Claudio Bini · Jaume Bech *Editors*

PHEs, Environment and Human Health

Potentially harmful elements in the environment and the impact on human health

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Preface

Research on potentially harmful elements (PHEs) in the environmental, agricultural and life sciences is extensively increasing since the last decades, owing to the larger consciousness of general population of the risks induced by anthropic activities to human health.

This book is dedicated to the occurrence and behaviour of PHEs in the different compartments of the environment, with special reference to soil as one of the most vulnerable ecosystems, and a precious resource with limited resilience capacity.

Current studies of PHEs in ecosystems have indicated that many industrial areas near urban agglomerates, abandoned or active mines, major road systems (highways and national roads) and ultimately also agricultural land act as sources, and at the same time sinks, of PHEs (particularly Zn, Cu, Cd). In these areas, large amounts of metals are recycled or dispersed in the environment, posing severe concerns to human health. Therefore, starting from the atmosphere (Chap. 1), through the aquatic environment (Chap. 2) and the different soil compartments (Chaps. 3, 4), the book also encompasses all the anthropic systems where PHEs play a significant role (mine and urban areas, Chaps. 5, 6). The soil-plant relationships, and the element fluxes from soil to plant and the food chain, including an overview on soil remediation, are explored in Chaps. 7, 8. In the last part of the book, trace elements join the food safety (Chap. 9) and the risk assessment (Chap. 10), concluding with potential risk to human health (Chap. 11), which is the main purpose of the whole book: to ensure a safe environment and a good quality of life to new generations.

The book provides new insight on the role and function of PHEs in the environmental and human health, following fundamental textbooks (e.g. Ferguson 1990; Adriano2001; Kabata-Pendias and Mukhejre 2007; Brevik 2013; Alloway 2013) and papers (e.g. Lag 1980, 1984; Nriagu 1988; Nriagu and Pacyna 1988; Thornton 1993; Oliver 1997; Abrahams 2002; Bernard 2008; Steinnes 2009) without forgetting recent thousands of contributions from several scientific domains, not only soil science, but also plant physiology, biology, epidemiology, medicine, and in particular oncology.

The book covers a list of most environmentally important elements involved in environmental and human health, subdivided in *key elements* and *emerging elements*. *Key elements* include: arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb), and selenium (Se). *Emerging* are those elements that have received less scientific attention, but nevertheless are of potential environmental significance, with reflection on human health: aluminium (Al), antimony (Sb), beryllium (Be), boron (B), cobalt (Co), copper (Cu), fluorine (F), iodine (I), manganese (Mn), molybdenum (Mo), nickel (Ni), thallium (Tl), tin (Sn), tungsten (W), vanadium (V), and zinc (Zn).

Thanks to the collaboration of numerous colleagues, the book outlines the state of art in PHE research in different environments and countries, and has been enforced with case studies and enriched with new data, not published elsewhere. The book will provide to stakeholders (both scientists and public administrators) and also to non-specialists a lot of data on the concentrations of metals in soils and the environment, and the critical levels so far established, in the perspective to improve the environmental quality, and the human safety.

We are grateful to colleagues who preceded us on this roadmap towards a more sustainable environment, and a better quality of life for human population.

University of Venice, Italy — Prof. Claudio Bini
University of Barcelona, Spain — Prof. Jaume Bech
Venice, 2014, June

Introduction

Chemical elements of both geogenic and anthropogenic origin are usually present in various amounts in different compartments of the environment according to the inputs, the fate and the distribution patterns that occur in the environmental ecosystems. Heavy metals, in particular, are considered to be among the most effective environmental contaminants, and their release into the environment is increasing since the last decades. Yet, they continue to receive attention due to the greater understanding of their toxicological importance in ecosystems, agriculture and human health.

Metals released in the environment may result from many different activities and sources and may enter into the environment by a wide range of processes and pathways. They can be transported, dispersed in the environment and accumulated in plants, and then may enter the food chain and from that may be taken in by human population as the final consumer, causing serious health problems as intoxication, neurological disturbances and also cancer (Bernard 2008; Steinnes 2009). Terrestrial and aquatic systems are prone to receive trace elements from emissions, airborne dust, suspended particles and solutes, and it is likely that they have higher inputs than outputs. Therefore, they can suffer from accumulation of potentially harmful substances.

Soils, in particular, are known to be an effective sink for trace elements, including those potentially harmful (PHEs), leading to their accumulation. At the same time, soils are a source of trace elements, both essential and toxic, to the biological systems. The concentration, chemical form, distribution and persistence of potentially toxic elements in soils depends on parent rocks, weathering, soil type and land use. The sulphur-seeking elements (Ag, Au, Bi, Hg, Pb, Tl) are expected to be more toxic than borderline (transition) elements, which in turn are more toxic than oxygen-seeking elements (alkaline and earth-alkaline) (Adriano 2001).

For trace elements that are essential for plant metabolism (e.g. Cu, Fe, Mo, Se, Zn), increasing concentration overcomes a possible deficiency status and so the biological activity increases until a critical point is achieved. Beyond this point, one or more trace elements will become toxic: biological activity decreases, metabolic functions are more and more lacking, and death is likely to occur (McGrath 1995).

Conversely, for trace elements that are toxic (e.g. As, Cd, Cr, Hg, Pb, Sb, Tl etc.), their concentration can be altered by mismanagement of industrial and mining activities, energy generation, traffic increase, overuse of agrochemicals, sewage sludge and waste disposal, causing contamination, environmental problems and health concerns.

On the other hand, however, also deficiencies of essential elements, such as zinc (Zn), copper (Cu) and manganese (Mn) and metalloids, such as selenium (Se) in agricultural soils may affect agricultural productivity and human health in many countries (Alloway 2013).

In contaminated soils, high concentrations of metals such as Pb, Cr, Zn, Cd, Cu, Hg and Ni are quite common. Metals such as B, Be, Al, V, Ag, Mo and Tl are less frequent. Metalloids such as As, Se and Sb and radionuclides such as U, Th, Ra, ^{137}Cs, ^{90}Sr and Po may also be present. Their availability to biological systems depends on the concentration, nature and distribution (local or diffuse contamination) of the potentially toxic elements, the site characteristics, soil type and soil properties, mainly texture, organic matter, pH and rH values, which control the balance between adsorbed and soil solution fractions.

An understanding of the natural (geochemical) and anthropogenic levels of heavy metals and metalloids in soils, their soil-plant relationships and possible toxicity or deficiency problems associated with them is nowadays a relevant concern for environmental protection, agricultural productivity and human health (Alloway 2013).

Toxicological effects of metals to humans, particularly those of As, Cd, Hg, Pb, have been well documented. Their ecological effects on aquatic, agricultural, and forest ecosystems are also well documented (Adriano 2001). Among essential elements, Cu, Fe and Zn are of considerable interest for both toxicity and deficiency, and have been thoroughly investigated. Other essential elements (Mn, Se, Cr, Co, Mo), instead, have received less attention, and need further information to ascertain their functions. Other elements such as Al, Be, Bi, Sb, Sn, Tl, V, W (here referred to as "emergent") and others are still under investigation; their role in human organisms is not yet defined, if they are somewhat essential, or critical, or even toxic.

It is generally accepted that the metal species (or the metal complex) influence in a determinant way the biological and toxicological activity of that metal. The effect induced by that element depends on its ability to enter the cell and to interact with target organs and tissues (e.g. lung, kidney, liver, brain), human fluids (blood, urine) and molecules such as enzymes and DNA. Crucial, therefore, is the knowledge of the chemical species and its characteristics: the oxidative state, solubility, binding properties and possibility to interact with other xenobiotics (Adriano 2001). Based on these assumptions, the key to achieve a more sustainable land use and, hopefully, to diminish health hazard is a better understanding of the biogeochemical processes that control trace element cycling, and the setup of a comprehensive dataset on the abundance of trace elements in abiotic and biotic environmental compartments (Kabata-Pendias and Mukhejre 2007).

A problem to address thoroughly is the lack of knowledge on residence time of trace elements, i.e. the most probable time period that any element will spend in ecosystems and, for animals and humans, the time of exposure and the likely dose-response effect of trace elements. Yet, the biological responses are complex, depending not only on metal availability and exposure, but also on the pathway of excretion, depletion, genetic adaptation and competition with other organisms (McGrath 1995). When applied to an ecosystem, toxicology becomes a new field of science – ecotoxicology – which refers to the study of effects, both direct and indirect, of toxic agents on organisms (Adriano 2001). In general, ecotoxicological research is based on single organisms and single metals, and is carried out at several levels of biological organization: molecular (e.g. RNA/DNA), cellular (enzyme, hormones, metallothioneins), individual (growth rates, target organs functioning, behavioural responses) and population (genetics, morbidity, mortality). Lower level effects, in general, respond more rapidly to toxicants, as shown by Franco et al. (2009) for DNA damage induced by PHEs.

Research in environmental geochemistry and health in the last 50 years has been addressed particularly on target PHEs such as Cd, Hg, Pb, and less attention has been paid to other PHEs; in our opinion, once the peak of knowledge on "traditional" toxic elements has passed, it is time to extend research to emerging elements for which basic knowledge concerning their occurrence and toxicity in the environment is fairly lacking: Cr, Ni, Sn, Tl (used in traditional industries but relatively little investigated); Al, Be, Bi, Sb, W (elements that are being used in new industrial processes). This is necessary in order to protect the environment, and to ascertain whether they may have influence on human diseases.

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Chapter 1
Potentially Harmful Elements in the Atmosphere

Giancarlo Rampazzo, Elena Innocente, Eliana Pecorari, Stefania Squizzato, and Gabrio Valotto

Abstract The atmosphere represents a complex system influenced by the chemical and physical processes that occur at the Earth surface. These processes include emissions, transport, lifetimes and fates of several anthropogenic and biogenic/geogenic chemicals emitted from a wide variety of sources. Among these chemicals, some are considered air pollutants, i.e. any substance present in ambient air and likely to have harmful effects on human health and/or the environment as a whole. Metals, and in general elements, are natural components of the earth's crust and constituents of all ecosystems. In the atmosphere, they are mainly related to particle phase but also they can be present in a liquid phase due to the dissolution of aerosol particles in the water drops. Whatever their origin, both natural and anthropogenic, most elements, and in particular heavy metals, are dangerous because they tend to bio-accumulate in the human body.

This chapter describes a general overview on elements and their sources and potential effects on human health in atmosphere. Furthermore, considering the increase of the interest on biological fraction of PM, a briefly description of bioaerosols will be made. Recently, the number of evidence that describes how this fraction may play a key role in the effects of PM on biological systems with negative impacts on human health and ecosystem functioning are increased.

Mathematical model applied to air pollution studies will be briefly described. Mathematical models (dispersion and transport model), that predict the concentration and the dispersion of primary and secondary pollutants in atmosphere, represent a fundamental tool in the atmospheric studies to develop health and/or environmental risk assessment and various control strategy actions. Moreover, some specific elements (Sb, Tl, V and Be) will be discussed investigating the effects on health, main sources application and reviewing the most recent studies.

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1 Introduction

In the last two centuries, the technological evolution accelerated sharply with the intensification of human activities after the Industrial Revolution. On one hand, scientific and technological knowledge increased in different areas, but on the other hand, several changes in atmospheric composition occurred, increasing interest on environmental issues. The idea of pollution is a paradox within the modern world, where the scientific and technological civilization promotes the improvement of human life quality and, on the contrary, contributes to endanger life on Earth.

Anthropogenic activities release several pollutants such as gases, aerosol and particulate matter. They are continuously emitted and the concentrations exceed those which would be naturally present in air. This leads to dangerous and harmful consequences for the living beings and also produce major threats to cultural heritage. To mitigate the underlying causes of this situation, a sustainable way must be conducted aiming to reduce the emissions from human activities (i.e.: transport emissions and industrial emissions) and to reach a compromise between industrial development and environmental well-being.

The atmosphere represents a complex system influenced by the chemical and physical processes that occur at the Earth surface. These processes include emissions, transport, lifetimes and fates of several anthropogenic and biogenic/geogenic chemicals emitted from a wide variety of sources. Among these, several substances may cause adverse effects on human health and environment as a function of chemical composition, reaction properties, emission, persistence in the environment and ability to be transported in long or short distances (Kampa and Castanas 2008). On this basis, atmospheric contamination represents a serious concern and may be invisible to humans as it begins to build and the concentrations of contaminants may be so gradual that it goes unnoticed (Farmer and Cook 2013). In addition, the chemical component is connected to the biological component. In effect, the atmospheric biological material commonly named “bioaerosol”, plays a role in air and cloud chemistry and meteorological dynamics and it’s frequently associated with allergic reaction and respiratory diseases with public health impact.

Air pollutant concentrations are strictly connected to the meteorological conditions (wind speed, humidity, temperature, solar radiation, height of the Planetary Boundary Layer, PBL) which influence both transport processes and formation processes. Under this point of view, air pollution description needs several information concerning the meteorological and geographical description of the study area and the application of chemical and physical aspects. Sampling all these variables and understanding the relationships among them could be really difficult from both logistic and economic point of view. Mathematical models represent the junction between these aspects and become fundamental tools in the atmospheric studies to develop health and/or environmental risk assessment and various control strategy actions. A description of the air pollution modeling system will be briefly described in the Sect. 3.

Among the air pollutants, most of the harmful chemical species are PM-bound, i.e. they are mainly related to the particle phase. It is generally acknowledged that specific chemicals present in PM, such as metals or polycyclic aromatic hydrocarbons (PAHs) and their derivatives, determine to a large extent the toxic potency of PM. Particulate air pollution, contains organic compounds, hydrocarbons, acid aerosols and metals attached to a carbonaceous core (De Kok et al. 2006). The World Health Organization (WHO) and the International Agency for Research on Cancer (IARC) depicts as carcinogenics or harmful for human health several elements present in atmosphere. IARC includes As, Be, Cd, Cr and Ni in Group 1 (carcinogenic to humans) and Pb, Sb, Co and V in Group 2 (probably carcinogenic to humans) (IARC 2013). Furthermore, in the Air Quality Guidelines for Europe (WHO 2000), As, Cd, Cr, Pb, Mn, Hg, Ni, Pt and V were considered in the evaluation of risk to human health. Despite this, in the European Community, just few elements have been considered in the recently UE Directive 2008/50/CE and previous ones (As, Cd, Hg, Ni, Pb). In this view, in the Sect. 4, some elements have been selected and describe considering the gap existing with respect to other much more studied elements especially in the analysis of atmospheric particulate and the potential toxicity and carcinogenicity: (i) Beryllium and related compounds are known to be human carcinogens; (ii) Vanadium is classified as possible human carcinogen by IARC (2006); (iii) Antimony and its compounds are considered pollutants of priority interest due to their potential toxicity and carcinogenicity and (iv) Thallium and related compounds are of particular scientific interest and environmental concern due to their high acute toxicity on living organisms.

1.1 Planetary Boundary Layer (PBL) and Pollutants Dispersion

Human activities and natural sources release most of the pollutants in a thin atmospheric layer well distinguishable for its chemical and physical properties. This layer, called Planetary Boundary Layer (PBL), can be defined as the portion of the troposphere directly influenced by the Earth's surface and responds to the release of energy emanating from the surface with the time scales of 1 h (Stull 1988) (Fig. 1.1). This layer is particularly characterized by well developed mixing (turbulence) generated by frictional drag as the Atmosphere moves across the rough and rigid surface of the Earth, and by the 'bubbling-up' of the air parcels from the heated surface (Oke 1987).

The reasons of the interest in PBL studies can be summarized as (Stull 1988):

- its composition needs to be continuously monitored, as the man spends most of his life in the PBL and most of human activities taking place in it;

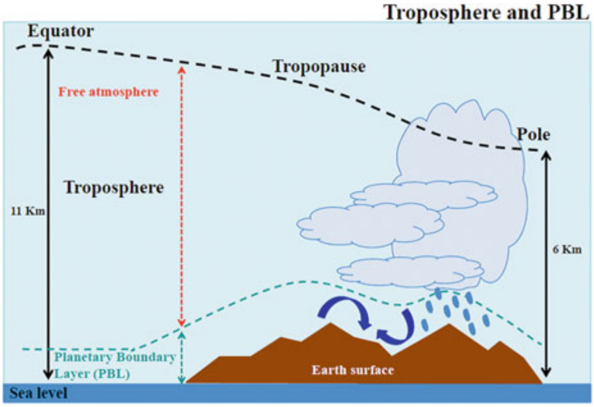

Fig. 1.1 Relationship between troposphere and planetary boundary layer

- most interest weather forecasts are that concerning the PBL;
- air pollutants emitted on the Earth surface can bet trapped in the PBL;
- processes involving fog and smog formation occur on PBL and influence what happens in it;
- the most important energy source for the Earth's atmosphere is the solar radiation that is absorbed by the Earth and transmitted to the rest of the atmosphere by thermodynamic processes that characterize the PBL;
- about 50 % of the kinetic energy of the atmosphere is dissipated in the PBL through friction and turbulence;
- the evolution of some weather phenomena, i.e. storms and hurricanes, is related to the increase of humidity in the PBL;
- most of the aerosol sources are located on the Earth surface, therefore relevant aerosol concentrations can be detected within the PBL;
- internal stratification, height and others PBL features are important in atmospheric models since they are used as input or in validation processes.

As a consequence, several studies have been conducted on PBL.

