of clouds exist and detailed classification schemes have been developed. The classification of clouds can be based on their altitude within the atmosphere (*low*, *mid-level*, *and high clouds*), their phase (*liquid*, *ice*, *or mixed*) or their manifestation. Cumulus and cumulonimbus clouds are called *convective clouds* because of the central role of convective updrafts in their development and structure. They usually show a relative large vertical extend compared to their horizontal dimension. In contrast to convective clouds, *stratiform clouds*, like stratus, stratocumulus, cirrostratus, and cirrocumulus, have a more layered appearance, they usually span much larger areas than convective clouds and thus account for most of the global cloud cover. Some cumulus clouds can be very deep and extend to the tropopause, where they generally spread out and form large cirrus anvils. Often also a distinction between *precipitating* and *non-precipitating clouds* is made. Strong precipitation events are connected to intense convection and long lasting rain covering larger areas is associated with *nimbostratus clouds* occurring in warm frontal systems of extratropical cyclones.

16.2.2 Cloud Formation and Composition

The detailed microphysical processes occurring in the life cycle of a cloud are quite complicated (Pruppacher and Klett 1997; Seinfeld and Pandis 2006), here only a few general remarks on their formation are made. The factors of prime importance in cloud physics are the air motion, available water vapour, and the number and composition of particles serving as cloud condensation nuclei or ice nuclei. Most clouds are formed by the lifting of moist air which cools adiabatically by expansion under falling pressure. Eventually, relative humidity approaches saturation and condensation becomes possible. The height where this condition is reached is called lifting condensation level. There are several ways how the necessary lifting of air masses can be achieved. Local ascent of warm, buoyant air parcels in a conditionally unstable environment leads to convective clouds. The associated updraft velocities are a few meters per second, but in large convective cloud systems also several tens of meters per second can be reached. Cloud lifetimes range from minutes to hours. Forced lifting by e.g., frontal movements leads to stratiform clouds. Here, the updraft velocities are much lower, typical values are in the range of a few centimetres per second to 10 cm s^{-1}. The lifetime of these clouds typically range between hours and tens of hours. Air masses passing hills or mountains experience a forced lifting, if clouds are formed in this way they are called orographic clouds. The spatial and temporal distribution of surface heating and the paths of large scale weather systems determine the type of clouds occurring in a region.

Clouds are composed of hydrometeors which differ in phase, size and shape. The basic hydrometeors in the atmosphere are water droplets, ice crystals, rain drops, graupel, hail and snow flakes, of which water droplets and ice crystals are cloud particles while the latter four hydrometeor types are called precipitation particles. Depending mainly on the vertical temperature profile, the different hydrometeors can be present in all clouds in a more or less distinct number concentration. Pure water clouds are observed at temperatures above 5°C and pure ice clouds below −40°C; in the broad temperature range of −5°C to −40°C mixed phase clouds can be present. The particles in clouds occur in a range of sizes leading to characteristic size distributions. To fully characterize a cloud the spatial and temporal distribution of its water content (liquid or ice) and the phase, size and shape of its particles needs to be known. Typical microphysical properties for different cloud types can be found in Quante (2004).

16.2.3 Cloud Distribution

The overall influence clouds have on climate, the hydrological cycle, and atmospheric chemistry depends on how (where and when) clouds of different types are distributed over the Earth. Global average amounts for different cloud types according to surface observation climatologies are shown in Table 16.1. The most common types are stratocumulus, altocumulus and cirriform clouds, the dominance of low-level stratus and stratocumulus over large areas of the oceans is obvious in the data. The annual average total cloud cover from surface observations (1982–1991) is 64% (54% over land and 68% over the oceans) (Warren and Hahn 2002). The annual total cloud amount from the International Satellite Cloud Climatology Project (ISCCP) considering data from 1986 to 1993 is 68% (58% over land and 72% over oceans) (Rossow and Schiffer 1999).

Table 16.1 Cloud type amounts from surface observations (After Warren and Hahn 2002)

Cloud type	Annual average amount (%)	
	Land	Ocean
Stratus	5	11
Stratocumulus	12	22
Cumulus	5	12
Cumulonimbus	4	4
Nimbostratus	5	6
Altostratus	4	
Altocumulus	17	22
Cirriform	22	13

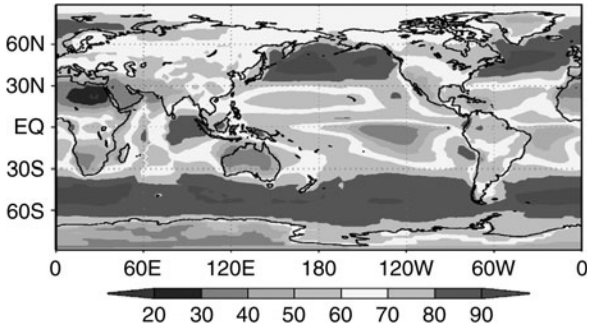

Fig. 16.2 Annual average cloud amount (1983–1997) in % from the International Satellite Cloud Climatology Project (Rossow and Schiffer 1999)

The global distribution of cloud amount as based on ISCCP results is shown in Fig. 16.2. As expected the cloud cover is continuously high in the equatorial belt due to strong convection along the Inter Tropical Convergence Zone (ITCZ). High cloud amounts also occur in the regions of the extratropical storm tracks along the polar fronts at mid-latitudes (50–60°). Minima of cloudiness are observed in the zones of downward motion in the subtropics associated with the Hadley cells. Lowest values of cloud amount are found over the desert areas. A further examination of the ISCCP data (figures not shown here) reveals in the tropics and subtropics the existence of low level often quite homogeneous stratocumulus fields at the western rims of the large continents over ocean areas, which are typically relatively cold. Largest coverage with high clouds is found in the tropics, many of these are sheared off the tops of large cumulonimbus towers. Consistent global climatologies for cloud water content or effective particle size over land and ocean areas are currently not available.

Concerning changes in global cloud occurrence during recent decades of rapid warming there are no clear results, yet, despite of some reported regional changes. Expected cloud changes are not straightforward to extrapolate, since they may be influenced by unforced dynamical variability instead of solely temperature and humidity. There is also a lack of a homogeneous observational record, which stretches over the recent decades (Norris and Slingo 2009).

Although focusing on the cloud–climate relation, Heintzenberg and Charlson (2009) is a recommended up-to-date reference for information on many additional aspects of clouds and cloud systems.

16.3 Cloud Venting

Pollutants may be transported horizontally and vertically through the atmosphere within cloudy air or even embedded in cloud droplets or ice crystals. In this section we restrict ourselves to cloud venting as a very effective way of vertical transport. Cloud venting refers to the process of transporting gaseous matter and aerosols from the lower troposphere to the cloud layer (Ching 1982; Cotton et al. 1995). It comprises convection below the cloud layer as well as the flow of interstitial air and partly transport of pollutants embedded in hydrometeors. Cotton et al. (1995) provide a comprehensive review on observational and modelling studies on cloud venting by a wide variety of cloud types ranging from ordinary cumuli to ordinary cumulonimbi, mesoscale convective systems (MSCs), mesoscale convective complexes (MCCs), and tropical and extratropical cyclones. It should be mentioned that besides reviewing observational and modelling studies Cotton et al. (1995) provide a theoretical framework for the quantitative estimation of cloud venting rates. They start from equations for mixing ratios of species in air, including turbulent transport, and develop the equations for species embedded in hydrometeors.

Deep convection plays a prominent role in cloud venting and thus is an important process in determining tropospheric distributions of many chemical species including aerosols. The strong updraft and downdraft generated by deep convection can directly and rapidly transport chemical species and aerosols from the planetary boundary layer to the middle and even upper troposphere or vice versa. A number of studies have revealed this effective role of deep convection in tropospheric redistribution of constituents (e.g., Gidel 1983; Dickerson et al. 1987; Wang and Prinn 2000; Barth et al. 2007). On this path, vertical transport can cross the whole troposphere within only 1 to a few hours. In deep convective clouds peak updraft velocities are typically between 10 and 30 m s^{-1}, in supercell thunderstorms vertical velocities of 40 m s^{-1} can be reached and persist for several hours.

The relative effectiveness of the larger scale cloud systems in transporting pollutants can be judged by looking at the air mass the systems extract from the boundary layer. According to Cotton et al. (1995), the typical boundary layer mass fluxes over characteristic cloud system lifetimes are: 1.34×10^9 kg s^{-1} for mesoscale convective systems (Houze 2004), 4.35×10^9 kg s^{-1} for mesoscale convective complexes (Houze 2004), 1.54×10^{10} kg s^{-1} for tropical cyclones, 2.33×10^{10} kg s^{-1} for extrapropical cyclones, and 5.00×10^{10} kg s^{-1} for ordinary thunderstorms. The overall boundary layer mass flux by all cloud venting systems is estimated to amount to 4.95×10^{19} kg $year^{-1}$ (this represents a venting of the entire boundary layer about 90 times a year). With a contribution of 2.36×10^{19} kg $year^{-1}$, extratropical cyclones dominate the global annual venting of boundary layer air. This underlines the importance of an advanced understanding of theses systems as well as of their adequate representation, when the transport of persistent pollutants is to be modelled. At lower latitudes, mesoscale convective systems are a major contributor to transporting boundary layer air into the upper troposphere.

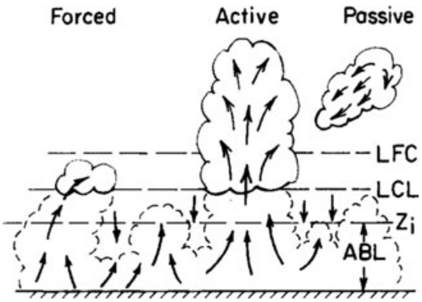

Fig. 16.3 Illustrative example of different types of fair weather cumulus clouds (forced, active, passive). Zi is the height of the atmospheric boundary layer (ABL), LCL denotes the lifting condensation level and LFC the level of free convection (From Stull 1985)

Also ordinary cumulus clouds contribute to vertical mass transport and thus to the transport of gases and aerosols. In Fig. 16.3, different states of fair weather cumuli are illustrated. Note, that only "active" cumuli (Stull 1985) contribute to relevant transport into the free troposphere. Only a few observations of ordinary cumulus cloud venting have been made either by in situ aircraft measurements or with airborne remote sensing platforms. As an example the results reported by Isaac et al. (1983) are given. In their study a cloud volume transport ratio (VTR) to present their findings has been defined. The VTR is the volume of sub-cloud air that is pumped through the base of cumuli into a region on an hourly basis divided by the volume of the sub-cloud air. For summer cumuli over Ontario, Canada, Isaac et al. (1983) found VTR values of 20% per hour. The respective values for stratocumuli in the region were slightly lower. Averaging over all cloud types in that study, it was found that in summer (winter) about 50% (20%) of the sub-cloud air was on an hourly basis vented through the cloud base. For comparison, a modelling study by Flossmann and Wobrock (1996) considering the transport from the marine boundary layer by a medium-sized convective cloud revealed that about 60% of the initial pollutant mass in the marine boundary layer surrounding the cloud was transported upward. One of the important effects of ordinary cumuli on the distribution of persistent pollutants is their transfer from the boundary layer cross the cloud base to the free troposphere, where the substances can eventually participate in long range transport.

16.4 Wet Deposition

There are two major processes by which pollutants are brought back from the atmosphere to the ground, namely dry and wet deposition. Dry deposition includes sedimentation, interception and turbulent transport, while in wet deposition always atmospheric hydrometeors (cloud and fog drops, ice crystals, rain and snow) are involved. According to Seinfeld and Pandis (2006) "wet deposition refers to the natural processes by which material is scavenged by atmospheric hydrometeors and is consequently delivered to the Earth's surface". Wet deposition is an important

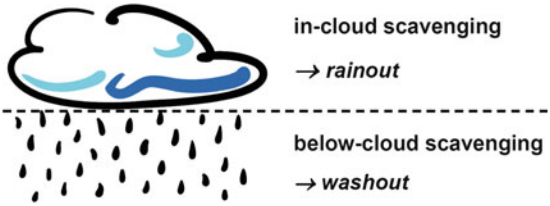

Fig. 16.4 Sketch which relates in-cloud and below-cloud scavenging to the often used terms rainout and washout

intermedia transport process responsible for the effective removal of aerosol-bound as well as gaseous air pollutants from the atmosphere (Tsai et al. 1991). In general it is distinguished between in-cloud scavenging and below-cloud scavenging. In-cloud scavenging is also known as rainout while washout usually refers to below-cloud scavenging by precipitation particles (Fig. 16.4). Often the term wet removal is used synonymously with wet deposition. In addition the term occult deposition is in use, which denotes wet deposition by settling fog droplets or direct interception of a cloud with structures and vegetation.

16.4.1 Conceptual Framework

In general there are three basic steps necessary in the wet deposition process. The chain is as follows: first the gas or aerosol needs to be brought into the presence of condensed water, then the material must be scavenged by the hydrometeors and finally the hydrometeors need to be delivered to the Earth's surface. Scavenging of pollutants is already possible during cloud formation; in this case nucleation scavenging is the expression generally used. To complicate matters, the compounds under consideration may undergo chemical reactions and subsequent transformations during each of the steps mentioned above. A conceptual framework of wet deposition processes, of which many are reversible, is shown in Fig. 16.5 (see Seinfeld and Pandis 2006 for a detailed discussion). As can be depicted from Fig. 16.5, wet deposition depends on quite a number of processes, which may involve different physical phases. In addition wet removal pathways are influenced on a variety of physical length scales, they reach from the cloud microscale (order of micrometers) to the size of total cloud systems, which may extent to hundreds of kilometres. The aqueous phase involved can be present as cloud droplets, ice crystals, rain, snow, sleet or hail. Each of these forms comes with a specific time dependent size resolution, depending on the details of the actual cloud microphysical processes and their history. Overall, wet deposition is among the most complex processes in the atmosphere. Aerosol removal by falling precipitation, below-cloud scavenging, remains an open subject for the scientific community in spite of many theoretical and experimental efforts made in the last few years. An example for the up-to-date implementation of a scavenging scheme into a global atmospheric chemistry model can be found in Tost et al. (2010).

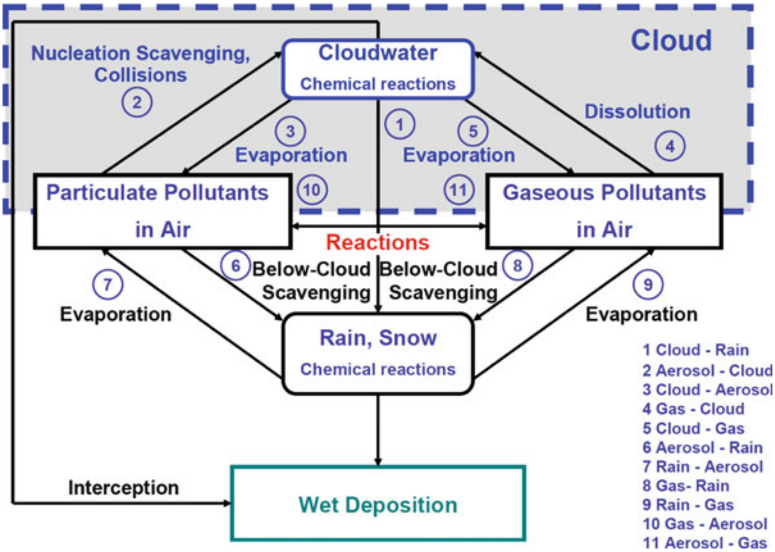

Fig. 16.5 Conceptual framework of the different processes involved wet deposition (Adapted from Seinfeld and Pandis 2006). Reprinted with permission of John Wiley & Sons, Inc.

16.4.2 Parameterisation of Wet Deposition

Seinfeld and Pandis (2006) develop a mathematical framework for the rather complicated wet deposition processes for the case of a warm raining cloud. As an illustrative example only a rather simple attempt (but nevertheless often used) to describe the wet removal process for the below-cloud scavenging case is be presented here. In this attempt the many processes determining the relationship between airborne species concentrations, meteorological conditions, and wet deposition rates are lumped into a few semi-empirical parameters.

The approximation of the rate of transfer of a soluble gas or a particle into rain droplets below a cloud may be expressed as follows:

$$\begin{aligned} W^i_{gas/rain} &= \Lambda_{ig} C_{i,gas} \\ W^i_{part/rain} &= \Lambda_{ip} C_{i,part} \end{aligned},$$

here $W^i_{n/m}$denotes the rates of transport of species i from medium n to medium m; Λ_{ig} and Λ_{ip} are the scavenging coefficients for species i in the gas and particle phase, respectively; $C_{i,gas}$ and $C_{i,part}$ are the concentration of species i in the gas and particle phase, respectively. The scavenging coefficients are time dependent functions of location, rain characteristics and the aerosol size distribution of species i.

If a horizontally homogeneous atmosphere is introduced as a further simplification, the concentration of a species C_g is only a function of altitude z and time t.

The below-cloud scavenging rate F_{bc} in this case is given by the following integral:

$$F_{bc}(t) = \int_0^h \Lambda_g(z,t)\, C_g(z,t)\, dz,$$

with the cloud base height h and the height and time dependent scavenging coefficient Λ_g.

If the overall wet flux from a precipitating cloud is needed the transfer of the species from the cloud droplets to rain has also to be considered and added to the below cloud scavenging. In-cloud scavenging requires the inclusion of several additional processes: nucleation, effect of phoretic forces, electrical forces, etc.

Additionally, in praxis it has to be distinguished whether a gas is irreversibly or reversibly soluble in the water droplets.

More complex parameterisations of below-cloud and in-cloud scavenging of atmospheric constituents can be found in a review article by Sportisse (2007). According to Sportisse (2007) the existing parameterisations are still characterized by many uncertainties. In praxis, the variability of cloud and precipitation parameters, i.e., liquid water content and size distributions of cloud droplets, and rain intensities enhance the overall uncertainty accompanying the estimation and modelling of wet deposition (Mircea et al. 2000).

16.4.3 Remarks on Wet Deposition of Polycyclic Hydrocarbons and Heavy Metals

Since polycyclic aromatic hydrocarbons (PAHs) and heavy metals are in the focus of this volume on persistent pollutants, a few remarks on wet deposition of these substances are made and some relevant references are given below.

Most of the PAHs in the atmosphere are present in both the gaseous and aerosol phases. Thus, both the processes of gas and particle scavenging may be important for these compounds. The gas scavenging of atmospheric trace organics can be predicted theoretically, by Henry's law, which describes the equilibrium distribution of a compound between gas and aqueous phases. The particle scavenging is more difficult to predict theoretically, since it is a complex process, which depends upon the meteorological conditions in the cloud as well as the chemical and physical properties of the aerosol (Ligocki et al. 1985). Concerning the relative importance of gas versus particle scavenging Poster and Baker (1996) and Offenberg and Baker (2002) argue that particle scavenging rather than gas scavenging is the dominant removal mechanism of PAHs from the atmosphere. This finding has been confirmed by more recent studies (e.g., Sahu et al. 2004; He and Balasubramanian 2009).

Concerning wet deposition of heavy metals Barrie and Schemenauer (1989) provide an excellent overview. Although the contribution seems to be outdated it covers the major aspects of the field. A special case is the wet removal of mercury from the atmosphere. It is generally accepted that Hg(0) is not susceptible to any major process of direct wet deposition. The gaseous divalent mercury is expected to be scavenged readily by precipitation. Particulate mercury is also subject to wet deposition due to in-cloud scavenging and below-cloud scavenging. Roughly half of Hg(p) may be scavenged by atmospheric water (e.g., Seigneur et al. 2003). Several studies have shown that wet deposition is a major removal pathway for atmospheric mercury (e.g., Keeler et al. 2005; Miller et al. 2005; Sakata and Marumoto 2005). But reported proportions of dry deposition or wet deposition vary greatly. In general it should be stated that still much uncertainty exists on the relative role of wet deposition of mercury. In recent years, there has been some progress in modelling mercury wet deposition; a basic approach is described in Bullock and Brehme (2002). The still existing uncertainties in mercury models including the wet deposition process are discussed by Lin et al. (2006).

16.5 Influence of Clouds on Photochemistry

The essential energy flux in atmospheric chemistry is the flux of solar radiation. Its energy levels are high enough (i.e., in the ultraviolet part of the solar spectrum) to break some chemical bonds, a process called photolysis or photochemical degradation. Solar radiation can either affect persistent pollutants directly or by creating reactive chemicals like the hydroxyl radical or ozone that in turn take part in the degradation of organic molecules. Since clouds interact strongly with solar radiation by absorption and scattering (Liou 1992), they have a profound influence on tropospheric photochemistry (Lelieveld and Crutzen 1991) and thus on the degradation of pollutants.

16.5.1 Photolysis Rate

Through the modification of solar radiation clouds directly affect photolysis rates (J-values) (Madronich 1987; Crawford et al. 1999; Liu et al. 2009). The photolysis rate is dependent on the wavelength λ of the radiation and may be calculated by the following equation:

$$J = \int f(\lambda)\ \sigma_0(\lambda)\ \phi(\lambda)\ d\lambda$$

here $f(\lambda)$ is the spectral actinic flux (photons cm^{-2} s^{-1} nm^{-1}), $\sigma_0(\lambda)$ is the absorption cross section (cm^{-2} molecule^{-1}) and $\phi(\lambda)$ is the quantum yield of the molecule of interest. The quantum yield is the fractional number (≤ 1) of molecules of a specific substance formed per photon of radiation absorbed at a given wavelength.

The actinic flux is the radiative flux from all directions on a volume of air; it is the relevant flux for photolysis, since it does not matter from which direction a photon comes. The actinic flux varies according to atmospheric absorption and scattering. Mie-scattering due to the presence of clouds plays a role in the sense that it can effectively redistribute the photons contributing to the actinic flux. Cloud amounts, their horizontal and vertical structure as well as their composition vary considerably in time and space. Modelling studies of the radiative effects of clouds on tropospheric chemistry have emphasized the need to account for the resulting spatial and temporal variability of the photolysis rates (e.g., Tie et al. 2003; Yang and Levy 2004; Liu et al. 2006, 2009). The cited studies come to the conclusion that photolysis rates are in general enhanced above and even in the upper portion of cloud layers and are reduced below optically thick clouds. Above optically thick clouds and within their top regions, photolysis rates can be twice as large as the corresponding clear-sky values. In the lower part of optically thick clouds and below them, photolysis rates can be reduced several fold (Neu et al. 2007).

Certain broken cloud fields may lead to enhanced photolysis rates below them. High excess solar radiation has been observed during summer months below layers of broken clouds. Largest excess radiation (sometimes by more than 500 W m^{-2}) is reached close to overcast situations with altocumulus clouds partly obscuring the solar disk, and preferably with cumulus clouds in lower levels (Schade et al. 2007).

16.5.2 Illustrative Example

Since tropospheric ozone (O_3) and the hydroxyl radical (OH) contribute to the degradation of some persistent pollutants (e.g., several polycyclic aromatic hydrocarbons), here an example for the influence of cloud modified photochemistry on the concentration of these gases taken from a modelling study by Tie et al. (2003) is presented.

In Fig. 16.6, photolysis rates for a specific ozone reaction in a cloudy sky and in a clear sky condition are compared for different cloud situations in the troposphere. In this example the cloud water content was set to be 0.1 g m^{-3} (resulting J-values are sensitive to the choice of this parameter). The impact of the clouds on the photolysis rates is obvious for all three displayed cases in Fig. 16.6. For the low level cloud layer the J values are significantly enhanced above the cloud as well as in the upper part of the cloud (maximum increase is 33% at cloud top, average increase is 12%). For the high level cloud case, there is a strong reduction in the J-values below the cloud down to the surface (maximum decrease 29%). Above the high level cloud layer again an increase in the photolysis rate can be seen. These two effects combine to a more complex J-value profile in the case of a two layer cloud system. Here, a slight increase of the photolysis rate below the high level cloud has to be noted, which is due to upward scattering by the lower cloud layer.

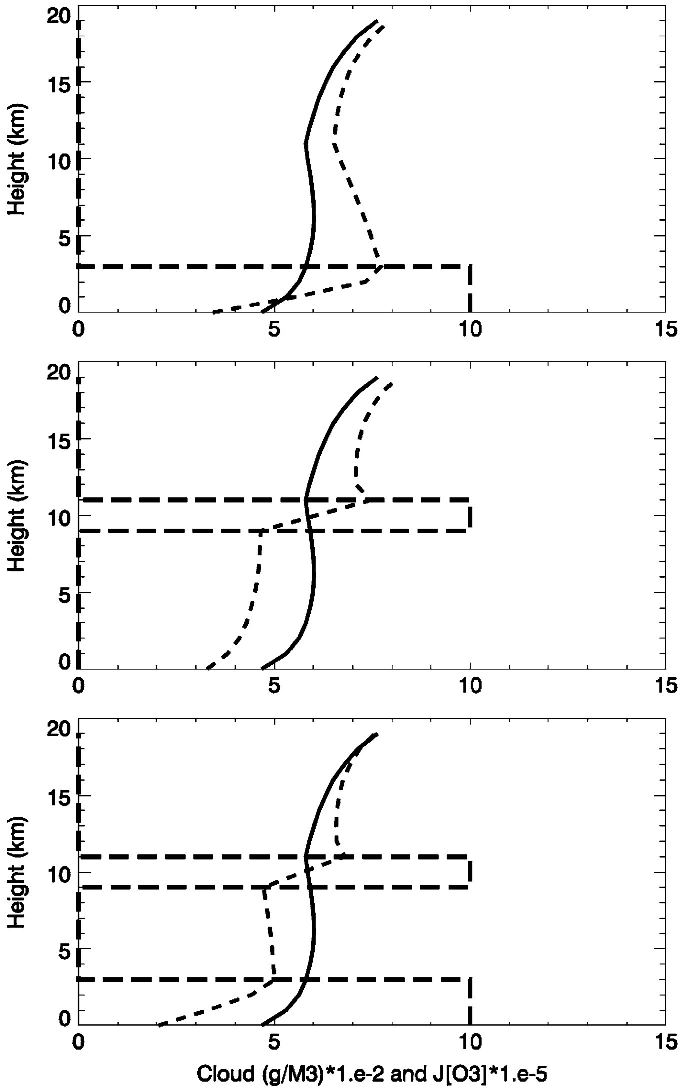

Fig. 16.6 Photolysis rate J($O_3 \rightarrow O(^1D)$) for a single low level cloud layer (*top*), a single upper level cloud layer (*middle*) and the combination of both (*bottom*); the cloud layers are indicated by *thick dashed lines*. The J-values of the clear sky condition are given by the *solid lines*; the *thin dashed lines* represent the J-values for the respective cloudy sky condition (Adapted from Tie et al. 2003)

In Fig. 16.7, the changes in the concentration of ozone and the hydroxyl radical due to the effects of clouds on tropospheric chemistry for 2 different months (June and December) are shown. It can be seen that for some latitude bands and certain altitudes the cloud effect on the gas concentrations can be considerable. It is also

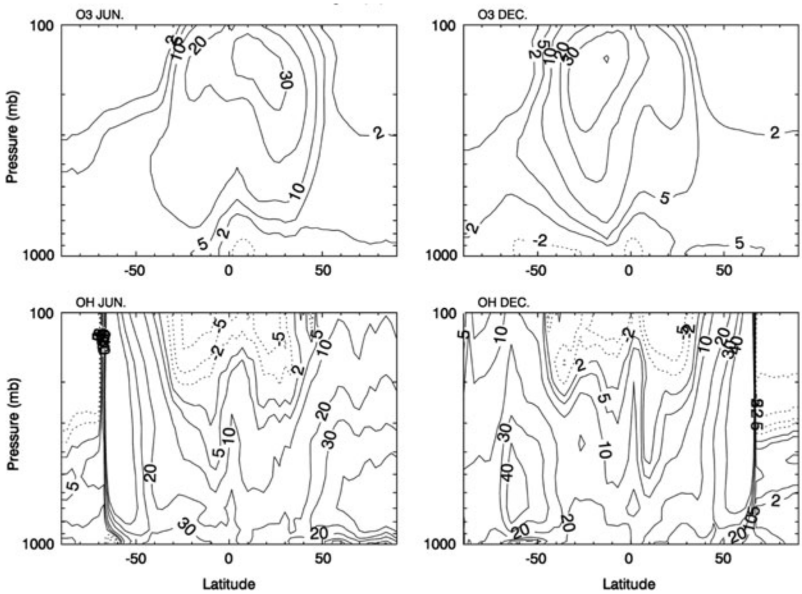

Fig. 16.7 Zonal means of modelled changes (given in %) in the O_3- (*top*) and OH-concentrations (*bottom*) due to the radiative effect of clouds for a June (*left*) and a December (*right*). Here, pressure has been chosen as the vertical coordinate (Adapted from Tie et al. 2003)

obvious that there is a seasonal shift in the overall pattern of the cloud effect, which reflects the influence of the changing position of the sun around the year. Of course the different angles of incoming solar radiation have an influence on the cloud fields developing during the 2 months. For ozone the maximum change with an increase in concentrations of about 30% when clouds are present is found in the upper troposphere of the tropics. Between 50°N and 50°S the changes in the free troposphere are larger than 5–10%. In the lowest layers of the troposphere changes concerning O_3 in general are found to be small, at some locations a decrease of about 2% in the ozone concentration has been modelled. Compared to cloud induced changes of ozone concentrations, changes in OH concentrations show a different pattern. Maximum OH changes with values of up to 30–40% occur in the middle and upper troposphere at higher latitudes. A strong seasonal effect is obvious. There is a general increase in OH concentrations when clouds are present with the exception of the upper troposphere at tropical latitudes, where a decrease in OH concentrations of a few percent has been modelled when clouds were included.