The height of the PBL (i.e. the depth of surface-related influence) is not constant with time, it depends upon the strength of the surface-generated mixing. It varies in time and space from a few hundred meters to a few kilometers following a day-night cycles. By day, when the Earth's surface is heated by the Sun, there is an upward transfer of heat into the cooler Atmosphere. This vigorous thermal mixing (convection) enables the boundary layer depth to extend to about 1 to 2 km. Conversely by night, when the Earth's surface cools more rapidly than the Atmosphere, there is a downward transfer of heat. This tends to suppress mixing and the boundary layer depth may shrink to less than 100 m. Thus in the simple case we envisage a layer of influence which waxes in a rhythmic fashion in response to the daily solar cycle (Oke 1987). On these bases, the PBL can be compare to a heat engine that is able to use solar energy as fuel to propel the air masses (Sorbjan 1989). The changes on thickness occurring in the PBL are attributable to the combination of a number of factors related to the interaction between the Earth surface and the layer of atmosphere overlying it. The influence of the Earth surface on the PBL is mainly determined from the following surface forcing, both natural and anthropogenic (Stull 1988):

- the aerodynamic drag (or air resistance) caused by viscous friction;
- the heat transfer to and from the soil, the evaporation and the evapotranspiration;
- the changes of the air flow induced by the surface roughness;
- the emissions of pollutants into the atmosphere, both from natural and anthropogenic sources, thermally inhomogeneous with respect to the surrounding environment.

As an obvious consequence PBL height and turbulence, and, consequently, pollutants dispersions, change in relation to the latitude considered, to the orography and to the land use of the local area. In particular, non-uniform terrain can produce advective effects causing changes in the thermal circulation systems considered. This peculiarity strongly affects the pollutants behavior that changes in relation to the latitude, climate and specific local meteorology.

As a result, the air pollution, mainly considered as particulate matter levels, is presented at the European level as often episodic situations. In northern Europe, thermal inversion conditions on the ground, stable atmosphere and low wind speed are the key factors leading to heavy pollution events. Moreover, even the local topography may affect, in some cases limiting the atmospheric circulation. In Northern and Central Europe, the resuspension of particles, for example from the road surface, is an important source of coarse particles. In South and Central Europe, stable atmosphere, low wind speed, meso-scale circulation patterns, topography and solar radiation are the most important factors that generate episodes of photochemical pollution, including the formation of ozone and new particles, which are commonly seen during the spring and summer (Valkama and Kukkonen 2004). Several authors have analyzed data on air quality with meteorological data relating them to interpret the levels of particulate matter and other pollutants in different European cities (e.g.: Querol et al. 2004; Kukkonen et al. 2005; Perrino et al. 2010) highlighting as the episodes of increased pollution are associated with high atmospheric pressures and events of thermal inversion.

Therefore, the episodes characterized by high levels of pollutants, especially particulate pollution, are in general primarily related to: (i) high traffic emissions, (ii) conditions of poor atmospheric dispersion at the local level (calm winds, thermal inversion), (iii) synoptic-scale climatic conditions that favor the long-distance transport of particles and (iv) natural sources of particles, in the coarse fraction, not easily controllable (sea-salt, wind dust) (Vardoulakis and Kassomenos 2008).

The concentration of any pollutant follows specific temporal cycles since the environmental phenomena and parameters that affect the dispersion of pollutants follow also cyclic behaviors (e.g.: the intensity of the solar radiation determines the variation in time of the photochemical pollutants). The variability of these factors influence above the average concentrations of pollutants in the short term (hourly or daily). These also can be caused by exceptional events that lead to high levels of pollution. The medium to long term (seasonal or annual) only marginally affected by these cyclical fluctuations or exceptional events, and changes in pollutant levels on a seasonal or annual variations can depend only on prolonged or high and specific abnormalities (Perrino et al. 2010).

Accordingly, the air pollution measured at a given site is the result of a set of processes and characteristics that make up an appropriate setting to provide an aerosol with unique features and specifications. The knowledge of local sources is a starting point for characterizing different properties of the aerosol and its components but must also be considered those phenomena that occur at larger scales (regional and long-distance). These processes may involve arrivals of air masses rich in particulate and inorganic and organic component both of natural and anthropogenic origin, which may change the characteristics of the aerosol at local level (Salvador et al. 2007).

1.2 Bioaerosol

A new field of investigation in atmospheric science consists on the study of the relationship between elements and biological component. Microbic fraction is ubiquitous in atmosphere (Polymenakou 2012) and it is commonly named "bioaerosol", as a mixture of viable and nonviable microorganisms (e.g. pollen, algae, bacteria, fungi, yeasts) as well as other types of biomass, including a wide range of antigenic compounds, dander, plant and insect debris, microbial toxins, and viruses (Lacey and West 2006; Peccia and Hernandez 2006) (Fig. 1.2). Among these, bacteria represent the most part of Earth's biomass and they have been found in every environment, even the most extreme, surviving at heat, cold, radiation, pressure, salinity, acidity, and darkness (Polymenakou 2012). Biological material is mainly originated from natural sources like soil, vegetation, water, human activity like livestock, agriculture, and industrial process as fermentation. Despite the wide variety of microorganisms, taxonomic composition of atmospheric microbial community is still poorly described, because taxonomic studies of bacterial diversity are a new interest and the knowledge about the functional potential of air microbiota is not well developed.

The interest for the biogenic fraction of aerosol has increased because the exposure at biogenic material is frequently associated with allergic reaction and respiratory diseases. It is well know that bioaerosol can be associated with a wide range of adverse health effects with public health impact, including contagious infectious diseases, acute toxic effects, allergies, flu, pneumonia, tuberculosis, legionellosis, asthma, rhinitis, bronchitis, cancer (Douwes et al. 2003; Peccia and Hernandez 2006) lead to death in debilitated people and children (Kim and Kim 2007; Burger 1990; Peccia et al. 2008). Although bacteria represent the less part of bioaerosol and infrequently can induce acute diseases, they can produce endotoxines, and peptidoglycan that seems to play a role in the change of occurrence in asthma, noninfectious airway diseases such as allergies. In the developed

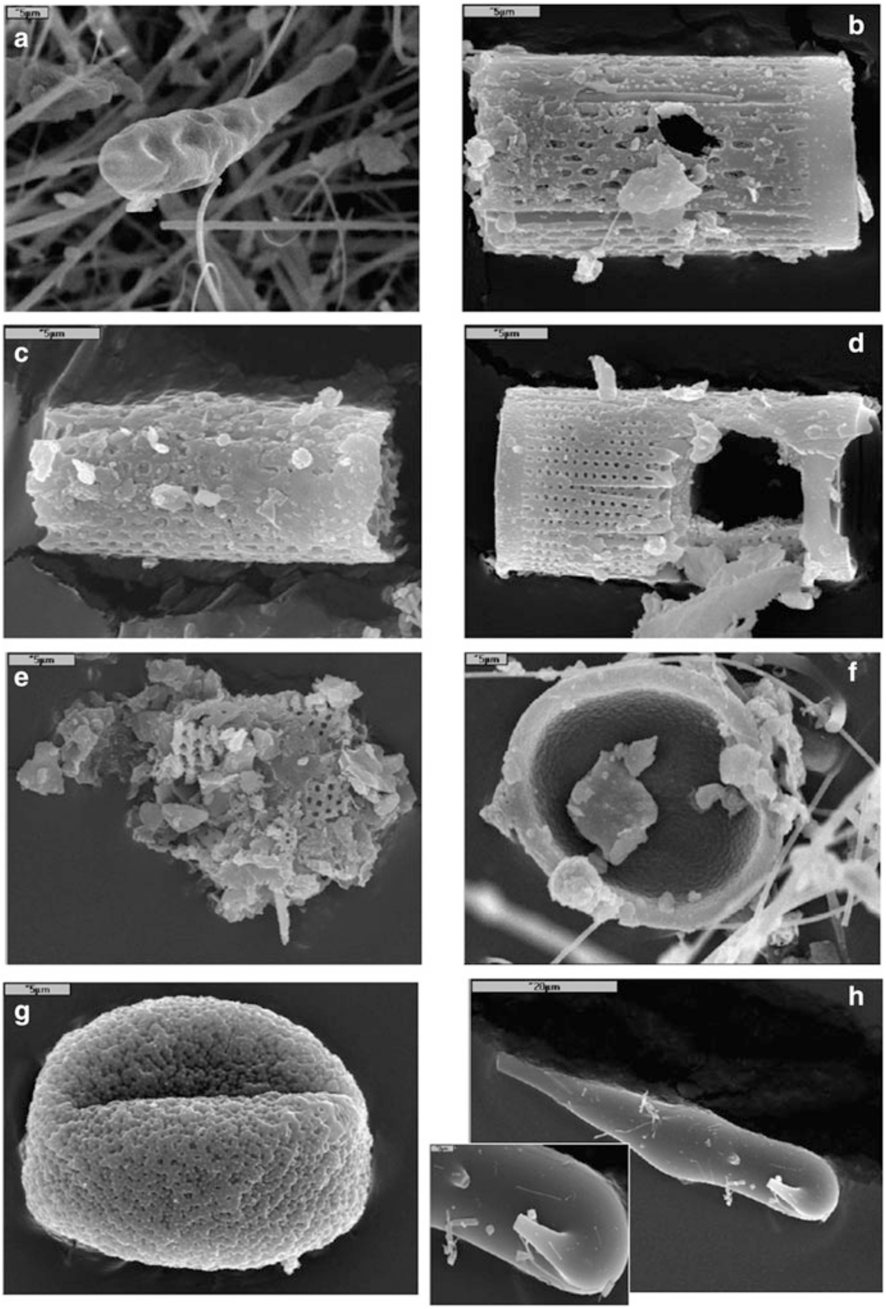

Fig. 1.2 SEM photographs of TSP and PMSEM photographs of TSP and PM 2.5, biogenic particulate matter or bioaerosols identified in dust filters from Tenerife (Canary Islands) during African dust intrusions. All samples from Las Cañadas (high mountain site), excepting **f** (Santa Cruz, coastal city). (**a**) Typically club-shaped Conidium of ascomycotan fungi (*Alternaria* sp., a cause of allergic fungal sinusitis). (**b–d**) Siliceous tests of freshwater diatoms ((**b**, **c**) *Aulacoseira*

world, allergies and asthma are a major cause of illness and disability, and the number of patient increase yearly.

In air, some studies report that bacteria, fungi and yeasts are viable in rainy drops, clouds and snow and have proposed that they play a role in air and cloud chemistry and meteorological dynamics (Amato et al. 2007a; Fuzzi et al. 1997; Deguillaume et al. 2008; Polymenakou 2012). Sattler (2001) collected bacteria from rain drop and demonstrated that bacteria, using carbon and nitrogen, are viable in rain droplet and can growth at low temperature. Moreover, bacteria are involved in chemical process in atmosphere, contributing to degradation of organic compounds (Ariya et al. 2002; Amato et al. 2007b) and transformation of dicarboxylic acids (Ariya et al. 2002).

When in air, bioaerosol can be transported by upper air currents over long distances across continents and they are find out in association with ambient particles, incorporated into water droplets of fog, clouds, and precipitation (Kuske 2006; Polymenakou 2012; Fuzzi et al 1997). Atmospheric bacteria can be deposited to earth surface via dry and wet deposition and they can generate adverse effect on ecosystem, human health or agriculture (Shinn et al. 2000).

Atmosphere represents a stressful environment for bacteria communities: low temperature are a limiting factor for cellular activity in the air even though studies have demonstrated that there is bacterial activity at subzero temperature. Another limiting factor is the presence in atmosphere of oxidants and solar radiation, although microbial cells can reduce the negative effects by the activity of specific enzymes (superoxidase or peroxydases). Bacteria are afforded to adopt several survival mechanisms: for instance at low temperature they can reduce cell size, and the thickness of capsular polysaccharide modifying their phospholipids composition. The damage due to solar radiation are prevented by the production of a wide range of pigments able to absorb from UV-B to red wavelengths, avoiding DNA damage (Polymenakou 2012).

In spite of chemical composition and the biogenic portion of atmospheric aerosol are the focus of many studies, the relationship between chemical composition and biological fraction has been poorly investigated and at today appear not clear. A recently published study (Bertolini et al. 2013) conducted in Milan, depicts that the bacteria communities were dominated by *Actinobacteridae*, *Clostridiales, Sphingobacteriales* and few *proteobacterial orders* (*Burkholderiales, Rhizobiales, Sphingomonadales* and *Pseudomonadales*). A higher abundance of *Actinobacteridae*, which are typical soil-inhabiting bacteria, has been detected in samples collected on cold days. The variation in community composition observed within seasons was comparable to that observed between seasons, thus suggesting

Fig. 1.2 (continued) granulata; (**d**) *A. islandica*), heavily eroded and worn due to the transport process. (**e**) Conglomerate of diatom test remains (presumably *Aulacoseira* spp.) with platy clay particles. (**f**) undetermined pollen grain, cross-section, containing mineral particles (Santa Cruz). (**g**) pollen grain, undetermined species. (**h**) fragmentary spicule-like particle (inset: magnification), origin (either abiotic or biological) and composition uncertain (From Delgado et al. 2010) that airborne bacterial communities show large temporal variability, even between consecutive days. The structure of airborne bacterial communities therefore suggests that soil and plants are the sources which contribute most to the airborne communities of Milan atmosphere, but the structure of the bacterial community seems to depend mainly on the source of bacteria that predominates in a given period of time. In addition, the results indicates that different bacterial communities could be found in different PM fractions, thus suggesting that a detailed investigation of the structure, temporal variability and potential sources of bacterial communities associated to PM of different sizes may disclose further insights into the ecology of bioaerosols (Bertolini et al. 2013).

2 Elements in Atmosphere

On average the atmosphere is mainly composed by a mixture of gases represented by nitrogen (which occupies 78 % of the volume of the dry air), oxygen (21 %), and other gases present in minor amounts, such as argon, neon, helium, xenon and hydrogen (Table 1.1). These gases present constant concentration in time and within the PBL. In addition, several substances can be detected in the atmosphere, in gaseous, solid or liquid phase, emitted from natural and anthropogenic sources and some of these are considered air or atmospheric pollutants (e.g.: greenhouse gases, chlorofluorocarbons (CFC), carboncompounds, carbonmonoxide (CO) and hydrocarbons).

Air pollutant can be defined as any substance present in ambient air and likely to have harmful effects on human health and/or the environment as a whole (European Community 2008). Primary pollutants or components are defined as those emitted directly into the air, e.g., SO_2, NO_x, CO, Pb, organics and combustion-generated particulate matter (PM). Once in the atmosphere, they are subjected to dispersion and transport and simultaneously to chemical-physical reaction forming secondary pollutants in gaseous or particulate phase. Both primary and secondary components are removed from the atmosphere via wet or dry deposition and can impact a variety of receptors, for example, humans, animals, aquatic ecosystem, forest and agricultural crops, and materials. Briefly, air pollutants can be grouped in four categories: (i) gaseous pollutants; (ii) persistent organic pollutants; (iii) heavy metals and (iv) particulate matter. Heavy metals, include basic metals elements such as lead, mercury, cadmium, silver, nickel, vanadium, chromium and manganese (Kampa and Castanas 2008) and the main emission sources are combustion of fuels in stationary sources for As, Cd, Cr, and Ni (more than a half of the total anthropogenic emissions) and combustion of gasoline for lead (Pacyna et al. 2007).

Metals, and in general elements, are natural components of the earth’s crust and constituents of all ecosystems. In atmosphere, they are mainly related to particle phase but also their can be present inside a liquid phase due to the dissolution of aerosol particles in the water drops. They cannot be degraded or destroyed, and can be transported by air, and enter water and human food supply (Kampa and Castanas

Table 1.1 Chemical composition of the atmosphere

Constituent	Fractional concentration by volume
Nitrogen (N_2)	78.08 %
Oxygen (O_2)	20.95 %
Water vapor (H_2O)	0–4 %
Argon (Ar)	0.93 %
Carbon dioxide (CO_2)	0.04 %
Neon (Ne)	18 mg L^{-1}
Helium (He)	5 mg L^{-1}
Methane (CH_4)	1.7 mg L^{-1}
Hydrogen (H_2)	0.5 mg L^{-1}
Ozone (O_3)	0.4 mg L^{-1}
Nitrous oxide (N_2O)	0.3 mg L^{-1}

2008), moving between atmosphere, hydrosphere, lithosphere, and biosphere. The dispersion and distribution of metals are highly dependent on the size of the particles and on the surface properties of the substrate on which the metals are deposited. Figure 1.2 represents fluxes and transfers of elements between the major environmental pools in a urban environment. The represented conceptual model of urban biogeochemical cycles, proposed by Kaye et al. (2006), includes major elemental pools (boxes), transformations of materials within those pools (dotted arrows), fluxes among pools (solid arrows), and controls on these fluxes (bowties). The urban ecosystem can be 'black boxed' such that only inputs and outputs to the entire system are measured (the largest box in Fig. 1.3), or internal components (land, atmosphere and hydrosphere) of the system can be studied. Humans control five dominant drivers of biogeochemical cycling: (i) hydrology (humans build impervious surfaces and drainage networks that alter aqueous flow paths and elemental transport) (Fig. 1.3a); (ii) atmospheric chemistry (elevated CO_2, NO_x, ozone, organic aerosols and metals in urban atmospheres interact to alter plant growth and ecosystem carbon and nitrogen cycling) (Fig. 1.3b); (iii) climate (urban heat islands and irrigation alter evaporation, transpiration and probably other biogeochemical process rates) (Fig. 1.3c); (iv) nutrients (food and fertilizer cycling affect plant growth and interact with human-dominated hydrology and atmospheric chemistry) (Fig. 1.3d); and (v) vegetation and land-use (humans impose a variable distribution of land use types within and around cities, and within each land-use type, they exert strong control over plant composition and, thus, ecosystem function) (Fig. 1.3e) (Kaye et al. 2006).

Elements deposited on land in an urban setting can be readily relocated and dispersed by wind, rain, and surface runoff (Swaine 2000; Callender and Rice 2000). Therefore, metal compounds are also increasingly introduced in the environment and could finally accumulate in a/biotic systems. In addition, acidification (e.g. upon acid rain fall) may increase their bioavailability and possibly raise their toxic potential (Florea and Büsselberg 2006). Most elements, and in particular heavy metals, are dangerous because they tend to bio-accumulate in the human body. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the

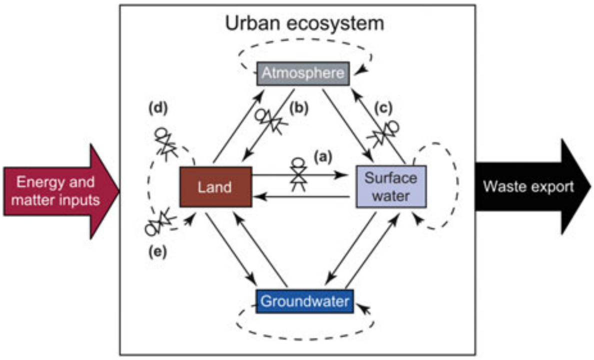

Fig. 1.3 Conceptual model of urban biogeochemical cycles (From Kaye et al. 2006)

environment. Compounds accumulate in organisms any time they are taken in and stored faster than they are broken down (metabolized) or excreted (Kampa and Castanas 2008).

2.1 *Overview on Main Emission Sources*

The atmosphere concentrations of PM and related elements are mainly a function of the emission sources. Natural emissions derive from different kind of processes acting on crustal minerals (e.g. erosion, surface winds and volcanic eruptions), as well as from natural burning and from the oceans. On a global scale, the contribution of resuspended surface dust represents about 50 % of natural emissions of Cr, Mn, V and more than 20 % of Cu, Mo, Ni, Pb, Sb and Zn. Similar, volcanic eruption release about 20 % of Cd, Hg, As, Cr, Cu, Ni, Pb and Sb. The marine aerosol, generated by the action of wind and waves, may contribute to approximately 10 % of the emissions of trace metals. The combustion of biomass can contribute to emissions of Cu, Pb and Zn (Grgić 2008).

The main anthropogenic sources are linked to high temperature combustion processes, biomass burning, fossil fuel combustion, incinerator and industrial activities. Anthropogenic processes release metals in vapour phase that can form new particles by condensation or gas-to-particle conversion processes. Fossil fuels combustion represents the most important anthropogenic sources of Be, Co, Hg, Mo, Ni, Sb, Se, Sn and V (Moreno et al. 2006; Grgić 2008) and contributes to the emissions of Cu, Mn and Zn. As, Cd, Cu, Ni and Zn primarily derived from steelworks (Moreno et al. 2006), coal combustion (Lin et al. 2005; Lim et al. 2010) and zinc metallurgy (Querol et al. 2007). V and Ni are linked to coal and oil combustion (Almeida et al. 2005; Elminir 2005; Hueglin et al. 2005; Moreno et al. 2007).

Vehicular traffic emits a wide range on elements deriving from exhaust gas of gasoline and diesel vehicles (Fe, Ba, Br, Pb, Cu, Zn, Cd) (Sternbeck et al. 2002; Moreno et al. 2006), tyre wear abrasion (Zn), lubrificant (Sb) and fillers (Ba, Ca)

(Thorpe and Harrison 2008), while Mn and Pb are related to the erosion of the road surface (Amato et al. 2009). PM_{10} metal emissions were dominated by crustal elements Si, Fe, Ca, Na, Mg, Al, and K, and elements associated with tailpipe emissions and brake and tire wear, including Cu, Zn, Sb, Ba, Pb, and S. Although the sum of Cu, Zn, Sb, Ba and Pb did not exceed 1 % of PM_{10} mass in tunnel studies, they may be important for health effects and can provide some indications of the sources of particulate matter emissions, such as brake wear (Lough et al. 2005). Moreover, in the last decades, the introduction of the use of catalytic converters has contributed to the emission of platinum group elements (Pt, Pd, Rh) (PGEs).

2.2 *Particulate Matter and Trace Elements: Health Effect*

As describe above, elements in atmosphere are mainly related to particle phase but also their can be present inside a liquid phase due to the dissolution of aerosol particles in the water drops. Briefly, elemental fraction represents one of the components of the atmospheric aerosol (commonly identified as Particulate Matter), defined as complex mixture of particles both on liquid and solid phase, dispersed in a gaseous medium. Particulate matter plays a central role in atmospheric processes affecting human health (Pope et al. 2009); visibility (Bäumer et al. 2008), air quality and climate change (IPCC 2007). It also influences ecosystems and cultural heritage, being involved in acid deposition (Larssen et al. 2006; Nava et al. 2010).

The chemical composition of atmospheric aerosol in a given area depends on PM sources, physical and chemical processes of transformation, and processes of transport and mixing caused by atmospheric motions. The large surface area of the finer fraction favors the adsorption of heavy metals, ammonium ions, sulfates, nitrates and numerous organic compounds such as polycyclic aromatic hydrocarbons (PAHs).

On these bases, the pollution from particulate matter is an important environmental risk factor for both human health, for the disorders generated by it, and the possible effects on climate and ecosystems (e.g.: acidification, eutrophication, effects on the radiative balance, corrosion and degradation of materials) (Lazaridis et al. 1999). Recently there is a growing interest of the scientific community for the levels of pollution from particulate air pollution, due to the strong correlation between morbidity, mortality and concentration of inhalable and respirable particles (PM_{10} and $PM_{2.5}$), highlighted from numerous epidemiological studies (Dockery and Pope 1996; Brunekreef et al. 1997; Englert 2004; Oberdoster et al. 2005). The association between the levels of concentration of the fine particles and the increase in risk has already been demonstrated, while the biological mechanisms that determine the health effects are still partially obscure. Elevated levels of particle in air have been associated with decreased lung function, increased respiratory symptoms such as cough, shortness of breath, wheezing and asthma attacks, as well as chronic obstructive pulmonary disease, cardiovascular diseases and lung cancer.

Factors which may influence the toxicity of airborne particulate matter can be summarized as: (i) bulk chemical composition; (ii) trace element content; (iii) strong acid content; (iv) sulfate content; and (v) particle size distribution (Harrison and Yin 2000). The size of airborne particles is significant, as this determines in which parts of the respiratory tract the particles are deposited, as well as how rapidly and the manner in which they are cleared. Small airborne pollutant particles have small inertia and therefore are poorly impacted before entering the alveoli region of the lung; while in the alveoli, the probability of deposition is very high due to their high diffusion coefficient. A general trend of increasing element concentration with decreasing aerodynamic diameter was observed for elements V, Mn, Ni, Cu, Zn, Se, and Cd, indicating they were predominately concentrated in the nanoparticle size range. Other elements including Fe, Sr, Mo, Sn, Sb, Ba, and Pb were predominately concentrated in the fine-size range. Increased concentration of elements in the nano and fine particle size range is significant due to their ability to penetrate into the deepest alveolar area of the lungs. Moreover, particle size had an important effect on element bioaccessibility for the studied urban PM samples showing a general trend of increasing element bioaccessibility with decreasing particle size (Niu et al. 2010).

The particle composition may determine in what way the respiratory tract reacts, or the body responds. Some particles can act as carriers of adsorbed chemicals or gases which can act as triggers for various health effects (Morawska and Zhang 2002 and references therein). Cardiovascular effects have been mostly ascribed to particulate components (Bhatnagar 2006; Brook 2008; Araujo and Nel 2009). Various mechanisms have been proposed to explain how inhalation of ambient particulate could result in systemic cardiovascular effects such as: (1) activation of pulmonary receptors resulting in autonomic nervous system imbalance and the development of dysrhythmias; (2) induction of pulmonary and systemic inflammation; (3) access of particles or their chemical constituents to the systemic circulation (Araujio 2011).

Many elements, such as V, Cr, Mn, Fe, Ni, Cu, Zn, Cd, and Pb are widely distributed in PM and, therefore, are suspected to be an important source of PM toxicity. Elemental PM Components have been reported to produce and release inflammatory mediators by respiratory tract epithelial cells and/or to catalyze oxidative stress resulting in potential tissue injury. Toxicological studies have suggested that it is the soluble trace element content instead of the total element content of PM that has more direct links to harmful. The production of radicals by soluble elements and their mediated Fenton chemical reaction is the primary pathway to generating oxidants, where particle size plays an important role in element bioaccessibility and, therefore, finally in bioavailability and toxicity (Niu et al. 2010 and references therein).

Trace elements found in association with fine particles and of toxicological concern include As, Cd, Cr, Hg, Mn, Ni, Pb, and V, exposure to which in occupational environments has been suspected of causing sinusitis, asthma and chronic bronchitis, pneumonia, lung hemorrhage, lung cancer, and brain hemorrhage (Charlesworth et al. 2011 and references therein). Furthermore, trace elements are important because of their dual role in the health of plants, animals and humans, namely, their essentiality and their potential to be harmful. Consideration must be given to essentiality, non-essentiality and toxicity that depend on concentrations, the form of the element speciation, pH and oxidation–reduction conditions and other factors. For essential trace elements, there is an optimal range of concentration for healthy growth of organisms, varying for different plants, animals and humans. Concentrations less than the lower end of this range would give deficiency, while those above the upper end of the range could lead to harmful effects (Swaine 2000). A human health concern is usually associated with excessive exposures to metals that cause toxic effects to biological organisms, herein referred to as trace metals of environmental concern. These trace metals may include non-essential ones, such as Cd and Pb that can be toxic even at trace levels, and biologically essential elements, such as Cu and Zn, which might cause toxic effects at elevated concentrations. Other indirect consequences of trace metal contamination of the urban environment include the subsequent migration of the pollutants to receiving bodies of water via urban runoff, resulting in the trace metal enrichment of sediments (Wong et al. 2006).

Physicochemical properties of metal compounds govern uptake, intracellular distribution and binding of these in the organism. Interactions with proteins (e.g.: with zinc finger structures) appear to be more relevant for metal carcinogenicity than binding to DNA. In general, metal genotoxicity is caused by indirect mechanisms. In spite of diverse physico-chemical properties of metal compounds, three predominant mechanisms emerge: (1) interference with cellular redox regulation and induction of oxidative stress, which may cause oxidative DNA damage or trigger signaling cascades leading to stimulation of cell growth; (2) inhibition of major DNA repair systems resulting in genomic instability and accumulation of critical mutations; (3) deregulation of cell proliferation by induction of signalling pathways or inactivation of growth controls such as tumour suppressor genes. In addition, specific metal compounds exhibit unique mechanisms such as interruption of cell–cell adhesion by cadmium, direct DNA binding of trivalent chromium, and interaction of vanadate with phosphate binding sites of protein phosphatases (Beyersmann and Hartwig 2008).

Exposure to heavy metals is potentially harmful especially for those metal-compounds, which do not have any physiological role in the metabolism of cells. The ingestion of metals via food or water could modify the metabolism of other essential elements such as Zn, Cu, Fe and Se. Furthermore, most metals are capable of forming covalent bonds with carbon, resulting in metal-organic compounds. Transformation (by methylation or alkylation) influences their mobility, accumulation as well as their toxicity (e.g. Pb, Zn, Cu, Cd, As, Sb, Cr, Ca, Na, Au, Cl, Br). Prolonged exposure to metals and metal compounds could result in dysregulation of cellular pathways causing subsequent toxicity. Metals and metal compounds interfere with functions of the central nervous system (CNS), the haematopoietic system, liver and kidneys. Recently, more attention and concern is given to metal compounds that have toxic effects at low levels of exposure.

3 Modelling Air Pollution

A mathematical model is a description of a system using mathematical concepts and language. The process of developing a mathematical model is termed mathematical modelling. A model may help to explain a system and to study the effects of different components, and to make predictions about behaviour. The model use equations to represent the interconnections in a system with several approaches that have lead to the creation of different model types: dynamical systems, statistical models, differential equations, etc. Models represent an important tools in environmental research giving a complementary instrument useful in data interpretation and are of great importance in natural science giving a complementary instrument useful in scenarios representation and data interpretation (Ford 2009).

Air pollution description needs several information concerning the meteorological and geographical description of the study area, the emission sources and the application of chemical and physical aspects involved on pollutant interactions. In this view, air quality is a complex phenomena and the use of modelling represent a fundamental tool for both research and applied objectives (e.g.: policies, action plans, risk assessment).

In order to modelling air pollution a modelling system must be implemented. A model system is composed of sub models that are necessary to create the input for the chemical model (Fig. 1.4).

The main steps to create a model input are: (i) the creation of an appropriate emission inventory; (ii) the simulation of the meteorological fields and (iii) the simulation of the dispersion and transport. Very important are also the characterization of the topographical and land use coefficients that characterize the study domain as well as the geometric representation of the emission sources (as point, line and area source).

3.1 Air Pollution Modelling System

3.1.1 Emission Inventory and Emission Modelling

An *emissions inventory* is a database that lists, by source, the amount of air pollutants discharged into the atmosphere of a community during a given time period (EPA 2011). The development of a complete emission inventory is an important step in an air quality management process. Emission inventories are used to help determine significant sources of air pollutants, to establish emission trends over time, target regulatory actions, and to estimate air quality through

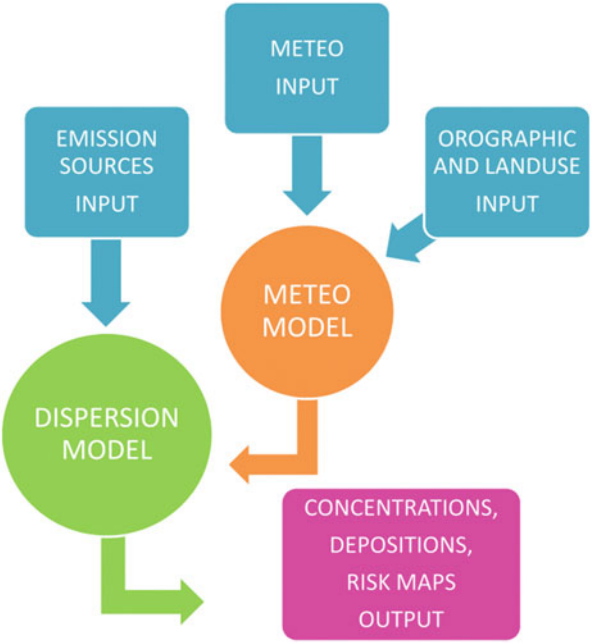

Fig. 1.4 A flow diagram of a typical modelling system used to simulate air pollutants dispersion

computer dispersion modeling. An emission inventory includes estimates of the emissions from various pollution sources in a specific geographical area. A complete inventory typically contains all regulated pollutants. Different methods for calculating the emissions inventories are available, and the choice of method depends on the availability of data, time, staff and funding.

The methods may include, but are not limited to: continuous monitoring to measure actual emissions; extrapolating the results from short-term source emissions tests and combining published emission factors with known activity levels. An emission factor may be used to estimate emissions when actual emission data is not available. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category.

In Europe, the third edition of the emission inventory guidebook (prepared by the United Nations European Environment Agency Task Force on Emissions Inventories and Projections) (EMEP 2009) provides a comprehensive guide to state-of-the-art atmospheric emissions inventory methodology to support reporting under the UNECE Convention on Long-Range Transboundary Air Pollution and the EU directive on national emission ceilings. In the U.S., the EPA Clearinghouse for Inventories & Emission Factors contains information on emissions inventories, emissions factors, software and tools used for emissions inventories, and emissions modeling (EPA 2011).

In the context of air quality modeling, *emission modeling* is the process by which emissions estimates are prepared for use in an air quality model. In general terms, the emissions model is the suite of tools that are used to estimate and spatially and temporally allocate emissions for use in deterministic and statistical air quality models (Sarma 2008). Yet, the emissions estimates, that result from the emissions modeling process, are the critical link in the air quality modeling process. The emissions estimates model is a computerized system that utilizes data to estimate emissions from a specific source. The emissions modeling system is a computerized framework under which emissions estimates models operate.

3.1.2 Meteorological Models

Modeling air quality requires an accurate modeling of all the factors that control the concentrations of these chemical species, including the movement of these airborne species from one location to another. Hence, accurate air quality modeling is predicted by accurate meteorological modeling. The phrase meteorological modeling (or atmospheric modeling or numerical weather prediction, NWP) refers to any numerical representation of the atmosphere and its processes. A numerical representation is based on dynamical, thermodynamical, physical and chemical properties of the atmospheric system. Even though atmospheric modeling started out examining just the atmospheric processes, it is commonly understood that the atmospheric motions depend on the properties of the earth surface as well as the dynamics of the oceans. Therefore, it is appropriate to extend the definition of meteorological modeling to include the effects of the surface of the earth and the oceans (Sarma 2008). Meteorological models are developed and used for two main purposes: (i) to understand and forecast local, regional, or global meteorological phenomena and (ii) to provide the meteorological input required to run air pollution models. Numerical meteorological models can be divided in two groups: (i) diagnostic models, i.e., models that are based on interpolation/extrapolation of available measurements and contain no time-tendency terms and (ii) prognostic models, i.e., models that perform space-time integration of the conservation equations of mass, heat, motion, water, and if necessary other substances, such as gases and aerosols.