The above example was extracted from one specific modelling study. A few other studies on the effect of clouds on photochemistry using different models and cloud representations have been published. In general they qualitatively confirm the influence of clouds on tropospheric chemistry but come to quantitatively differing results when global averages of the effect on oxidant concentration are considered. See e.g., the introduction in Voulgarakis et al. (2009) for a discussion of the ozone case. Considerable uncertainties in adequately modelling cloud properties and coverage contribute to the large differences in oxidant concentrations simulated by different chemistry models. The selected example shall only illustrate possible cloud effects on photochemistry and thus the oxidation capacity of the atmosphere.

16.5.3 Relevance

Overall it can be stated that clouds regionally have a significant influence on tropospheric photochemistry and subsequently on the concentration of certain persistent pollutants. The photolysis rate above clouds typically is enhanced while below optically thick cloud layers it is considerably reduced. This leads to a change in the oxidation capacity pattern of the atmosphere, which certainly will have resulting regional effects on the degradation of specific persistent pollutants. A reliable quantification of the cloud effect on the different persistent pollutants still remains to be derived.

16.6 Concluding Remarks

Besides their important role in the energy budget of the Earth and the global and regional water cycles clouds have through their profound influence on the transport of (persistent) pollutants and on atmospheric chemistry an additional significant effect on our environment.

By horizontal and vertical transport and wet deposition clouds alter effectively the spatial distribution of pollutants in the atmosphere. Without clouds the concentration and deposition pattern of many species would look quite different. The role convective clouds play in vertical transport has to be emphasized. Due to typically quite large vertical wind velocities associated with them, convective clouds can rapidly pump up air from the lower to the middle and upper troposphere, while vertical wind velocities in the cloud-free atmosphere or in non-convective clouds are in general quite low.

Convective clouds play overall a twofold role in the cloud–chemistry relation, on one hand they transport trace species rapidly between the boundary layer and the free troposphere on the other side they provide an effective way of cleansing the atmosphere through wet deposition, since often intense precipitation is connected with this cloud type. Because of these important processes an adequate representation of convection is of primary importance for modelling studies addressing the distribution of persistent pollutants. Current global and regional models still show a high range of variability concerning their results in a comparison of different convective schemes (Lawrence and Rasch 2005; Tost et al. 2010).

The possible transformation of pollutants by aqueous chemistry in cloud and precipitation particles is another way by which clouds may alter the concentration of substances of interest. Even if persistent pollutants are not directly altered by cloud chemistry the concentration of other relevant substances (i.e., oxidants) which may have an effect on their lifetime may well be altered by aqueous chemical reactions.

The lifetime of persistent pollutants in the atmosphere may also be influenced by the effect clouds have on photolysis rates. Related changes in the oxidation capacity (e.g., the concentration of ozone and the hydroxyl radical) have certainly an impact on the fate of certain persistent pollutants. In general, the actinic flux is enhanced above and in the top of cloud decks, while it is reduced below clouds. In the case of highly structured cloud fields quite complex changes in the pattern of photolysis rates may occur. High excess solar radiation has been observed during summer months below layers of broken clouds close to overcast.

Nowadays many studies addressing the distribution of persistent pollutants are based on numerical modelling. In this context, it should be emphasized that it is important to adequately represent cloud-related physical and chemical processes when modelling atmospheric transport and transformation of pollutants as well as their wet deposition on land or on oceans and seas. This statement is made being aware of the many uncertainties which are still existing in cloud and precipitation modelling.

Cloud amounts, spatial distributions and composition may very well change in a changing climate. A better understanding of the cloud–climate relation and improvements of its implementation in chemistry-climate models are essential for realistic projections of the impacts clouds will have on the fate of persistent pollutants in future climate.

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Part V
Persistent Pollution and Health

Chapter 17
Natural Substances of Marine Origin with Toxic Properties

Heike Helmholz

17.1 Introduction

The marine environment covers more than 70% of the earth surface and is one of the richest biospheres of the world. Biological and chemical investigations of marine ecosystems have provided insights into a fascinating and complex world underwater. The biological and chemical diversity is very high due to the array of natural conditions. It encompasses a high thermal range from −1.5°C to 350°C and a pressure range of 1–1,000 atm. The food conditions vary between nutrient rich and nutritionally sparse regions and photic and non-photic zones. Marine organisms have to adapt to these wide variety of living conditions. The adaptation capabilities are different from those of land-based organisms (Lindequist and Schweder 2001). Marine organisms live in close associations and therefore in nutrition and substrate competition (Ianora et al. 2006). In order to ensure survival and fitness it is necessary to produce secondary metabolites. The variety of secondary metabolites provides a biochemical reflection of the biotic interactions. The function of secondary metabolites is manifold. Allelochemicals are used for intra- and interspecies signaling and communication, for the deterrence of predators and herbivores or the suppression of competing neighbors. Bacterial and fungal invasion can be inhibited. Secondary metabolites can also be used for protection against UV radiation.

As manifold the ecological function of secondary metabolites are as manifold are their possible applications in the pharmaceutical field as cytotoxic, antiproliferative, immunmodulatory or antibacterial agents or in the biotechnological field as enzymes, pigments or biosurfactants (König and Wright 1996; Bongiorni and Pietra 1996; Procksch et al. 2003; Nakamura et al. 2009).

The road of isolation and structural elucidation of pharmacologically active or toxic metabolites from marine organisms is a complex procedure (Knutsen and Hansen 1997; van der Wielen and Cabatingan 1999; Riguera 1997; Ebada et al. 2008).

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The process of substance discovery and identification starts with the collection and taxonomical identification of marine organisms. The quality of the sample collection procedure is of fundamental importance and influences all further steps. A careful documentation of the habitat and its physical conditions is necessary and contamination has to be avoided. The collected material should be immediately frozen or kept in an appropriate solvent to prevent biological and chemical degradation and modification of the secondary metabolites (McConnell et al. 1994). In the next step substances will be extracted from the biological sample according to their physical and chemical characteristics with solvents of increasing polarities.

The obtained extracts should than be tested in a screening method to prove the bioactivity. Fast, economic and representative primary assays should be applied for the selection of potential substances. It is advantageous when minute amounts of biological material are sufficient.

The final isolation and chemical identification of active compounds is a time and material consuming process. Different isolation procedures have to be performed and combined to develop a multidimensional isolation strategy. Sequential solvent partition, structure-selective as well as activity-guided chromatographic techniques can be feasible. These isolation procedures should lead to the purity of compounds which is a prerequisite for the structural elucidation with spectroscopic methods like mass spectrometry and nuclear magnetic resonance spectrometry.

17.2 Sources of Marine Natural Substances

As divers the flora and fauna of marine habitats are, as manifold are the potential producers of natural marine substances (Blunt et al. 2009). Most of the major animal phyla are represented in the marine environment and eight phyla are exclusively aquatic. To date only a small part of marine organisms are known and only a small percentage of them have been evaluated for their biochemical properties and biological activity.

Especially the huge group of marine microorganisms including bacteria, fungi and protists and also the different groups of algae are prolific producers of natural marine substances which can assemble to biofilms in a very high individuum density (Davidson 1995; Bremer 1997; Engel et al. 2002; Schulz et al. 2008). Algae as autotroph organisms are primary producers whereas bacteria and fungi fulfil their ecological role as decomposers. They are at the lower level of the marine food web and represent food and nutrition for higher organisms. Certain marine microorganisms inhabit extreme environments like thermophile, methano- or halobacteria and therefore the synthesis of unusual secondary metabolites is very likely. Marine microorganisms can live as symbiotic, endobiotic, parasitic or commensally organisms in close collaboration with higher plants and animals and therefore they are often the original producer of the secondary metabolites isolated from other organisms (Burgess et al. 1999; Sponga et al. 1999; Yasumoto and Satake 1998;

König et al. 2006). Among these higher organisms the most potential group as producer of bioactive compounds are sponges (porifera) (Costantino et al. 2004). Nearly 40% of the so far known compounds of marine origin have been found in sponges. They consume food by filtration and major parts of the sponge's biomass are microorganisms. Other promising sources for bioactive and toxic substances are cnidaria, molluscs, bryozoans, tunicates and crustacean (Munro et al. 1999; Bongiorni and Pietra 1996; Procksch et al. 2003).

Due to the overall diversity of these organisms and habitats, the taxonomy and systematic are extremely important to ascertain the producer. Another challenge for the isolation and identification of natural marine substances is the influence of habitats, seasonal and geographical factors on the synthesis, quantity and chemical structure of bioactive compounds (Halstvedt et al. 2008). In order to minimize environmental impacts the biotechnological production or chemical synthesis of bioactive compounds should be preferred if possible when the natural product is applied for technical or pharmaceutical purposes. Prerequisite for the synthesis is the elucidation of the chemical structure (Hamann 2003). The development of biotechnological production processes is not only favoured to ensure a continuous allocation of biological material but is also necessary to avoid the exploitation of marine habitats (Sipkema et al. 2005).

Another challenge for substance identification from marine resources is the trace nature of extremely bioactive compounds and also unexpected and diverse functional groups and complex chemical structures.

17.3 Preparation of Biological Samples

General procedures for the preparation of biological samples are (1) the cultivation and harvest of microorganisms and their cultivation medium, (2) the collection and preparation of fresh, natural material and (3) in case the substance of interest is known from a controlled biotechnological process.

Advantages of the cultivation of microorganisms such as algae, bacteria or fungi are the continuous production and provision of the biological sample under controlled conditions. Marine fungi are a prolific resource of bioactive substances. They growth as saprophytes in various habitats and are accessibly by cultivation (Saleem et al. 2007). The cultivation conditions can be optimized to achieve a high production rate and activity of the compounds of interest and of biomass for the subsequent extraction and substance isolation processes. An example for the successful modification of cultivation conditions is given for the facultative, marine basidiomycete *Nia vibrissa* (Moore & Meyers) where different culture media with variable environmental factors such as salinity, pH and light were studied (Helmholz et al. 1999). Parameter for optimal cultivation conditions were the yield of biomass and immunmodulatory activity of an ethanolic extract of the mycel. It could be shown that a the cultivation of the fungi in a synthetic cultivation medium (SMII) increases both the production of mycel and the bioactivity of the ethanolic

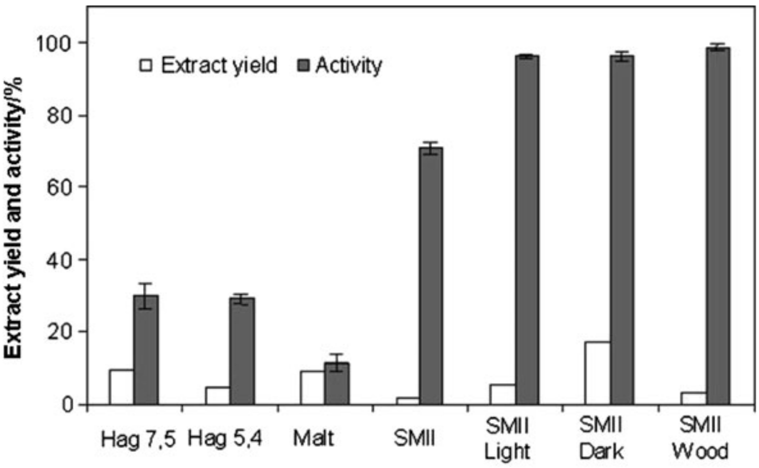

Fig. 17.1 Cultivation of *Nia vibrissa* in different media (*Hag* Hagem-medium, *Malt* maltmedium, *SM II* synthetic medium typ II) yield of ethanolic extract of mycel in relation to mycel dry weight, bioactivity as relative inhibition of the binding of FITC-labeled LPS onto CD14 positive CHO cells

extract whereas the growth in conventional malt medium increases only the biomass but not the biological activity (Fig. 17.1).

The utilization of fresh material could be recommended when enough biomass could be obtained from the same sampling area.

The preparation of fresh bioactive, organic material from jellyfish is described as a practical example (Helmholz et al. 2007). Jellyfish belonging to the phylum cnidaria produce a variety of toxic metabolites used for prey capture and defence. They are a major component of the marine food web preying on zooplankton organisms, fish eggs, larvae and small fish. Another important interaction is the potential competition on prey among cnidaria and zooplanktonivorous fish species especially when they occur as jellyfish blooms (Bamstedt et al. 1994; Purcell and Arai 2001).

A further concern is the stinging capacity of jellyfish and the resulting public health hazard. At tropical and subtropical coast lines life-threatening and frequent contact between humans and jellyfish are an ongoing field of attention (Bailey et al. 2003).

Envenomations in the northern coastal territories are considered to be much less serious, although with the observed larger population numbers an increasing amount of stings is expected (Mills 2001; Burnett 2001). The cnidarian venom (toxin mixture) is preserved in specialized cell organelles (cnidocysts) which are harboured in cnidocytes situated as batteries at fishing and mesenteric tentacles (Fig. 17.2). Adequate chemical and mechanical signals induce the fast discharge of cnidocysts resulting in immediate paralysis of its prey. Human can respond with cutaneous irritations and pain up to cardiovascular system failure after accidental

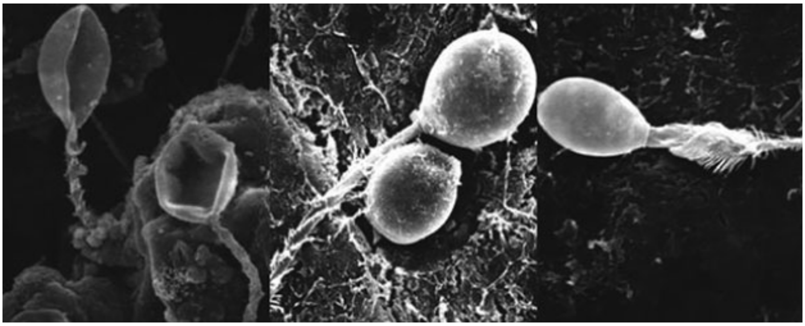

Fig. 17.2 Various types of *Cyanea* spec cnidocysts, raster electron micrographs

contact with Cyanea spec. one of the most abundant jellyfish in the North Sea (Burnett 2001). The complex nature of the venom and the supposed multitude of pharmacological effects require the application of various in vitro assays to cover different modes of effects. The causative substances for the toxic reactions are mainly unknown especially for the jellyfish of the northern temperate coastal zones.

In the recent investigation jellyfish of the species *Cyanea capillata* (L.) and *Cyanea lamarckii* (Péron & Léslueur) were collected at a research cruise to the Orkney Islands, Scotland and at the German North Sea Island Helgoland. Mesenteric and fishing tentacles were sliced and collected for the preparation of intact cnidocysts. A concentrated mixture of intact cnidocyst was obtained by maceration of the tissue in distilled water, filtration and thoroughly washing with sterile filtered seawater. Discharge and lysis of the cnidocysts was performed by sonication. The resulting suspension was centrifuged; the supernatant containing the toxin mixture is used as extract for protein determination and bioactivity assays or stored at 80°C until further use. Ratio of discharged capsules in the remaining residue was counted microscopically.

The preparation of jellyfish cnidocytes and venom extracts is a special case were specialized cells are utilized as target for sample preparation. Normally fresh organic material from whole organisms, organs or tissues is extracted with solvents of increasing polarity or freeze dried material is used for sample preparation and extraction.

17.4 Testing the Biological Activity

The bioactivity of the prepared crude extracts has to be determined in cytotoxicity assays showing the viability of cells after exposure to toxic agents either of natural or anthropogenic origin. For a fast overview, sensitive and robust assays that can be run in a high throughput are required. For a detailed analysis of mode of actions specific test systems with targeted responsive elements have to be developed. Cell-based assays are one possibility for a fast and representative conclusion on the bioactivity of extracts obtained from biological samples. Various methods which can be applied at different levels of specificity are described in the following section.

There are different options to measure the general cell response (Lindl and Bauer 1994). The easiest method is the microscopically inspection of the treated cells after staining with vitality dyes such as trypanblue. Trypanblue is incorporated into affected cells and the relation of viable to dead cells can be calculated. A simple quantitative method are dye uptake assays where special vitality dyes such as Neutral Red are incorporated into living cells and after cell lysis the released dye can be photometrically determined. Electronic cell counter can also be used to quantify the proliferation and survival rate of cells after exposure to toxic components.

More precise information onto the metabolic activity of cells can be made with cells assays detecting the incorporation of radioactive precursors (e.g., ^{3}H-thymidine) in nucleic acids or cell assays measuring the metabolic activity of cellular enzymes.

These assays can be applied for primary and for permanent cell lines. The latter have the advantage of a continuous culture ensuring the same experimental conditions and properties of the cells for comparative studies. Liver cells are often a target for testing cytotoxic effects because they are involved in detoxification and metabolism processes. The formerly described extracts of jellyfish cnidocytes were tested in a dye uptake test system to detect the acute toxicity of the extracts (Helmholz et al. 2007). Cells of a continuous culture of the hepatoma cell line HepG2 were sowed into a microtiter plate and allowed to settle for 24 h. After this adaptation step extracts were applied to each well in increasing concentrations. Positive controls as well as solvent or buffer controls have to be performed in order to measure the relative toxicity and compare test to test variations. After a certain incubation period with the toxic components the cells were incubated with the dye Neutral Red solution for 3 h and washed to remove the unspecifically adsorbed dye. Cell disruption was performed with lysis solution containing 50% (v/v) ethanol 1% (v/v) acetic acid and rigorous shaking. The released Neutral Red was measured in a microtiter plate reader at 550 nm indicating the capability of vital cells to store the dye and consequently the toxic potential and effects of the test substances. Different cytotoxic effects induce the reduction in cell viability. The inhibition of the cell proliferation, the inhibition of enzymatic activities or the influence on cell membrane stability can cause the observed cytotoxic effect.

Another example for a representative and common cytotoxicity assay is the measurement of the metabolic activity of mitochondrial enzymes which reduce a yellow terazolium salt into a red formazan derivative (Scudiero et al. 1988). The test principle is equivalent to the dye uptake assay. Cells of a continuous culture were exposed to increasing toxin concentrations. After certain incubation time the tetrazolium salt is added and the coloured formazan derivate can be determined photometrically. With this assay the inhibition of cell growth, the metabolic activity of mitochondrial enzymes and also the adherence of cells onto the flask surface can be indicated as toxic effects.

These two described assays are end point methods. To monitor the cell response in real time cytosensor measurements are of great advantage. The cells growth on a sensor chip surface and the metabolic activity can be measured following the acidification of the culture medium. Oxygen consumption indicates the mitochondrial respiration and also the cell adhesion and confluence can be detected. This system allows not only the measurement of the cell response directly after exposure to toxins but also cell recreation (Thedinga et al. 2007).

Besides the general cell response the detection of lytic, cell-membrane activity is a useful method to measure cytotoxicity. The toxic potency of approximately one third of all described proteinaceous toxins is based on membrane interaction. Toxins need to be secreted as water-soluble proteins but they have to be transformed into membrane proteins for the purpose of membrane insertion. It can be supposed that the toxin is concentrated on the membrane by means of special cell surface features such as a protein receptor, lipid clusters or carbohydrate side chains (Parker and Feil 2005). An indicator for such lytic, pore-forming toxins is the release of haemoglobin from red blood cells (erythrocytes).

The described jellyfish toxin preparations were also applied to a haemolysis assay according to (Emura et al. 2004). Human and animal red blood cells were exposed to increasing toxin concentrations in a microtiter plate format. Cnidocyst extracts and erythrocytes were mixed in the round bottom wells of a microtiterplate and incubated over night at room temperature. The supernatant containing the released haemoglobin indicating the cell lysis potential of the toxins was measured photometrically.

Membrane-active, pore-forming proteins have been found in different cnidaria species, mainly in sea anemones (Anderluh et al. 1996; Lanio et al. 2001; Hinds et al. 2002). Such proteins express an affinity to the phospholipids in cell-membranes and small cavities are engraved in the cells thus reducing the membrane integrity (Athanasiadis et al. 2001; Suput et al. 2001). A membrane affinity can also serve as an indicator for a membrane-active, lytic effect as observed in the haemolysis assay. Membrane-binding and can be detected by Biospecific Interaction Analysis (Anderluh et al. 2003). These binding interactions can be resolved by the physical phenomenon of Surface Plasmon Resonance (SPR) in real time and without labelling using the Biacore® technology. For membrane association studies, liposomes are immobilized on modified gold surfaces. This methodology has been employed in a variety of applications. Vanhoye et al. (2004) investigated Gly-Leu-rich peptide orthologes in order to analyse the influence of net charge on cytotoxicity (Vanhoye et al. 2004). Drug/lipid membrane interactions were performed to evaluate the degree of absorption (Danelian et al. 2000; Baird et al. 2002; Abdiche and Myszka 2004). A differentiation between pore formation and lysis was demonstrated by Papo and Yechiel (2003).

This selection of different assay principles for cytotoxicity with cultured cells or as biosensor studies indicates the huge variety of possible methods to detect cytotoxic effects. To clarify the mode of action more specifically different cell types e.g., immunocompetent, cancer or nerve cells or molecular assays e.g., specific enzyme activities are recommended.

These functional assays serve as an indicator for a biologically driven discovery of bioactive substances and can be used to guide the isolation process to purify causative substances from crude mixtures and extracts.

17.5 Isolation of Natural Substances

The isolation of bioactive substances is possible with chromatographic separation processes. Chromatography is the collective term for a family of laboratory techniques for the separation of substance mixtures. It was introduced in 1903 with the separation of plant pigments and become an essential tool in biochemical and analytical sciences. In general the chromatographic process involves the passing of a substance mixture solubilised in a mobile phase through a stationary phase and results in the separation of an analyte, to be measured from other molecules in the mixture. Chromatography can be differentiated according to the mobile phase into gas- and liquid chromatography and according to the stationary phase into column, paper and thin layer chromatography. The mobile phase is a low molar buffer system or mixtures of water and organic solvents that allows the solubilisation of the analyte, a continuous flow and specific interaction with the stationary phase. The stationary phase is the column packing material inducing the retention and retarded flow of compounds. Stationary phases can be biopolymers such as cellulose and dextran, synthetic polymers or anorganic polymers such as silica or glass beads. Depending on the purpose different dimensions of liquid-column chromatography systems (LC) are available for preparative separation and for sensitive analytical applications.

Chromatographic principles of separation are based on molecule characteristics. The molecule charge depends on the number of ionic groups. Hydrophobicity describes the “water hating” character of a molecule. The interaction of special binding structures with other trapping molecules determines the affinity.

The separation principle of size-exclusion chromatography (SEC) also known as gel permeation chromatography or gel filtration is the molecular weight which is related to the size of a molecule. It is a non-interactive technique. The retention of the analyte is determined by the accessibility of the sample to particle pores. The substances elute in order of size. Analytes with the highest molecular weight elute first. SEC is often used as the first step in downstream processing.

In the ion exchange chromatography process the molecules bind by the reversible interaction of electrostatic charges on the outer surface of the analyte and the opposite charge on the ion exchanger particle. The higher the net charge of the analyte the higher the ionic strength of the mobile phase has to be.

Reversed phase chromatography is also an interaction chromatography were the particles of the stationary phase are modified with non-polar molecules such as alkyl chains (C2–C18) or phenyl rings. The hydrophobic part of the analyte adsorbs to these particles and with increasing concentrations of the organic modifier in the mobile phase desorption occurs.

A special separation procedure, where the binding behaviour of characteristic molecule structures is utilized, is the affinity chromatography. It can be applied whenever molecules form specific binding such as between enzymes and substrates or lectins and glycoconjugates. Advantages of this separation procedure are the high resolution, the reduction of separation steps and the application of physiological, bioactivity preserving conditions. A special mode of affinity chromatography is the lectin-affinity chromatography (LAC) that enables the isolation of glycoproteins and the conservation of their function and natural glycosylation pattern by using mild chromatography conditions (Helmholz et al. 2008). An LAC process starts with the lectin immobilization on a solid support. A mixture containing the glycosylated compound is applied and the unbound material is washed out. Following this, the specifically adsorbed product can be desorbed with an elution buffer containing the corresponding monosaccharide (Helmholz et al. 2003; Rosenfeld et al. 2005).

To obtain and isolate a pure bioactive substance these described chromatographic principles have to be combined in a multidimensional downstream process. Purity of a compound is essential for the elucidation of the chemical structure and for the assignment of the toxic or biological effect to a certain substance. In a bioactivity-guided isolation procedure the preservation of the activity has to be proven with an appropriate bioactivity assay.

17.6 Examples of Marine Substances with Toxic Properties

In the following section, a number of different examples for natural substances of marine origin with toxic properties are presented. A selection is done according to the ecological importance of the organism group or the particular occurrence, distribution, chemical functionalization and bioactivity of the substances.

17.6.1 Phycotoxins Produced by Harmful Algae Blooms

Phycotoxins are a group of natural products of algal origin, which can be responsible for a devastation of microfauna in marine food webs and intoxication syndromes by sea food. Some phycotoxins are accumulated through the food web by vectors that are not affected by such substances. Especially when the producer occurs in masses as algae blooms the ichthyotoxins can have an enormous effect on fish populations. The primary function of these phycotoxins is assumed to be chemical defence meaning that they act as allelochemicals (Daranas et al. 2001; Cembella et al. 2003).

A well known example of phycotoxins is saxitoxin (SXT) and its approximately 24 naturally occurring analogues (Fig. 17.3). SXT's are produced in marine dinoflagellates e.g., in Alexandrium and Gymnodium species. They act as neurotoxins

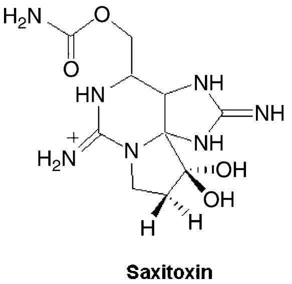

Fig. 17.3 Formula of saxitoxin

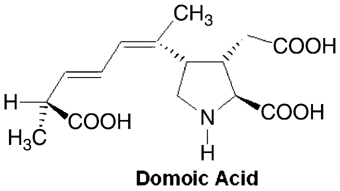

Fig. 17.4 Formula of domoic acid

blocking voltage activating Na+ channels. SXT's are associated with the intoxication syndrome of paralytic shellfish poisoning (PSP) (Luckas et al. 2003).

Another example of a well studied phycotoxin is the domoic acid, a secondary amino acid produced in diatoms (Fig. 17.4). With its function as a glutamate agonist it acts neuroexcitatory. Intoxication syndromes (amnesic shellfish poisoning – ASP) in humans can be observed at a concentration range of 1–5 mg/kg. It is known as a vermifuge and insecticide and effects many levels in the marine food web but the ecological function of this toxin is not clear (Quilliam 2003).

17.6.2 Proteinaceous Toxins

Bioactive peptides and proteins represent a valuable source of potent cytotoxic, antimicrobial and neuroactive compounds with complex chemical structures related to a variety of biological properties (Aneiros and Garateix 2004).

Among the most extensive and well studied marine toxins are the conotoxins. There are potentially 50.000 different conotoxins present in the venoms of living species in the genus Conus. The cone snails prey on fish and invertebrates and the stings of these molluscs are known to cause human fatalities. Various cone snail venoms contain different biologically active compounds and per species 100–300 different toxins can be supposed.

According to their mode of action and some structural features they can be grouped (Olivera and Cruz 2001; Putzier and Frings 2002). The "shaker peptides" containing ω-conotoxins inhibit the Ca-conductance. The ω -conotoxin GVIA has probably become the most widely used toxin in neuroscience and the ω-conotoxin MVIIA may become a therapeutic drug as analgesic. Contulakin-G belonging to the group of "sluggish peptides" is an O-glycosylated peptide acting as a neurotensin receptor agonist. Contulakin was shown to be a potential analgesic in animal models. Another group are the "sleeper peptides". Conantokin-G belonging to this group is a 17 amino acid peptide is an NMDA receptor antagonist with therapeutic potential for epilepsy.

Proteinaceous pore-forming cnidarian cytolysins, which have been mentioned before, were mainly found in sea anemones. Up to now 32 species of sea anemones have been reported to contain cytolysins ((Anderluh and Macek 2002). The equinatoxins from Actinia equina are a prominent example for such marine cytolysins grouped as actinoporins. These are monomeric, cystein-less proteins. Actinoporins act as pore forming toxins in a two step procedure. The first step is the binding of monomers onto cell membranes and in a second step pores are formed by oligomerization. The binding onto membrane components is selective because sphingomyelin containing membranes are preferred. The pore formation leads to the disintegration of cells and finally to destroyed cells (Parker and Feil 2005; Macek 1992; Turk 1991).