3.1.3 Diffusion and Transport Model

Air quality models use mathematical and numerical techniques to simulate the physical and chemical processes that affect air pollutants as they disperse and react in the atmosphere. Based on inputs of meteorological data and source information like emission rates and stack height, these models are designed to characterize primary pollutants that are emitted directly into the atmosphere and, in some cases, secondary pollutants that are formed as a result of complex chemical reactions within the atmosphere. These models are important to the air quality management system because they are widely used by agencies tasked with controlling air pollution to both identify source contributions to air quality problems and assist in the design of effective strategies to reduce harmful air pollutants. For example, air quality models can be used during the permitting process to verify that a new source will not exceed ambient air quality standards or, if necessary, determine appropriate additional control requirements. In addition, air quality models can also be used to predict future pollutant concentrations from multiple sources after the implementation of a new regulatory program, in order to estimate the effectiveness of the program in reducing harmful exposures to humans and the environment.

The most commonly used air quality models include the following:

- Dispersion Modeling – These models are typically used in the permitting process to estimate the concentration of pollutants at specified ground-level receptors surrounding an emissions source (e.g.: Lagrangian models).
- Photochemical Modeling – These models are typically used in regulatory or policy assessments to simulate the impacts from all sources by estimating pollutant concentrations and deposition of both inert and chemically reactive pollutants over large spatial scales (e.g.: Eulerian models).
- Receptor Modeling – These models are observational techniques which use the chemical and physical characteristics of gases and particles measured at source and receptor to both identify the presence of and to quantify source contributions to receptor concentrations.

EPA (2011) suggests specific models for each type but several models are developed in the entire world. Differences on modeling output are highlighted in Fig. 1.5.

Models are typically applied to study impacts of individual sources, multiple-source industrial facilities, metropolitan areas, or larger regional areas up to sub-continental scale. The spatial scales range from up to few kilometers (for large industrial point sources), to hundred kilometers (for individual urban areas), to few thousand kilometers (for larger regional areas). When applying models to regional-scale domains, the spatial scale of important atmospheric phenomena that ultimately contributes to regional air quality problems must be accurately analyzed.

Nested grid capabilities, an important feature of contemporary regional models, allow them to resolve important phenomena and concentration gradients in areas of the domain where significant sources are present. The time scales of concern are related to ambient air quality standards, which have averaging times ranging from 1 h to 1 year.

3.2 Chemical Transport Model for Particulate Matter (PM)

A particular subject in air quality modelling is the simulation of PM (Particulate Matter) transport and chemical reaction. Particulate matter constitutes a multi-component system of material in solid or liquid state that could enter in the air by natural or anthropogenic causes. A crucial issue in understanding and managing atmospheric PM is the ability to link emissions of primary PM and precursors of

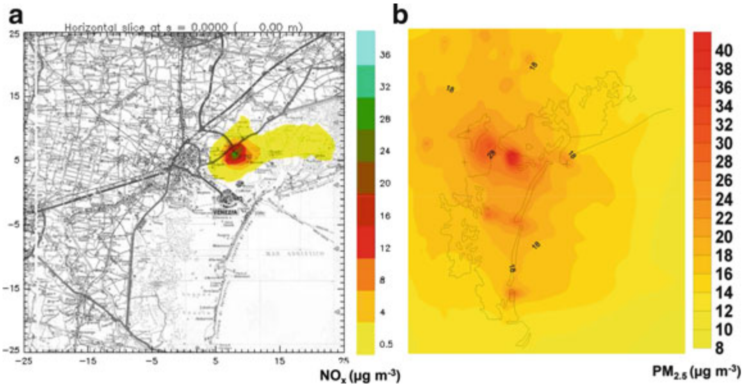

Fig. 1.5 An example of a Lagrangian dispersion simulation of an aircraft emission (**a**) (Pecorari 2010) and of an Eulerian $PM_{2.5}$ dispersion simulation (**b**) (Pecorari et al. 2013)

secondary PM quantitatively to ambient PM concentrations and other physiologically and optically important properties. Air quality models used to study PM distribution are generally called C*hemical-Transport Models* (CTMs). For PM they are an important quantitative tool with which to address this relationship. CTMs consist of mathematical representations of the relevant physical and chemical atmospheric processes, which are solved using numerical algorithms to obtain pollutant concentrations as a function of space and time for a given set of pollutant emissions and meteorological conditions (e.g.: Peters et al. 1995; Seinfeld and Pandis 2006; Jacobson 1999; NARSTO 2000; Russell and Dennis 2000). CTMs are prognostic models that, given the emission rates of selected pollutants and their precursors and prevailing meteorological conditions, predict the atmospheric concentrations of those pollutants based on a combination of fundamental and empirical representations of the relevant physicochemical atmospheric processes. Although most current CTMs tend to treat the same major physicochemical processes, there are significant differences among CTMs in their characterization of PM chemical composition and size distribution. Air-quality models that neglect atmospheric chemistry are often termed dispersion models, and such models are limited to the treatment of chemically inert species. An air quality modeling system is the set of emission, meteorological, and air-quality models needed to simulate air quality. In addition to PM, CTMs have been developed for other pollutants, including photochemical oxidants and chemicals deposition (wet and dry). As a general rule, all of the atmospheric processes relevant to photochemical oxidants and chemicals deposition are also relevant to PM, but some processes relevant to PM (for example, size-dependent droplet chemistry) are usually neglected in CTMs for photochemical oxidants or chemicals deposition. Consequently, PM CTMs are normally more complex than CTMs developed for other air pollutants, and they are often able to predict these other pollutants as well as PM. For this reason, they may also be referred to as “one atmosphere”, “multi-pollutant”, or “unified” air quality models (Seigneur and Moran 2004).

4 Selected Target Elements

4.1 *Beryllium (Be)*

4.1.1 Health

The primary route of human exposure to Beryllium and related compounds is through inhalation of dusts and fumes although it may be present in drinking water and food. As reported by the U.S. Department of Health and Human Services (HHS 2011), Beryllium and related compounds are known to be human carcinogens. Indeed several epidemiological studies indicate an increased risk of lung cancer in occupational groups exposed to this element or beryllium compounds. Workers more exposed to this metal are: beryllium miners, beryllium alloy makers and fabricators, phosphorus manufacturers, ceramics workers, missile technicians, nuclear reactor workers, electric and electronic equipment workers, and jewelers. Moreover, Beryllium metal and several beryllium compounds such as beryllium-aluminum alloy, beryllium sulfate and beryllium oxide cause lung tumors in rats, transgenic mice and rhesus monkeys by either inhalation or intratracheal instillation (HHS 2011).

The bioavailability (related to its solubility) of this element is strongly pH dependent. At pH of about 7, beryllium is poorly soluble but with decreasing pH, it becomes more soluble (Bohdalkova et al. 2012).

4.1.2 General Usage

The abundance of beryllium in the ecosystems and in the Earth's crust is low (Ryan 2002). Due to its peculiar properties (such as the lightness and a high melting point) Beryllium and related compounds are very useful for different applications in industry, computer science, telecommunications and aerospace (HHS 2011). Moreover Beryllium is useful in the production of nuclear weapons and in sealed neutron sources due to its small neutron cross-section.

According to the Agency for Toxic Substances and Disease Registry (ATSDR), 9.5 metric tons of beryllium and beryllium compounds is released annually to the atmosphere: the 54 % is from natural sources (windblown dust and volcanic particles) and the 81 % of the anthropogenic beryllium coming from electric utilities (ATSDR 2002). However, the open-pit coal mining and the coal combustion in power plants are the main regional sources of atmospheric pollution of this element. Furthermore the metallurgical plants could be also important point sources of this pollution (Aneja et al. 2012; Bohdalkova et al. 2012).

4.1.3 Results of Some Recent Studies

The majority of studies concerning the Be in the atmosphere are related to the isotope ^{7}Be that arise as a result of the spallation processes of light atmospheric elements in the upper atmosphere and is a relatively short-lived ($T_{1/2} = 53.3$ day) (Vecchi and Valli 1997; Papastefanou and Loannidou 1996 and references therein). The production rate of this isotope is maximum in the stratosphere, at about 20 km, and decreases exponentially with decreasing altitude but a significant quantities is still formed in the upper troposphere.

^{7}Be participates in the formation and growth of the accumulation mode aerosols (0.07 to 2 μm aerodynamic diameter). The size of particles which contain this isotope increases when there is high concentration of other pollutants, when the relative humidity increases and with large residence time of ^{7}Be in the atmosphere. Its removal occurs when aerosol is collected on droplets during condensation of moisture in the lower parts of the troposphere and by wet precipitation (dry fallout plays only a minor role) (Conaway et al. 2013). Due to these features and to its relative simplicity in measurement using high-resolution gamma-ray spectrometry, ^{7}Be is a powerful and commonly used tracer to study the nature of large scale atmospheric circulation and tropospheric aerosol scavenging processes (wet and dry deposition and trapping by above ground vegetation).

For example, Conaway et al. (2013) have investigated the temporal and spatial variability of ^{7}Be accumulation in atmospheric deposition at sites near northern Monterey Bay on the central California coast. They found values of activities and deposition fluxes comparable to those of other coastal locations with comparable latitude and Mediterranean-type climate (annual ^{7}Be atmospheric deposition was approximately 1,900 Bq m^{-2} yr^{-1}, with most deposition via rainwater (>95 %) and less via dry deposition). Further, Vallés et al. (2009) identified similar seasonal variations of ^{7}Be and ^{210}Pb concentrations by characterizing the radioactivity of airborne particulate matter sampled in the Barcelona area from 2001 to 2005: the maximum values were recorded during the summer months and dry periods supporting that washout of atmospheric aerosols by rainfall carries these radionuclides. These results were not completely in agreement with those of Hernandez et al. (2005) that characterized the atmospheric particulate of Tenerife Island for a comparable sampling period. Indeed they found a linear correlation between ^{7}Be and ^{210}Pb but concentration lower than expected for a continental site at the same latitude and altitude and the maximum values were not detected during summer season. Subsequently, Hernandez et al. (2008) focused on the study of the time variation of ^{7}Be concentration to better characterize the long range transport of North African and oceanic aerosols. This research confirms that the downward transport from the mid-troposphere is a key mechanism for the increase of these radionuclide concentrations in the lower atmosphere. Moreover, this paper suggests that the flow of re-suspended particles in the aerosol transport zone can enhance the scavenging effect of ^{7}Be and then its atmospheric particulate concentration.

As regard the air concentration of Beryllium (not only the isotope ^{7}Be), Pandey et al. (1998) showed that this element is associate with Cadmium, Chromium, Nickel and Vanadium in the atmospheric particulate of Bhilai (an urbanized and industrialized city of India) suggesting that the most likely sources are: non-ferrous metallurgical operations, diesel exhaust and residual oil combustion.

Although Beryllium has been historically machined, handled and stored in facilities at Lawrence Livermore National Laboratory since the 1950s, the atmospheric concentrations of this element over three decades were comparable to those found elsewhere in the natural environment (Sutton et al. 2012). Indeed, the atmospheric concentrations show a typical seasonal periodicity characterized by high levels in late summer and early fall (related to elevated temperatures, wind speed, and lower precipitation), and lower ones in the winter (related to lower temperatures, wind speed, and greater precipitation). Moreover the mean annual concentrations decrement revealed at the National Laboratory since 1990 correspond to the national decrease in PM_{10} since the implementation of the EPA's 1990 Clean-Air-Act. On these bases, the laboratory operations have had a negligible impact on the Be content of airborne particulate near the monitored area and so, the detected beryllium mainly comes from soil resuspension and previous coal fired power station burden.

Lately, Bohdalkova et al. (2012) measured soluble and insoluble Be concentrations in rime and snow (these two matrices contribute to the scavenging of pollutants from the atmosphere (Brewer et al. 1983)) of mountains remote from residential and industrial areas of the Czech Republic (Europe). They revealed that on average about 34 % of total Be deposition occurred in soluble form (bioavailable) and that soluble concentrations in rime were 7 times higher compared to snow (6.1 vs. 0.9 ng L^{-1}) because the larger overall surface of water droplets in rime more efficiently scavenges pollutants from the atmosphere.

4.2 Vanadium (V)

4.2.1 Health

The environmental exposure to Vanadium and related compounds occurs via inhalation or through consumption of contaminated foods (IARC 2006). In Ress et al. (2003) was highlighted a spectrum of non-neoplastic lesions in rats and mice exposed to V_2O_5 by whole-body inhalation for 2 years and a clear evidence of carcinogenicity in male and female mice and some evidence of carcinogenicity in male rats. As concerns the human, the reactive oxygen species induced by Vanadium have been reported to trigger or potentiate cell apoptosis (evolutionary conserved homeostatic process involved in distinct physiological processes including organ and tissue morphogenesis, development and senescence), and to induce lipid peroxidation and oxidative DNA damage (Franco et al. 2009 and references therein). Specifically, the results of the research of Ehrlich et al. (2008) suggest that the workers from a V_2O_5 factory are at increased risk for cancer and other diseases that are related to DNA instability due to the inhalation of this compound. Indeed this metal oxide is classified as possible human carcinogen by IARC (2006).

4.2.2 General Usage

According to IARC (2006), Vanadium is found in several minerals (prevailing in phosphate rock and iron ores) and in fossil fuels (oil, coal, shale) with an average concentration in the earth's crust of 150 mg kg^{-1}. In ores V is mainly in pentoxide form and sometimes as sodium or ammonium vanadates, in crude oil and residual fuel oil the most common oxidation state of Vanadium is +4. Only a few Vanadium compound are of commercial significance and the Vanadium pentoxide (V_2O_5) is the dominant one. This is a poor soluble compound of atmospheric particulate matter prevailing emitted by oil – coal burning and metallurgical plants (Ress et al. 2003). It is used in the production of metal alloys, electronic material, lithium batteries, high-pressure lamps, glass, paint, ceramics, in petrochemistry, for the enameling, for the synthesis of chemicals compounds as an oxidation catalyst in heterogeneous and homogeneous catalytic processes, as a corrosion inhibitor and in the photographic field (IARC 2006; Ehrlich et al. 2008 and references therein).

4.2.3 Results of Some Recent Studies

The main atmospheric natural source of V is the continental dust, followed by the sea spray salt and the volcanic emission. The anthropogenic ones are the activities related to the production-consumption of materials abovementioned. Specifically, the largest contributors are metallurgical works, coal and residual oil burning. During the combustion, V is mainly released as vanadium pentoxide or may be associate with sulfate in form of fly ash particulate. The common atmospheric concentration of this element is of the order of ng m^{-3} although in unpopulated areas such as Antarctica it was found at pg m^{-3} and near large metallurgical plant at μg m^{-3} (IARC 2006 and references therein).

Usually, this element is used as a tracer to identify the heavy oil combustion sources (Wang et al. 2006; Moreno et al. 2010; Fernzandez Espinosa et al. 2002; Lupu and Maenhaut 2002; Mazzei et al. 2008; Hedberg et al. 2005; Jang et al. 2007; Rajšić et al. 2008) or coke combustion (Alastuey et al. 2007). However, most studies carried out in urban and suburban environments identified this element clustered with a mixture of more general anthropogenic tracers of industry or traffic sources (Viana et al. 2008; Sternbeck et al. 2002; Amato et al. 2010). Moreover, Hao et al. (2007) shown that V in the TSP of Qingdao (China) is mainly derived from soil with a minor contribution from ship emissions. Specifically, this element was characterized by a strong seasonal variation with the lowest mean value in fall, the highest in winter, a significant increase of concentration during the Asian dust episodes and statistical analysis highlighted a significant correlation with Fe, Ti, Mn, and Ni.

Fernandez Espinosa et al. (2001) shown that Vanadium is prevailing concentrated in fine fraction (<0.61 μm) of atmospheric particulate of Seville at the end of twentieth-century. Similar size distribution was found for nickel, lead and cadmium suggesting as a potential source the combustion process. As regard the chemical speciation of Vanadium in fine fraction, about 50 % of this element is present in the "soluble and exchangeable fraction" (the most easily available to human body through breathing), about 25 % in the "carbonates, oxides and reducible fraction" (also bioavailable through the lung), and about 13 % in the "bound to organic matter, oxidable and sulphidic fractions" (Fernandez Espinosa et al. 2002). Moreover, a significant correlation between Ni and V in the chemical fraction of metal bound to organic matter or sulphidic metal was found, confirming that these metals have a strong relationship with the combustion of fuels used in the industrial activities of the city.

Also Okuda et al. (2007), by studying the TSP and $PM_{2.5}$ of Yokohama (Tokyo metropolitan area) found that almost all the Vanadium was contained in fine fraction. Moreover, they showed that this element was relatively high water-soluble and good correlated with Ni. According to Jang et al. (2007), the authors identify as a major source the heavy oil combustion. Furthermore, Moreno et al. (2010) showed that sometimes anomalous high values of V/Ni ratio (>4) can detect the influence of near high-V petcoke and fuel oil combustion sources. Indeed, in urban background PM the use of this ratio is limited due to the substantial contribution of other source. Finally, also Cheng et al. (2011) and Vecchi et al. (2008) found significant concentrations of V in PM_1.

Moreno et al. (2008a) used Vanadium and some Lanthanide elements as geochemical markers in PM_{10} and $PM_{2.5}$ to better characterize the emission contributions of natural and anthropogenic sources in several cities of Spain (Moreno et al. 2008a, 2010) and Mexico City Moreno et al. (2008b). Specifically, atmospheric particles derived from fuel oil and petcoke combustion in power stations exhibit very low La/V ratios (<0.1) because the fly ash is enriched in V, the mineral PM derived from uncontaminated crustal materials or coal combustion are characterized by La/V = 0.2–0.3 and emissions from oil refineries using zeolitic fluid catalytic converters can be enriched in La to such an extent that the La/V value is above the normal crustal ratios. Another useful tool to improve the abovementioned source characterization is the three-component Ce-La-V or Ni-La-V plot where the sample are placed as a function of the concentration of three elements (Moreno et al. 2008b, 2010).

Finally, Sella et al. (2006), by characterizing the total suspended particulate (TSP) sampled in two site of a coastal region of Rio de Janeiro (Brazil), found that the atmospheric concentration of Vanadium was of ng m^{-3} order and increased by approaching to the ocean (unlike the other elements studied) especially during upwelling events. The authors suggested that the sea spray is an important source of V in particular during upwelling events when the presence of some marine tunicate, that bio-accumulate this element, is high.

4.3 Antimony (Sb)

Although, there are several reviews that characterize the Sb in different areas and the relative interest in the environmental field is growing in the last decade, a gap exists with respect to other much more studied elements especially in the analysis of atmospheric particulate. Between the various reviews is interest to mention Franco et al. (2009) and De Boeck et al. (2003) where the toxicity and carcinogenicity of this element is defined; He et al. (2012) where the Antimony pollution in several samples of soils, sediments, waters, plants and atmospheric particulate collected in China are characterized; and Smichowski (2008) where the research carried out on the determination of Sb and its predominant chemical species in atmospheric aerosols are summarized and discussed.

4.3.1 Health

United States Environmental Protection Agency and the European Union consider Antimony and its compounds as pollutants of priority interest due to their potential toxicity and carcinogenicity (He et al. 2012 and references therein). Indeed, due to its chemical similarity with As (same periodic group and oxidation states) it is plausible that the DNA damage induced by Sb follows similar pathways as those for arsenic. Moreover, Sb exposure induce apoptosis whose deregulation also participate in the etiology of several human diseases (e.g. neurodegenerative and autoimmune disorders) (Franco et al. 2009 and references therein). Specifically: elemental Sb is more toxic than its salts, inorganic species are more toxic than the organic ones, Sb(III) species are more toxic than Sb(V) compounds (Smichowski 2008 and references therein), Sb(III) and Sb(V) compounds are generally negative in non-mammalian genotoxicity tests instead they are generally positive and negative in vitro in mammalian test systems, respectively. Generally, population is rarely exposed to antimony but in case of occupational exposure, inhalation and skin contact are the main routes. Due to the frequent co-exposure to arsenic the human carcinogenicity is difficult to evaluate. Finally, antimony potassium tartrate (APT) has been used worldwide as an anti-shistosomal (anti-helminthic agent) drug until the 1990s and the pentavalent antimony compounds such as sodium stibogluconate have replaced the more toxic trivalent compounds for the treatment of leishmaniasis (De Boeck et al. 2003 and references therein).

4.3.2 General Usage

Sb and its compounds has been used since the Early Bronze Age in medicine, veterinary and cosmetics. In modern times, they are used in the manufacture of alloys, pigments, paints, ceramics, glass, glazing for pottery and tiles, colouring matter for paper and cloth, pharmaceutical preparations, ammunitions, fireworks, bearings, tires, brake linings cable covering, as opacifying agent for enamels, as a flame retardant in rubber, plastics, pigments, adhesives, textiles, and paper (Sb_2O_3), as catalyst in the manufacture of polyethylene terephthalate, as component of brake linings (Sb_2O_3) (He et al. 2012; De Boeck et al. 2003; Smichowski 2008 and references therein).

Due to the natural dispersion process and its broad use in human activities, Antimony is ubiquitous throughout the environment. The main natural source of this element is the atmospheric volcanic emission, followed by the rock weathering and soil runoff (Smichowski 2008 and references therein). About the anthropogenic ones, in addition to those strictly related to the production and the use of the abovementioned objects, relevant sources of Sb are: the electronic waste, the non-ferrous metals refining, the smelting processes, the incineration of waste and sewage sludge, the fossil fuel combustion (especially coal of which China is one of the major production and consumers centres in the world) and the Sb mining (the majority of the world's reserves are located in China, the others are in Bolivia, Russia, South Africa and Tajikistan). It is therefore evident that China plays an important role in global anthropogenic Sb emissions. Indeed, severe environmental contamination have been reported in many areas (He et al. 2012 and references therein).

4.3.3 Results of Some Recent Studies

Generally, in unpolluted environments of China, Sb was detected in concentration of the order of ng m^{-3} but in mining areas and in fly ashes from waste incinerators elevated concentrations were found (mg m^{-3} order). At the beginning of the twenty-first century, in Beijing (where the main sources of Sb was the brake abrasion and the coal combustion) the mean concentration in total suspended particulate was of the order of μm m^{-3} (He et al. 2012 and references therein). Conversely, in $PM_{2.5}$ of Palermo (Sicily, Italy) sampled from November 2006 to February 2008 the mean concentration was of ng m^{-3} order, although this element was characterized by an elevated Enrichment Factors (calculated by dividing the relative abundances in atmospheric particulate by the relative average abundances in local soils – EF $>$ 1,000). Moreover, a close linear relationships between this element, Cu and $PM_{2.5}$ and between the respective enrichment factors were observed. Due to these findings, the authors suggested that Sb is probably originated from brake wear debris (Dongarrà et al. 2010).

By characterizing the elemental composition of atmospheric particulate sampled inside and outside an elementary school in Flagstaff (AZ – USA), Majestic et al. (2012) showed that Sb mass in PM_1 was significantly higher indoor (86 times greater than outdoor) with an air concentration of 17 ng m^{-3}. Because indoor Sb concentration was higher in the submicron fraction compared with the supermicron one and due to the lack of significant correlations with other elements in the PM_1 where Cu:Sb ratio is 0.08 (Cu:Sb ratio of crustal origin = 125, traffic = 2.3–10.1, fly ash ~ 20) they suggested as indoor source the re-suspension of flame retardants embedded in the carpeting characterized by a Cu: Sb ratio of 0.18.

Little is known about the chemical speciation of this element and its reaction in the atmosphere; it is supposed that Sb is oxidized to Sb_2O_3 by reaction with atmospheric oxidants (Smichowski 2008 and references therein). Varrica et al. (2013) defined the speciation of Sb in several samples of brake linings, brake pad wear residues, road dust, PM_{10} and $PM_{2.5}$ (of Palermo – Italy) by combining several techniques including Synchrotron Radiation X-ray Absorption Spectroscopy (SR-XAS). They found that these samples were composed by an admixture of Sb(III) and Sb(V) oxide in different relative abundances. Specifically, brake linings contain Sb(III) oxide (Sb_2O_3) and stibnite (Sb_2S_3) Stibnite was also detected in some samples of atmospheric particulate. Moreover, they suggested that Sb_2S_3 during the brake abrasion process is easily decomposed forming more stable Sb mixed oxide compounds.

Similar results were found by Marconi et al. (2011) that quantified the Sb(III) and Sb(V) species concentrations in some samples of PM from brakes, road dust and atmospheric particulate by ion chromatography – inductively coupled plasma – mass spectrometry (IC-ICP-MS). They found that Sb(III) is predominant in brake pads while Sb(V) is the dominant form in dust from brake linings and in road dust. In most samples of atmospheric particulate both species were detected with ratio (Sb(III)/Sb(V)) that ranged from 0 to 1.5. Moreover, they showed that total Sb concentration was characterized by a bimodal pattern with the peaks centred at 0.65–1.6 and 4.4–10 μm.

4.4 Thallium (Tl)

4.4.1 Health

Due to their high acute toxicity on living organisms, Thallium and related compounds are of particular scientific interest and environmental concern. Nevertheless, this element has been less studied compared to other toxic elements mostly due to the poorer sensitivity of classical analytical methods. Tl is characterized by a relatively high solubility of all its forms and in natural waters it occurs almost exclusively as monovalent cation. Due to this it can be easily transported through aqueous routes and transferred from soils to crops, by entering the food chain (Peter and Viraraghavan 2005 and reference therein).

The main routes of absorption of this element are through the skin, the mucous membrane and by nutrition (mostly by assimilating home-grown fruits and green vegetables contaminated). Subsequently it is widely distributed throughout the body and accumulates in bones, in renal medulla and, in the central nervous system. Significant inhalations of thallium occur mostly during mining, ore processing and product application of this element or in the workplace where Tl-rich dusts are handled or produced such as those originated from the roasting of pyrite (Peter and Viraraghavan 2005 and reference therein).

An elevated exposure by inhalation can produce several nervous system effects such as numbness of fingers and toes. In Peter and Viraraghavan (2005) and Kazantzis (2000) there are a long list of effects related to acute and chronic exposure to Thallium, among those it is worth remember tiredness, fatigue, headache, insomnia, vomiting, diarrheal, temporary hair loss, and effects on the nervous system, lungs, heart, liver, and kidneys.

4.4.2 General Usage

Thallium is a natural widely spread constituent of the earth crust where is found in trace amounts (average concentrations in the continental and oceanic crust are 991 0.49 ppm and 0.013 ppm, respectively), (Delvalls et al. 1999). It is mainly present in the sulphide ores of zinc, copper, lead and also in coal indeed Thallium was detected in base-metal mining effluents.

As described in the review of Peter and Viraraghavan (2005) and in Kazantzis (2000), Thallium and related compounds were used in medicinal purpose in the treatment of ringworm of the scalp, venereal diseases, syphilis, tuberculosis and malaria. Moreover they were used in many areas such as in the manufacture of insecticides, poison for rodents, imitation jewellery, low-temperature thermometers, ceramic semiconductor materials, special glass, laser equipment, crystals, alloys, optical systems, electronic devices, radioactivity detectors, infrared spectrometers, fireworks (thallium nitrate), pigments (thallium chromate) and dyes, impregnation of wood and leather against fungi and bacteria. Although the steady increase in use of Tl in these industrial sectors favoured the mobilization and the dispersion of this element, the main anthropogenic atmospheric source are the coal burning power plant (in particular those using brown coal or coal from the Jurassic 1006 period), (Kazantzis 2000), the brick work and cement plants, the ore processing and the ferrous and non-ferrous smelting operations (Cheam et al. 1995; Kazantzis 2000). The efficiency of retention of Tl-rich particles by electrostatic precipitators or other emission control facilities is limited because Tl-compounds are characterized by high temperatures of volatilization (Peter and Viraraghavan 2005 and references therein).

4.4.3 Results of Some Recent Studies

In the review of Juda-Rezler and Kowalczyk (2013) that discuss the parameters affecting the size distribution and the chemical composition of fly ash particles emitted from the combustion of hard coal pulverized in boilers, it is claimed that Thallium is volatile inside the boiler but subsequently a fair amount of this condenses on fly ash particles in electrostatic precipitators (Meij and Winkel

2007). The behavior of this element during the combustion and the relative enrichment factors are similar to those of As, Cd, Ge, Mo, Pb, Sb and Zn.

Kazantzis (2000) reported that higher concentration of Thallium are recognized in finer particles fraction. Indeed, in Hagler et al. (2007) concentrations of the order of magnitude of some ng m^{-3} and very high enrichment factors were observed for Thallium (and Zn, Br, Sn, As, S, Pb, Se) in $PM_{2.5}$ of Hong Kong suggesting anthropogenic origin linked to the coal burning.

Santacatalina et al. (2012) by characterizing the chemical composition of PM_{10} in the southeast of Spain (arid region with a great number of cement, ceramic and related industries) before and during the last economic crisis highlighted a significant decrease of several atmospheric pollutants in concordance with the reduction of industrial production. Specifically, during the crisis they have shown a reduction of the components that have as their main sources the soil-related industries and the crustal material re-suspension such as CO_3^{2-}, Ca, Sr, Tl and Pb. According to Querol et al. (2007), Sanchez de la Campa et al. (2010), Conesa et al. (2008) and Gutiérrez-Cañas et al. (2009) that used Thallium as a fingerprint for ceramic emissions and also as a semi-volatile metal escaping as dust from the clinker exit line depuration systems (Conesa et al. 2008; Gutiérrez-Cañas et al. 2009), Santacatalina et al. (2012) ascribed the Tl reduction to the decrease in the construction sector affecting the ceramic and cement industry. Moreover, by studying the relation between Vanadium and Thallium concentrations, they identified that the crisis has led to a larger decrease in ceramic production (bricks and tiles) than in clinker production because in that period the correlation between two element and the ratio V/Tl were higher.

The oxidation states of Thallium are Tl(III) that is characterized by strong oxidizing properties and is slowly converted to Tl(I) that generally form most stable compounds. Furthermore, the monovalent ion are dominant one in most natural environments (Peter and Viraraghavan 2005 and references therein). Zhu et al. (2001) by studying $PM_{2.5}$ collected in Salt Lake City (USA) by time of-flight secondary-ion mass spectrometry (TOF-SIMS) found that some particles contain ions of thallium such as Tl_2O^+, Tl_2O^{2+}, Tl_2O^{3+}, Tl_3^{O+}, indicating the oxide nature of this element.

Finally, Pappas et al. (2006, 2007) by analyzing the content of Tl, Cd, and Pb in different types of cigarettes found that Thallium was present in concentration of the order of magnitude of some ng $cigarette^{-1}$. Specifically their data show that the levels of all three metals in smoke particulate were proportional to their tar delivery category (full flavor > light > ultralight) and that the respective concentrations were far greater for counterfeit than the authentic brands (in some cases by an order of magnitude), even after the normalization by the nicotine concentration.

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Chapter 2
Harmful Elements in Estuarine and Coastal Systems

Md. Badiuzzaman Khan, Mauro Masiol, Angelika Hofer, and Bruno Pavoni

Abstract Estuaries and coastal zones are dynamic transitional systems which provide many economic and ecological benefits to humans, but also are an ideal habitat for other organisms as well. These areas are becoming contaminated by various anthropogenic activities due to a quick economic growth and urbanization. This chapter explores the sources, chemical speciation, sediment accumulation and removal mechanisms of the harmful elements in estuarine and coastal seawaters. It also describes the effects of toxic elements on aquatic flora and fauna. Finally, the toxic element pollution of the Venice Lagoon, a transitional water body located in the northeastern part of Italy, is discussed as a case study, by presenting the procedures adopted to measure the extent of the pollution, the impacts on organisms and the restoration activities.

Keywords Harmful elements • Coastal areas • Aquatic organisms • Health effects • Venice Lagoon

1 Introduction

Estuarine and coastal areas being the interaction zone between fresh and marine waters are highly complex due to tidal currents and waves (Morris et al. 1995). According to Ridgway and Shimmield (2002), they are dynamic systems where various ecological and physicochemical functions occur. In many ways, estuaries are very important ecosystems (Legorburu et al. 2013) being a vital site for primary

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production (Bricker et al. 2008) and a suitable habitat for many species (Lotze 2010). In addition, they control exchange processes of elements between river and coastal areas (Das et al. 2010) and supply goods and services (Pinto et al. 2010). Recently, researchers throughout Europe have given priority to estuaries and coastal areas especially after the European Commission, in the European Water Framework Directive (WFD, 2000/60/EC), has emphasized the objective of achieving "Good Ecological and Chemical Status" in all European water bodies by 2015 (Borja et al. 2009; Tueros et al. 2009).

However, river banks and estuaries have always been a focus for human settlement and industrial development, recreation, tourism, development of port and boating facilities, agriculture, housing, mining and forestry. Estuaries are becoming polluted by various human activities due to a quick economic growth and urbanization (Xu et al. 2013). Estuarine and coastal areas act as a sink for trace metals and other pollutants incoming from adjacent catchments, up-watershed activities and nearby terrestrial areas, but also they are a source for the same materials to the adjoining coastal marine areas (Kennish and Fertig 2012). Moreover, estuaries have been frequently used as dumping grounds for sewages, rubbish and industrial wastes. All these activities are responsible for the pollution of estuaries and coastal marine areas. Waste discharges, accidental spills, urban and agricultural runoff and ground water flow carry a wide range of pollutants to the coastal marine areas (Water and River Commission 1997). Therefore, substantial amount of nutrients and trace metals are transported through riverine input and submarine groundwater discharges to coastal sea waters due to progressive anthropization in coastal areas (Moore 2006). Trace elements are taken by river and ultimately mixed into coastal marine areas after transportation and alteration in estuarine areas (Swarzenski et al. 2006).