One of the most lethal marine organism groups are the box jellyfish. Especially species of the genus Chironex and Carybdea can cause systemic symptoms in humans such as severe pain, cardiovascular diseases, dermal reactions, excruciating muscle cramps in all four limbs, the abdomen and chest. These animals occur at tropical Indo-Pacific coasts. They are pale blue and transparent. The name box jellyfish is deduced from the bell or cube shape of the body with four distinct sides and long tentacles on each corner. The venom composition as well as the molecular mechanisms of the toxins is not fully understood. Up to know a few proteinaceous hemolytic cytotoxins have been isolated and sequenced in the molecular weight range of 42–46 kDa (Nagai 2003; Brinkman and Burnell 2007).

17.6.3 Halogenated Compounds

Halogenated secondary metabolites are frequently reported compounds in marine organisms. These compounds span a range from halogenated indols, terpens, fatty acids, phenols, etc. to volatile halogenated hydrocarbons (Gribble 2003; Vetter 2006). In many cases these halogenated marine metabolites possess a high variety of biological and toxic activities. Up to now more than 3,800 naturally organohalogen compounds are known to exist. They are rare in terrestrial plants but very common in marine organisms. The natural origin of a halogenated compound is not always easy to prove. In several cases the natural producer is still unknown or natural halogenated compounds found in higher organisms are produced in microorganisms and accumulated through the food web. Their detection in top predators indicates that the natural halogenated compounds share some of the adverse properties of anthropogenic halogenated substances such as persistency and bioaccumulation.

Their ecological role is not clear but an importance as a defence system can be supposed. Halogenated compounds could be utilized by the producer to reduce microbiological infections, herbivore grazing and fouling by epiphytes. A protection role against self generated hypochloride and hydrogen peroxides is also possible.

Biogenesis of organohalogens is performed by haloperoxidase enzymes isolated from a variety of marine organisms. This group of enzymes can be classified according to the most electronegative halide they can oxidize. Chloroperoxidases utilize chloride, bromine and iodine whereas iodoperoxidases utilize only iodine. Haloperoxidases contain vanadium or a ferrum-heme complex as a prosthetic group and function in a two step mechanism. At first the halide is oxidized and than an appropriate organic substrate is halogenated (Butler and Carter-Franklin 2004).

Besides the ecological role as defence system many natural halogenated compounds possess biological activities of pharmacological interest such as antifungal, antibacterial, anti-inflammatory activity or cytotoxicity.

The halogenated terpenoids with MHC-1 (mixed halogenated compound 1) for example are mutagenic in the Ames test. A component of this group telfairine is 100% lethal to mosquito larvae at 10 ppm or procomene is an insecticide expressing a four times stronger activity compared to lindane. MHC-1 were firstly detected in commercial fish samples (pollack and salmon) under sea food control. Fish oil capsules, hooded seals and human milk from the Faeroe Islands contain also the organohalogen terpenoids but the original source is probably a marine red algae (Vetter et al. 2008).

Dimethyl-bipyrrols (DBP) express moderate dioxin-like effects. There is no uniequivocal proof of natural production for this substance group. However the distribution pattern of these substances is different from anthropogenic contaminants, the concentration in the marine environment is very high, the mixed halogenated pattern is relatively rare for industrial chemicals and the related tetrabromopyrrols are known from a marine bacterium. DBP were identified in sea bird eggs from Canadian Pacific and Atlantic coast and can also be detected in bird tissues, egg yolk, canned fish, marine mammals and human milk (Gribble 2003; Vetter 2006).

Another group of halogenated pyrrols are the heptachloro-1′methyl-1,2′-bypyrrols (Q1; Fig. 17.5). Although the natural producer of Q1 is still unknown Q1 has only be abundant in marine samples which strongly suggest a natural source. It was detected in the highest concentration (14.000 ng/g) of a halogenated natural product in marine samples from Oceania, but it could also be detected in fish samples, deep

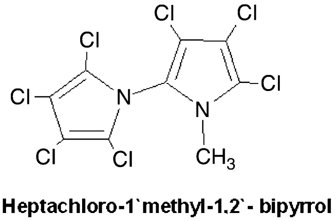

Fig. 17.5 Formula of heptachloro-1′methly-1,2′-bypyrrols (Q1)

sea fish and commercial fish oil capsules. Due to the planar and symmetrical structure very little activity in the arylhydrocarbon receptor – assay is expressed (Vetter 2002, 2006).

Halogenated compounds which express antibacterial activity against different microorganisms and show enzyme inhibition are the brominated methoxy diphenylether (MeO-BDE's). They are structural similar with anthropogenic (poly)brominated diphenylether used as flame retardants. The original producers of the natural compounds are probably cyanobacteria and algae. Similar to other organohalogens they can be accumulated and detected in sponges and molluscs feeding on sponges, in fish samples and sea eagle from the Swedish Baltic coast.

With more than 300 substances the halogenated fatty acids are a very large group of natural halogenated compounds (Dembitsky and Srebnik 2002). They can be isolated from microorgansims, algae, invertebrates and some animals. Halogenated fatty acids act as chemical defensives and express a high toxicity against potential predators and harmful bacteria. Another ecological function is the support of mesomorphic cell membrane states in algae that are important for the survival in extreme environments. Chlorinated fatty acids are major constituents among organohalogen compounds in fish (flounder, eel, salmon), in molluscs, some invertebrates and seaweed. In the Moon Jellyfish Aurelia aurita six isomers of saturated chlorinated fatty acids with a chain length of C16–C18 exist. In the American Lobster Homarus homarus dichlorotetradeconoic acid can be found in the digestive glands.

Functionally interesting derivatives of halogenated fatty acids are the chlorinated monocyclic oxilipids that are prostaglandin like substances to be found in soft corals, sponges and molluscs. Aurantosides, dichloro polyenes from a marine sponge Theonella spec. express a cytotoxicity against different cell lines. Very long chain (C24–C28), unsaturated brominated fatty acids can be found in sponges but also in sea anemones. Components of this group are cytotoxic against murine leukaemia and human carcinoma cell lines. Another potent cytotoxin is grenadadiene, a cyclopropyl derivate from the cyanobacterium Lyngbbya majuscula.

17.7 Summary

The marine environment is regarded on the one hand as a sensitive responder that is threatened by hazardous substances having adverse effects and on the other hand as a rich resource for marine natural substances. Marine natural substances play an important role in ecological interactions and communication processes of marine organisms. Since most of these substances and even the producing organisms are still unknown it is a promising field for the discovery of potential bioactive substances with toxicological and pharmacological relevant effects. Due to the huge diversity of marine organisms and the expected variety of chemical structures multidimensional preparation and isolation processes have to be combined with sensitive analytical methods and arrays of bioactivity test systems for a comprehensive characterization of natural marine substances with toxic properties.

It has become increasingly apparent that secondary metabolites have important ecological functions and may contribute as much as primary metabolites to the survival of the producing organism. Therefore further efforts are necessary to isolate and to investigate the structural and the functional properties of these natural marine compounds. Especially novel genetic and sophisticated analytical techniques have to be utilized in order to reveal the ecological role and enable the application as potential biotechnological and biomedical products.

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Chapter 18
Effects of Persistent Polutants on Marine Mammals

Veronika Hellwig

18.1 Introduction

This contribution is intended to give an impression of various aspects of the effects of persistent pollutants on marine mammals with a special emphasis on the challenges and methods to confirm cause–effect relationships and biomarker reactions as well as to monitor contaminant levels and biological effects of persistent pollutants in marine mammals. The intention is not to present a comprehensive review with complete citation, but to establish an understanding of the context. Illustrating examples are primarily chosen from research and studies on seal species from the North and Baltic Sea.

The diverse group of marine mammals comprises more than a hundred species, including the cetaceans (whales, dolphins and porpoises), the sirenians ("sea cow"), the pinnipeds (seals and walrus) and several otters. Depending on definition, polar bears can also be considered among the marine mammals due to their high level of adaptation to the marine habitat.

In the Middle Ages, hunting of marine mammals began for commercial use of whale oil, and later on, in the beginning of the twentieth century, also of their meat. Hereby, many species were unfortunately hunted (nearly) to extinction. Nowadays, marine mammals are considered a part of the marine ecosystem which deserves to be protected. To save the remaining populations hunting of endangered marine mammals, especially of whales, is only allowed to a limited percentage of certain species. However, marine mammals are threatened indirectly by the anthropogenic impact of fishery, limitations of food sources and habitat, noise and – most important in the context of this article – chemical pollution.

All marine mammals, independent of their degree of adaptation to marine life, use the ocean as food resource (see Fig. 18.1). As top predators, they are a target for bioaccumulation and biological effects of persistent pollutants, with damaging

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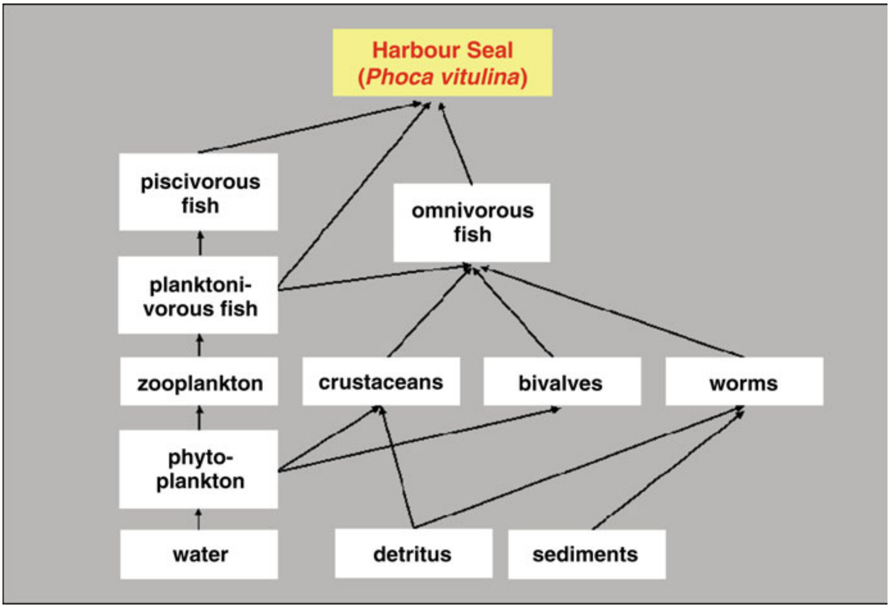


Fig. 18.1 Harbour seal food chain in the Wadden Sea (Ross 1995)

toxic and subtoxic or sublethal effects to individuals with consequences up to population level. For example, persistent pollutants have been shown to cause endocrine-disrupting as well as immunotoxic effects leading to morphological abnormalities, reproductive impairment and population declines in marine mammals. Regarding seemingly natural endangerments, the epidemic outbreak of virus diseases is relevant for mass mortalities. However, it is widely believed that persistent pollutants are responsible for an increased susceptibility to infectious diseases and therefore are also responsible for the recurring virus outbreaks and mass mortalities amongst marine mammals.

Due to the alarming population decline of certain marine mammals and the unpredictable outbreak of epidemic diseases, monitoring of marine mammals regarding population development, health and contaminant levels has become very important in the last decades. Therefore, research projects should aim at developing novel parameters and tools to monitor (contaminant-induced) disorders and to help to predict any possible mass mortality events. Furthermore, marine mammals are considered sensible (pollution) indicators for environmental changes in the marine ecosystem due to their position as top predators in the marine food web (see Fig. 18.1), their long life span, relatively low reproduction rate and their propensity to bioaccumulate pollutants (Ross 2000; Mossner and Ballschmiter 1997). These animals suffer from severe and sublethal effects of persistent pollutants (Van den Berg et al. 1998), as they have to perform the main part of their detoxification and biotransformation within the food web of the ecosystem. Marine mammals are often parameters in general marine monitoring programs reflecting marine mammal health but also ecosystem health, as it is highly desirable to have early warning systems for alterations in the ecosystem. Harbour seals often serve as a bioindicator species due to their wide distribution and ease of capture since they live both aquatically and ashore. This allows capturing wild-ranging individuals alive for sampling blood, but also skin and – in some regions – liver biopsies in a rather non-destructive manner. Findings from these samples of living animals (e.g., blood status, serology, hormone profiles, bacteriological, virological, and parasitological findings, contaminant levels, toxicological biomarker reactions) are particularly important for the early detection of disorders. For the development of a non-invasive monitoring strategy for wildlife populations of marine mammals the establishment of (species) specific biomarker reactions is essential (Fossi and Marsili 1997).

To monitor the status of the Wadden Sea for example, harbour seals (*Phoca vitulina*) are used as one of the bioindicator species in the framework of the Trilateral Monitoring and Assessment Program (TMAP) (Reijnders et al. 2005). The program which in 1997 was agreed on between the Netherlands, Germany (Schleswig-Holstein and Lower Saxony) and Denmark, focuses on the development and protection of the Wadden Sea ecosystem. Harbour seals are one of the three indigenous species among the marine mammals in the Wadden Sea, the other two being the grey seal (*Halichoerus grypus*) and the harbour porpoise (*Phocoena phocoena*). The population size and reproduction rate of harbour seals are monitored on a regular basis: Aerial surveys at low tide showed a total of about 20,000 individuals for 2008 in the Wadden Sea (Reijnders et al. 2007b, 2008). In the recent past, their population was smitten twice – in 1988 and 2002 – by a virus distemper epidemics (Härkönen et al. 2006; Seibel et al. 2007). In response, health monitoring programs were established, e.g., in Schleswig-Holstein, Germany, based on post-mortem findings from continuous pathological investigations of dead seals and regular investigation on seals captured alive or during rehabilitation in a seal station (Siebert 2003; Siebert et al. 2007).

For identifying (species-)specific biomarkers causal connections between contaminant exposure and biological effects in marine mammal populations have to be demonstrated. However, this has proven to be challenging due to the limited access to marine mammals for experiments, sampling, and collection of data. Hence, it is not surprising that the cause–effect relationships of pollutants in marine mammals are not completely understood and that the question about the most suitable way to monitor corresponding effects has yet to be answered. However, there is clear evidence from other mammalian species, including humans and other marine organisms as well as from studies with marine mammals, that pollutants have adverse effects on marine mammals (Reijnders et al. 2007a). Research on biomarkers in marine mammals most often starts with reproducing the monitoring strategies from other organisms, but then species-specific processes have to be considered as well.

In most regions, sacrificing of animals for research purpose is not allowed. Therefore, independent of the kind of samples needed (i.e., living cells or tissue samples), it is tedious and often virtually impossible to obtain sufficient large numbers of comparable samples concerning statistical significance. Frequent variations in sampling conditions (e.g., alternating sampling time after death for biopsies) may worsen the situation. It is labour-intensive to obtain detailed pathological findings of the sampled wild-ranging animals.

Almost no direct exposure or feeding studies are possible due to ethical or logistic reasons, but must be substituted by other approaches, some of which will be discussed in the following sections:

- Monitoring of contaminant levels in (tissue) samples is performed to show the food web contamination by persistent pollutants. The process of bioaccumulation and release of pollutants from the fat tissue (blubber) as well as other factors influencing the bioavailability and by this also the contaminant levels are described in Sect. 17.3.
- These analyses provide the basis for the establishment of cause–effect relationships and biomarker reactions, which are presented in Sect. 17.4. For the development of biomarkers upregulated proteins or metabolites due to the biotransformation and detoxification of pollutants as well as other biological effects (i.e., impairment of reproduction) are utilized. Toxicoproteomic approaches are often performed in combination with in vitro cell culture models.
- Determination of contaminants as well as of biomarkers levels is important for understanding and predicting effects on population levels. In the past, semi-field feeding studies were performed for tracking selected parameters in a controlled way in free-ranging animals, here shown for those in an immunological context. To consider factors which are responsible for an impaired immunocompetence and an increased susceptibility to infectious diseases in vitro exposures on immune cells may help for early registration of effects relevant for population level. This is discussed in Sect. 17.5.

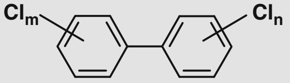
18.2 Bioaccumulation of Contaminants in Marine Mammals

Desired properties of persistent organic pollutants (POPs) for industrial and commercial application, e.g., as pesticides, surfactants and fire-retardants, are their low water solubility, high lipid solubility and semi-volatility together with a long-life cycle. However, the same features also account for their persistence and wide distribution in the environment, including the resistance to abiotic and biotic degradation and their bioaccumulation in the food web ending up in top predators such as marine mammals, in which they are stored in the blubber. InfoBox 18.1 presents a selection of compound classes which are found as xenobiotics in tissue samples of marine mammals. Table 18.1 contains exemplary data from the North and Baltic Sea.

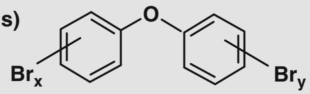
The sources and pathways of persistent pollutants in the marine ecosystem are manifold. The main part enters the sea by riverine input from land-based industrial, agricultural and urban sewage sources, while sources at sea include accidental and deliberate discharges and dumping. The highest concentrations of contaminants are often found in estuaries and coastal areas, the habitats for a significant part of the marine mammal population. POPs are distributed worldwide through the atmospheric transport and are even detected in the Polar Regions. They are therefore not only found in biota samples taken from areas of direct anthropogenic activity, but also from remote areas even after the release of many POPs has been stopped.

InfoBox 18.1 Selection of compound classes found in marine mammals

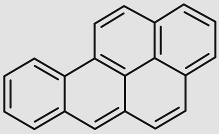
Polychlorinated biphenyls (PCBs)



Polybrominated biphenyl ethers (PBDEs)

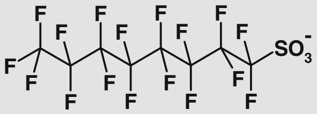


Polyaromatic hydrocarbons (PAHs)



Benz[*a*]pyren

Perfluorinated acids (PFAs)



Perfluorooctyl sulfonate (PFOS)

Therefore, there is an ongoing need for chemical analyses of concentration levels of persistent pollutants as well as for the evaluation of related biological effects in marine mammals. Both, their concentration levels and related biological effects, depend on their fate and interaction in the organism. In the following, some factors will be discussed, which have to be taken into account when measuring and comparing concentration levels of contaminants in marine mammals.

After a xenobiotic has entered an organism, it is stored or bioaccumulated mainly in the fat tissue or excreted, the latter in the majority of cases after a biotransformation or detoxification step. Bioaccumulation of a substance occurs if the absorption rate is higher than the rate for its excretion or degradation. Biomagnification across the marine food web starting from water and sediment results in high loads of these fat soluble and persistent compounds in the top predator organisms, especially in marine mammals. The diet of marine mammals varies with the species and consists of fish or zooplankton. Certain marine mammals like transient killer whales (or: orcas) have the highest position in the food chain, eating other marine mammals like seals or sea lions.

Table 18.1 Selected studies on organic contaminant concentrations in tissues of marine mammals in the North and Baltic Sea

Area	Year of sampling	Biological species	Sampled tissue	Concentration range (ng/g)^{a,b}	Reference
PCB					
German coast North Sea (1), Baltic Sea (2)	1994–1995	*Phocoena phocoena*	Blubber	ΣCB^{c}: 4480–39,130^{b} (1), 5,610–38,550^{b} (2) CB 153: 3,010^{b} (1), 2,930^{b} (2)	Bruhn et al. 1999
UK coast (North Sea)	1988 PDV epizooty	*Phoca vitulina*	Blubber	PCB-153: 30–28,000^{a}	Hall et al. 1992, 1999
Estonian coast (Baltic Sea, 1), Froan. Norwegian Sea (East Atlantic, 2)	1998 1997	*Halichoerus grypus (pups)*	Blubber	PCB-153: 921–11,050^{b} (1), 204–760^{b} (2) ΣPCBs^{d}: 2,625–26,732^{b} (1), 655–2,932^{b} (2)	Sørmo et al. 2003a
PBDEs					
UK coast (North Sea)	1996–1999	*Phocoena phocoena*	Blubber	BDE 47: n.d. – 6,110^{a} BDE 99: n.d. – 1,287^{a} BDE 100: n.d. – 634^{a}	Law et al. 2002
(Law et al. 2002)	1998–2000	*Halichoerus grypus (pups)*	Blubber	BDE 47: 3.3–1,200^{b} BDE 99: 1.5–100^{b} BDE 100: 2.2–110^{b}	Kalantzi et al. 2005
Perfluorinated compounds (here: data for PFOS)					
Bothnian Bay (Baltic Sea)	Not specified	*Phoca hispida* *Halichoerus grypus*	Liver, blood	Liver: 130–1,100^{a} (P. h.), 140–360^{a} (H. g.)	Kannan et al. 2002
Dutch Wadden Sea (North Sea)	2002 PDV epizooty	*Phoca vitulina*	Liver, kidney, blubber, muscle, spleen	Liver: 46–488^{a} Blubber: 19–297^{a}	Van de Vijver et al. 2005
German Bight (North Sea)	2007	*Phoca vitulina*	Blood, liver, muscle, lung, kidney, blubber, heart, brain, thymus, thyroid	Liver: 559–1665^{a} Blubber: 0–23^{a} Blood: 48–887^{a}	Ahrens et al. 2009

[a] (ng/g) wet weight

[b] (ng/g) lipid

[c] Sum of 46 individual congeners and three groups of coeluting CBs

[d] Sum of the PCB congeners 47, 52, 74, 99, 101, 118, 128, 138, 149, 153, 170, 180, 183, 187

Currently, marine mammals are heavily polluted and suffer from chronic poisoning even years after the reduction or stop of the emission of many of these compounds. For instance, Ross et al. estimated – using individual and life-history-based models – that not before the twenty-second century levels of contamination of 95% of the endangered southern resident killer whales, the most PCB-contaminated marine mammals in the world, will fall below the currently valid thresholds, above which adverse health effects are to be expected (Ross et al. 2007).

The xenobiotics are deactivated regarding biological effects, while being stored in the fatty tissue, but they are reactivated and bioavailable again in periods of emaciation, when they are released again from the declining blubber. For detoxification and elimination of xenobiotics an organism needs an appropriate biotransformation system. In general, organisms on a lower trophic level as well as birds and fish have lower biotransformation ability than mammals. Mammals have developed an enzymatic system especially in the liver to transform lipophilic substances, e.g., xenobiotics, to hydrophilic congeners. For most POPs, the top predators have to perform the main part of detoxification and biotransformation work. Due to the species specificity of transformation and metabolism steps the contaminant pattern found in marine mammal species varies and differs both from the technical mixtures originally released into the environment and from the pattern in their prey (Aguilar 1987; Boon et al. 1997; Storrhansen et al. 1995). With increasing contaminant levels, the rate of metabolism may be elevated by increased induction of detoxifying enzymes, which are often used as biomarkers for pollution impact (Nyman et al. 2000). For more detailed information on biotransformation see Sect. 17.4.

Not all studies of pollutant levels in marine mammals include related data from lower trophic levels and vice versa. Studies, often of the Arctic and Antarctic food web, show representative accumulation factors, the impact of substance specific biotransformation, and the global distribution of POPs (Fisk et al. 2001; Muir et al. 1988). A time series on organochlorine levels in representatives of the antarctic biota showed that biomagnification of most POPs in the Weddell seal (*Leptonychotes weddellii*) and southern elephant seal (*Mirounga leonina*) is 30–160 times that of krill; while hexachlorobenzene was the only exception with levels in seals lower than in fish, indicating specific elimination of this compound in the food web (Goerke et al. 2004).

In addition to substance- and species-specific elimination processes, other factors (e.g., nutrition status) may influence the concentration levels to be measured in tissue samples of marine mammals and have to be considered when evaluating the contaminant loads in marine mammals.

If comparing concentrations from blubber samples and biopsies, background information on season and blubber thickness has to be taken into account. Sample analyses from blubber show a gradient of compound levels from the inner to the outer layer instead of a homogeneous distribution (Czub and McLachlan 2007; Severinsen et al. 2000). In periods of fasting or emaciation, bioaccumulated POPs are released from the blubber and may cause acute poisoning or medical disorders. For instance, Sørmo showed that the organochlorine concentration in seal pups is related to the nutritional condition of the individuals (Sørmo et al. 2003a). Analyzing the concentrations of organochlorine compounds in seal blubber showed that the levels are negatively correlated to blubber thickness (Hall et al. 1992) and varies by season (Ryg et al. 1990).

For most POPs, the stored amount is different for males and females due to placental and lactational transfer. The mobilization of compounds stored in the fatty tissue during the gestation and lactation period is one important elimination and detoxification mechanism for certain persistent pollutants in females. On the other hand, the organisms of pups or calves have to cope with a considerable amount of xenobiotics during the early period of life, when their immune system is still under development (see Sect. 17.5). To obtain data on transfer of xenobiotics from mother to pups, repeated sampling of milk, serum and blubber biopsies of mother and offspring during the gestation, lactation and weaning periods is necessary. Several seal species fast during lactation, so that all the xenobiotics transferred from mother to pup are derived from the stored substances in the fat tissue. Due to placental transfer (Debier et al. 2003) detected higher serum levels of PCBs in newborn grey seal pups in comparison to their mothers, which even increase during the lactation process. Also (Sørmo et al. 2003b) investigated the partitioning of POPs in mother-pup pairs of grey seals and found that high-chlorinated and hydrophobic compounds were passed less into the milk than low-chlorinated and more water-soluble compounds due to lower concentrations of the first mentioned compounds in pup blubber than in maternal blubber. In summary, females accumulate POPs until the stage of sexual maturity and reproduction with the level of certain compounds either remaining stable or declining during the gestation and lactation period. In comparison, the levels of persistent pollutants in adult males increase continuously and are for most of the POPs higher than those in adult females.

As the concentration of POPs in harbour seals are dependent of age and gender, Ross et al. propose to sample free ranging pups (3–6 weeks) for monitoring purposes to ensure that their POP levels can directly be traced back to placental and lactational transfer (Ross et al. 2004).

However, not all substance classes are subject to placental and lactational transfer within the same range. No differences in PBDE (polybrominated diphenyl ethers) concentration levels were detected for male and female individuals in stranded beluga whales (*Delphinapterus leucas*) in the St. Lawrence Estuary, Canada, indicating a barrier that prevents transfer from mother to calf (Lebeuf et al. 2004).

In summary, the contaminant levels in marine mammals vary for different groups of chemicals and types of sampled tissue as well as for different biological species, regions and habitats. They also vary seasonally by factors as sex, age and general health status of the individuals. Various tissues and body fluids are sampled from marine mammals for the determination of contaminant levels, among which are liver tissues, e.g., blubber biopsies, serum and milk.

There are two main objectives of measuring and monitoring the persistent organic pollutant levels in marine mammals. First, POP levels in marine mammals reflect the status of their global distribution and the anthropogenic stress on the coastal and marine environment. Second, these data may be a prerequisite to providing cause–effect relationships of the POPs in marine mammals as well as to assess the health status of marine mammals up to the population level and should be completed with measurements of effect-orientated biomarkers (see Sect. 17.4). The type of sample depends on the scope of the study. A comparison of results from different studies remains difficult due to the use of different sampling techniques, tissues and organs. Different monitoring programs also comprise different groups of substances. It is very important to have a large data set of uniform data and to focus on the effects more independently of the substance classes, as they can often hardly be assigned to a single compound (Reijnders et al. 2007a).

Pollutants found in indigenous marine mammal species in the North and the Baltic Sea include pesticides, polychlorinated biphenyls (PCBs) and other organochlorine compounds, PBDEs and perfluorinated organic acids (see Table 18.1; data concerning concentrations of metal pollution are summarised by Kakuschke and Prange (2007)). Most of these data are collected together with data regarding biological effects and pathological findings (see Sects. 17.4 and 17.5).

18.2.1 Polychlorinated Biphenyls

PCBs were among others used as heat-resistant coolants, electrical insulators and plasticizers, before they were banned in the 1980s at least in Western Europe and the USA. The PCBs used commercially were mixtures of 209 different congeners with differing toxicity and transport behaviour in the environment. PCBs impair the immune, reproduction, neurological and endocrine system of mammals, cause cancer and are also suspected to have immunotoxic effects at lower concentration levels (Safe 1993). They are still regarded to be most harmful in the context of marine mammals (Reijnders et al. 2007a), as they are linked to severe effects in seals, such as infertility and intestinal ulcers, but also induce less obvious effects including endocrine disruption and immunosuppression.

18.2.2 Polybrominated Diphenyl Ethers

PBDEs are still in use as flame retardants in mixtures of Deca-BDEs, while Octa-BDE and Penta-BDE have been already banned. PBDEs are structurally related to PCBs and have similar properties concerning lipophilicity and bioaccumulation, but are more susceptible to environmental degradation. Their mammalian toxicity increases with decreasing number of bromine atoms, causing more and more toxic and bioaccumulative congeners to be formed during degradation. Regarding human health, PBDEs are assumed to affect the hepatic, the immune as well as the reproductive systems by causing cancer, decreasing thyroid hormone levels and acting as endocrine disrupting substances. Ross et al. (2009) suspect large environmental reservoirs of BDE-209 in sediments, which may be a long-term threat to biota, if breaking down into the lighter congeners.

18.2.3 Polycyclic Aromatic Hydrocarbons

PAHs are mainly released after incomplete combustion of carbon-containing fuels. They show mutagenic and carcinogenic as well as endocrine-disrupting activity (Santodonato 1997). High loads of PAHs are found in macroinvertebrates; while in organisms at high trophic levels the concentrations of PAH are down due to metabolic transformation. Here biological effects caused by PAH metabolites are of more relevance (damages on DNA or cellular level).