The estuarine and coastal seas play a vital role in the biogeochemical cycles of various essential and non-essential elements, by favouring physico-chemical and biological processes such as variations in the chemical speciation, inorganic scavenging, sedimentation, bio-alteration, bio-accumulation and bio-magnification (Costa et al. 2012). Trace metals are natural elements of crustal materials which enter the aquatic environment via erosion process (Di Leonardo et al. 2009; Rocha et al. 2011; Weber et al. 2009). Although some metals are vital to biota, all are potentially toxic when concentrations exceed a certain limit. Metals are received in the estuaries through rivers, many of them are persistent, toxic and bioaccumulative in nature (Liang 2011). Trace metals enter the aquatic systems mostly from anthropogenic inputs such as leaching of impervious urban surfaces (roads, parking lots and roofs) and soil surfaces by runoff and to sewage overflow from sanitary sewer systems during high rainfall events, locally treated wastewater discharge and industrial effluents (Bay et al. 2003; Bothner et al. 2002; Nicolau et al. 2012). The entrance of trace elements from river to open ocean via estuaries depend on the partitioning of trace metals between dissolved and particulate phase, riverine and anthropogenic inputs, coastal and seafloor erosion, biological activities and also physical – chemical transport and biological interaction within these areas. Trace elements may be accumulated in sediments after recycling due to chemical and biological processes and also may return back to the water column after resuspension (Förstner 1984; Tessier and Campbell 1987).

There are two processes controlling the partitioning of metallic species between the solution and suspended particulate matter (SPM) phase during estuarine mixing. Firstly, the removal of metals by flocculation of humic and fulvic acid-metal complexes and desorption of metals from river particles or from resuspended sediments (Roux et al. 1998). The features of a river or estuary's watershed such as climate (e.g., rain frequency and intensity), morphology, hydrology, geology and land use drive estuarine dynamics, particularly flushing times of waters and particle concentrations and residence times, which are among the most important factors controlling metal reactivity in estuaries (Elbaz-Poulichet 2005). Redox conditions (Zwolsman et al. 1997) and the presences of dissolved organic matter (DOM) also control the fate of metals in estuaries.

Keeping the above points in mind, the sources, chemistry, sediment accumulation and removal mechanisms of the harmful elements in estuarine and coastal seawater are described below. Elements are discussed in the following chapter in an order that reproduces a decreasing impact on the organisms and ecosystems. However, the chapter of the book first discussed metal, then non-metal (As) followed by organotin compounds (Tributyltin and Triphenyltin).

2 Harmful Elements in the Estuary and Coastal Areas

2.1 Mercury

Mercury is a widely distributed hazardous pollutant and has received great attention globally because of its persistence in environments, high toxicity to organisms, reactivity and tendency of forming more toxic organic mercury compounds and also biomagnifications capability along the food web (Jiang et al. 2006; Craig 1986; Beckvar et al. 1996). Although the use of Hg has declined considerably during the past several years, still now the metal has to be considered important in several sectors such as energy generation, incineration and mobilization from mining activities (Hines et al. 2012; Fitzgerald et al. 2007). Mining, industrial activities and urban expansion in estuarine and coastal zone are the main anthropogenic sources of Hg (Luo et al. 2012).

The coastal zone plays a vital role in the global mercury cycle (Mason et al. 1994) both as sink for terrestrial Hg and as source of methylated Hg to the ocean (Mason and Benoit 2003). Approximately 50–80 % of the total Hg coming from rivers is deposited within the estuarine zone (Cossa et al. 1996; Benoit et al. 1998). Input of Hg in the coastal zone is influenced by various natural and anthropogenic activities such as coastal and seafloor erosion, river and sewage/mining discharge, and atmospheric Hg deposition (Ci et al. 2011). Hg can exist in different forms which control its availability, complex distribution, and toxicity.

The most important forms of Hg are elemental Hg (Hg^0), inorganic Hg (Hg^{2+}), monomethylmercury (CH_3Hg^+) and dimethylmercury (CH_3HgCH_3) (Leermakers et al. 2001). All of these are influenced by various factors such as redox and pH conditions, and concentrations of inorganic and organic complexing agents (Horvat et al. 2003).

Approximately 10–30 % of the Hg exists as elemental Hg in ocean water (Mason and Fitzgerald 1993), where Hg^0 is mainly formed from the reduction of Hg (II) by aquatic microorganisms (Mason et al. 1995) and from photoreduction of Hg (II) (Amyot et al. 1997; Costa and Liss 2000) followed by geotectonic activity (Ferrara et al. 2003; Horvat et al. 2003). Abiotic methylation may take place in an environment loaded with humic organic matter (Weber 1993). Methylmercury (MeHg) is produced from inorganic mercury due to the activity of sulfate reducing bacteria (Mason et al. 1993; Morel et al. 1998; King et al. 1999). Although methylmercury is present in estuarine water at very low concentrations (Cossa and Coquery 2005), it is the most toxic form of Hg and may be accumulated in human body through the consumption of sea foods (Baldi 1997; Morel et al. 1998). Methyl mercury is a unique example of metal biomagnification in food chains due to its special characteristics such as (i) high lipid solubility and easy transfer through membranes and (ii) longer biological half-life. There are several factors controlling the production of MeHg such as temperature (35 °C is the optimum temperature in river), salinity (methylation rate decreases at increasing salinity due to the formation of chloride complexes), redox/sulphide levels (MeHg is higher in moderately anoxic sediments and increased proportionately with sulphide concentrations up to 1.8 mg S g^{-1}) (Callister and Winfrey 1986; Compeau and Bartha 1984; Breteler et al. 1981; Craig and Moreton 1983).

Dimethylmercury is an organic form of Hg found in seawater and mainly produced in oxygenated environments (Mason et al. 1995). There is little evidence of the production of dimethylmercury in surface water. However, it comes to the surface from deep water through deep water upwelling and deep thermocline mixing and degrades quickly due to its low stability with light and higher surface water temperature (Fitzgerald and Mason 1997). There is also evidence of the demethylation of the methylmercury (Marvin-DiPasquale et al. 2000; Barkay and Wagner-Dobler 2005) mediated by the bacteria through both reductive process (products: Hg^0 and CH_4) and also oxidative process (products: Hg^{2+} and CO_2) (Barkay et al. 2003).

The concentration of dissolved mercury ranged from 0.5–3 ng L^{-1} to 2–15 ng L^{-1} in ocean and coastal sea-water, respectively (WHO 1989), whereas its concentrations varied from 20 to 100 μg kg^{-1} in ocean sediments. The concentration of methylmercury in UK estuarine sediments is less than 0.02 μg g^{-1} (Langston 1982). Dissolved mercury has strong attraction for organic matter and suspended sediment and becomes accumulated in sediment after adsorption onto these particles. After deposited in sediment, inorganic Hg is transformed into methylmercury, which is bioavailable and toxic to aquatic organisms (Campbell et al. 1986). Methyl mercury can be accumulated at concentrations 10 (*Fucus vesiculosus*) and 100 (*Mytilus edulis*) times higher than sediment concentrations in estuarine algae and invertebrates (Langston et al. 1996). The concentration of total mercury in the Isonzo River (northern Adriatic Sea) ranged from 1.72 to 31.4 ng L^{-1}, whereas the average value was 9.2 ± 7.9 ng L^{-1}. On the other hand, the concentration of methyl mercury ranged from 1.65 to 17.2 ng g^{-1} in sediments. However, the concentration of methylmercury varied from 0.21 to 6.28 ng g^{-1} which is 0.121 % of total Hg (Bratkič et al. 2013).

2.1.1 Effects of Mercury on Aquatic Organisms

The European Water Framework Directive – 2000/60/EC (2000) indicates mercury as a priority harmful substance. In addition, mercury is included in the first 20 compounds of the priority list of dangerous substances published by the Agency for Toxic Substances and Disease Registry (ATSDR 2007). This metal behaves as a resistant cation, which forms complexes and can interact with proteins, enzymes and cell membranes in biological systems. It is present under different oxidation states such as Hg^{2+}, Hg^{+} or Hg^{0} in the methylated forms dimethylmercury $(CH_3)_2Hg$ and methylmercury CH_3Hg^{+}. This two derivates are persistent and bioaccumulable. The methylmercury with its ionic form is hydrophile and quite mobile in the environment, while the dimethylmercury is lipophylic and volatile. In mammals, depression and irritability indicate a low intoxication of mercury, whereas damages to the nervous system such as blindness, madness, paralysis, as well as effects on the DNA (Renzoni et al. 1998) can indicate a heavy intoxication of mercury. Elemental mercury is less dangerous because it is easily eliminated with the urine. As described by (Grieb et al. 1990), the methylmercury accumulates in muscle tissues, liver and kidney of fishes (Mackey et al. 1996) with a biological half life varying from 2 to 3 years (USEPA 1984 and references therein). Considering the trophic chain, the methylmercury contained in the benthos or the smaller fish tissues will deposit in different tissues of the predator (e.g. kidney, bile, muscle). As the level of intoxication in fish depends on its diet (Adams et al. 2010), age, weight and length, as well as on the physical-chemical parameters of the water body, no definitive intoxication parameters can be established, but a stress condition can be proved (Das et al. 1980), because a significant impairment of metabolitic functions, and a modified morphology and behaviour can be detected (Alam and Manghan 1992; Scott and Sloman 2004). Adams et al. (2010) reported that at levels higher than 5 μg g^{-1} of wet weight in fish muscles impairment in the reproduction can be observed. In the benthos, some difficulties were found in determining the toxicity of Hg, rather than of a mixture of metals (Suchanek et al. 2008). Brown and Ahsanullah (1971 and Arizzi Novelli et al. 2002b) demonstrated that Hg is the most toxic element compared to others such as Cu, Cd, Zn, Pb for larvae of Ophryotrocha and Artemia as well as for sperm cells and embryos of *Paracentrotus lividus*, respectively.

2.2 Cadmium

Great attention has been given to cadmium due to its toxic behavior in the environment (Steinnes 1989; Flyhammer 1995; Porter et al. 2004). The main dissolved forms of Cd are chloride complexes whereas the most available species is the free ion (Cd^{2+}), the proportion of which increases with decreasing salinity (Engel and Fowler 1979; Cross and Sunda 1985). Many scientists reported that there was a relationship between the Cd concentration in sediment and biota. A linear relationship was found between the concentration in the polychate *Nereis diversicolor* and in surface sediment from estuaries in Devon and Cornwall (Bryan and Hummerstone 1973a).

The concentration of Cd in Ocean was found to range from 0.02 to 0.12 $\mu g\ L^{-1}$ (Bruland et al. 1979), whereas the concentration was 0.01–0.17 $\mu g\ L^{-1}$ in UK coastal waters. However, the concentration of Cd in estuary fluctuated from 1 to 50 $\mu g\ L^{-1}$ (Morris 1984; Bryan and Gibbs 1983). Although chlorinity is a vital parameter controlling Cd behavior in estuaries, other factors such as ionic strength (increase of Ca^{2+} and Mg^{2+} concentrations competing with Cd^{2+} for adsorption onto particles), pH, redox potential, microbial activity, organic matter degradation and the residence time of the particles in the mixing zone (type of estuary) can be involved.

Cd has higher affinity for the chloride ion rather than to organic ligands (Bilinski et al. 1991; Tipping et al. 1998). During the mixing of river water with sea water, mobilization processes occur from particulate matter by the formation of highly stable and soluble Cd-chloride complexes. The formation of chloride complexes increase with the increase of salinity which regulates the activity of the free ion (Paalman et al. 1994; Thouvenin et al. 1997; Lemaire et al. 2006). An organic complex is occurred at low salinity condition. There was also evidence of Cd desorption in the estuary (Boyle et al. 1982).

2.2.1 Effects of Cadmium on Organisms

This metal can be complexed by the seawater and form soluble forms such as $CdCl^{+}$, $CdCl_2(aq)$ and $CdCl_3^{-}$. Under these forms, Cd can be taken up from different organisms living in the aquatic environment, stored in liver, kidney and gills, and cause problems in the enzymatic regulation of the carbohydrate metabolism. Cd is one of the elements next to Mn and Ni which can disrupt the storage or mobilization of metabolic substrates like glucose, glycogen, lactate, lipids and proteins (Scott and Sloman 2004). As Cd and Zn have the same positive loading, it can substitute Zn in some enzymes causing an alteration of their structure, which compromises their activities. Moreover, Cd (in addition to Cu, As, Hg, Pb) influences reproduction processes of fishes (Das et al. 1980). Cd is accumulated in small amounts in the fishes' muscle but in higher amounts in other tissues and organs (USEPA 2001). In mammals, Cd can cause caught, nausea, thoracic diseases, but in small quantities it is bound by proteins and eliminated easily with the urine. When exposed to high quantities, red blood cells can be destroyed and the kidney can be damaged. Therefore, Cd is considered a potentially toxic element (Mackey et al. 1996). In benthic organisms, Cd was linked to lysosomal damage and mortality of the organisms (Thompson et al. 2007).

2.3 Lead

Lead is one of the major anthropogenic pollutants and is now considered as ubiquitous (Chakraborty et al. 2012; Snape and Townsend 2008; Lobinski and Marczenko 1996). Nutritionally or physiologically lead is not an essential nutrient for either humans or other organisms. It is toxic, bioaccumulative and persistent. The contamination of lead from gasoline burning has declined in different environmental matrices, including aerosols (Migon et al. 1993; Grousset et al. 1994), seawater (Boutron et al. 1991; Wu and Boyle 1997) and rivers (Singh and Singh 2006).

Various uses of lead such as in storage batteries and as organic antiknocking additives (tetraalkyllead) to petrol, cables, solders, steel products, ammunition, shielding systems from radiation and x-rays, circuit boards in computers and electronics equipments, superconductor and optical technology, insecticides, pigments, paints, ceramics, enamels, glass, plastics and rubber products, coal-fired power stations, wastes from runoff and incineration and other industrial effluents have contributed significantly for the wide distribution of lead in the environment (Ritson et al. 1999; Hansmann and Köppel 2000). Although legislations have been implemented to enforce the use of alternative petroleum additives and recover lead from used batteries, the uses of lead are continuing in other areas of application.

Various forms of lead are available in the environment. Organometallic forms of lead are more lipophilic and can easily penetrate biological membranes. As a result, alkyllead species may be bioaccumulated in food chains. The main dissolved forms of Pb are $PbCO_3$ and PbOH (Nurnberg and Valenta 1983), whereas the most available inorganic form is the free ion Pb^{2+} (Freedman et al. 1980). Pb can be accumulated in the sediments by the deposit-feeding species. Pb levels in the polychaete *Nereis diversicolor* were correlated linearly to the Pb/organic matter ratio in the sediment (Bryan 1985). The availability of lead decreases with the increases of sediment organic matter concentration. This is due to the complexation of the free ion Pb^{2+} in the interstitial water, or possibly in the gut following sediment ingestion (Windom et al. 1982). Fe oxides have also effect on Pb concentration and its availability decrease with the increase of Fe oxides (Luoma and Bryan 1982). Inorganic lead may be a source for the contamination of birds. Tetramethyllead and tetraethyllead are the two main lead compounds introduced into the environmental. Both of these compounds are used as gasoline antiknock additives. However, tetramethyllead and derivatives of methylatedlead are the two main compounds found in the environment as organometallic compounds of lead.

Methyllead compounds are only found in the immediate vicinity of anthropogenic sources which are normally present at nanograms per gram level and decay occurs via R_3Pb^+ and R_2Pb^{2+}, with inorganic lead as the final products (Craig 1986). The principal factors governing the biological activity of lead in aquatic environment depend on its geochemical behavior. The physical and chemical properties of surface water and sediments such as pH, total hardness, porosity, Eh and organic matter affect the concentration of lead. Lead carbonates, lead sulfates and lead sulfides are predominant in sediments, whereas lower amount of lead were detected in surface water in dissolved form. Lower pH helps for the mobilization of inorganic lead.

Flegal and Patterson (1983) conducted an experiment and found the concentration of Pb in Ocean to be in the range 0.001–0.014 μg L^{-1}. The dissolved concentration of Pb ranged from 0.015 to 0.135 μg L^{-1} along the east coast basin of Britain, whereas in the Humber estuary the concentration fluctuated from 0.010 to 0.055 μg L^{-1} (Balls 1985). However, the highest portion of lead in coastal waters and estuaries is connected with particles. The concentration of inorganic Pb in UK estuarine sediments ranged from 25 μg g^{-1} to more than 2,700 μg g^{-1} of sediment (Bryan et al. 1985). Organolead compounds have also been detected in sediments such as the concentrations of tetraethyl, triethyl and diethyl Pb in Canada were 1.15, 0.19 and 0.022 μg g^{-1}, respectively (Chau et al. 1984). Riley and Towner (1984) conducted an experiment and found higher concentrations of tri and dialkyl Pb than those of dissolved inorganic Pb.

2.3.1 Effects of Lead on Organisms

When present in its ionic form Pb^{2+}, it becomes hazardous for the environment as it is easily taken up by organisms. Therefore, it is also included in the priority list of ATSDR (2007). In mammals, Pb is distributed firstly in the soft tissues, then in the bones, where it takes the place of Ca^{2+}. It may cause damage to liver and the reproductive system and to the DNA as well. In fish, the lead poisoning can cause permanent and severe damages in the reproductive system (Das et al. 1980) after long term exposure, depending on the species, size and age of the fish (Alam and Manghan 1992). Temperature, depth and movement of the water body influence the possibility for marine organisms to take up Pb, stored in liver, hepatopancreas and hard tissues and finally influence the metabolism of the organism (Prosi 1989). However, lead (Pb^{2+}) also influences the cytoskeleton, mitochondria, the nucleus in liver cells, causing the cell death, whereas in the kidney it inhibits only some enzymes (Rabitto et al. 2005).

2.4 Zinc

Zinc acts as metal cofactor for many enzymatic processes of both eukaryotic and prokaryotic organisms (Vallee and Auld 1993) and is used in nucleic acid transcription and repair protein (Anton et al. 2007). It also participates in nutrient uptake mechanisms especially for the uptake of CO_2 through the enzyme Carbonic Anhydrase (CA) (Morel et al. 1994) and also for the uptake of phosphate through the enzyme alkaline phosphatase (Shaked et al. 2006).

There are several forms of available Zn in the aquatic system. However, the most bioavailable and dissolved one is the free ion Zn^{2+} (O'Brien et al. 1990). The concentration of zinc in coastal areas and estuaries are much higher than in the ocean (less than 1 μg L^{-1}, Bruland et al. 1979). The concentration of zinc in a North Sea transect was 0.3–70 μg L^{-1} (Duinker and Nolting 1982), whereas the concentration varied from 11 to 23 μg L^{-1} in Bristol Channel-Seven Estuary (Morris 1984). The Zn concentration of sediment in Restronguet Creek, UK, ranged from less than 100 to around 3,000 μg g^{-1}. In interstitial waters, the concentration of Zn in Creek sediments veried from 262 to 396 μg g^{-1}, whereas it fluctuated from 67 to 216 μg g^{-1} at a depth of 10 cm (Bryan and Gibbs 1983). The average Zn concentration in the western coast of Mauritius was 107 mg kg^{-1} (Ramessur 2004).

Generally dissolved Zn is predominant in river water, whereas in estuaries a larger portion of the zinc is adsorbed to suspended particles where concentrations of suspended particles are higher (CCREM 1987). Zinc may be mobilized from sediments in low saline estuarine areas, due to the microbial degradation of organic matter and also displacement by calcium and magnesium. Zinc also can be deposited with flocculated particles during high tubidity and may accumulate in anaerobic sediments.

2.4.1 Effects of Zinc on Organisms

Zinc is a micronutrient for marine organisms, important in the enzymatic and metabolic regulation, but at high concentrations it becomes toxic and can cause different permanent and severe damages, e.g. in the reproduction processes (Das et al. 1980). Low concentrations of Zn were observed to stimulate the growth of the organisms in the marine environment. The water hardness (hardness <1 mg L^{-1} as $CaCO_3$), when Zn is present only at low concentrations can influence the egg production and the fertilization process in fish (Sprague 1971 and references therein). An irregular development of some marine organisms has been detected when the concentration of Zn increases (Volpi Ghirardini et al. 2005). Further, it seems that diet borne Zn is not toxic, but it can influence the concentrations of Fe and Cu in the fish. However this feature is still depending on species, age, length and weight of the organism. However, in fish Zn is principally accumulated in the digestive tract after short-term and long-term exposure. Then, gills, liver, kidney, spleen and skeletal tissues divide the second position in Zn accumulation (Clearwater et al. 2002).

2.5 Chromium

Chromium is an important component in industrial sectors and used for the production of ferrochrome, electroplating, pigment production and tanning. The major sources of Cr in the marine environment are the wastes of these industries, dumping of solid wastes and municipal wastes. Different forms of chromium are available in the aquatic environment, but the main biologically important forms are Cr (III) and Cr (VI). Trivalent species participates in glucose, lipid and protein metabolism (Eisler 1986), whereas hexavalent Cr is comparatively more toxic than the trivalent form due to its oxidizing potential, solubility and capability to cross cell membrane (Levy and Venitt 1986). The main forms of Cr (III) are $CrOH^{2+}$, $Cr(OH)_3{}^0$ and organic and inorganic complexes, whereas $HCrO_4{}^-$and $CrO_4{}^{2-}$are the main forms of Cr(VI) in aquatic system (Rai et al. 1987, 1986).

In offshore waters, the average concentration of Cr ranged from 0 to 234 μg L^{-1}, while the concentration of Cr varied between 30 to over 200 μg g^{-1} in UK estuarine sediments (Murray et al. 1983). The total concentration of Cr in the upper 500 m water of the Sargasso Sea (Near to the Bermuda in the North Atlantic Ocean) ranged from 2.5 to 4.5 nM where the concentrations of Cr (III) and Cr (VI) were 1.2 and 2.4 nM, respectively (Connelly et al. 2006). The main way of the removal of Cr (III) from the sea water is adsorption to suspended particles such as oxides of Fe or by surfaces (Peternac and Legovic 1986; Mance et al. 1984). The adsorption of trivalent Cr increases with pH. However, adsorption process may decrease with the increases of competing cations. On the other hand, the adsorption of hexavalent Cr decreases with pH and the presence of dissolved anions. Chromium migrations are controlled by several processes such as competition between complexation, dissolution/precipitation, redox process and adsorption/desorption mechanisms. The migration of trivalent chromium occurs under acidic conditions and it occurs as dissolved organic complexes. On the contrary, Cr (VI) migrates rapidly but the process may slow down due to the presence of Fe (II) and high organic matter concentration (Richard and Bourg 1991). With the presence of dissolved oxygen, oxidation of Cr (III) to Cr (VI) is very low but increases with the presence of MnO_2. On the other hand, the reduction of Cr (VI) to Cr (III) increases with the presences of organic matter-rich environment. Finally, after settling of the Cr in sediment, remobilization of Cr occurs either as chromate or as organic Cr (III) complexes (Fig. 2.1).

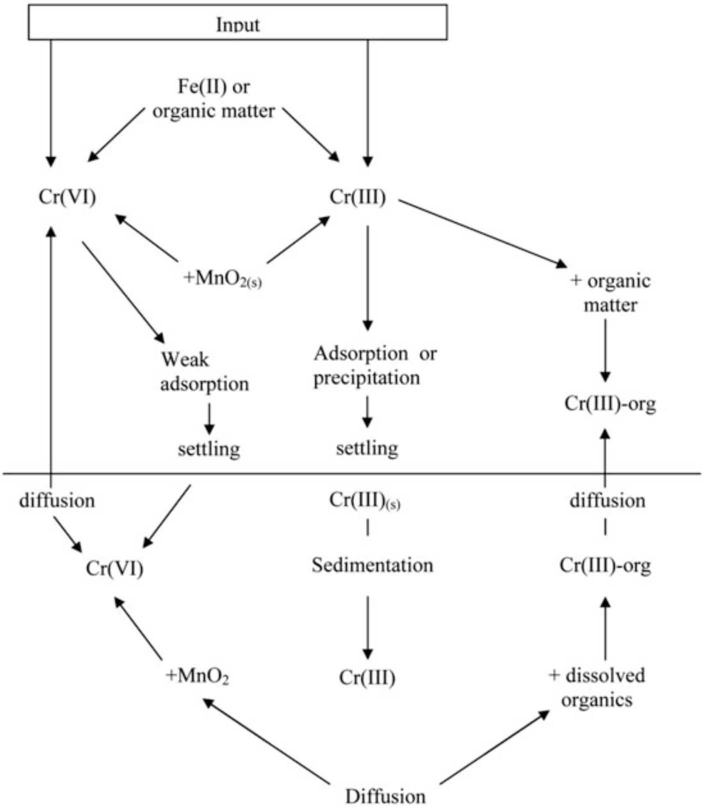

Fig. 2.1 Chromium cycling in the aquatic environment (Adapted from Richard and Bourg 1991)

2.5.1 Effects of Chromium on Organisms

Cr is present in the environment mainly in its inorganic forms Cr(III) and Cr(VI). The latter is a highly toxic compound as it is soluble at each value of pH. Therefore, it is also a quite mobile species. Cr(III) is important in the metabolism of fish, whereas Cr(VI) has increased the maximum lifespan of females in the study of Perez – Benito (2006). As reported by USEPA (1980), *Daphnia magna* is highly sensitive to Cr(VI) in the water body. Further, the photosynthesis in algae and the growth of some fish species varies with the concentration of Cr(VI). However, the uptake of Cr(VI) in a marine organism depends on the conditions of the water body in terms of temperature, salinity and pH.

2.6 Nickel

Nickel is a ubiquitous and nutritionally essential nutrient for plants, animals and micro-organisms. Nickel is used for the production of stainless steel and nickel alloys which are ultimately used in vehicles, processing machinery, armaments, tools, electrical equipment, household appliances and coinage. Moreover, it is also used in catalysts, pigments and batteries. The main sources of nickel to the environment are the uses of coal and oil for power generation, incineration of wastes, nickel mining, steel manufacturing, electroplating, cement manufacturing. However, nickel from all of these activities finally reaches the marine environment due to dumping of wastes, surface-runoff of wastes and incineration (WHO 1991).

Nickel may exist in several forms in the aquatic system. However, Ni (II) is the prevalent oxidation state under normal environmental conditions. The other forms exist in oxidation of 1−, 1+, 3+ and 4+ (Young 1995; Clayton and Clayton 1994; Coogan et al. 1989). The concentration of Ni in fresh water ranged from 2 to 10 μg L^{-1}, whereas it ranged from 0.2 to 0.7 μg L^{-1} (WHO 1991) in Ocean. In coastal, bay and estuary waters it varied from 0.20 to 5.3 μg L^{-1} (Domínguez-Lledó et al. 2007). The concentration of nickel in sediment of Ria Ferrol (NW Spain) were in the range 11.3–67.2 μg g^{-1}, whereas the average concentration was 32 μg g^{-1} (Barciela-Alonso et al. 2003).

Nickel exists in aquatic systems as soluble salts, absorbed on clay particles or together with organic materials such as humic and fulvic acids and proteins. However, sediments also act as a source of nickel through desorption (WHO 1991). The fate of nickel in sea water is controlled by several factors including pH, pE, ionic strength, type and concentration of organic and inorganic ligands, and the presence of solid surfaces for adsorption (Barciela-Alonso et al. 2003).

2.6.1 Effects of Nickel on Organisms

Ni is an essential element for all organisms, aquatic or not, which becomes toxic at high concentrations. In addition, it has been indicated as possible carcinogenic (Coogan et al. 1989; Denkhaus and Salnikow 2002). A long term exposure of marine organisms can modify their morphology and behavior (Alam and Manghan 1992) and disrupt the storage and/or mobilization of essential metabolic substrates (e.g. glucose, proteins) (Scott and Sloman 2004). However, there is no strong evidence about the relationship between the concentration of nickel and its toxicity in the organism (Griffitt et al. 2008).

2.7 Cobalt

Cobalt is an essential component for human and other organisms since it is an important component of Vitamin B-12. Cobalt has both natural and anthropogenic sources. The main human sources are coal and oil burning, industrial activities, vehicular exhausts and sewage sludge. Cobalt is used in steel and alloys, metallurgy, electroplating, nuclear technology, fertilizers, medicine, drier for paint, foam stabilizer in beer brewing (Tsalev and Zaprianov 1985; ATSDR 1999).

The main forms of cobalt in seawater are Co^{2+} and its sulfate-, chloro- and carbonate-complexes (Ahrland 1975) and is removed quickly from seawater with MnO_2 (Knauer et al. 1982). About 90 % of the cobalt can be found in the sediments and in suspended particulate matter in sea waters (Robertson et al. 1973). Sometimes cobalt acts as a limiting nutrient for marine phytoplankton when present at low concentration in the ocean waters (Knauer et al. 1982).

The mean concentration of cobalt detected in seawater was 0.3 μg L^{-1}, whereas it varied from 0.1 to 10 μg L^{-1} in fresh water. The concentrations of cobalt in estuarine sediments ranged from 15 to 60 nM (Huynh-Ngoc et al. 1989), whereas Duchart et al. (1973) found the cobalt concentration 34–650 nM in estuarine sediments. The cobalt concentration in surface marine water is 18–300 pM, whereas it ranged from 20 to 50 pM at depth (Donat and Bruland 1995). The concentration of cobalt is comparatively higher in estuarine and coastal waters than in ocean. Achterberg et al. (1999) measured 140–310 pM cobalt in coastal water near Washed Humber Estuary.

The mobilization of cobalt in estuarine and coastal areas depends on the partitioning of the metal between dissolved and particulate phases (Martino et al. 2002). This is influenced by various factors such as types of metal ion, metal concentration, pH, salinity and dissolved oxygen (Stumm 1992). The primary ways of removal process of cobalt are particle scavenging and biological uptake. However, the metal is also released from the sediment to the dissolved phase due to desorption as a consequence of salinity changes (Kraepiel et al. 1997)

2.7.1 Effects of Cobalt on Organisms

Cobalt seems to be an essential element for certain blue-green algae, nitrogen-fixing bacteria and symbiotic systems as well as for animals. It can be found in two oxidation states, Co^{2+} and Co^{3+}. Co^{3+} is found rarely in organisms as it is thermodynamically unstable in natural waters and cannot be taken up easily. Co can also substitute other trace metals (e.g. Cu, Pb, Zn, Cd) in a wide variety of minerals due to its similar geochemical properties, to form complexes (EnvGovCa 2003). In addition, it can influence negatively the growth rate of, and the Ca-uptake in aquatic herbivores (De Schamphelaere et al. 2008)

2.8 Vanadium

Vanadium is a vital component for aquatic organisms such as marine phytoplankton (Moore et al. 1996), macroalgae (Patrick 1978; Nalewajko et al. 1995) and other organisms (Taylor et al. 1997). Vanadium is present in many enzymes such as haloperoxidases (Butler and Carter-Franklin 2004), nitrate reductases (Antipov et al. 1999) and nitrogenases (Rehder 2000) and also participates in metabolic activity of many components such as chlorophyll synthesis (Meisch et al. 1977; Wilhelm and Wild 1984), cell division (Meisch and Benzschawel 1978), phosphate uptake kinetics (Lee 1982), sulfoxidation (Andersson et al. 1997). Vanadium, on the other hand, is a very important metal for technology. Approximately 75–85 % of the vanadium is used in ferrous metallurgy (alloy additives in steel). The main inputs of vanadium into environment are the burning of fossil fuels, crude oil spillages and industrial activities (atomic energy industry, air craft construction and space technology, as catalyst for the production of sulfuric acid and plastics) (Kalogeropoulos et al. 1989; WHO 1988).

Vanadium in the aquatic environment exist in the form of many species, but the predominant stable oxidized forms are V(IV) and V(V). However, V(V) is more toxic than V(IV) (Pinto et al. 2013). El-Mosehy (2006), who collected sediment samples from the coastal area of the Egyptian seas (Mediterranean and Red Seas) found a mean concentration of 52.61 μg g^{-1} in the Red Sea sediments, whereas the mean value was 40.58 μg g^{-1} in the Mediterranean Sea. The concentrations of dissolved and particulate vanadium in the seawater of English Channel were in the ranges 15–28 nmol L^{-1} and 2–32 nmol L^{-1}, respectively (Auger et al. 1999).

The speciation of vanadium is influenced by redox condition of the aquatic environment (Taylor and van Staden 1994; Pettersson et al. 2003). Various redox pairs such as NO_3^-/NH_4^+, Fe^{3+}/Fe^{2+}, MnO_2/Mn^{2+}, SO_4^{2-}/H_2S play a significant role in vanadium speciation and cycling in coastal seawaters. The solubility of vanadium decreases with decreasing oxidation number. Most of the vanadium present in ocean waters has a conservative behavior, which turns into a non-conservative one in coastal water (Paulsen and List 1997). As most of the vanadium is accumulated in the sediment and only 10 % is present in a soluble form, it is evident that a continuous removal from the sea water occurs (WHO 1988).

2.8.1 Effects of Vanadium on Organisms

Vanadium is an essential element for mammals depending on its concentration and it is bioavailable in the environment. In marine mammals Vanadium was detected at concentrations around 0.2–1.2 μg g^{-1}, wet weight, in liver tissues, where the concentration is proportional to the animal size and age. Furthermore, V shows a good correlation with the concentration of Hg in tissues of marine organisms and it forms complexes with phosphorus. These complexes cause the inhibition of

ATPase. It accumulates in bones, liver, kidney, muscles (Mackey et al. 1996). When V is present at low quantities, it stimulates the biosynthesis of chlorophyll in green algae in the presence of light (Meisch and Bielig 1975). Further, V^{3+} and V^{4+} show antimicrobial activities at low pH values. Therefore, a Vanadium accumulation in the tissues of an organism can be a defense against predators, bacterial infections and biofouling competitors (Odate and Pawlik 2007). At low concentrations (0.041 mg L^{-1}), Vanadium stimulates the growth and reproductive performance in fish, whereas high concentrations (11.2 mg L^{-1}) are toxic (Perez-Benito 2006).

2.9 Iron

Iron is one of the most important essential plant nutrients and plays an important role in various metabolic processes such as photosynthesis, respiration, nitrogen fixation and detoxification of reactive oxygen species (Sunda 2001; Crichton 2001). Iron enters the aquatic environment from weathering as well as from human activities such as burning of coke and coal, acid mine drainage, mineral processing, sewage, iron related industries and the corrosion of iron and steel (CCREM 1987).