18.2.4 Perfluorinated Compounds

Perfluorinated compounds are another group of "modern" pollutants with growing concerns for different organisms. Perfluorinated compounds are in use since 1960 as e.g., surfactants and fire retardants. They are today widely distributed even in remote Polar Regions (Giesy and Kannan 2001). Relatively little is known on the toxicity of this group of compounds to mammalian organisms, but serious chronic toxicity was found in laboratory animals. The hepatic peroxisome proliferating capacity of several congeners is correlated to hepatocarcinogenesis. Perfluorooctane sulfonate (PFOS) is the predominant compound found in marine mammals, while perfluorinated carboxylic acids (PFCAs) are found in much lower concentration levels. The (eco)toxicological role for marine mammals has not yet been completely established.

18.3 Biomarkers for Pollutants in Marine Mammals

Monitoring the influence of (changing) anthropogenic factors like persistent pollution on marine mammals and their health status can provide an early warning system for the partially threatened populations of these animals as well as for the whole ecosystem which they inhabit. This requires not only the determination of concentration levels, but also the knowledge of related biological effects of contaminants.

At present, the question of (adverse) effects of persistent pollutants on marine mammals has not been fully answered because of the complex physiology of marine mammals and the difficulties to sample a sufficient number of appropriate individuals for cause–effect studies (Reijnders et al. 2007a). Anthropogenic contaminants have partly caused severe visible effects in marine mammals such as infertility and intestinal ulcers. Recently, less noticeable effects like immunosuppression have also pushed to the fore (see also below in Sect. 17.5), which reflect subtle changes in the ecosystem at an early stage. Such sublethal effects may be caused by lower concentration levels of the same pollutants, but must be considered as possible forerunners to more severe effects. For a complete and reliable risk assessment in the future an integrated set of biomarkers is needed which could simultaneously consider various mechanisms of action of pollutants and their sublethal effects. This is at best detectable after minimal invasive sampling of marine mammals captured alive (Fossi and Marsili 1997). Therefore there is an urgent need for the development of (species-specific) diagnostic techniques for early indication of damaging effects on individuals and to be able to predict those for an entire population and ecosystem.

In this section, in a short general introduction the terms *bioindicator* and *biomarker* are defined and some pollutant biomarkers are introduced. Then more detailed information is provided on the use of established biomarkers in marine mammals. Finally, an in vitro approach is presented to reveal proteins upregulated by contaminants in marine mammals.

The health status and population size of bioindicators is supposed to reflect the status of ecosystem health and environmental integrity (e.g., marine mammals as top predators are considered sentinel bioindicators for marine pollution in the marine ecosystem (Mossner and Ballschmiter 1997; Ross 2000).

Biomarkers or biochemical indicators are quantifiable tools to define and monitor the biological function and health of such a bioindicator organism. Their main task has up to now been to display the dysfunction produced by contaminants in a dose- or time-dependent manner, while in future other (anthropogenic) influences should be considered as well.

From a biochemical point of view, there are several levels, on which biomarkers or related indicator reactions could be monitored (see Fig. 18.2): visible by eye are only morphological characteristics, while the metabolome, the proteome and the genome are targets of modern bioanalytical methods, which have been developed in the last decades. The rather static genome contains the whole hereditary information, which is encoded in the DNA. The proteome comprises all the expressed proteins of a cell or an organism at a given point in time under defined conditions. This implies that the same genome yields different proteomes as modifications of external conditions (stress, chemical substances, temperature) may alter the pattern

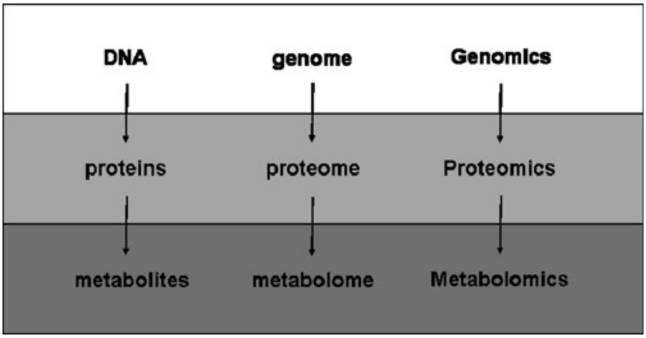


Fig. 18.2 Levels to take a snapshot of an organism: The proteome and metabolome

of protein expression. Therefore, the proteome or protein expression pattern and also the transcriptome at the mRNA level allow monitoring the effect of external stress factors on an organism. Comparison of the protein pattern under varying external conditions may lead to appropriate biomarkers, mostly in form of a set of proteins instead of a single protein. The metabolome refers to the complete set of small-molecule metabolites (such as metabolic intermediates, hormones and other signalling molecules as well as secondary metabolites). The metabolite spectrum is also changed as certain proteins are needed as enzymatic catalysts to synthesize or to biotransform metabolites: Changing in the pattern of proteins or metabolites may indicate pathological impairments and result in morphological visible changes.

Considering the indigenous marine mammals in the German North Sea in this context, histopathological and histological parameters are established parameters for monitoring of the health status of harbour porpoises and harbour seals (Siebert et al. 2001, 2007). Considering cellular parameters, Hasselmeier et al. (2008) collected haematology profiles on several hundred harbour seals in the last years to contribute to the assessment of marine mammal health. Further investigations on blood to evaluate the immunocompetence of harbour seals are described in Sect. 17.5. Current research is aimed to confirm biochemical indicators for application in the monitoring of marine mammals, their health status and pollution impact. mRNA expressions of selected proteins (e.g., cytokines, acute phase proteins) were analyzed in blood of harbour seals and harbour porpoises using real time RT-PCR (Fonfara et al. 2008; Fonfara et al. 2007a, b).

Evaluation and application of biochemical markers on the level of protein expression is illustrated in detail in the following. Several groups of protein biomarkers which are currently discussed for monitoring the exposure to or effects of persistent pollution in marine mammals are already established in easily accessible organisms. The most important group are proteins involved in xenobiotic biotransformation and metabolism (see Fig. 18.3), which happens predominantly in the liver. Analogous to drug metabolism, xenobiotic metabolism is proceeding in two phases: Hepatic enzymes are responsible for the metabolism of xenobiotics by catalyzing the transformation of lipophilic substances to water-soluble products for excretion. In Phase I the functionalisation of the xenobiotic is catalysed (oxidation, reduction, hydrolysis or hydration), after Phase II the conjugation of the active secondary metabolite (with glucuronic acid, sulphuric acid or glutathione) is followed by excretion in bile or urine. The expression levels of the involved enzymes are only upregulated in case of need for the fast detoxification and elimination of xenobiotics as in exposed organisms. The production, content and variation of such enzymes do often not only depend on the presence of xenobiotics, but vary with species, diet, sex, age, season and tissue. In addition, genetic polymorphism may also lead to differences in the enzymatic activity of isoenzymes. This is in agreement with the fact that the resulting contaminant pattern varies (see Sect. 17.3). Figure 18.3 summarizes such enzymes which catalyse biotransformations and which are in use as biomarkers due to the high upregulation of their expression level as a consequence of exposure with pollutants in certain organisms. In comparison to other enzymes, xenobiotic metabolizing enzymes possess rather low

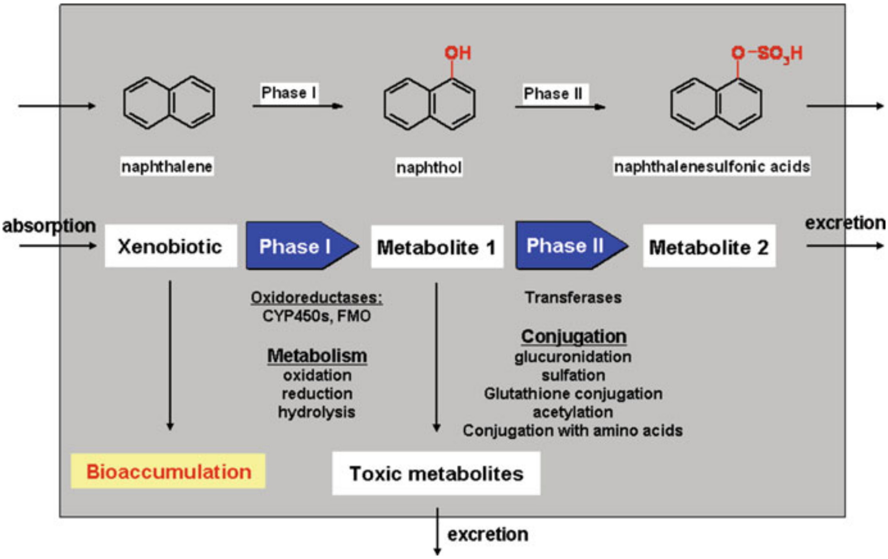


Fig. 18.3 Xenobiotic metabolism

substrate specificity and can catalyse the biotransformation of a whole range of xenobiotics. However, in spite of the low specificity these enzymes often only transform xenobiotics and upregulation is characteristic for the presence of xenobiotics. The low specificity comes along with a rather weak binding of the substrate and relatively low turnover rates, which are compensated by a rather high upregulation of protein expression, which is advantageous for their use as biomarker.

The hepatic microsomal cytochrome P450 proteins play a central role in xenobiotic metabolism. These membrane proteins are associated with membranes in many organs and are commonly found in the endoplasmic reticulum of the liver. As monooxygenases they are responsible for detoxification mainly by hydroxylation and epoxidation of hydrophobic substances. Their expression is induced via the aryl hydrocarbon receptor (AhR) pathway (see Fig. 18.4; Hahn 1998; Okey 2007): The induction of cytochrome P450 expression is based on the binding of hydrophobic and planar organic compounds as ligands at the binding site of the Ah receptor. The activated complex between xenobiotic and receptor translocate into the nucleus, dimerize with the AhR nuclear translocator (ARNT) and binds in the cell nucleus in the promoter region of the gene. Upregulated expression yields higher levels of mRNA and CYP1A protein, but also other proteins which are related to modifications in the steroid metabolism, in the level of thyroid hormones and in the function of other receptors. In summary, analogous biological effects of the various xenobiotic classes are a result from the same molecular mechanism at the Ah receptor. The highly conservative receptor is existent in all mammals and most vertebrates (fishes, amphibians, reptiles), but is lacking in invertebrates and some lower vertebrates. Organisms (invertebrates, knock-out mice) lacking the receptor react

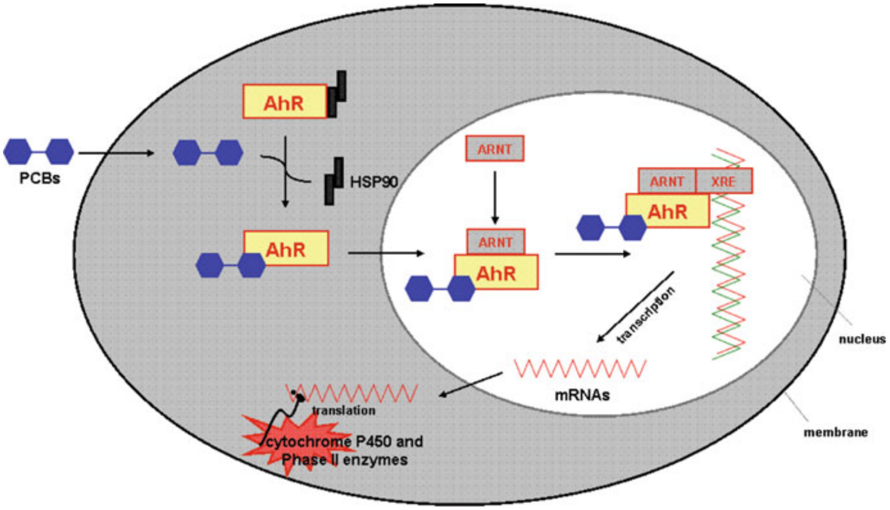


Fig. 18.4 *AhR* aryl hydrocarbon receptor, *ARNT* AhR nuclear translocator, *HSP* heat shock protein, *mRNA* messenger RNA, *PCBs* polychlorinated biphenyls, *XRE* xenobiotic-responsive element

less sensitive to these groups of xenobiotics. In mammals the physiological relevance of the Ah receptor is not completely elucidated, but it seems to be important for the development of the blood system and in the regulation of cell cycle, growth and differentiation.

The components of the pathway are partly identified for two Phoca species. To investigate the mechanistic basis for planar halogenated aromatic hydrocarbons toxicity in harbour seals (*Phoca vitulina*), Kim and Hahn (2002) sought the aryl hydrocarbon receptor (AhR). To understand the regulation mechanism of AhR and AhR nuclear translocator (ARNT) expression in individuals of the wild Baikal seal (*Pusa sibirica*) population, Kim et al. (2005) investigated hepatic mRNA expression levels of AhR and its heterodimer, ARNT genes, in association with biological index (age, gender and body weight), accumulation of planar halogenated aromatic hydrocarbons, and expression levels of cytochrome P450 (CYP1A and 1B).

In vertebrates various cytochrome P450 isoenzymes with different functions exist. CYP1A induction has been extensively used as a biomarker of exposure to polycyclic aromatic hydrocarbons and planar halogenated aromatic hydrocarbons as it catalyses epoxidation and hydroxylation of the xenobiotics. It is advantageous that the protein can be detected in several kinds of tissues and even in blood, which can be obtained in a non-destructive way (van den Brink et al. 2000).

The induction and resulting pattern of cytochrome P450 isoenzymes may vary for different organs, individuals and species, but also with factors like diet, season, age, sex, tissue, making species-specific investigations necessary (Fink-Gremmels 2008) before using upregulation of cytochrome P450 expression as a biomarker for pollutants.

Cytochromes P450, P420 and mixed-function oxidases were early evaluated as biomarkers of polychlorinated biphenyl (PCB) exposure in harbour seals (*Phoca vitulina*) (Troisi and Mason 1997) and other marine mammals, and the related cytochrome P450 1A genes were identified in several marine mammal species (Teramitsu et al. 2000).

Nyman et al. (2000) et al. analyzed hepatic microsomes and found that the expression level of CYP1A apoprotein as well as its catalytic activity were increased up to fivefold in Baltic ringed and grey seal populations in comparison with the levels in ringed seals from Svalbard and grey seals from Sable Island as less polluted areas. This data strengthened the concept that CYP1A is markedly induced in seals living in polluted waters and can be used as exposure biomarkers in blubber or plasma of both species (Nyman et al. 2003).

Investigations of Ross and co-workers on cytochrome P450 1A (CYP1A) expression level in liver and skin biopsies of captive harbour seal pups as well as in skin biopsies of free-ranging seals indicated that CYP1A in skin may be used as a biomarker of contaminant exposure (Assuncao et al. 2007; Miller et al. 2005), but the authors also stated that a higher sample number as well as the transfer to real samples derived from free ranging seals is needed for confirmation.

Also in skin biopsies from bottlenose dolphins (*Tursiops truncatus*) CYP1A1 expression appear to be determinated by PCB concentrations (Wilson et al. 2007), but the endothelial CYP1A1 expression varied along the length of the biopsy.

For understanding and predicting the toxic effects of xenobiotics, possible metabolites of biotransformation have to be considered as well. Therefore PCB biotransformation is studied in two contrasting ringed seal populations; on the one hand in the highly contaminated Baltic Sea and on the other hand in the less contaminated Svalbard (Routti et al. 2008). McKinney et al. (2006) investigated the formation of potentially toxic oxidative PCB and PBDE metabolites in hepatic microsomes of beluga whales and in a rat model, which may be contributing to contaminant-related stress effects.

Many persistent pollutants show endocrine disrupting bioactivity in addition to other toxic effects interacting with hormone receptors in the organism and are then also classified as estrogenic endocrine disruptive chemicals (EDCs). This may lead to feminization of males and masculinization of females respectively, disruption of the physiology concerning vitamin A and thyroid hormone and alteration of the distribution of its essential metabolites.

In the past, marine mammal population in highly polluted areas showed rather high infertility rates. High levels of PCBs in the western part of the Wadden Sea due to pollution input by the river Rhine were thought to be responsible for the low reproduction rate in Dutch common seals in the 1970s. This motivated a feeding study, in which reproductive disorders in seals were observed after feeding on polluted fish (Reijnders 1986). Two groups of twelve female common seals were fed with fish caught in the western part of the Wadden Sea and from the less polluted north East Atlantic respectively. Three males receiving Atlantic fish were alternated between both groups during the mating period. Although the difference in diet did not influence the hormone pattern, the reproductive success was significantly lower in the group of females fed with the more polluted fish. The reproductive mechanisms are affected in the post-ovulation phase. The period around implantation seemed to be the most sensitive stage.

In the 1980s the population of the grey seals in the heavily polluted Baltic Sea was declining from approx 100,000 in the beginning of the century to less than 4,000 seals. Even after banning hunting, the population continued to decrease due to health problems, particularly sterility among females. Pathological analyses showed prevalence of uterine obstructions and uterine tumours (leiomyomas; Bergman 1999; Backlin et al. 2003). There are also indications, that PCBs are involved in the development of leiomyomas (Bredhult et al. 2008). From 1980 to 2006 a breeding project was performed in Sweden for grey seals. The seals were fed fish from the Atlantic to show that reproduction is possible if the food for the animals is imported from an area with lower pollutant load. The pups were released to the wild primarily in the southern Baltic, where the population of grey seal was weak (Roos and Ekström 2006). In the meantime the reproductive health has improved again [population increasing at about 8% a year since 1990 (Backlin et al. 2008)].

For biomonitoring the endocrine disrupting or estrogenic activity of persistent pollution different biomarkers of exposure are relevant in fishes and mammals. In fishes the egg yolk precursor protein vitellogenin is expressed in male fishes by anthropogenic estrogenic chemicals in a dose dependent manner (Sumpter and Jobling 1995). In marine mammals and other fish-eating wildlife Vitamin A (retinol) physiology is a touted biomarker of contaminant-related estrogenic activity (Simms and Ross 2000), as retinol metabolites are required for growth and development as well as for the reproduction and endocrine system, immune function, vision and epithelial maintenance. Reference retinol levels as well as confounding factors must therefore be characterized before retinoids can be used as an effective indicator of adverse health effects in marine mammals due to persistent pollutants. In a study with young harbour seals, Mos and Ross (2002) demonstrated that vitamin A physiology could be monitored using skin and biopsy samples. In another study, Mos et al. (2007) showed that concentrations of circulatory vitamin A (retinol) in plasma and stored vitamin A in blubber were negatively associated with blubber PCB concentrations. The harbour seal retinoic acid receptor a (RAR alpha) expression in blubber was elevated in more contaminated animals. Both may serve as sensitive biomarkers of PCB-associated toxic effects.

Another group of proteins which is used in a whole range of organisms as effect-specific biomarkers for proteotoxic stress is not involved in biotransformation or direct detoxification processes. Many heat shock proteins (HSPs) assist the protein folding in their function as molecular chaperones and are upregulated in expression levels by heat or other (e.g., chemical) stress as a response to the denaturation of proteins (Wiegant et al. 1994; Kinder et al. 2007) if the proportion of un- or misfolded proteins is increased. Their protein sequences are highly conserved in all organisms. Heat shock proteins are not in routine use in monitoring of marine mammals, but some studies indicate, that heat shock proteins are related to the impact of exposure with contaminants in marine mammals as well.

Nowadays proteomics-based approaches are often used to reveal novel biomarkers in various fields of applications. In an ecotoxicological context the goal of such toxicoproteomic approaches is to identify pollutant-induced modifications in protein expression in appropriate tissue or biofluid samples that are characteristic for exposure with pollutants. Considering the whole range of the proteome allows for the detection even of subtle changes in protein patterns from chemical stress. The results can be used to confirm biomarker reactions and can contribute to the understanding and establishing species-specific cause–effect relationships (Wetmore and Merrick 2004; Nesatyy and Suter 2007; Monsinjon and Knigge 2007; Gonzalez-Fernandez et al. 2008). For toxicoproteomic approaches it is essential to provide samples which can be traced back unambiguously to the pollutant source and in which other confounding factors on the protein expression can be excluded. While samples from feeding experiments with organisms from lower trophic levels [e.g., mussels (Amelina et al. 2007), fish (Mi et al. 2005)] are readily accessible in sufficient number, this still presents a challenge for studies with free ranging marine mammals. In vitro approaches with cell material from marine mammals can offer an alternative to extensive exposition studies.

To identify protein patterns as additional sensitive and reliable biochemical markers for an effect-oriented monitoring strategy in harbour seals (*Phoca vitulina*), an in vitro approach using primary hepatocytes has been established. Hepatocytes of other organisms are generally accepted to reflect in vivo responses to xenobiotics. Primary hepatocytes maintain relevant liver functions such as detoxification of exogenous or endogenous substances (Li 1998) and protein synthesis (Farkas et al. 2005). The primary seal hepatocytes were isolated with techniques such as non-perfusion techniques and biopsy techniques which are suitable for liver samples obtained from wild-ranging individuals, which had died or had to be euthanized by a designated seal ranger or a veterinarian due to severe illness. The subsequent exposition of the cells with persistent pollutants should reflect the in vivo response in the hepatic system and therefore provide a means to examine species-specific effects and corresponding molecular structures as potential biomarkers. In Behr et al. (2008), the in vitro approach is described comprising the comparison of protein expression levels in cells incubated with a technical mixture of polychlorinated biphenyls in three concentration levels with those in internal controls from the same individual. Some of the upregulated proteins are putatively identified to belong to the group of cytochrome P450 enzymes. The species-specific protein pattern found to be corresponding to its impact has to be reconfirmed in corresponding tissue and blood samples before using such samples in monitoring.

Brenez et al. (2004) propose a similar proteomics-based strategy using blood cell cultures (lymphocytes) to study the effects of persistent pollutants on the immune system of seals (see also Sect. 17.5). After establishing fibroblast cell cultures from skin biopsies of cetacean species of the Mediterranean in a non-lethal sampling, Marsili et al. (2000) and Fossi et al. (2006) treated such cells with organochlorine contaminants and polybrominated diphenyl ethers (PBDEs) to evaluate effects on the expression levels of CYP1A and CYP2B proteins by western blot and immunofluorescence techniques.

In summary, the detection of biomarkers is an important alternative and completion for measurements of exposure to persistent pollutants (see Sect. 17.3). Concentrations of biomarkers can be measured at the sub-organism level to indicate adverse effects on population level. Measurements of biomarkers are related to the bioavailable part of the chemical compounds, which is responsible for biological effects and considerable for consequences on the ecosystem.

18.4 Immunotoxicology of Persistent Pollutants in Marine Mammals

The chronic intake of contaminated diet yields high pollutant levels in marine mammals, which may cause severe effects such as morphological changes of organs, but also to an imbalance of the immune system (Beineke et al. 2006) and an increased susceptibility to infectious diseases. Regarding epidemic disease outbreaks it is evident that they are caused by virus infections, but in recent times the immunotoxicity of persistent organic pollutants in marine mammals is in focus (De Guise 2005).

To confirm the impact of POPs on the immune system, often long-lasting studies and collection of data are needed. Some feeding studies with distinguished groups fed with contaminated or less-contaminated diet respectively have been performed up to now. Nowadays even in vitro approaches are employed.

Statistical correlations of pathological findings with contaminant levels often utilise the data collected in monitoring programs. As mentioned earlier (see Sect. 17.2), the population size of marine mammals as well as their health status considering deceased animals and living animals are regularly monitored in various regions due to official rules. Several studies from different geographical sites evaluate the impact of environmental contaminants in marine mammal species by revealing morphological changes of certain organs or an increased susceptibility to infectious diseases of animals inhabiting contaminated regions or with higher body burdens of pollutants (see Table 18.2). Hereby contaminant levels and data concerning the health status, which are collected in a continuous monitoring or on the occasion of certain events, could be correlated. This kind of

Table 18.2 Selected studies on correlation of pollution impact and disease outbreak

Reference	Title
Hall et al. (1992)	Organochlorine levels in common seals (*Phoca vitulina*) which were victims and survivors of the 1988 phocine distemper epizootic
Aguilar and Borrell (1994)	Abnormally high polychlorinated biphenyl levels in striped dolphins (*Stenella coeruleoalba*) affected by the 1990–1992 Mediterranean epizootic
Jepson et al. (2005)	Relationships between polychlorinated biphenyls and health status in harbor porpoises (*Phocoena phocoena*) stranded in the United Kingdom
Beineke et al. (2005)	Investigations of the potential influence of environmental contaminants on the thymus and spleen of harbor porpoises (*Phocoena phocoena*)

investigations is often motivated by the concern that further disease outbreaks can occur.

De Swart et al. (1994, 1996) performed a feeding study under semifield conditions with harbour seals consuming herring from areas of different contamination levels. Two groups of eleven harbour seals each were housed in two similar basins over a two and a half year period, so that the same individuals could be repeatedly sampled for monitoring of haematological and immunological parameters in regularly taken blood samples. After an adaptation period of 1 year, during which all animals were fed with relatively uncontaminated herring, the control group was continued to be fed with relatively uncontaminated herring from the North Atlantic, while the other group was fed with herring from the Baltic Sea. The authors found higher body burdens of potentially immunotoxic organochlorines and impaired immune responses in those seals which were consuming more contaminated food showing suppression of natural killer cell activity as first line of defence and suppression of T-cell response representing specific immune response. Ross (2002) concludes that immunotoxic substances in contaminated prey lead to suppression of the immune system of the individuals within a population. Emergence of infectious diseases and virus replication is facilitated, which may contribute to a decrease in population size.

In a feeding study with West Greenland sledge dogs (*Canis familiaris*) it was shown that daily feeding with minke whale (*Balaenoptera acutorostrata*) blubber, which is heavily loaded with organohalogen contaminants and mercury causes an impairment of the non-specific and specific cellular immune system (Sonne et al. 2006). As in the study exposure levels are similar to those of Inuit and polar bears (*Ursus maritimus*), the authors assume that it is reasonable to infer that Inuit and polar bears suffer from a similar decreased resistance to diseases.

In an immunotoxicological study (Mos et al. 2006) compared blood and blubber samples from free-ranging harbour seal pups (*Phoca vitulina*) that were live-captured from two remote and two near-urban sites in British Columbia, Canada, and Washington state, USA. Univariate correlations between immune parameters (phagocytosis, respiratory burst, T-lymphocyte function, lymphocyte signalling, lymphocyte counts) and polychlorinated biphenyl concentrations suggested chemical-associated immunotoxicity.

Another approach aside from feeding studies are in vitro exposures of immune cells obtained from the blood of marine mammals (see review of De Guise 2005). These experiments revealed the susceptibility of various immune cells of different marine mammals to chemicals, which can be exposed separately or in mixtures. Immunotoxic pollutants may lead to two main types of effects: immunosuppression and immunostimulation.

To give an example, Hammond et al. (2005) exposed mononuclear (PBMCs) as well as polymorphonuclear (PMNCs) leukocytes from harbour and grey seals to Aroclors. The phagocytic as well as the respiratory burst activity of harbour seal PMNCs was decreased, while there was no effect on the grey seals. The observed differences may have implications for the previously recorded differences in disease susceptibility between grey and harbour seals.

Using lymphocytes from blood samples of harbour seals from the Wadden Sea, Kakuschke et al. (2005) investigated the T-lymphocyte response to metals using an lymphocyte transformation test (LTT): MELISA® (memory lymphocyte immunostimulation assay). Lymphocytes from blood samples of wild-ranging seals were isolated and incubated with different metal salts.

Those lymphocytes, which have already been sensitized by certain metals derived from environmental pollution, were transformed to lymphoblasts and became so called "memory cells". In the incubation experiment the added metal salts act as antigens and can induce an immune reaction related to hypersensitivity: the lymphoblasts proliferate rapidly. In 13 of 31 animals investigated, metals induced such a metal-specific hypersensitivity reaction. The combination of a high metal concentration in blood with a metal-specific sensibilization strongly suggests chronic metal exposure. The proposal is to use metal-hypersensitivity as indicator of immunomodulation in harbour seals (*Phoca vitulina*) in the North Sea. Kakuschke et al. (2008) investigated also the immunosuppressive effect of metals in pups during rehabilitation. Metals showed a strong immunosuppressive effect on the lymphocytes of the newborns, but this effect decreased during their rehabilitation until the release into wildlife.

In summary, in vitro exposure experiments only provide information of the direct toxicity of persistent pollutants on immune cells, but are important for more accurate risk assessment in combination with exposure data (De Guise 2005).

18.5 Future Perspectives

It is generally accepted that persistent pollutants cause disorders in marine mammals regarding morphological changes in organs, reproductive disorders and possible impairment in the function of the immune system. Although the levels of persistent pollutants are declining in marine biota since they have been banned, marine mammals will continue to suffer for a long time due to bioaccumulation (Hickie et al. 2007). For defining threshold limit values of pollutant levels sublethal irritations and long-term effects as vulnerability of the animals have to be considered in case of marine mammals due to their long-life and expected long-term effects on reproduction and the immune system.

Due to the position of marine mammals as top predators in the marine food web, alterations and impairments in their health status may also be used for monitoring ecosystem health. The confirmation of cause–effect relationships and biomarker reactions presents a challenge in the field of marine mammal research. Achievements in in vitro technologies and bioanalytical methods may help to overcome such difficulties.

It is very important to test and evaluate the impact not only of single compounds, but also of mixtures of various compound classes. Also the possible toxic effects of the metabolites after biotransformation have to be considered (McKinney et al. 2006; Routti et al. 2008).

Monitoring exposures to toxic pollutants is often still considered independently of other potential stress factors. In the future effects of interactions between contaminants and various stress factors and dependence of the vulnerability of the organisms from environmental changes has to be considered as well (Couillard et al. 2008a, b). The distribution, bioavailability and transformation of pollutants may be altered due to environmental factors (e.g., temperature, sedimentation). Changes in such factors may also lead to increased vulnerability of marine organisms to pollutants by influencing the response mechanism regarding toxic injury or by modifying their predation behaviours (Couillard et al. 2008a). If both concentration and effect levels are detected, changes considering the bioavailability of persistent pollutants and the vulnerability of the bioindicator organism can be recognized at an early stage.

While a positive trend respecting reproductive health could be recognised, effects on the immune system are in focus which may be caused by yet unidentified toxic factors (Bergman 1999).

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Part VI
Future Aspects

Chapter 19
Emerging Persistent Organic Pollutants in the Marine Environment

Norbert Theobald

19.1 Introduction

At present, more than 18 million organic compounds are known. Consequently, even if only a small portion of these substances exhibit properties leading to environmental problems, the number of organic contaminants is high and, in principle seams unlimited, as the development of new substances continues. Approximately 2,000 substances are presently estimated to be environmentally relevant, of which 100–300 compounds are summarised in lists of substances to be treated with priority by various international organisations, such as the EU (EU-Water Framework Directive: EU-WFD), OSPAR Commission (for the protection of the Marine Environment of the North-East Atlantic, (OSPAR 2005, 2009) and HELCOM Commission (Baltic Marine Environment Protection Commission).

Most of these compounds are relatively new, which means that their observation in the environment began since the mid 90s of the last century. Only 12 pollutants are considered as "classical" POPs which are, e.g., treated and regulated by the UN POP Convention (UNEP 2005). While "classical" POPs are mostly non-polar, lipophilic compounds and belong to a few compound classes only – such as chlorinated hydrocarbons (PCB, DDT, dioxins, HCH, etc.) or policyclic aromatic hydrocarbons (PAHs) – new, emerging pollutants exhibit properties which are different from "classical" pollutants. The new compounds are often more polar, less volatile and belong to many quite different compound classes and origin from a great number of different applications. This renders their treatment and monitoring much more demanding and difficult. Especially for investigations in the marine environment, a number of analytical challenges and administrational, logistic and financial parameters have to be considered and optimised.

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19.2 Selection Processes for Emerging Pollutants

Due to the fact that there are so many compounds of potential concern it is necessary to apply effective procedures for selecting new pollutants for monitoring investigations. For the selection process various approaches with emphasis on scientific, rational economical, or administrational aspects can be applied. All three have their pros and cons, therefore a combination of all three will produce the optimal results; especially, as they are partially interconnected.

The scientific approach starts from scientific investigations which specifically are looking for possible new pollutants. These can start for example from structural considerations, looking for analogues or homologues of known pollutants (e.g., brominated flame retardants, fluorinated compounds such as perfluorooctane sulfonate [PFOS]). Other approaches use results of toxicological investigations, non-target screening surveys or the combination of both – toxicity guided analysis (Biselli et al. 2005). All these are innovative but expensive as experimental studies are necessary.

The economic rational approach starts from products, which are suspected to pose possible environmental problems. This would apply for examples for substances which are likely to show biological effects – such as pesticides or pharmaceuticals. A second aspect concentrates on large volume compounds that show a possible threat just by their great amounts used and released to the environment. A prominent, classical example for this is mineral oil. More recent examples are surfactants (e.g., nonylphenol ethoxylates), additives to polymers (e.g., phthalates) or personal care products (e.g., fragrances). Although this way is in principle straight forward it is in reality often very difficult to obtain information such as production volumes from companies as these often consider this information as confidential.

The administrative way uses agreed lists of compounds of possible concern or list for priority action. Generally, these are based on tools using elements of the two other approaches. Therefore, it is a sound approach, but because of the harmonising process it is slow and presents the smallest common denominator.

Nevertheless, for monitoring authorities the lists of priority pollutants of international organisations, such as the EU, OSPAR Commission and HELCOM Commission are the most important starting points for the investigation of novel contaminants. Prioritisation procedures within the commissions help to rank the numerous compounds. For the evaluation and before establishing a monitoring programme on a routine basis, first limited surveys are needed to investigate the occurrence and distribution of new pollutants in the marine environment. Generally, these studies are first carried out on national basis.

The procedure OSPAR (and similarly HELCOM) is dealing with new hazardous substances is shown in the scheme in Fig. 19.1. The Hazardous Substance Committee (HSC) uses an evaluation process called DYNAMEC (OSPAR 2006) to identify and evaluate hazardous substances. In a step wise process it reduces a larger list of “substances of possible concern” to a small and more feasible list for “priority action”. Criteria used for the evaluation are mainly persistency, bioaccumulation

Fig. 19.1 Prioritisation processes within OSPAR and involvement of national agencies (e.g., Germany)

and toxicity (PBT compounds, Fig. 19.1, circle on the left). On the national level the German Environmental Agency (UBA) and the Federal Maritime and Hydrographic Agency (BSH) are involved in these processes. The BSH mainly contributes by gaining information on concentrations of the hazardous substances in the marine environment, which are essential for the "background paper". If no information is available, "one off surveys" will become necessary.

This procedure underlines that the process of implementing new pollutants into monitoring programs depends on field studies which identify and analyse emerging pollutants in advance or during the official prioritisation processes.

19.3 Analytical Challenges

The investigation of organic pollutants in the marine environment poses some special analytical challenges. In addition to the large number of target compounds, the very low concentrations observed in the open sea (water: pg/L, sediment: ng/kg) renders the analysis quite demanding. As consequence, special sampling and highly selective and sensitive analytical techniques are needed for the determination of both "classical" and new (emerging) organic pollutants. As concentrations in the open sea are generally two or three orders of magnitude lower than on land, for nearly all new compounds the development of new methods or at least improvements of existing procedures are necessary.

All analytical procedures use a combination of an *extraction/enrichment* step and a very sensitive and specific *analysis* (determination) technique. For "classical" non-polar pollutants the extraction is generally done by liquid–liquid extraction (LLE) with a non-polar solvent, the analysis is usually done by gas chromatography coupled with mass spectrometry (GC-MS) techniques. For most new pollutants these techniques are not successful as the mostly polar compounds are not well extracted by LLE and are too nonvolatile for GC techniques. As shown by Fig. 19.2

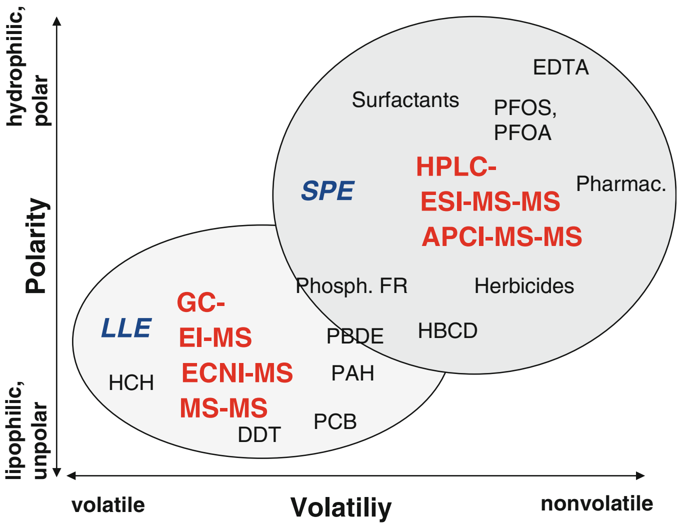

Fig. 19.2 Analytical approaches appropriate for analysis of classical and novel contaminants

for these chemical properties high performance liquid chromatography (HPLC)-MS techniques are the methods of choice. For the extraction/enrichment step a solid-phase extraction (SPE) with appropriate adsorbing phases like C18-coated silica, polymer resins, ion exchange resins or carbon phases are used.

With these techniques, ultra-trace analysis down to concentrations of about 50 pg/L is possible affording a reasonable amount of effort. However, below concentrations of ca. 10 pg/L problems are getting considerably bigger, as blanks problems increase and selectivity of normal GC-MS reaches a critical limit. To overcome these limits the following principles are used:

- Larger sample amounts
- Additional clean-up steps
- More selective detection systems

For analysing large sample amounts of 10–100 L it was necessary to develop new sampling systems. Figure 19.3 shows examples for a 100 L sampler for LLE (Theobald et al. 1990) and a SPE-extraction system for 1–30 L, which were developed by the BSH. By using larger sample amounts blank and sensitivity problems can be solved, as the signal strength of the detector increases proportional to sample amount. However, as the signals of disturbing matrix compounds increase in parallel, the selectivity finally becomes the limiting factor. By MS techniques like MS-MS or ECNI (electron capture negative ionisation) it is often possible to increase the selectivity by a factor of 10 and more. By this, additional clean-up steps which are labour intensive and susceptible to errors often can be avoided.

Fig. 19.3 Glass bowl sampler for 100 L (*left*) and SPE system for 1–30 L (*right*) water samples

Table 19.1 Analytical Methods for the analysis of WFD substances and their limit of quantitation (LOQ)

Substance	Method	LOQ (ng/L)
Brom. diphenylether	GC-ECNI-MS	–
C_{10-30}-chloroalkanes	GC-MS-MS	–
Anthracene	LLE GC-MS	0.003
Naphthalene	LLE GC-MS	0.05
PAH (6–16 compounds)	LLE GC-MS	0.003
Trichlorobenzenes	LLE GC-MS	0.005
Pentachlorobenzene	LLE GC-MS	0.005
Hexachlorobenzene	LLE GC-MS-MS	0.001
Hexachlorobutadiene	LLE GC-MS	0.01
Hexachlorocyclohexane	LLE GC-MS	0.01
Di(2-ethylhexyl)phthalate	LLE GC-MS special	5.0
Organotin compounds	LLE/Derivat. GC-AED	0.5
Nonylphenols	LLE/Derivat. GC-MS	2
Octylphenols	LLE/Derivat. GC-MS	0.5
Atrazine	SPE HPLC-MS-MS	0.3
Simazine	SPE HPLC-MS-MS	0.4
Diuron	SPE HPLC-MS-MS	0.1
Isoproturon	SPE HPLC-MS-MS	0.1
Alachlor	SPE HPLC-MS-MS	0.1
Pentachlorophenol	SPE HPLC-MS neg.	0.2
Chlorfenvinphos	SPE GC-ECNI-MS	0.02
Chlorpyrifos	SPE GC-ECNI-MS	0.01
Endosulfan	SPE GC-ECNI-MS	0.03
Trifluralin	SPE GC-ECNI-MS	0.005

With the described two extraction/enrichment techniques (LLE and SPE) and the two analysis principles (GC-MS(-MS) and HPLC-MS-MS) a powerful and quite universal analytical tool kit is available. By this, a large range of compounds with quite different chemical properties can be analysed. As demonstrated in Table 19.1, all organic substances of the WFD priority pollutants list can be determined by these techniques. However, as can be seen, it is not possible to use only one or two procedures, but in combination more than eight different GC-MS and HPLC-MS procedures are used, combined either with LLE (for non-polar substances) or SPE (for polar compounds) enrichment procedures. Limits of detection (LODs) are varying, ranging from 1 pg/L–5 ng/L and are generally sufficient to determine most pollutants in marine waters (high LODs, e.g., for phthalate esters are generally limited by blank problems).

The combination of these techniques provides a very good repertoire of methods which also allows implementing upcoming emerging contaminants relatively fast.

While it is necessary to apply a highly specific method for the determination of target compounds in order to discriminate from other pollutants and matrix compounds this high selectivity makes the analysis “blind” for other compounds. By this, new, yet unknown contaminants cannot be detected during routine analysis. In order to minimise this “blind” spot and to obtain a most comprehensive description of the environmental pollution load, samples should be additionally screened by an undirected search for new compounds (non-target screening). This is best done by GC-MS analysis in combination with a library search of the observed mass spectra. Due to the very high complexity of the sample extracts it is often necessary to pre-separate the extract into sub-fractions by a micro-preparative HPLC fractionation which are then screened by GC-MS separately (Theobald et al. 1995, Theobald 1998). By this, however, the complete screening becomes very complex and time consuming and only few selected samples can be analysed on a routine basis. In principle, such a screening should be additionally applied on polar, non-volatile compounds by HPLC-MS. However, as there are presently no comprehensive ESI- or APCI-mass spectra libraries available such a screening can be done for the present time only at a very limited basis.

In the scheme in Fig. 19.4 the different techniques are put together to a comprehensive analytical procedure enabling both target analysis and non-target screening of polar compounds. As can be seen, there is a separation between strait forward routine analysis (left side) and comprehensive screening investigations (right side).

19.4 Examples for the Investigation of Emerging Pollutants

By the methods described in Sect. 19.3, a great number of new compounds has been detected in the water phase of the North and Baltic Seas during the last 15 years. Both target and non-target analyses have been used for these investigations. In the following, a few examples for the occurrence and distribution of some of these new pollutants are presented.

19.4.1 Target-Analysis

As most of the emerging hazardous substances are more polar than the “classical” pollutants the investigations were mainly done by HPLC-MS-MS. Only trifluralin

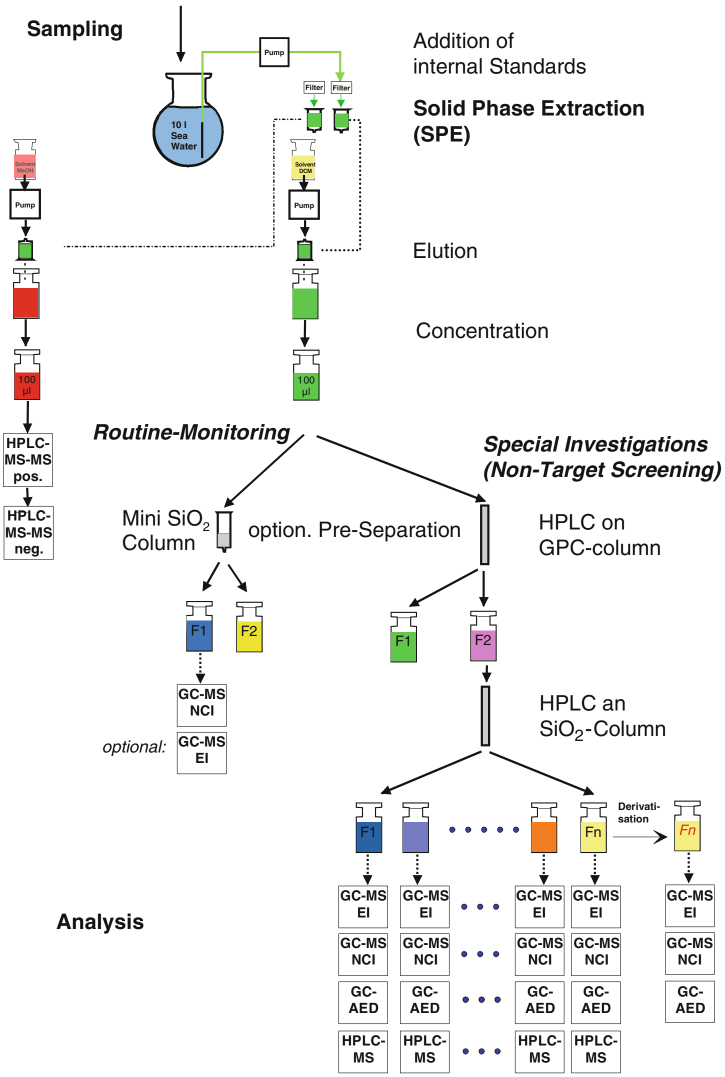

Fig. 19.4 Methods for the investigation of (polar) organic pollutants in sea water

was determined by GC-ECNI-MS. The compounds have been selected by processes described in Sect. 19.2. Examples are presented for different herbicide classes and perfluorinated compounds in the North and Baltic Seas.

Herbicides are a group of plant protection agents which are used at rather high volumes (>1,000 t/a in Europe). Compounds of all three major herbicide classes (triazines, phenylureas and phenoxyacetic acids) are found in the surface waters of the North and Baltic Seas. As an example, in Fig. 19.5 the geographical distribution

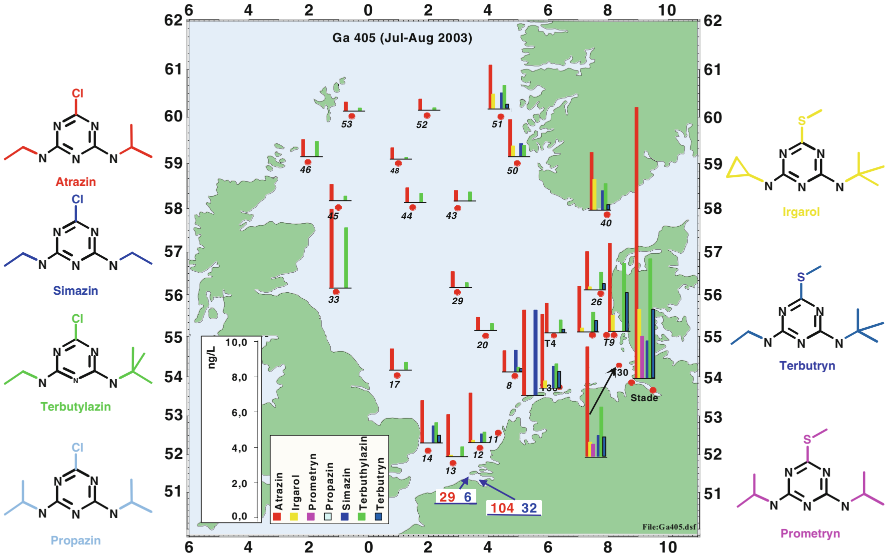

Fig. 19.5 Concentrations of triazine herbicides (ng/L) in surface water of the North Sea in Jul/Aug 2003

of the concentrations of seven triazine herbicides are shown for the surface water of the North Sea in summer 2003. The dominant herbicide was atrazine with concentrations between 4.9 ng/L (coastal) and 0.9 ng/L (open sea). In rivers like Elbe or Rhine concentrations between 30 and 104 ng/L were observed. This and the strong decreasing gradients from the coast to the open sea demonstrate that these rivers are the major input sources. The high concentrations of atrazine (and simazine as well) are quite remarkable as the use of these compounds are forbidden since the mid nineties in most European countries. As shown in Fig. 19.5 several structurally similar triazines are detected, of which terbuthylazine is the predominant one. Most compounds exhibit a very similar distribution pattern with strong gradients from the coasts to the open sea.

However, for some herbicides specific distribution patterns have been observed as well. For example, the trifluralin concentration in the surface water of the German Bight exhibits a distribution (Fig. 19.6) which does not correspond to the usual pattern with higher values along the north-Frisian coast, which is caused by inputs from the river Elbe. Instead, high values are observed at the western part of the German Bight, which can be explained either by inputs from the river Rhine or by atmospheric deposition only. In addition, this herbicide shows a remarkable seasonal variation with high values during winter time, which are more than ten times higher than in summer. The reason for these high winter concentration may be the use as pre-seeding herbicides with application times in winter and a slower degradation in winter time.

In Fig. 19.7 the distribution of the phenylurea herbicide diuron and the phenoxy acetic acid herbicide 2,4-D are shown for the surface water of the Baltic Sea. The

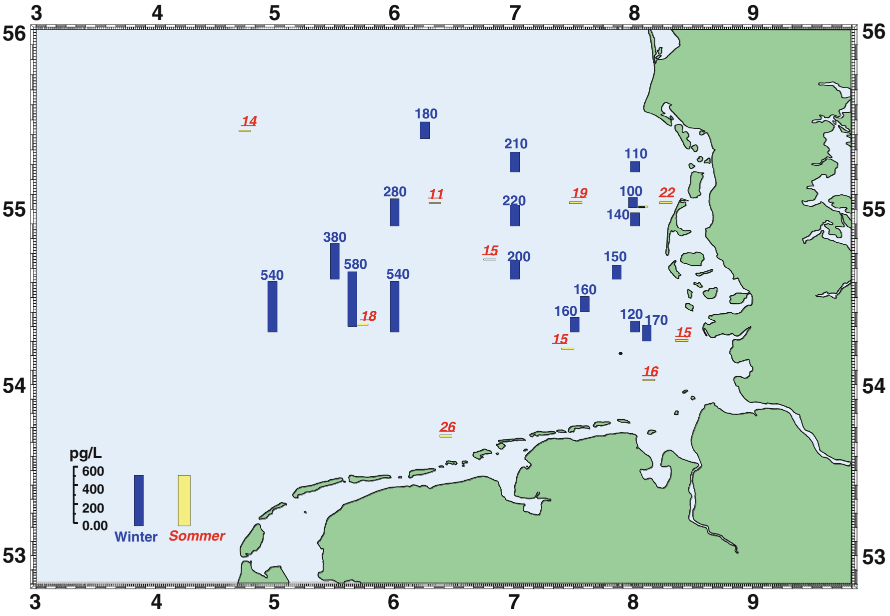

Fig. 19.6 Distribution of trifluralin concentrations (pg/L) in summer and winter (2004–2005; individual samples)

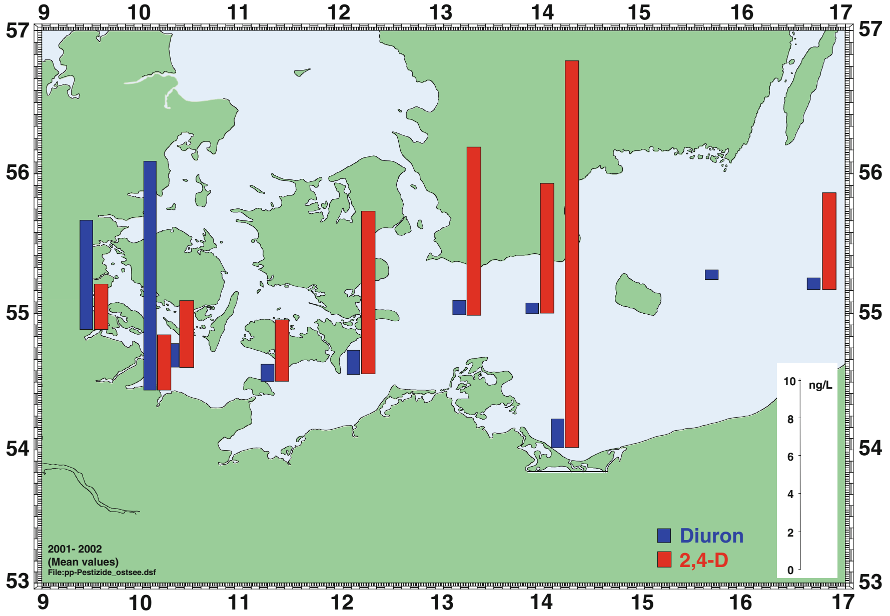

Fig. 19.7 Concentrations of Diuron and 2,4-D (ng/L) in surface water of the western Baltic Sea (Mean values 2002–2003)

two compounds show completely different spatial patterns. 2,4-D evidently has a source in the river Odra. In contrast, diuron shows high concentrations in the western region. As diuron is used not only in the agriculture but in addition as constituent of antifouling ship paints this could be explained by high ship densities and shipyards activities around Kiel and Flensburg.

Perfluorinated compounds (*PFC*s) like perfluorooctanoic acid (PFOA) and PFOS have attracted large attention as emerging pollutants during recent years. Owing to their very strong and stable carbon-fluorine bonds, these compounds are chemically nearly inert and are highly persistent in the environment. Perfluorinated organic acids are used in a large number of industrial and consumer applications, e.g., in surface treatment of textiles, carpets, and paper, and in lubricating oils, pigments, polishes, food packaging and fire fighting foams. PFOS is both an important perfluorinated surfactant and a precursor to other PFCs. Besides PFOS, also perfluorooctane sulfonamide (PFOSA), PFOA, perfluorononanoic acid (PFNoA) and perfluorohexane sulfonate (PFHxS) are used as precursors in the synthesis of PFCs or directly in numerous applications. Owing to their unique properties, large amounts of PFCs have been synthesised and used since the 1950s. Because it is bioaccumalative and toxic OSPAR and OECD classified PFOS as a PBT compound.

Nine PFCs were investigated and detected in the waters of the North Sea and western Baltic Sea (Theobald et al. 2007). In the German Bight, concentrations of the major compounds PFOA and PFOS ranged from 30 pg/L to 6 ng/L, with strong gradients from the coasts to the open sea (Fig. 19.8). The rivers Elbe and

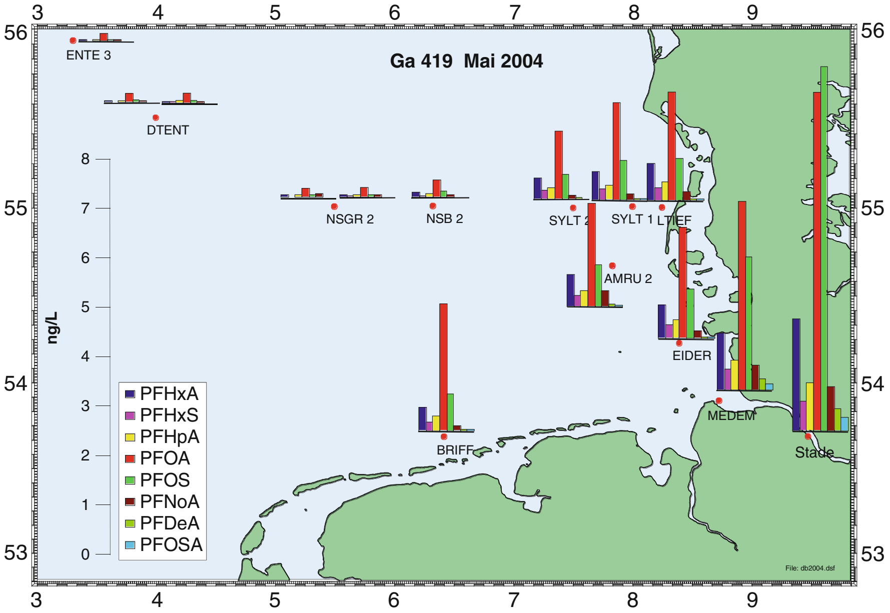

Fig. 19.8 Concentrations of perfluorinated compounds (PFCs) (ng/L) in surface water of the German Bight in May 2004

Rhine/Schelde were identified as significant input sources for the southern North Sea. In the Elbe, PFOA and PFOS concentrations ranged from 8 to 30 ng/L.

19.4.2 Non-Target Screening

As described in Sect. 19.3, non-target-screening is a very complex analysis. By screening a 100-L water extract from the Elbe estuary it was possible to separate and detect some thousand individual substances. The most abundant compounds were of natural origin and many compounds could not be identified because either no library entry matched or the spectral information was insufficient for structure elucidation. Nevertheless, many new compounds could be identified, which might be possibly of environmental concern. As examples, a few compounds identified by screening surveys of the Elbe estuary during the last years are summarised in Fig. 19.9.

The substances are grouped either according to use (pesticides, pharmaceuticals) or structural similarities (phosphorous or sulphur containing compounds). It is quite remarkable to see the large structural variety and the many application fields from which the detected substances originate.

After tentative identification of the compounds by their spectra and final proof by comparison with standards for some of the new substances quantification methods were established and their spatial distribution was investigated.

In Fig. 19.10 the concentration distribution of the pharmaceutical agent carbamazepine is shown for the German Bight. This distribution pattern with high concentrations (6–23 ng/L) along the North-Frisian coast and decreasing values to the open sea (0.08 ng/L) is typical for persistent contaminants imported by the river Elbe. The concentrations observed are considerably higher than classical pollutants like HCH or PAHs.

A further remarkable group of compounds are alkyl phosphorous esters like TBEP, TBP, TCPP (Tris-2-chloro-isopropyl)-phosphate) and TDCP, which are used as flame retardants or plasticizers. Their distribution pattern in the German Bight is different from that of carbazepine. Although there are high concentrations in the river Elbe (e.g., 132 ng/L for TCPP) and along the North-Frisian coast (15–36 ng/L) (Fig. 19.11), indicating an input by the Elbe, the decrease in concentration is less steep than for e.g., carbamazepine (see Fig. 19.10). Such a pattern can be explained by an additional input from the south west of the North Sea, e.g., by the river Rhine. The concentrations observed for TCPP are among the highest values of anthropogenic compounds in that area so far.

The examples shown so far are only a part of new substances detected in the marine environment during the last 15 years. In Table 19.2 some more examples are summarised together with their concentration ranges observed in the German Bight and in its (generally) most important input source, the river Elbe.

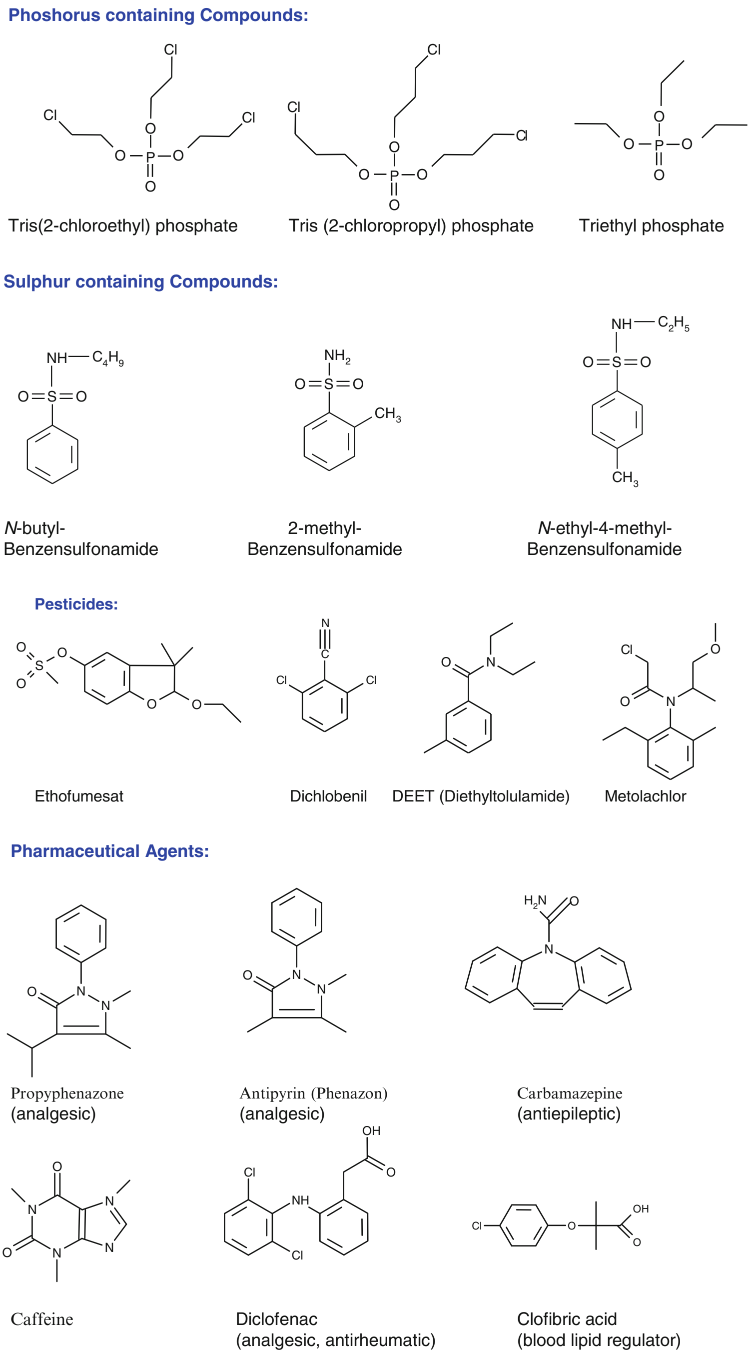

Fig. 19.9 Examples of compounds identified by non-target screening in the Elbe estuary

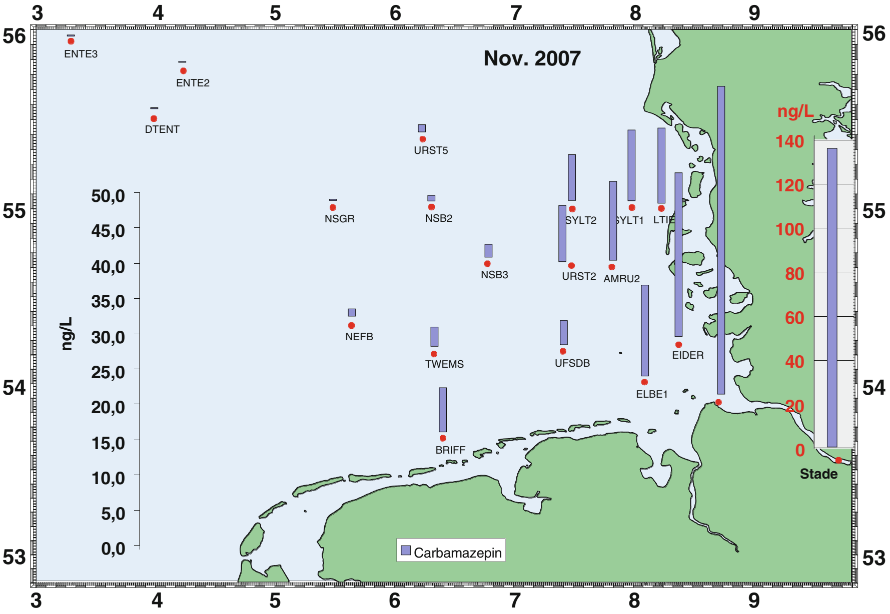

Fig. 19.10 Concentrations of carbamazepine (ng/L) in surface water of the German Bight and river Elbe in Nov. 2007 (Notice: For the Elbe a different scale is used!)

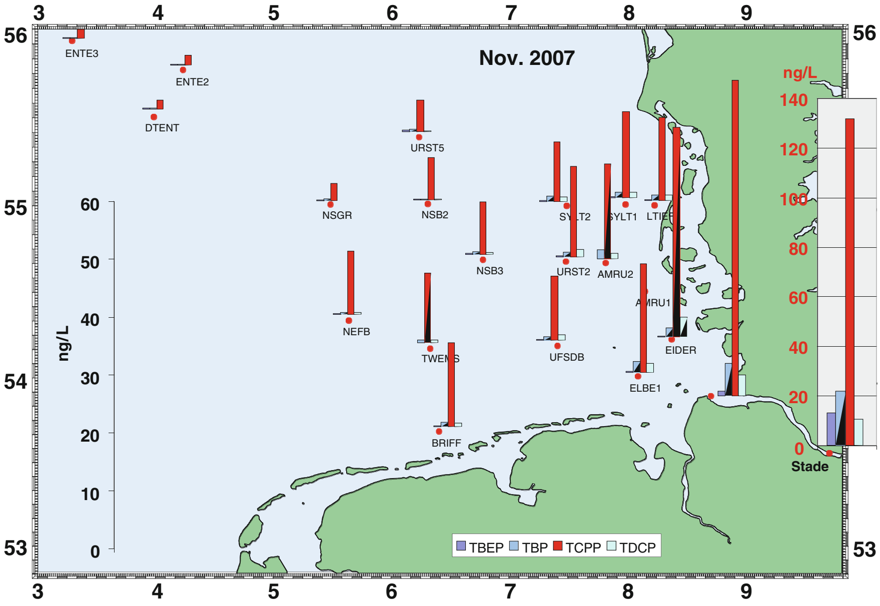

Fig. 19.11 Concentrations of alkyl phosphorous esters (ng/L) in surface water of the German Bight and river Elbe in Nov. 2007 (Notice: For the Elbe a different scale is used!)

Table 19.2 Concentrations of emerging pollutants (ng/L) in water of the river Elbe and the German Bight

Compound	List of priority substances	Min (seawater) (ng/L)	Max (seawater) (ng/L)	Max (Elbe at Stade) (ng/L)
Miscellaneous compounds				
2,5-Dichloroaniline		<0.01	0.65	8.54
3-Chloronitrobenzene	OSPAR	<0.01	0.19	0.7
4-Chloronitrobenzene	OSPAR	<0.01	0.61	8.8
2-Chloronitrobenzene	OSPAR	<0.01	0.59	8.9
2,5-Dichloronitrobenzene	OSPAR	<0.01	1.04	7.7
3,4-Dichloronitrobenzene	OSPAR	<0.01	0.27	6.1
Xanthenone		0.09	0.68	3.7
Benzothiazol		0.2	2.2	2.7
Methylbenzothiazol		0.04	1.37	55.0
Benzotriazol		0.347	25.6	183.8
Bis-(4-chlorophenyl) sulfone		0.18	2.2	0.7
Bisphenol A	OSPAR	<0.1	6	40
Tetrachloro-bis(propyl) ethers (sum of 3 isomers)		0.02	4.45	8.98
Trichloro-bis(propyl) ethers (sum of 2 isomers)		<0.001	0.2	0.46
Dichloro-bis(propyl)ethers (sum of 2 isomers)		<0.001	0.26	7.1
Bis(ethylhexyl) phthalate	EU-WFD, OSPAR	<18	38	72
Surfactants				
Nonylphenols (sum of isomers)	EU-WFD, OSPAR	0.3	63	84
Nonylphenol-monoethoxylates (sum of isomers)	OSPAR	0.7	29	46
Nonylphenol-diethoxylates (sum of isomers)	OSPAR	0.2	4.6	11
Octylphenol	OSPAR	0.1	16	18
Octylphenol-monoethoxylate	OSPAR	0.1	11	11
Octylphenol-diethoxylate	OSPAR	0.1	19	20
Pesticides				
Monobutyltin	OSPAR	<0.2	0.5	9.2
Dibutyltin	OSPAR	<0.3	1.0	12
Tributyltin	EU-WFD, OSPAR	<0.3	2.8	47
Triphenyltin	OSPAR	<0.01	0.1	0.23
Monooctyltin	OSPAR		<0.5	<0.5
Dioctyltin			<0.3	<0.3
Tricyclohexyltin			<0.05	<0.05
Atrazine	EU-WFD	<0.2	3.40	48.6
Deethylatrazine		<0.1	1.11	8.81
Irgarol		<0.02	0.25	5.75
Simazine	EU-WFD	<0.3	1.1	10.5
Terbuthylazine		<0.04	1.15	18.3

(*continued*)

Table 19.2 (continued)

Compound	List of priority substances	Min (seawater) (ng/L)	Max (seawater) (ng/L)	Max (Elbe at Stade) (ng/L)
Diuron	EU-WFD	<0.15	5.9	35.1
Isoproturon	EU-WFD	<0.04	3.4	12.7
2,4-D		<0.5	0.72	2.56
MCPA		<0.3	0.79	6.65
Mecoprop		<0.15	1.30	5.06
Bentazon		<0.05	1.34	4.61
Alachlor		<0.1	<0.1	<0.5
Trifluralin	EU-WFD	0.010	0.58	0.08
Pentachlorophenol	EU-WFD	<0.2	0.4	1.40
Chlorpyrifos-ethyl	EU-WFD	0.007	0.10	0.18
Endosulfan I	EU-WFD	<0.02	0.05	0.05
PFC				
PFBS		<0.05	3.93	0.65
PFOA		0.131	5.89	9.0
PFOS		0.037	3.13	7.9
Phosph. Esters				
TBEP		0.070	0.25	13.0
TBP		0.142	1.93	21.9
TCPP		1.536	36.29	131.5
TDCP		0.050	3.39	10.5
Pharm./Pers. Care Prod.				
Clofibrinic acid		0.000	0.78	3.52
Carbamazepine		0.078	23.15	135.4
Oxazepam		0.018	1.78	8.32
Diclofenac		0.014	1.02	46.2
Primidon		0.021	5.68	22.8
HHCB (musk fragrance)		0.15	4.8	95
AHTN (musk fragrance)		0.08	2.6	67

The “new” compounds origin from various sources and are used originally as products or intermediates in the chemical industry, as agriculture chemicals (herbicides, insecticides), surfactants, flame retardant and pharmaceuticals. Their spatial distributions in the German Bight are often very similar to those shown in Figs. 19.10 and 19.11 with more or less strong gradients from coast to open sea. As shown in Fig. 19.12 the concentrations of the new compounds are often considerably higher than those of “classical” pollutants such as PAHs and CHCs.

19.5 Discussion

The few examples described above demonstrate that a lot more pollutants are present in marine waters than the few “classical” pollutants, which are monitored since ca. 1975. They underline the necessity of constantly updating analytical procedures for investigating new, emerging pollutants in the marine environment.

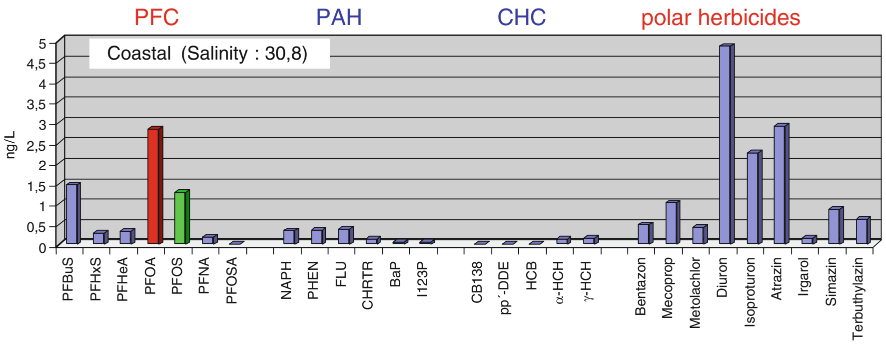

Fig. 19.12 Mean concentrations (years 2004–2005) of selected "classical" pollutants (PAH, CHC) and "new" pollutants (PFCs, herbicides) in coastal waters of the German Bight

The detected substances show quite different chemical structures and originate from many different applications and uses. Their detection in the marine environment – far from direct input sources – demonstrates that these compounds must be quite stable and persistent. The detection of these new compounds does not always mean that these compounds are really new. In many cases they are present for some years but their detection became possible by the progress of analytical techniques only.

The results show that it is worth to screen sample extracts by different MS techniques in order to identify unknown contaminants which are not yet in lists of priority substances (non-target screening). In this respect, it is essential to use any scientific information available to identify new possible pollutants and to obtain a more comprehensive picture of the contamination burden.

Although the single concentrations are mostly below acute and chronic toxic effects it should be realised that altogether, there is a complex cocktail of hazardous compounds in the marine environment with concentrations far above background values; this puts additional stress to the ecosystem, in particular, as some compounds are suspicious to be endocrine disruptors or carcinogenic.

19.6 Summary

Due to the great number of possible organic pollutants and the very low concentrations observed in the marine environment the analysis of emerging (new) pollutants is a complex and continuously demanding task. Both specific target analysis and undirected non-target screening are used to identify and determine new pollutants. While "classical" pollutants (e.g., PAH, CHC) are mostly unpolar and volatile, most of the emerging contaminants are polar and non-volatile. Therefore, many of the new compounds cannot be analysed by the commonly used GC-MS techniques but have to be analysed by HPLC-MS techniques. Since this technique is available for routine use since about the year 2000 there was a rapid evolution in detecting new pollutants. Many of the "new" pollutants are not really new compounds but their detection was new only (because of previous restriction in analysis). By the enhanced analytical possibilities many new pollutants with a great variety of chemical structures and from many different primary applications and uses have been detected in recent years. Remarkably, many of the newly detected compounds exhibits far higher concentrations in the water phase than the old, “classical” pollutants.

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Chapter 20
Analytical Methods for the Determination of Emerging Organic Contaminants in the Atmosphere

Zhiyong Xie and Ralf Ebinghaus

20.1 Introduction

Emerging organic contaminants (EOCs) include several groups of organic compounds that have been wildly distributed in the environment and attracted tremendous attention over the past decades. Analyses of EOCs in water have been reviewed in several special issues of Analytical Chemistry (Richardson and Ternes 2005; Richardson 2007). These important articles highlighted the current issues in the developments of instrumental technologies related to the detection of EOCs. In another important issue, Environmental Science and Technology published an excellent perspective in "what is emerging?" (Muir et al. 2006). This article pointed out that the longevity of a contaminant's emerging status is typically determined by whether the contaminants are persistent or have potentially harmful human or ecological effects. The EOCs discussed in this paper are selected on the basis of the reviews made for emerging contaminants in water analysis (Richardson and Ternes 2005; Richardson 2007) and review for potential candidates of persistent organic pollutants (Muir et al. 2006). The EOCs include polyfluorinated alkyl substances (PFASs), (perfluorooctanoic acid (PFOA), perfluorooctanesulfonate (PFOS) and others), brominated flame retardants (BFRs) and their degradation products, polybrominated dibenzo-p-dioxins (PBDDs), and polybrominated dibenzofurans (PBDFs), synthetic musk fragrances, organophosphate esters, alkylphenols (APs) and bisphenol A (BPA). The acronyms of individual compounds are listed in Table 20.1.

Per- and polyfluoro alkyl substances (PFASs), e.g., perfluorooctanoate (PFOA), perfluorooctane sulfonate (PFOS) perfluoro alkyl sulfonamide (PFOSA) and N-substituted sulfonamides and fluorotelomer alcohols (FTOHs) have been produced in high volumes for several decades and are widely used to make consumer products such as polymerisation aids, stain repellents in carpets, textile, and leather

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Table 20.1 Abbreviation of polyfluorinated alkyl substances, brominated flame retardants, synthetic musk fragrances, organophosphate esters, and alkylphenols

Compound	Abbreviation	CAS number	Chemical formula
Neutral PFAS			
4:2 Fluorotelomer alcohol	4:2 FTOH	2043-47-2	$C_4F_9C_2H_4OH$
6:2 Fluorotelomer alcohol	6:2 FTOH	647-42-7	$C_6F_{13}C_2H_4OH$
8:2 Fluorotelomer alcohol	8:2 FTOH	865-86-1	$C_8F_{17}C_2H_4OH$
10:2 Fluorotelomer alcohol	10:2 FTOH	678-39-7	$C_{10}F_{21}C_2H_4OH$
12:2 Fluorotelomer alcohol	12:2 FTOH	39239-77-5	$C_{12}F_{25}C_2H_4OH$
N-methyl perfluorooctane sulfonamide	NMeFOSA	31506-32-8	$C_9H_4F_{17}NO_2S$
N-ethyl perfluorooctane sulfonamide	NEtFOSA	4151-50-2	$C_{10}H_6F_{17}NO_2S$
N-methyl perfluorooctane sulfonamidoethanol	NMeFOSE	24448-09-7	$C_{11}H_8F_{17}NO_3S$
N-ethyl perfluorooctane sulfonamidoethanol	NEtFOSE	1691-99-2	$C_{12}H_{10}F_{17}NO_3S$
Ionic PFAS			
6:2 Fluorotelomer unsaturated carboxylic acid	6:2FTUCA	–	$C_8H_2F_{12}O_2$
8:2 Fluorotelomer unsaturated carboxylic acid	8:2FTUCA	70887-84-2	$C_{10}H_2F_{16}O_2$
10:2 Fluorotelomer unsaturated carboxylic acid	10:2 FTUCA	–	$C_{12}H_2F_{20}O_2$
6:2 Fluorotelomersulfonate	6:2FTS	29420-49-3	$C_8H_4F_{13}SO_3^-$
Perfluorosulfonamide	PFOSA	754-91-6	$C_8H_2F_{17}SO_2N$
Perfluorobutane sulfonate	PFBS	29240-49-3	$C_4F_9SO_3^-$
Perfluorooctane sulfonate	PFOS	2795-39-3	$C_8F_{17}SO_3^-$
Perfluorohexane sulfonate	PFHxS	355-46-4	$C_6F_{13}SO_3^-$
Perfluorodecane sulfonate	PFDcS	335-77-3	$C_{10}F_{21}SO_3^-$
Perfluorohexanoic acid	PFHxA	68259-11-0	$C_6HF_{11}O_2$
Perfluoroheptanoic acid	PFHpA	375-85-9	$C_7HF_{13}O_2$
Perfluorooctanoic acid	PFOA	335-67-1	$C_8HF_{15}O_2$
Perfluorononanoic acid	PFNA	375-95-1	$C_9HF_{17}O_2$
Perfluorodecanoic acid	PFDcA	335-76-2	$C_{10}HF_{19}O_2$
Perfluoroundecanoic acid	PFUnA	2058-94-8	$C_{11}HF_{21}O_2$
Perfluorododecanoic acid	PFDoA	307-55-1	$C_{12}HF_{23}O_2$
Perfluorotridecanoic acid	PFTrA	72629-94-8	$C_{13}HF_{25}O_2$
Perfluorotetradecanoic acid	PFTeA	376-06-7	$C_{14}HF_{27}O_2$
Alkylphenol			
Tetraoctylphenol	*t*-OP	140-66-9	$C_{14}H_{22}O$
Nonylphenol	NP	25154-52-3	$C_{15}H_{24}O$
Nonylphenol monoethoxylate	NP1EO	104-35-8	$C_{17}H_{28}O_2$
Nonylphenol diethoxylate	NP2EO	20427-84-3	$C_{19}H_{32}O_3$
Bisphenol A	BPA	80-05-7	$C_{15}H_{16}O_2$
Brominated flame retardant	BFR		
2,2 ′,4-tribromodiphenyl ether	BDE-28	41318-75-6	$C_{12}H_7Br_3O$
2,2′,4,4′-tetrabromodiphenyl ether	BDE-47	5436-43-1	$C_{12}H_6Br_4O$
2,2′,4,4′,6-pentabromodiphenyl ether	BDE-100	189084-64-8	$C_{12}H_5Br_5O$
2,2′,4,4′,5-pentabromodiphenyl ether	BDE-99	60348-60-9	$C_{12}H_5Br_5O$
2,2′,3,4,4′-pentabromodiphenyl ether	BDE-85	182346-21-0	$C_{12}H_5Br_5O$
2,2′,4,4′,5,6′-hexabromodiphenyl ether	BDE-154	207122-15-4	$C_{12}H_4Br_6O$
2,2′,4,4′,5,5′-hexabromodiphenyl ether	BDE-153	68631-49-2	$C_{12}H_4Br_6O$
2,2′,3,4,4′,5′-hexabromodiphenyl ether	BDE-138	67888-98-6	$C_{12}H_4Br_6O$
2,2′,3,4,4′,5′,6-heptabromodiphenyl ether	BDE-183	68928-80-3	$C_{12}H_3Br_7O$
2,2′,3,3′4,4′,5,5′,6,6′-decabromodiphenyl ether	BDE-209	1163-19-5	$C_{12}Br_{10}O$
1,2-bis(2,4,6-tribromophenoxy)ethane	BTBPE	37853-59-1	$C_{14}H_8Br_6O_2$
2,3,4,5,6-pentabromoethylbenzene	PEB	85-22-3	$C_8H_5Br_5$

(*continued*)

Table 20.1 (continued)

Compound	Abbreviation	CAS number	Chemical formula
Tetrabromobisphenol A	TBBPA	79-94-7	$C_{15}H_{12}Br_4O_2$
Hexabromocyclododecane	HBCD	3194-55-6	$C_{12}H_{18}Br_6$
Polybrominated dibenzo-p-dioxins	PBDDs	–	
Polybrominated dibenzofurans	PBDFs	–	
Synthesized musk fragrances			
Galaxolide	HHCB	1222-05-5	$C_{18}H_{26}O$
Tonalide	AHTN	1506-02-1	$C_{18}H_{26}O$
Traseolide	ATII	68140-48-7	$C_{18}H_{24}O$
Celestolide	ADBI	13171-00-1	$C_{16}H_{22}O$
Phantolide	AHMI	15323-35-0	$C_{17}H_{23}O$
Cashmeran	DPMI	33704-61-9	$C_{14}H_{18}O$
HHCB-lactone	HHCB-lactone	–	$C_{18}H_{21}O_2$
Musk xylene	MX	81-15-2	$C_{12}H_{15}N_3O_6$
Musk ketone	MK	81-14-1	$C_{14}H_{28}N_2O_5$
Organophosphate ester			
Trimethyl phosphate	TMP	512-56-1	$C_3H_9O_4P$
Tripropyl phosphate	TPrP	513-08-6	$C_9H_{21}O_4P$
Tributyl phosphate	TBP	126-73-8	$C_{12}H_{27}O_4P$
Tris(chloropropyl) phosphate	TCPP	13674-84-5	$C_9H_{18}Cl_3O_4P$
Tris(2-chloroethyl) phosphate	TCEP	115-96-8	$C_6H_{12}Cl_3O_4P$
Tris(1,3-dichloro-2-propyl) phosphate	TDCPP	13674-87-8	$C_9H_{15}Cl_6O_4P$
Triphenyl phosphate	TPP	115-86-6	$C_{18}H_{15}O_4P$
Tris(2-butoxyethyl) phosphate	TBEP	78-51-3	$C_{18}H_{39}O_7P$
Tris(2-ethylhexyl) phosphate	TEHP	78-42-2	$C_{24}H_{51}O_4P$
Di-n-octylphenyl phosphate	DOPP	6161-81-5	$C_{28}H_{45}O_4P$
Methyl diphenyl phosphate	MDPP	115-89-9	$C_{13}H_{13}O_4P$

and paper products. Scientific concern about PFAS increased due to their global distribution and ubiquitous detection in the environment (Hansen et al. 2002; Giesy et al. 2006; Skutlarek et al. 2006; So et al. 2004; Yamashita et al. 2005), fish and marine mammals (Houde et al. 2006; Martin et al 2004; Bossi et al. 2005), as well as in human blood (Kannan et al. 2004; Kubwabo et al. 2004; Calafat et al. 2007). Some PFAS have been shown to cause developmental delays and cancer in lab animals (Luebker et al. 2005; Molina et al. 2006). Recent studies conducted in the presence of PFAS in wildlife from the Arctic (Young et al. 2007) have demonstrated that these chemicals are widespread in these regions and accumulated in the food chain (Tomy et al. 2004). More studies are required to resolve how PFAS transport from the sources to remote regions (Wania 2007; Shoeib et al. 2004; Jahnke et al. 2007a).

The brominated flame retardants (BFRs), particularly polybrominated diphenyls (PBDEs), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD) have been used in a variety of commercial application to prevent fire EBFRIP (2006). PBDEs have 209 congeners and can be distributed into three commercial products (penta-, Octa- and deca-BDE) based on the number of bromines in the chemical structure (de Wit 2002). They are more likely to leach out of the products during the lifetime. HBCD is mainly used on expanded and extruded polystyrene for thermal insulation forms, in building and construction in order to meet required high fire safety standards. A very small application of HBCD is in high impact polystyrene, which is used for electrical and electronic appliances (EBFRIP 2006). HBCD has a strong potential to migrate into the environment (Covaci et al. 2006). Moreover, landfills containing deposited construction and demolition waste are possible sources of HBCD to air, surface waters and groundwater (Remberger et al. 2004). There is increasing evidence that penta-BDE and HBCD are globally distributed based on measurements in biota in open oceans and in the Arctic (Verreault et al. 2007). TBBPA is used primarily as a reactive flame retardant in printed circuits boards (90%) but also used as an intermediate in the production of other brominated flame retardant systems, TBBPA derivatives and brominated epoxy oligomers. TBBPA is mostly chemically bound in these applications and has no potential for emissions to the environment, while TBBPA used as an additive flame retardant in plastics can be released into the environment by emission (EBFRIP 2006). PBDDs and PBDFs are formed by thermal reactions in the presence of bromine compounds. Their chemical structures are similar to those of polychlorinated dibenzo-p-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs), implying they have similar physicochemical properties, toxicity and behaviour in the environment. PBDDs may also have a natural source in marine environment (Haglund et al. 2007).

Synthetic musk fragrances are used as low cost fragrance in personal care products and household cleaning products. The four major synthetic musk fragrances are 2,4,6-trinitro-1,3-dimethyl-5-tert-butylbenzene (musk xylene, MX), 4-aceto-3,5-dimethyl-2,6-dinitro-tert-butylbenzene (musk ketone, MK), 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8-hexamethylcyclopenta-γ-2-benzopyrane (Golaxolide, HHCB) and 7-acetyl-1,1,3,4,4,6-hexamethyl-1,2,3,4-tetrahydronaphthalene (Tonalide, AHTN) which account for 95% of those used (Rimkus 1999). Though many of these compounds can be partly removed in sewage and wastewater treatment plants, both nitro and polycyclic musk fragrances have been detected in surface water, air and biota (Peck 2006a). Atmospheric transport is supposed to be the major path for their presence in remote regions (Xie et al. 2007a).

Organophosphate esters are used on large scale as additive flame-retardant agents, plasticizers or both in diverse products, such as application in plastic material, lubricants, and electronic goods. The broad application range of organophosphate esters and the fact that they are utilized as additives may result in them spreading diffusively into the environment by volatilization, leaching and abrasion (Carlsson et al. 1997). Organophosphate esters have previously been detected in indoor air and snow (Fromme et al. 2004; Marklund et al. 2005a). It has been suggested that organophosphate esters are subject to long-range air transport (Marklund et al. 2005a).

Alkylphenol ethoxylates (APEOs) are nonionic surfactants and are used in a wide range of applications. The main application was in industrial and household detergents. Moreover, APEOs was used in many other industrial applications, e.g., as wetting agents, emulsifiers of pesticides, dispersants, solubilizers, foaming agents and polymer stabilizers (Ying et al. 2002). Concentrations of APs and their ethoxylates have been determined in different environmental compartments including air (Dachs et al. 1999). Studies have shown that volatilization and atmospheric transport should also be considered as a mechanism when determining the environmental fate of APs. Thus, methods for determination of APs in air are reviewed.

Particular attention has recently focused on bisphenol A (BPA) which is one of the chemicals with high production rate world-wide for use in many plastic products. BPA is mainly detected in aquatic ecosystems, whereas efforts have also been made to determine BPA in air (Berkner et al. 2004).

Recently, studies for understanding the distribution and transport of the EOCs from source regions to urban, rural and remote regions have become a significant issue for environmental science. Many efforts have been dedicated to developments in analytical, sampling and sample preparation techniques with the purpose to quantify and identify trace levels of these chemicals in the atmosphere. In view of the physicochemical properties of these EOCs, most common analytical methods include separation by gas chromatography (GC) followed by online mass spectrometry (MS), flame ionisation detection (FID) and electronic capture detection (ECD). GC-MS with electron capture negative ionization (ECNI) has been recognized as a sensitive and highly selective detection system for PBDEs (Richardson 2007; Hyötyläinen et al. 2002; Covaci et al. 2003). GC with nitrogen-phosphorus detection (GC-NPD) (Björklund et al. 2004) shows low detection limits, high selectivity and sensitivity for determination of organophosphate esters in air. GC-MS-MS has been recognized as a powerful tool for determination trace organophosphate esters in air upon its high sensitivity and ability for identification (Björklund et al. 2004). High performance liquid chromatography coupled to mass spectrometry (HPLC-MS/MS) and GC-MS and GC-MS/MS are the common techniques for determination of PFAS (de Voogt and Sáez 2006). Liquid chromatography-time-of-flight-mass spectrometry (LC-TOF-MS) is used for relatively polar compounds such as ionic PFAS (Barber et al. 2007; Jahnke et al. 2007a). Tollbäck et al. have developed and validated methods using LC-MS for determination TBBPA and organophosphate esters in air sample (Tollbäck et al. 2006a, b). The currently used sampling, sample preparation and analytical instruments are mentioned in Fig. 20.1.

The scope of this article focuses on the application of currently used or novel developments of analytical method in the determination of EOCs in the atmosphere. The main literature sources are the reviews and research articles reporting new developments in determination of EOCs in air within the period 2002–2007. Sampling, sample preparation and new technologies are reviewed for several classes of EOCs.

20.2 Sampling Techniques

Because the concentrations of EOCs in air are commonly at lower ng m^{-3} or pg m^{-3} levels, appropriate sampling and pre-concentration techniques are necessary to match the sensitivity of the analytical instruments. Air sampling is usually performed with active or passive sampling techniques. Active sampling techniques can

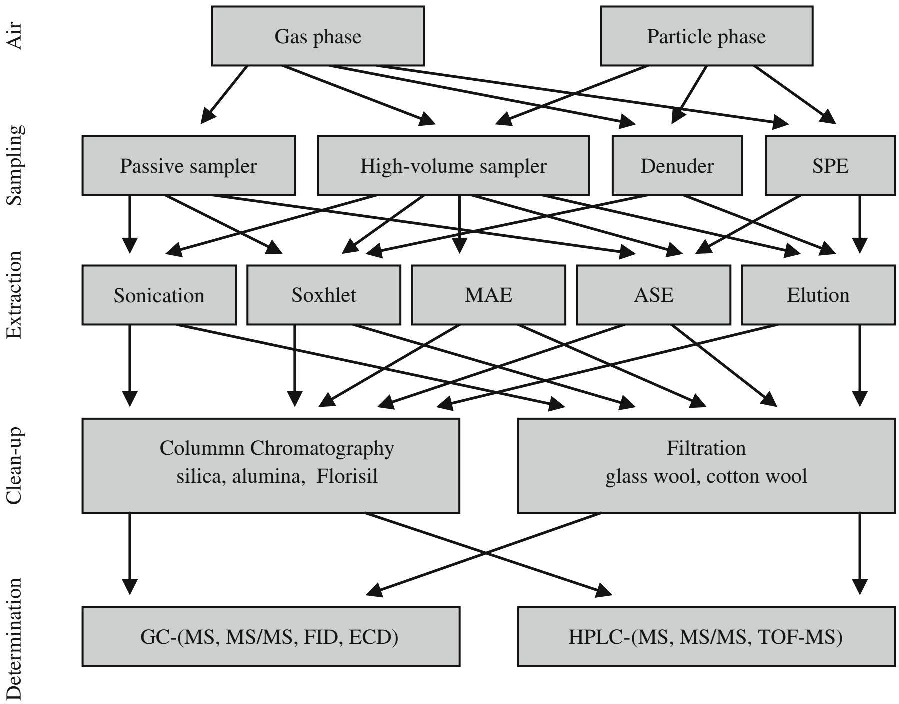

Fig. 20.1 Sampling, sample preparation and analytical instruments for the determination of emerging organic contaminants in air

collect air samples conventionally and achieve large sample volume within a couple of days. While they can be only deposited in a very limited number of sites, require electricity and are expensive. Recently, a various kind of passive air samples have been developed and applied in determination of classic persistent organic pollutants and EOCs (Harner et al. 2006). The passive sampling techniques have advantage in monitoring the distributions of EOCs in a large scale and the variation through a long time period. Nevertheless, they are usually used to collect only the EOCs in the gas phase, so that the information of the concentrations of EOCs in the particle is absent. Up to date, both active and passive sampling has been applied in the determination of EOCs in the air, which is discussed in the context.

20.2.1 Active Sampling Techniques

20.2.1.1 High Volume Sampling

A high volume sampler generally contains a high volume pump, a filter and a column with solid adsorbents. Glass fibre filters (GFF) and quartz fibre filters (QFF)

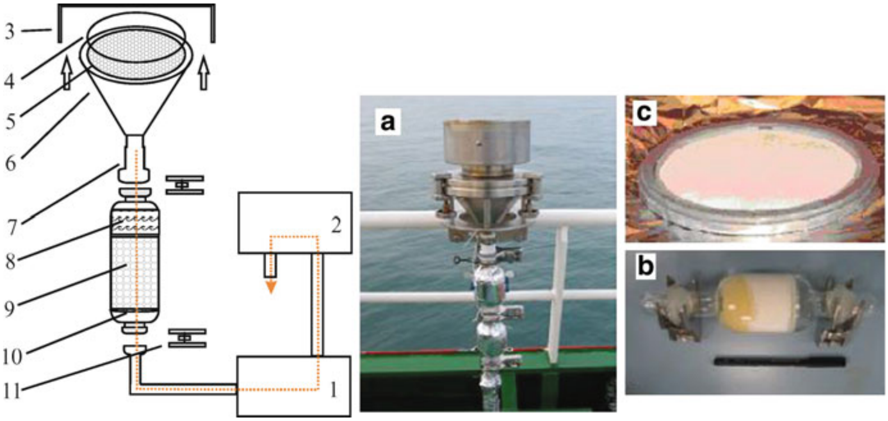

Fig. 20.2 Schematic drawing of a high-volume sampler (*left*) and operation on board (*right*). *1* High volume pump, *2* flow meter, *3* filter shelter, *4* filter (GFF/QFF), *5* metal frame for holding up the filter, *6* stainless steel filter holder, *7* connector (Teflon or other material), *8* PUF sheet, *9* XAD-2 resins, *10* glass frit, *11* adjustable clip, (**a**) air sampler, (**b**) PUF-XAD-2 column, (**c**) filter and particles

are used for collecting airborne particles, and the solid adsorbents, e.g., XAD resins, polyurethane foam (PUF) and PUF-XAD combination are applied for the gaseous phase (Strandberg et al. 2001; Sjödin et al. 2001; Martin et al. 2002). A currently used high-volume sampler is shown in Fig. 20.2. Different air flows from 100 to 500 L min^{-1} are used for collecting volumes of 500–2,000 m^3 in a matter of days to 2 weeks (Lohmann and Jones 1998). Nevertheless, long sampling duration may enhance the risk of losing compounds due to breakthrough and degradation losses of certain EOCs (Bildleman 1988). Breakthrough can be monitored by connecting two or more columns in series for sampling, or extracting the lower PUF independently of the upper one. Sometimes, the PUF is cut in two pieces and extracted separately for breakthrough check. Limited selection of new materials is applied in high volume sampling. XAD-4 has been once tested for determination of PFAS in air samples (Kaiser et al. 2005).

20.2.1.2 Diffusion Denuder

Diffusion denuder is an alternative to the high-volume sampler, which consists of a series of parallel tubes or concentric cylinders that have walls coated with a solid adsorbent or a organic liquid with high boiling point (Bildleman 1988). Vapors diffuse to the walls and are stripped from the airstreams. Particles passing through the denuder can be collected by a filter behind the denuder. Volatilized semivolatile organic compounds (SOCs) are collected in an adsorbent trap behind the filter. Thus, the sum of SOCs in the filter and backup trap represents the particle-bound fraction in the air. This technique is essential to investigate gas-particle partitioning in the atmosphere. Diffusion denuder sampling techniques have been applied to determine polycyclic aromatic hydrocarbons (PAHs), PCDDs, PCDFs and alkynes in the air (Poor et al. 2004; Possanzini et al. 2004; Volckens and Leith 2003). So far, diffusion denuders have been developed in various shapes and sizes including parallel plate (Dasgupta et al. 1997), multicapillary (Krieger and Hites 1994) and honeycomb (Mader and Pankow 2001) that are coated with various adsorbents. More recently, Tobias et al. (2007) have developed a novel method using thermal desorption of SOCs (hexachlorocyclo-hexanes (HCHs), polychlorinated biphenyl (PCBs) trapped in diffusion denuders, coupled with cryogenic preconcentration on Tenax-TA, and detection with GC-ECD. This technique can be used to determine trace concentrations of SOCs in ambient air over a range in temperature and humidity. Though application of diffusion denude in the determination of EOCs is rare at present, some advantages such as low sampling volume and short sampling time requirement, low solvent consumption, and the feasibility of online injection will lead diffusion denude to be an alternative sampling technique for the determination of EOCs in the air.

20.2.1.3 Solid-Phase Extraction

In comparison to the high-volume sampler, a number of materials were used in low volume sampling. Solid phase extraction (SPE) disks and cartridges with different adsorbents have been extensively used for indoor air monitoring and for sampling volatile organic compounds (VOCs) close to the local source (Demeestere et al. 2007). SPE C8 membrane, SPE with Isolute NH_2 and SPE disk (Empore™ Disk C_{18}) have been used for the determination of organophosphates in indoor air sampling (Solbu et al. 2007; Marklund et al. 2005b; Saito et al. 2007). The performance of SPE with Isolute ENV is evaluated for air sampling before determining PFAS in indoor and outdoor air. Tenax TA and chromosorb 106 have also been applied in the determination of organophosphate esters (Solbu et al. 2007). After sampling, Tenax TA was connected to an automatic thermodesorption unit coupled to GC-MS system.

20.2.1.4 Passive Air Sampling

Responding to a growing need for inexpensive and simple monitoring of semivolatile organic compounds (SOCs) in the atmosphere, various passive air sampler (PAS) designs and sampling media have been developed very quickly in the past 15 years. Ouyang and Pawliszyn (2007) have reviewed the design and calibration methods for passive sampling techniques. Esteve-Turrillas et al. (2007) have reviewed the perspectives and application of semipermeable membrane passive samples. In general, sampling media include semipermeable membrane devices (SPMDs), PUF discs and XAD-resin. Most of these approaches employ some kind of structure to support or shelter the sampling medium from sunlight, precipitation, and large particles.

20.2.1.5 Solid Phase Microextraction

Solid-phase microextraction (SPME) has been developed as a time and cost effective technique for sampling organic compounds in air (Pawliszyn 1997). It is widely used for sampling VOCs, or SOCs, especially in quantitative studies, using the relevant partition coefficients, Kfs, for the specific fibre and analytes involved to derive their concentrations (Ouyang and Pawliszyn 2007). Isetun et al. have developed and evaluated a sampling method using SPME with polydimethylsiloxane (PDMS) fibers for the determination of organophosphate esters in air (2004). Studies have demonstrated that accurate, highly repeatable measurements of gaseous organophosphate esters can be obtained using SPME under non-equilibrium conditions with a 100 μm PDMS fibre and sampling period of just 60 min. SPME at equilibrium using a 100 μm PDMS fibre requires at least 6 h for sampling the most volatile organophosphate esters. For accurate non-equilibrium sampling, the linear airflow must be either known or be higher than 7 cm s^{-1}. Though difficulties remain for using SPME, SPME is still an attractive sampling tool because the advantages such as no clean-up, extraction or use solvent prior to GC analysis are required.

20.2.1.6 Semi-permeable Membrane Device

Semi-permeable membrane devices (SPMDs) have been successfully tested for persistent organic pollutants (POPs) which predominantly occur in the gaseous phase, such as polychlorinated biphenyls (PCBs), hexachlorobenzene (HCB), hexachlorocyclohexanes (HCHs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-p-dioxins and –furans (PCDD/Fs) (Ockenden et al. 1998a, b; Lohmann et al. 2001). The sampling rates ($R_S = m_{SPMD}/(t{\cdot}C_{air})$), m^3 day^{-1}) of SPMDs can be estimated by comparison of the data in PAS (mSPMD, mass) and those for actively measured air concentrations (C_{air}, mass m^{-3}). SPMDs samplings have been conducted through the European Continent along a latitudinal transect from the south of the U.K. to the north of Norway to monitor the latitudinal and temporal trends of POPs including PBDEs in background air during 2000–2004 (Jaward et al. 2004; Gioia et al. 2006).

20.2.1.7 PUF Discs-Based PAS

PUF discs were an alternative and more feasible approach used in passive air sampling for monitoring the regional and global distribution of SOCs. Figure 20.3 shows the PUF discs-based PASs designed in Environment Canada (Shoeib et al. 2005; Wilford et al. 2004). The shelter for the indoor air samplers consists of a tripod support, open to the air at all sides, to minimize restriction of the generally low indoor air flows, while preventing gravitational deposition of coarse particles. The outdoor chamber design dampens the wind speed effect on uptake and protects the sample medium from precipitation, coarse aerosols and ultraviolet radiation.

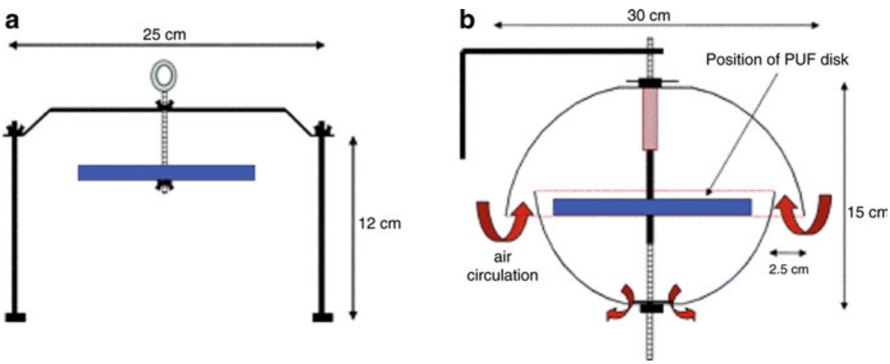

Fig. 20.3 Schematic diagram of indoor (**a**) and outdoor (**b**) PUF-based passive air samplers (Shoeib et al. 2005)

The PUF–air partition coefficient of organic compounds, KPUF-A is well correlated to their K_{OA} values (Shoeib and Harner 2002). The sampling uptake rate was 2.5 m^3 day^{-1} determined from the indoor PUF discs with PBDEs, and 3–4 m^3 day^{-1} for outdoor PUF discs determined with PCBs. Studies have shown that the indoor PAS samples mainly the gas phase with only a small contribution from fine particles. The wind effects on sampling rates were discussed in Tuduri et al. (2006).

PAS with PUF discs have been successfully applied for the determination of PBDEs over northern Europe (Gioia et al. 2007), along a north–south transect in Chile (Pozo et al. 2004) and across Asia (Jaward et al. 2005). Pozo et al. have performed a global atmospheric passive sampling study using PUF discs to assess the spatial distribution of POPs and EOCs on the planet (Pozo et al. 2006). Studies for comparison of passive and active air sampling showed that the PAS-derived concentrations of PBDEs in air in the Laurentian Great Lakes are consistent with previously reported values using high-volume air samplers (Gouin et al. 2005). Moreover, PUF discs have been used to study PFASs in indoor and outdoor air in Canada (Shoeib et al. 2005).

20.2.1.8 XAD-2-Based PAS

Wania et al. have developed a novel XAD-2-based PAS technique for POPs which is shown in Fig. 20.4 (Wania et al. 2003). Sixty milliliters of wet XAD-2 (in methanol) was packed in a mesh cylinder. The effects of wind velocity, temperature, and relative humidity on the sampling rate and efficiency of this design over the sampling period were studied. The sampling rates ranged from 0.52 to 1.97 m^3 day^{-1}. XAD-2-based PAS has been used for investigation of regional distribution of POPs (Shen et al. 2004, 2005) and PBDEs (Shen et al. 2006) in air in North America.

Other Passive air samples, such as thin film PAS (Farrar et al. 2005) and PDMS coated stir bars or silicone tubing (Wennrich et al. 2002) has been introduced for

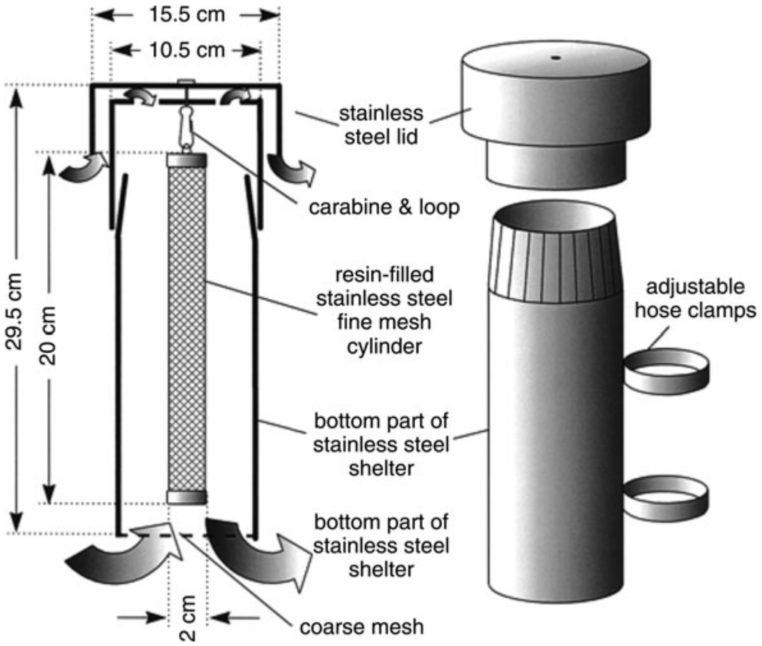

Fig. 20.4 Design and dimensions of the XAD-2-based passive air sampling system for persistent organic pollutants (Wania et al. 2003)

monitoring classic POPs. A flow-through sampler (Xiao et al. 2007) has recently been developed. The sampler consists of a horizontally oriented, aerodynamically shaped, stainless steel flow tube mounted on a post with ball bearings, which turns into the wind with the help of vanes. A series of polyurethane foam (PUF) discs with relatively large porosity mounted inside the flow tube serve as the sampling medium. The sampled air volume is calculated from wind speed recorded. Under typical wind speed conditions, the sampler can collect 100 m^3 day^{-1}, which is approaching the sampling rates of conventional high volume samplers. Application of these PASs will be interesting for the determination of EOCs.

20.3 Sample Preparation

Soxhlet and sonication have been common methods for the extraction of sampling media. Accelerated solvent extraction (ASE) and microwave-assisted extraction is becoming more important for particle samples. Thermodesorption coupled to online injection is often employed for volatile organophosphate esters and siloxane. The SPE disk and cartridge could be eluted with appropriate solvents. Next to the extraction, clean-up for the extracts has received intensive study in order to remove the matrix components. Silica, Florisil, alumina and combinations of these materials are often used to purify the extracts. Leeuwen and de Boer (van Leeuwen 2007) have reviewed the clean-up procedures for the determination of PFASs. For air samples, clean-up of extracts is not commonly applied. In some cases, glass wool (Barber et al. 2007) or cotton wool (Jahnke et al. 2007a) is used to filtrate the extracts to remove the particles.

20.4 Analytical Method for Determination of Emerging Organic Contaminants

20.4.1 Polyfluorinated Alkyl Substances

Martin et al. (2002) first developed a method for airborne fluorinated organic compounds including FTOHs (6:2, 8:2, and 10:2) and polyfluorinated sulfonamides (NEtFOSA, NEtFOSE, NMeFOSE) using GC-MS with both positive chemical ionisation (PCI) and negative chemical ionisation (NCI). Air samples were collected using high-volume air sampler employing sampling modules containing quartz-fiber filters (QFF) to collect the particle phase and glass columns with PUF-XAD-2 resins (25 g)-PUF sandwich (PUF-XAD-PUF) to collect the gaseous phase. A special procedure was applied for the extraction of both QFF and PUF-XAD-PUF columns. Instead of using classic soxhlet extraction, the authors (Martin et al. 2002) extracted XAD and PUF slits separately with methanol and ethyl acetate following soaking for 1 h. Pentadecafluoro-1-octanol (PDFO) was spiked as internal standard before roti-evaporation. The extracts were filtered through glass wool, and generally no further clean-up was necessary. Based on this sampling and sample preparation procedure, satisfying recoveries were achieved for the target compounds that ranged from 87% (10:2 FTOH) to 136% (8:2 FTOH). Breakthrough is not a concern for the high-volume sampling used in this method. Both PCI and NCI modes were optimised for determination of target analytes. The method detection limits ranged from 0.4 pg m^{-3} (4:2 FTOH) to 6.2 pg m^{-3} (NEtFOSE). It is reported that PCI was the most sensitive mode for detection of FTOHs, but NCI was the most responsive mode for NEtFOSA, NEtFOSE, and NMeFOSE. Most analytes can be confirmed by the corrected ratio relative to a standard injection in both PCI and NCI mode with the exception of 4:2 FTOH and NEtFOSA. This study highlighted the basic methodology and stirred more studies for the determination of PFASs in air.

In order to monitor the losses of target compounds during sampling and transport, Jahnke et al. (2007b, c) spiked the sampling material with five mass labelled internal standards, 6:2 FTOH (M + 4), 8:2 FTOH (M + 4), 10:2 FTOH (M + 4), NMeFOSA (M + 3), NEtFOSA (M + 5). For FTOHs in gaseous phase, the volatile 6:2 FTOH (M + 4) was generally below 50%, and the recoveries of 8:2 FTOH (M + 4) and 10:2 FTOH (M + 4) were around 100%. Satisfying recoveries were also achieved for NMeFOSA (M + 3), NEtFOSA (M + 5). These results are consistent with the breakthrough tests spiked with standard mixture, where less than 50% of 4:2 FTOH were retained on the upper columns. Considerably high recoveries were found for the N-substituted FOSEs, which are also reported in Martin et al. (2002). Reasonable explanation has been addressed to signal enhancement led by the matrix effect. Whereas the high recoveries are especially present in the extracts of PUF-XAD-PUF columns, suggesting that other unrealised reasons might exist. More recently, Dreyer et al. have optimized a method to avoid the solvent-induced response enhancement for the determination of PFASs with GC-MS (Dreyer et al. 2008). The use of acetone, dichloromethane, methyl tert-butyl ether (MTBE), and acetone: petroleum ether (1:1, v/v) resulted in recoveries bellow 100%. A mix of acetone: methyl tert-butyl ether (1:1, v/v) was chosen as suitable extraction solvent. Obviously, the data were much more reliable using the recovery correction with the coordinate internal standards. To minimize the losses of volatile PFAS, Isolute ENV + solid phase extraction (ENV + SPE) was tested for sampling indoor air (Jahnke et al. 2007c), while recoveries are more variable in comparison to those in previous work.

A method using GC-MS-EI (Shoeib et al. 2004, 2006) has been developed for the determination of sulfonamides, e.g., MeFOSE, EtFOSE and MeFOSEA. Significant changes in sensitivity were observed especially for MeFOSE and EtFOSE after numerous successive injections, whereas no change in response was observed from MeFOSEA. In another study, a passive sampler was applied for the determination of PFASs in outdoor and indoor air, which is discussed in the context (Shoeib et al. 2005).

In contrast to GC-PCI, LC-MS and LC-TOF-MS are versatile tools for the determination of ionic PFAS in air samples (Barber et al. 2007; Boulanger et al. 2005). Detailed blank problems were discussed in Barber et al. (2007) (see Table 20.2). The determination of ionic PFAS in field and lab blanks represented a much more serious contamination problem. One source of contamination related to the solvent such as methanol that may contact with the PTFE liner of the bottle cap. Another source is found to be the pressure reduction valve on the nitrogen bottle used for sample volume reduction. Additional possible sources of the contamination are not yet isolated. The method quantification limits (MQLs) of most ionic PFAS were often <1 pg m^{-3} or a few pg m^{-3}, but PFHxA, PFOS and PFNA had highly variable MQLs, even up to 56, 47 and 22 pg m^{-3} in the worst case.

For air sampling near the working place, Barton et al. (2006) used the OSHA versatile sampler (OVS) to collect gas phase and a high volume cascade impactor for particles along the fence line of a fluoropolymer manufacturing facility. Approximately 60% of the detected PFOA was associated with the <0.3 μm particle size. Both XAD-2 and XAD-4 were tested for air sampling (Kaiser et al. 2005). The column was eluted with methanol. The method was valid in the range of 0.474–47.4 μg m^{-3} for a 480 L sample.

Clean-up of air sample extracts is not commonly performed. Shoeib et al. (2006) cleaned up the extracts using 1 g alumina column (10% deactivation). Good recoveries were achieved for FTOHs (4:2–10:2), MeFOSE, EtFOSE and MeFOSEA. Boulanger et al. (2005) performed clean-up using florisil columns and eluted with ethyl acetate. Recoveries of PFOA and PFOS from clean-up and blowdown showed

Table 20.2 Typical procedure for the determination of polyfluorinated alkyl substances in air

PFCs	Sampling	Extraction	Clean-up	Separation/ detection	Column	Recovery (%)	MDL (pg m^{-3})	References
FTOHs NEtFOSA/E NMeFOSE PFOSF	PUF-XAD-2-PUF GFF	Methanol and ethyl acetate	Glass wool	GC-MS-PCI (NCI)	DB-Wax (30 m × 0.25 mm i.d., 250 μm)	87 (10:2 FTOH)-136 (8:2 FTOH)	0.15–6.2	Martin et al. 2002
FTOHs NEtFOSE, NMeFOSE, NMeFOSE	PUF-XAD-2-PUF GFF	Petroleum ether/ acetone (1/1) and dichloromethane	1 g alumina	GC-MS-PCI	DB-Wax (30 m × 0.25 mm i.d., 250 μm)	99 (8:2 FTOH)– 155 (EtFOSE) 83 (4:2 FTOH)–104 (10:2 FTOH) for clean-up	0.3–3.5 GFFs: <1.7	Shoeib et al. 2006
FTOHs NEtFOSA/E NMeFOSA/E	PUF-XAD-2-PUF GFF	Ethyl acetate	Na	GC-MS-PCI	DB-Wax (30 m × 0.25 mm i.d., 250 μm)	6:2 FTOH 8–60 8:2 FTOH 24–89 10:2 FTOH 47–100 NEtFOSA 97–155 NMeFOSA 54–145	–	Jahnke et al. 2007b
FTOHs NEtFOSA/E NMeFOSA/E 10:2 FTolefin	Isolute Env+SPE	Ethyl acetate	Na	GC-MS-PCI	DB-Wax (30 m × 0.25 mm i.d., 250 μm)	38–137 390 for 10:2 FTOH	0.3–2.1 (175 m^3)	Jahnke et al. 2007c
NEtFOSA NMeFOSA/E NMeFOSEA	PUF and GFF	Petroleum ether/ acetone and DCM	Filtration	GC-MS-EI/NCI	DB-5 (60 m × 0.25 mm i.d., 250 μm)	47–60 for soxhlet extraction	0.3–20	Shoeib et al. 2004
NEtFOSA NMeFOSA/E NMeFOSEA	PUF-based PAS	Petroleum ether/ acetone and DCM	Filtration	GC-MS-EI/NCI	DB-5 (60 m × 0.25 mm i.d., 250 μm)	47–60 for soxhlet extraction	Na	Shoeib et al. 2005
PFOA PFOS PFOSulfinate FOSA NEtFOSA/E NEtFOSAA PFOSAA	XAD-2 and GFF	Acetone/hexane	Florisil	HPLC-MS	Zorbax Extend C18 (150 mm × 2.1 mm (5 μm)) Mobile phase: 2 mM ammonium acetate and methanol	6 (PFOA), 79 (PFOS), 63 (PFOulfinate), 2 (PFOSAA), 0 (NEtFOSAA), 99 (FOSA), 106 (NEtFOSE), 102 (NEtFOSA)	Na	Boulanger et al. 2005

that PFOS, PFOSulfinate, FOSA, NEtFOSE and NEtFOSA had acceptable recoveries for both steps allowing for quantitative determination of the air sample. PFOA, PDOAA and NEtFOSAA had relatively low recoveries (0–6% for clean up), indicating strong retention on the florisil column (see Table 20.1). Powley et al. (2005) have reported a matrix effect-free method for extraction PFCAs in solid samples. Extracts are purified using dispersive solid-phase extraction with recoveries ranging from 70 to 120%. This method may be a perspective for the purification of air sample extracts.

20.4.2 Brominated Flame Retardants

BFRs, especially PBDEs, have been determined in atmospheric samples in North America, Europe, Asia-Pacific regions, and over the oceans. As shown in Table 20.4, the sampling technique usually contents of a high-volume pump, GFF/QFF for collecting particles, and a resin cartridge, a PUF plug or a mixture of resins and PUF sheet for collecting analytes in the gaseous phase. Because the concentrations of BFRs are usually from lower pg to lower ng m^{-3}, the high volume sample is necessary for the instrumental analysis. Recently, PASs has been applied in monitoring the temporal and aerial trends of PBDEs in air.

Mass spectra of PBDEs obtained from NCI mode are dominated by the ion Br^- and does not show any molecular ion, therefore the ion masses at m/z 79 and 81 are monitored in NCI mode. In contrast, EI provides better structural information, giving the molecular ions and the sequential losses of bromine atoms. The two most abundant isotope peaks correspond to molecular clusters for mono to tri-BDEs and $(M\text{-}Br_2)^+$ for tetra to hepta-BDEs. The main advantage in using NCI mode is that it provides dramatically lower detection limits than using EI mode, however, higher specificity and accuracy were obtained with EI mode. Tandem mass spectrometry techniques provide analytical specificities, but it was not widely used due to its poor sensitivity and reproducibility (Hyötyläinen and Hartonen 2002). Potential chlorinated and brominated interferences on PBDE determinations by GC-MS were discussed in Eljarrat et al. (2003). For example, coelutions occurred among BDE-47/CB-180, BDE-126/BDE-155 and BDE-153/TBBPA. Thus, the EI mode was often used to solve the bromine interference in NCI mode with additional information for the fragments of coeluted substances.

So far the measurements performed were mostly focused on the occurrence of PBDEs, very limited measurement for HBCD and TBBPA in the atmosphere have been performed solely or together with PBDEs (see Table 20.3).

20.4.2.1 PBDEs

Strandberg et al. (2001) have developed and validated a sensitive method for the determination of PBDEs in the air of the Great Lakes. QFFs and XAD-2 columns

Table 20.3 Overview of typical procedure for the determination of brominated flame-retardants in ambient air

BFRs	Sampling	Extraction	Clean-up	Separation/ detection	Column	Recovery (%)	MDL (pg m^{-3})	References
PBDEs	XAD-2 and QFF	Acetone/hexane (1:1 v:v)	Silica	GC-MS-EI/ECNI	DB5-MS (30 m × 0.25 mm, 0.25 μm) DB5-MS (15 m × 0.25 mm, 0.1 μm) for BDE 209	85–110	Na	Strandberg et al. 2001
PBDEs	PUF and QFF	Acetone/hexane	2 g alumina + 3 g silica acid	GC-MS-ECNI (methane)	DB5-MS (15 m × 0.25 mm, 0.1 μm)	99±1	0.5–3.4	Cetin and Odabasi 2007
PBDEs	PUF and GFF	DCM	Silica and Biobeads SX-3 GPC column	GC-MS-NCI (ammonium)	DB5-MS (30 m × 0.25 mm, 0.1 μm)	Na	0.3–47	Gouin et al. 2002
PBDE	PUF and QFF	DCM	Six layer column	GC-MS-NCI (methane)	12.5 m CP-Sil 13 CB (BDE 209)	67.8–114.2	0.16–0.50 (for 2,051 m^3)	Wang et al. 2005
PBDEs	PUF and GFF	DCM	Silica/alumina and GPC column	GC-MS-NCI (ammonium)	DB5-MS column	77–98	0.06–0.25 (for 1,000 m^3)	Lee et al. 2004
PBDEs	PUF and GFF	Acetone/hexane (10/7 v/v)	Acid/basic dual-layer silica	GC-MS-NCI (methane) GC-ECD	CP-Sil-8 (25 m × 0.25 mm, 0.1 μm) DB5-HT (15 m × 0.25 mm, 0.1 μm) for BDE 209	90	–	ter Schure et al. 2004
PBDEs	PUF and GFF	MAE for PUF acetone/hexane (3:2 v:v)	Silica	GC-EI-MS/MS ion trip system	CP-Sil-8 (10 m × 0.53 mm, 0.25 μm)	>75	0.04–0.7	Wurl et al. 2006
PBDEs TBE PEB	XAD-2 and QFF	Acetone/hexane (1:1 v:v)	Silica	GC-MS-EI/ECNI	DB5-MS (60 m × 0.25 mm, 0.25 μm)	>80	0.04 ng for TBE 0.01 ng for PEB	Hoh and Hites 2005; Hoh et al. 2005
PBDEs	Tissuquartz filter and XAD-2	DCM	Silica	GC-MS-NCI	–	–	–	Cahill et al. 2007
TBBPA	PUF/XAD-2, GFF	Hexane/diethyl ether (4:1 v:v) and DCM	Silica	GC-MS-EI/NCI (methane)	HP5-MS (30 m × 0.25 mm, 0.25 μm)	79	0.04 (EI)	Xie et al. 2007b
TBBPA	PUF and GFF	Ultrasonication with acetonitrile	Na	LC-MS	XterraMS C18 (150 mm × 2.1 mm, 3.5 μm) HPLC column	107 (PUF) 79 (GFF)	–	Tollbäck et al. 2006a
HBCD	PUF and GFF	Acetone	H_2SO_4 and silica	GC-MS-ECD/EI		52	1	Remberger et al. 2004

HCBD	PUF/XAD-2 and GFF	Acetone/hexane (1:1 v:v)	Silica	GC-MS-ECNI HPLC-MS-MS-ESI (Negative ionization)	DB5-MS (60 m × 0.25 mm, 0.25 μm) Eclipse XDB-C18 (250 mm × 4.6 mm) HPLC column	50–60	0.015	Hoh and Hites 2005
PBDEs	SPMD-based PAS deployed for 2 years	Dialysate in hexane for 2 × 24 h	Silica and Biobeads SX-3 GPC column	GC-MS-NCI	DB5-MS (30 m × 0.25 mm, 0.25 μm)	55–88	–	Jaward et al. 2004
PBDEs	PUF-based PAS 3 weeks for indoor air 3 months for outdoor air	Petroleum ether	Glass wool and Na_2SO_4	GC-MS-NCI	DB5 (60 m × 0.25 mm, 0.25 μm)	89–116	1.2–18 for indoor air 0.11–3.9 for out door air	Wilford et al. 2004
PBDEs	PUF-based PAS deployed for 3 months	DCM	Silica and Biobeads SX-3 GPC column	GC-MS-NCI	DB5-MS (30 m × 0.25 mm, 0.25 μm)	89–116	0.03–0.64 ng PAS^{-1}	Jaward et al. 2005
PBDEs	XAD-2-based PAS deployed for 1 year	Methanol and DCM	Silica	GC-MS-NCI (methane)	DB5-MS (60 m × 0.25 mm, 0.10 μm)	85–100	0.27–7.0 ng PAS^{-1}	Shen et al. 2006

were used to collect particle and gaseous phase compounds. After soxhlet extraction, PCB 14, 65, and 166, δ- hexachlorocyclohexane and dibutyl-chlorendate as internal standards were spiked into the samples. The extracts were cleaned up and fractionated using 3.5% water deactivated silica. GC-MS was operated in the electron capture negative ionization (ECNI) mode for quantification of BDE-209 and EI for determination of other PBDEs. BDE-209 was analyzed on a shorter DB-5-MS column to eliminate the potential risk for degradation in GC. Good recoveries were achieved for most selected PBDE congeners. This method was referred in the following studies (Hoh and Hites 2005; Cetin and Odabasi 2007). No breakthrough of PBDEs was observed for sampling media such as PUF, XAD-2 and PUF/XAD-2, suggesting the conventional high volume sampling techniques are essential for the sampling of PBDEs.

GC-MS-NCI is another efficient technique for the determination of PBDEs in air samples (99,100) with MDLs ranging between 0.3 and 47 pg m^{-3}. ter Schure et al. (2004) determined PBDEs in air samples using both GC-ECD and GC-NCI. Results from mass spectrometry determination were comparable to those with GC-ECD determination, suggesting GC-ECD is an alternative technique for determination of trace PBDEs. Wang et al. (2005) have determined PBDEs in the particle phase in the Arctic. The extracts were purified using a well-designed multilayer column chromatography composed of from bottom to top: 6 cm neutral alumina; 2 cm neutral silica; 5 cm alkaline silica; 2 cm neutral silica; 8 cm acidic silica; and 0.5 cm Na_2SO_4.

Soxhlet extraction was performed with acetone/hexane (10:7, 3:2, 1:1, v/v), DCM. The recoveries of the lower BDEs (tri- to hexa-) were between 85 and 110%, whereas the recoveries of the higher BDEs were from 50 to 60%. These results may be due to (1) strong retention of high BDEs on the sampling media, or (2) losses during column chromatography clean-up. Wurl et al. have used microwave–assisted extraction (MAE) (with 40 mL of hexane/acetone (2:3, v:v)) for extraction of PBDEs from PUF (Wurl and Obbard 2005; Wurl et al. 2006). Their recoveries were >75%. Detection was conducted using a GC-MS-MS ion trap system equipped with a CP-Si18-fused silica capillary column (10 m × 0.53 mm i.d., 0.25 μm film thickness). The MDLs of PBDEs ranged from 0.04 to 0.7 pg m^{-3}. Obviously, MAE could save solvent and extraction time, so that can be an alternative for the extraction.

Cahill et al. (2007) have developed new sampling method for determination of PBDEs in indoor and outdoor air at near-source sites. For the indoor air samples, air (13–18 L min^{-1}) was pulled through a 47 mm Tissuquartz filter to collect the particulate phase and then 6 g of XAD-2 resin to collect the gaseous phase. The sampling apparatus was constructed from stainless steel to reduce adsorption or contamination. The outdoor air samples were collected with a Tissuquartz filter for the particles and 90 g XAD-2 resin mounted in an aluminum holder for the gaseous phase. Moreover, applications of PASs for determination of PBDEs have been reviewed in the context (Jaward et al. 2004; Gioia et al. 2006; Shen et al. 2006).

20.4.2.2 HBCD

Remberger et al. (2004) have validated an analytical method and sampling procedure for the determination of HBCD in atmospheric samples taken in Sweden. The recovery of HBCD in the air samples was estimated by the added surrogate standard (ε-HCH) and was calculated to be 52%. There was no detectable HBCD present in the sample blanks. Hoh and Hites (2005) measured HBCD in air samples from east-central United States. ECNI mode at m/z 79 and 81 was used to detect and quantify HBCDs, and m/z 560.80 and 562.80 were monitored for identification. Relative HBCD isomers (α, β and γ) were analyzed using HPLC-MS with an Eclipse XDB-C18, 250 mm × 4.6 mm column for separation. The mass spectrometer was operated in negative electrospray ionization mode with multiple reaction monitoring. The $(M\text{-}H)^- \rightarrow Br^-$ transition at m/z 640.8→78.8 was monitored from the three-unlabelled HBCD isomers. $\gamma\text{-}^{13}C_{12}$-HBCD was used as internal standard and monitored at 652.8–778.8.

20.4.2.3 TBBPA

Methods for the determination of TBBPA in environmental samples have been developed based on gas chromatography-mass spectrometry (GC-MS) following derivatization of the phenolic group with diazomethane, methyl chloroformate and silylation agent (Covaci et al. 2003). Sjödin et al. (2001) have measured TBBPA in indoor air using GC-MS. A low volume sampler equipped with sampling heads of anodized aluminum containing a GFF and two PUF plugs was used. GFFs and PUFs were solvent extracted during sonication in 2 × 5 mL acetonitrile. TBBPA was first separated from the neutral substances, and allowed to react with diazomethane for 1 h in a refrigerator. The derivatives were further cleaned up on a silica/sulfuric acid column (2:1 w/w, 0.3 g). Quantification of TBBPA derivatives were performed by GC-MS-ECNI. Moreover, Tollbäck et al. have validated an analytical method using LC-MS for determination of TBBPA in air. Sampling and extraction procedures are similar to those used in Sjödin et al. (2001). The concentrated extracts passed through a syringe filter (nylon with 1 μm glass fiber filter) which resulted in recoveries of ~75%. LC-MS was operated in electrospray ionization mode. This method provided advantages that no further clean-up is required, no derivatization is necessary and enable ^{13}C-labelled TBBPA can be used as internal standard. These methods are efficient for the determination of TBBPA in indoor air or in the environment around the local source.

Xie et al. (2007b) have validated a new analytical method and sample preparation procedure for detecting TBBPA at pg m^{-3} level. Air samples were collected with GFFs and PUF-XAD-2 columns. ^{13}C-labelled TBBPA was spiked onto the PUF before sampling to monitor the entire recovery through the sampling, sample preparation and determination procedure. Derivatization has been performed with N, O-bis (trimethylsilyl) trifluoroacetamide and 1% Trimethylchlorosilane (BSTFA + 1% TMCS). Both EI and NCI modes were studied for GC-MS determination.

The mass spectra of TBBPA derivative from NCI was simple as compared to that from EI, while EI gave elevated sensitivity. The MDL was 0.04 pg m^{-3} for an average sample volume of 1,000 m^3. This method simplified the derivatization procedure and enable the authors to use ^{13}C-labelled TBBPA as internal standard and to use both EI and NCI modes for detection.

*20.4.3 Polybrominated Dibenzo-*p*-Dioxins and Dibenzofurans*

PBDDs/PBDFs have been thought to occur at very low concentrations in air as compared to PCDDs/PCDFs, and thus they are not included in monitoring programs. Harless et al. have first validated an analytical method for the determination of PBDDs/PBDFs in air (Harless et al. 1992). Samples were collected using high volume sampler with QFF and PUF plugs. After soxhlet extraction, clean-up of extracts was accomplished using an acid/base procedure followed by micro columns of silica, alumina and carbon. Samples were analyzed using high resolution GC-MS (HRGC-HRMS) operated in EI mode. Li et al. (2007, 2008) have determined PBDDs/PBDFs in air around an electronic waste dismantling area and in ambient air of Shanghai in China. The extracts were sequentially cleaned by passing through an acid silica bed, a multilayer silica column, and a Florisil column. Recoveries of labeled PBDDs/PBDFs ranged from 55 to 110%.

20.4.4 New Brominated Flame Retardants

New BFR substances have also been highlighted in recent studies (Sjödin et al. 2001). During the course of determining PBDEs in air samples, Hoh et al. (2005) realized some brominated compounds, the retention time and mass spectra of which did not match with those of any other PBDEs. Now they are known as 1,2-bis(2,4,6-tribromophenoxy)ethane (TBE or BTBPE) and pentabromoethylbenzene (PEB or PBEB). TBE and PEB in air samples were identified using GC-MS with EI mode and quantified with ECNI mode. Sjödin et al. (2001) have determined TBE in indoor air. The concentration levels of TBE were higher than those of most PBDEs, and comparable to those of BDE 209 and TBBPA.

20.4.5 Synthetic Musk Fragrances

Developments in the determination of synthetic musk fragrances in environmental matrices have been reviewed by Peck (2006). Ambient air samples were collected using high volume samples with GFF for particles and PUF, XAD-2 or PUF-XAD-2 for the gaseous phase (Xie et al. 2007a; Kallenborn et al. 1999; Peck and

Hornbuckle 2004, 2006a; Chen et al. 2007). Indoor air samples were collected using low volume samples (5 L min^{-1} for 2 m^3) with PUF (Fromme et al. 2004). Samples were extracted using DCM, hexane/diethyl ether (9:1 or 4:1, v/v) or acetone/hexane (1:1, v/v). Fromme et al. (2004) extracted the PUF using DCM with an accelerated solvent extract (ASE). Extracts were cleaned up with chromatographic column containing deactivated silica (2.5 g), silica/alumina (2:1), 8 g silica covered with 1 g Na_2SO_4, or a Pasteur pipette containing 0.75 g Florisil. Determination of synthetic musk fragrances using GC-MS with different ionisation modes has been studied in Kallenborn et al. (1999). GC-MS-EI is sensitive to both nitro musk fragrances and polycyclic musk fragrances, while GC-MS-NCI is more sensitive to nitro musk fragrances. Evaluation for the performance of two capillary columns for the determination of polycyclic musk fragrances showed that HHCB and ATII could be coeluted on a 25 m HP Ultra 2 capillary column, whereas good separation between HHCB and ATII was achieved on a J&W DB5-MS column. Several internal standards were applied to monitor the losses during sampling or sample preparation, which are musk xylene-d_9, fluoranthene-d_{10}, acenaphthene-d_{10}, phenanthrene-d_{10}, AHTN-d_3, hexamethylbenzene (HMB). It is noted that the use of AHTN-d_3 may be not suitable due to the occurrence of proton exchange during sampling treatment or GC-MS determination (Bester 2005; Buerge et al. 2003). Recoveries and detection limits are summarized in Table 20.4. Various method detection limits were determined by field or laboratory blanks related to the conditions of sampling and the laboratories. The concentrations of synthetic musk fragrances in indoor air ranged from below the MDL (10 ng m^{-3}) to 299 ng m^{-3}. HHCB and AHTN were also determined in air samples from a clean lab yielding concentrations of 1,750 and 540 pg m^{-3} (Xie et al. 2007a).

20.4.6 Organophosphate Esters

Analytical methods and sampling procedures have been developed for the determination of organophosphate esters in indoor air (Carlsson et al. 1997; Saito et al. 2007; Hartmann et al. 2004; see Table 20.5). Generally, indoor air samples were collected using GFFs for particles and backed up with a small piece of PUF for the gaseous phase. Various methods have been evaluated for detecting organophosphate esters in air samples, where the most commonly used method for quantification so far has been GC with nitrogen-phosphorus detection (GC-NPD). Björklund et al. (2004) have developed a novel analytical method using GC-MS-MS employing a softer ionisation technique, e.g., PCI for collision-induced dissociation (CID). The MDL of GC-MS-MS (PCI-CID) ranged 0.1–1.4 ng m^{-3}, which is 50 times lower than that of GC-MS-EI. Additionally, this method enables to use isotopic mass labelled compounds for quantification. LC-MS has been applied for the determination of organophosphate esters in indoor air (Tollbäck et al. 2006b). Air samples were collected on a SPE membrane and extracted on line with the cell connected to a LC-MS system via the switch valve of the LC-MS detector.

Table 20.4 Overview of typical procedure for the determination of synthetic musk fragrances in air

Musk fragrances	Sampling	Extraction	Clean-up	Separation/ detection	Column	Recovery	MDL (pg m^{-3})	References
MX, MK, HHCB, AHTN, ATII	PUF and GFF	Hexane/diethyl ether (9:1 v/v)	Silica (8 g)	GC-MS-NCI/EI	DB5-MS (30 m × 0.25 mm, 0.2 μm) Ultra 2 (25 m × 0.2 mm, 0.11 μm)	>80	Polycyclic musks: 20–50 (NCI), 5–10 (EI) Nitro Musks: 0.2–0.5 (NCI), 6–12 (EI)	Kallenborn et al. 1999
MX, MK, HHCB, AHTN, ADBI, ATII, AHMI, DPMI	XAD-2 and GFF	Hexane/acetone (1:1 v/v)	0.75 g Florisil	GC-MS-EI	HP5-MS (30 m × 0.25 mm, 0.25 μm)	56–86	–	Peck and Hornbuckle 2004, 2006b
HHCB and AHTN	PUF/XAD-2 and GFF	Hexane/diethyl ether (4:1 v/v) for PUF/XAD-2 DCM for GFF	2.5 g silica	GC-MS-EI	HP5-MS (30 m × 0.25 mm, 0.25 μm)	94–114	1	Xie et al. 2007a
HHCB, AHTN, ATII, ADBI, AHMI, MK	PUF	Hexane/diethyl ether (9:1 v/v)	–	GC-MS-EI	HP5-MS (30 m × 0.25 mm, 0.25 μm)	91–100	10,000	Fromme et al. 2004
DPMI, ADBI, AHMI, ATII, HHCB, AHTN	PUF and GFF	DCM	Silica-alumina (2:1)	GC-MS-EI	HP-5 (30 m × 0.32 mm, 0.25 μm)	57–108	–	Chen et al. 2007

Table 20.5 Typical procedure for the determination of organophosphate esters in air

Organophosphate ester	Sampling	Extraction	Clean-up	Separation/detection	Column	Recovery	MDL (pg m^{-3})	References
TMP, TEP, TPP, TBP, TCPP, TCEP, TEHP, TBEP, TDCPP, TPhP, TCP	GFF and SPE disk (Empore™ Disk C_{18}, 47 mm)	Sonication with acetone	Na	GC-FPD	DB-17 (30 m × 0.53 mm, 1 μm)	90.4–99.6	240–3,500	Saito et al. 2007
TiBP, TnBP, TPP, ToCP, TmCP, TpCP	GFF and Chromosorb 106	DCM	Na	GC-MS-EI	VF5-MS (30 m × 0.32 mm, 1 μm)	95	13,000	Solbu et al. 2007
TMP, TEP, TiPP, TnPP, TiBP, TnBP, TCEP, TCPP, TPP, TTP	GFF	DCM	Na	GC-NPD GC-PCI-CID-MS	VF5-MS (30 m × 0.25 mm, 0.10 μm)	–	100–1,400	Björklund et al. 2004
TMP, TEP, TClEP, TPP, DeuTPhP, TPhP, TBP, TClPP, TTP	C_8 SPE membrane	Hexane/diethyl ether (9:1 v/v)	Na	HPLC-MS	Apollo C18 (250 mm × 4.6 mm, 5 μm particle size)	72–107	1–19	Tollbäck et al. 2006b
TPB, TCEP, TPP, TBEP, TEHP, TCP, TCPP, TDCP	PUF	Methylene chloride	Na	GC-MS-EI	DB-5 (30 m)	62–100	–	Hartmann et al. 2004
TPeP, TMP, TPrP, TBP, TCPP, TCEP, DCPP, TPP, TBEP, TEHP, DOPP, TEEdP	SPE (25 mg Isolute NH_2)	DCM	Na	GC-NPD	DB-5 (30 m × 0.25 mm, 0.25 μm)	34–110	100–3,900	Marklund et al. 2005a
TEP, TnPP, TiBP, TnBP, TCEP, TCPP	SPME (PDMS 100 μm or 30 μm)	Thermal desorption	Na	GC-NPD	DB-5 (30 m × 0.25 mm, 0.2 μm)	–	<10	Isetun et al. 2004
TiBP, TnBP, TCEP, TCPP isomers, TBEP, TPP, TBEP, TEHP	GFF and PUF	DCM for Soxhlet and Ultrasonic extraction	Glass wool	GC-NPD GC-MS-EI/PCI GC-AED	DB-5 (30 m × 0.25 mm, 0.1 μm)	>95	–	Carlsson et al. 1997
TnBP, TCPP, TPP, TCEP, TBEP, TEHP	GFF	DMAE-SPE with Methanol	Na	LVI-GS-NPD	DB-5 MS (30 m × 0.25 mm, 0.1 μm)	97–103	61–186	Ericsson and Colmsjö 2003

The MDLs were between 1 and 8 pg m^{-3}. Saito et al. (2007) collected indoor air using QFF and SPE disk (Empore™ Disk C18, 47 mm), and extracted the filters using acetone. Extracts were analyszed with GC-FPD with a P-filter. MDLs ranged from 0.26 to 3.5 ng m^{-3}. Experiments demonstrated that the adsorbents Chromosorb 106, silica and XAD-2 all provided very good desorption efficiency of organophosphates with selected solvents such as DCM and MTBE. Chromosorb 106 showed a big advantage during sampling handling and preparation. Dynamic microwave assisted extraction (DMAE) coupled to SPE was used to extract and clean airborne particles for the determination of organophosphate esters (Ericsson and Colmsjö 2003). The system was further connected to a GC including large-volume injection. The recoveries of the organophosphate esters were greater than 97%, and the MDLs were in the range of 61–182.2 pg m^{-3}. Application of solid-phase microextraction (SPME) with PDMS for the determination of organophosphate esters was evaluated in Isetun et al. (2004). The equilibrium SPME has the advantage of making the sampling time insignificant, suggesting that this is an alternative technique for long term field sampling.

20.4.7 Alkylphenols and Bisphenol A

Air samples for determination of APs and BPA were usually collected using high volume sampler with GFF, QFF, XAD-2, PUF or PUF-XAD-2 (Dachs et al. 1999; Berkner et al. 2004; van Ry et al. 2000; Xie et al. 2006). Samples were extracted using petroleum ether and DCM, hexane/diethyl ether (9:1 or 4:1, v/v) and DCM, and hexane and hexane/acetone. Recoveries of APs in the gaseous phase were generally high than 70%, while the recoveries of APs were very variable for particle samples (Xie et al. 2006). Berkner et al. (2004) compared the efficiency of soxhlet extraction, ASE and ultrasonic extraction for particle samples. ASE showed unexpected low recoveries, which may be addressed to the fact that APs are lost in the tubing through which the extract is delivered to the vial. Both Soxhlet and ultrasonic extraction showed good recoveries. Clean-up was performed using alumina and silica. Derivatization was conducted to eliminate adsorption in the liner to improve the peak shape and increase the sensitivity of the GC-MS (Xie et al. 2006). The MDLs were in the low pg m^{-3} range. APs were also determined in indoor air and in particles with a low volume pump for air sampling (Rudel et al. 2003). Saito et al. (2004) used QFF and SPE disks (Empore disk C_{18}) to collect indoor air samples. 4-t-butylphenol, 4-n-pentylphenol, 4-n-hexylphenol, 4-n-heptylphenol, NP1EO and NP2EO were determined together with t-OP and NPs using GC-MS-EI (see Table 20.6).

Determination of BPA in air samples has been involved in (Berkner et al. 2004). Samples were collected with XAD-2 resins and GFF. BPA was derivated with BSTFA and then analyzed using GC-MS-EI. BPA-d16 was spiked as internal standard. An obvious matrix effect during the determination of BPA was observed for spiked XAD-2 resin and GFF. The average recovery in real particle samples was

Table 20.6 Typical procedure for the determination of alkylphenols and bisphenol A in air

Substances	Sampling	Extraction	Clean-up	Derivatization	Separation/ detection	Column	Recovery	MDL (pg m^{-3})	References
NPs *t*-OP	PUF and QFF	Petroleum ether DCM	8 g Alumina	No	GC-MS-EI	DB-5 (30 m × 0.25 mm, 0.25 µm)	72–90	1–5	Dachs et al. 1999; Van Ry et al. 2000
NPs *t*-OP BPA	XAD-2 and GFF	Hexane, DCM Hexane/ acetone (1:1 v/v)	3 g silica	BSTFA + TMCS PFBBr Acetic anhydride	GC-MS-EI	DB-5 (30 m × 0.25 mm, 0.25 µm)	72–78	6–44	Berkner et al. 2004
NPs NP1EO NP2EO	XAD-2 and GFF	DCM	–	BSTFA	GC-MS-EI	DB-5.625 (30 m × 0.25 mm, 0.25 µm)	60–150	3,000–6,000	Rudel et al. 2003
4-*t*-BP, 4-n-PeP, 4-HxP, *t*-OP, 4-n-OP, 4-n-NP	SPE disk and QFF	Acetone	–	BSTFA	GC-MS-EI	Ultra-1 (12 m × 0.20 mm, 0.33 µm)	83.6–94.1	150–4,500	Saito et al 2004
t-OP NP NP1EO	PUF-XAD-2 and GFF	Hexane/ diethyl ether (9:1 v/v) DCM	2.5 g Silica	BSTFA + TMCS	GC-MS-EI	HP-5 (30 m × 0.32 mm, 0.25 µm)	69–105	0.6–8	Xie et al. 2006

26% lower than for clean spiked GFFs, which is probably due to the fact that BPA could strongly bind to particles. Obviously, more efforts are necessary for achieving a moderate recovery to ensure the reliability of environmental data of bisphenol A.

20.5 Conclusion

The number of scientific papers on the determination of EOCs in air samples has rapidly increased. High volume samplers with GFF/QFF and PUF, PUF-XAD-2 combination have been extensively used for station or ship-borne sampling. New materials should be selected to make the high volume samplers suitable to sample polar compounds or relative volatile compounds, such as ionic PFASs and organophosphate esters. Care should be taken to avoid the losses of the highly volatile FTOHs. More recently, PASs have been favourably used for air sampling for evaluation of the regional and global distribution of classic POPs, while the application of PASs for the determination of EOCs is expected. Sampling media should be selected for developing new PAS techniques suitable for polar EOCs.

Studies have shown that matrix effects can enhance or suppress the responses when using LC-MS-EI and GC-MS-PCI to determine PFASs, which leads to considerable inaccuracies. Suitable clean-up steps should be set up to remove the complicated matrices from the extracts. Alternatively, matrix-assisted addition may also help to eliminate signal enhancement or suppression. Nevertheless, a robust non-discriminatory sample clean-up step must be given high priority.

PBDEs have been determined in air samples with high-volume sampling and PAS coupled to GC-MS. TBBPA, HBCD isomers and other new BFRs have been detected in air samples. Further work monitoring the levels of BFRs in air is required. Investigation should include their degradation products. Synthetic musk fragrances and alkylphenols have been measured in a few laboratories. Organophosphate esters were only measured in indoor air or near the source. Obviously, effective studies are necessary to achieve more environmental data of EOCs. Challenges towards this task will request efficient sampling with low contaminations and newly developed analytical methods.

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