Coastal waters receive iron from river water, groundwater inputs and terrestrial runoff. Generally iron exists in sea water in two oxidation states such as iron (II) and iron (III). These oxidation states play a significant role in the formation of soluble organic and inorganic complexes, colloids, insoluble ferric oxyhydroxides and particle phases (Bruland and Rue 2002; Achterberg et al. 2001). The iron (III) oxidation form is predominating in oxygenated waters, but it becomes insoluble after formation of oxyhydroxides.

The largest portion of dissolved iron (III) (80–99 %) occurs in the form of complexes with organic ligands probably produced by iron limited phytoplankton (Rue and Bruland 1995) or bacteria (Granger and Price 1999), whereas only a small portion is found in free hydrated (Fe^{3+}) or inorganically complexed form (Gledhill and Van den Berg 1994; Rue and Bruland 1995; Nolting et al. 1998). On the other hand, iron (II) is thermodynamically unstable in oxygenated water and is quickly oxidized to iron (III). The main sources of iron (II) in sea water are photoreduction of iron in surface water, atmospheric deposition and diffusion from sediments (Miller et al. 1995; Zhuang et al. 1992). This iron (II) contributes for about 50 % of the total dissolved iron in sea water (Gledhill and Van den Berg 1994; Hong and Kester 1986).

The concentration of iron in unpolluted oceanic seawater was found to range from 1.9–2.8 ng L^{-1} to 224–1,228 ng L^{-1} and higher concentrations could be found in estuarine water (Whitehouse et al. 1998). The mean concentration of iron was 20.8 μg g^{-1}, which was found in coastal salt marshes. Ergul et al. (2010) found an iron concentration of 0.033 ng g^{-1} and 25.1 μg g^{-1} in sea water and sediment samples, respectively.

The greater part of the dissolved iron in river waters exists as small colloidal particles, whereas the estimated value of dissolved iron (Fe) input of rivers in the

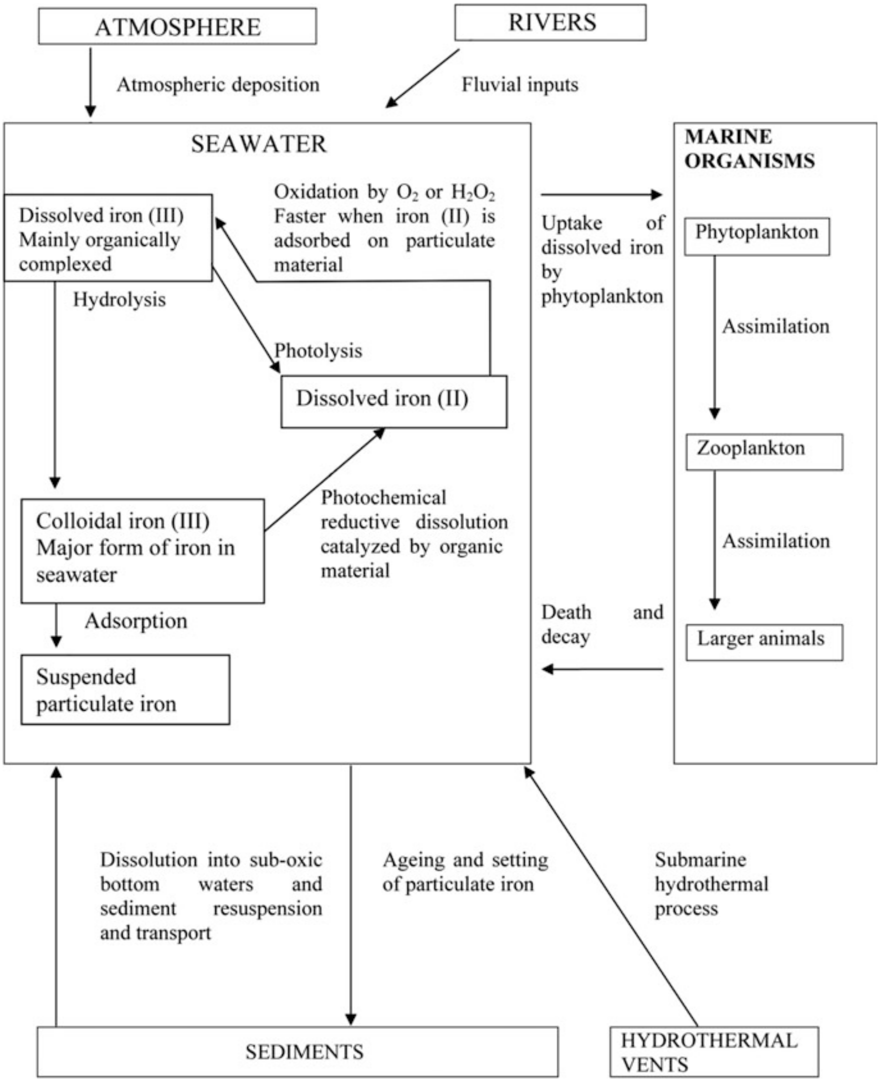

Fig. 2.2 Schematic diagram of biogeochemical iron cycling in the ocean (Adapted from Achterberg et al. 2001)

world oceans is 26 × 10^{19} mol year^{-1} (de Baar and de Jong 2001). Removal of particulate Fe occurs through flocculation during the estuarine mixing of the river water with seawater (Sholkovitz 1978). The biogeochemical cycle of Fe in oceanic environment is given in Fig. 2.2. Organic complexation is one of the key factors of biogeochemistry of Fe in estuarine waters and keeps iron in dissolved phase at high salinities beyond the flocculation zone. This dissolved phase is being flushed from the estuary, whereas the non-organically complexed fraction becomes aggregate and adsorb to particles, thus it remains within the internal cycle of estuary for a longer period of time (Morris et al. 1986). In anoxic marine waters, ferrous iron is mobilized from sediments and diffuses into the water column.

2.9.1 Effects of Iron on Organism

The bioessential element iron is not toxic itself, but it enhances the uptake of As(III) in some marine organisms, which causes adverse health effects for the organism, while it inhibits those of As(V) (Khang et al. 2012). Further, zero-valent iron has been tested by Gheju (2011) as a promoter of the reduction of the heavily toxic and mobile Cr(VI) into the less toxic Cr(III), a process which depends straightly of the environmental conditions of the aquatic system. The same effect was detected when marine organisms were exposed to Cd bound to ferric hydroxide which makes Cd less bioavailable for the organisms (Wu et al. 2012). Nevertheless, Fe is a fundamental element for many biological processes occurring in living organisms. One of them is the interference to the thyroid metabolism and to different enzymes in mammals and fish (Rejitha and Subhash Peter 2013).

2.10 Copper

Copper is a ubiquitous element existing in all natural waters and sediments. Copper is an essential plant nutrient and plays a vital role in the metabolic activities of the organisms. However, it may become toxic to aquatic organisms at concentrations 10–50 times higher than their normal recommended limit (Hall et al. 1997). Recently, the use of Cu as antifouling coating in ships has increased due to the ban of tributyltin and triphenyltin in antifouling coatings. Therefore, concerns are growing that copper has a detrimental effect on the aquatic environment and now it has become an issue in the European saltwater environment because of ecological risk from copper exposure (IMO 1997). Copper exists in various chemical forms such as free copper ions, or complexed with inorganic anions or organic ligands or as suspended particles when present as a precipitate or adsorbed onto organic matter (Mance et al. 1984). The free Cu^+ and Cu^{2+} ions are among the most toxic forms to marine life and toxicity decreases according to the order of Cu^+ and $Cu^{2+}>$ inorganic copper and organic copper (Jones and Bolam 2007; Zamuda et al. 1985). Actually dissolved copper exists in aquatic environment in different forms such as free hydrated cations, organic or inorganic complexes (Achterberg and Braungardt 1999), whereas particulate copper is bound to various mineral phases (clays, quartz, carbonates), iron/manganese oxides and organics (Millward 1995). There are many factors that control the bioavailability and concentration of dissolved Cu such as the cupric ion concentration. These include salinity, the presence of organic ligands and pH (Bryan and Langston 1992).

Hall and Anderson (1999) conducted a research on seawater and found that the concentration of Cu ranged from 0.26 to 16 μg L^{-1}, 0.28 to 5.48 μg L^{-1} and 0.069 to 5.56 μg L^{-1} in marina/harbor, estuary and coastal/open sea, respectively. The average highest concentration was found in a harbor (geometric mean 1.53 μg L^{-1}), the slightly lower concentration was observed in an estuary (geometric mean value 1.49 μg L^{-1}) and the lowest concentration was found in the open sea (0.68 μg L^{-1}).

In estuarine systems copper may be removed from solution by adsorption onto suspended particles which are deposited and accumulate in sediments. The bioavailability of copper increases with decreasing salinity due to the reduced competition from Ca and Mg for uptake sites (Wright and Zamuda 1987). The sea weed *Fucus vesiculosus* has the capability of desorbing and accumulating Cu adsorbed onto particles of suspended sediment (Luoma and Bryan 1982). Estuarine sediments are thought to be the most important depositional sites for particulate copper transported from rivers, although re-mobilization may occur when sediment is disturbed. Copper is removed from oceans' over time through the formation of sediments by the help of several biological and physiological processes (Martin and Windom 1991) or by particulate settling.

2.10.1 Effects of Copper on Organisms

Cu at low concentrations is essential for living organisms as it maintains cellular functions and it plays an important role as a cofactor for different metabolic enzymes (Monteiro et al. 2009). However at higher concentrations free cupric ions have been indicated as the most toxic forms of Cu present in the aquatic environment for marine organisms (Nor 1987), as they are supposed to damage intracellular proteins which lead towards apoptotic cell death (Monteiro et al. 2009). Other studies (USEPA 1985; James et al. 2008; Jorge et al. 2013) revealed a strong correlation between the concentration of Cu in the water body and physiological changes such as a lag in growth in the organisms they studied. Further, Cu can influence negatively the reproduction process of different marine organisms (USEPA 1985; James et al. 2008) as well as the community structure of phyto – and zooplankton (Moore and Winner 1989). However, Jorge et al. (2013) have verified adaptive or compensatory mechanisms when organisms are exposed even to higher concentrations of Cu for longer terms. Furthermore, the toxicity of Cu can be mitigated by the presence of humic matter in the aqueous environment as it complexes Cu (Nor 1987).

2.11 Manganese

Manganese is a vital micronutrient for marine organisms and plays a significant role in photosynthesis (Horsburgh et al. 2002; Kernen et al. 2002). It is also associated with some proteins and enzymes which regulate physiological functions (Frausto da

Silva and Williams 1991). However, a higher concentration of dissolved Mn is helpful to reduce the toxicity of copper (Sunda and Huntsman 1983; Stauber and Florence 1985), cadmium and zinc (Sunda and Huntsman 1996).

The uses of manganese show an increasing trend and recent yearly data account for more than 1,5,000,000 ton (Zhang 2007). Various forms of manganese are present in water such as Mn(IV) oxides, Mn(III) oxyhydroxide and Mn(II) (Post 1999). In marine oxygenated environments, manganese (IV, III) oxides exist as insoluble forms, whereas Mn(II) is available in soluble or dissolved condition. Marine sediments have an aerobic surface enriched with Mn (III, IV) phases. When these oxides enter into deeper layers become reduced to soluble Mn (II) (Burdige 1993). Dissolved Mn (II) may move towards the oxidized zone and precipitate again as Mn (III, IV) (Sundby and Silverberg 1985). In anoxic sediments, Mn is primarily available as Mn(II) carbonates and in solid solution with $CaCO_3$.

The sediment concentration of Mn in Galician rias (north-west Spain) was reported to vary from 93 to 500 mg kg^{-1} (Barreiro and Carballeira Real 1994; Belzunce-Segarra et al. 1997). Hartwell et al. (2000) conducted a research in Chesapeake Bay, USA and found that the total manganese level in sediment was from 940 to 2,400 mg kg^{-1}, dry weight. The total manganese level in the northern Adriatic Sea (Italy) ranged from 200 to 800 mg kg^{-1} dry weight, with an average value of 370 mg kg^{-1} dry weight (Fabbri et al. 2001). The average manganese concentrations in surface sediments of the Baltic Sea were 3,550 (Bothnian Sea), 5,070 (Gulf of Finland) and 8,960 (Bothnian Bay) mg kg^{-1} dry weight. The concentrations of dissolved Mn in sediment pore waters were in the range 0.2–24 mg L^{-1} (Eriksson and Baden 1998), whereas it fluctuated from 0.2 to 17 μg L^{-1} (Hall et al. 1996) in bottom water. Bryan and Hummerstone (Bryan and Hummerstone 1973b) measured manganese concentrations in seaweeds from south-west England varying from 128 to 393 mg kg^{-1} (geometric mean), whereas manganese concentrations were 350 and 29 mg kg^{-1} in a seaweed of North Sea (*Fucus vesiculosus*) and mussels (*Mytilus edulis*), respectively (Struck et al. 1997). The concentration of manganese in lobsters living on sediments was 92 mg kg^{-1} of body weight (Eriksson 2000).

In anoxic conditions the concentration of manganese in Chesapeake Bay, USA, was 237 μg L^{-1} (Eaton 1979), whereas it was approximately 700–800 μg L^{-1} in anoxic bottom water in the Baltic Sea (Kremling 1983). Roitz et al. (2002) conducted a research on the distribution of dissolved manganese within the San Francisco Bay and found manganese concentrations in the range 12–210 nM at the freshwater interface, from 35 to 756 nM at intermediate salinities and from 86 to 435 nM at the oceanic interface. Tueros et al. (2008) determined concentration of dissolved Mn according to the ranges in salinity in estuary and coastal waters within the Basque Country (northern Spain). The median value of Mn within the polyhaline range (18–50 PSU) was 5.8 μg L^{-1} while in the euhaline ranges (salinity $\leq$0.5 PSU) the value of Mn was 1 μg L^{-1}.

Dissolved manganese is particle reactive and may be removed from the water column by sorption onto inorganic and organic particles (Hunt 1983), bacteria

(Sunda and Huntsman 1990) and phytoplankton (Brand et al. 1983; Sunda and Huntsman 1996). However, there is also evidence of desorption of dissolved manganese from riverine suspended particles at the freshwater/seawater interface (Li et al. 1984; Yang and Sañudo-Wilhelmy 1998). The main sources of dissolved Mn in estuary are fluvial and atmospheric inputs, point and non-point source inputs and benthic fluxes from sediments.

Dissolved Mn shows a complex behavior in the estuarine mixing water zone where redox conditions play a vital role in the sedimentation, solubilization and dissolved-particulate partitioning processes. One of the main sources of dissolved Mn in the water column is the re-dissolution of Mn (II) ions (Laslett and Balls 1995). Desorption from suspended particulate matter (SPM) is favored in an environment with low dissolved oxygen and low medium salinity which also contributes for the formation of stably-dissolved Mn (III) chloride and sulphate complexes (Owens and Balls 1997). Mn (II) can be removed from the coastal areas through oxidative processes and the precipitation of Mn (IV) hydroxides (Laslett 1995; Nolting et al. 1999). However, the removal of Mn (II) has also occurred in estuarine reaches where dissolved oxygen increased. Changing of solubility of Mn ions due to the Fe (II)/Fe (III) solubilisation-precipitation processes affect the dissolution and co-precipitation of the other metals such as nickel and zinc (Laslett 1995; Audry et al. 2007). Generally the highest concentration was found in mesohaline-polyhaline ranges, whereas the concentration decreased gradually in the outer estuary and the coastal zone (Kraepiel et al. 1997; Nolting et al. 1999; Audry et al. 2007).

2.11.1 Effects of Manganese on Organisms

Manganese is an essential trace element which is involved in many metabolic processes in plants and animals, with the problem that an excess of the bioavailable ionic form Mn^{2+} can cause neurotoxic effects on marine organisms (Martin et al. 2008). Oweson and Hernoth (2009) detected immunotoxic effects of Mn in crustaceans. Mn was accumulated in the glands and the blood of the animals. This reduced the bactericidal capacity of the organisms, making them more susceptible to different infections. However, Mn was eliminated from the organism back into the water body when the Mn concentration of the latter decreased. Different aquatic organisms are widely used as bioindicators for the Mn concentrations prevailing in an aqueous environment (Steenkamp et al. 1994; Baden et al. 1999; Norwood et al. 2006). Mn-oxidizing bacteria also exist (Tyler 1970) in the aquatic environment. The resulting compounds can be faster taken up by organisms which use the oxidized Mn as energy source in their growth process (Kepkay and Nealson 1987).

2.12 Arsenic

Arsenic has received extensive attention during the last decades due to its relative mobility over a wide range of redox conditions, carcinogenic properties and also its occurrence in the aquatic environment (Wang et al. 2012). Arsenic is a ubiquitous element on earth with metalloid property and complex chemistry. In aquatic systems, arsenic can be originated from both natural and anthropogenic sources such as volcanism, weathering, as by-product of mining, metal refining process, burning of fossil fuels, wood preservation, herbicides, pesticides, fungicides, cement works, electronics industries, ammunition factories, chemistry (dyes and colors, wood preservatives, pesticides, pyrotechnics, drying agent for cotton, oil and dissolvent recycling), pharmaceutical works (medication) (Savory and Wills 1984; Pacyna 1987; Winter 1998; Cullen and Reimer 1989).

Arsenic is found in the atmosphere mainly in four oxidation states such as arsenate (As^{V}), arsenite (As^{III}), arsenic (As^{0}), and arsine (As^{III-}) (Sharma and Sohn 2009). In Earth, arsenic is commonly disseminated as the arsenides of copper, nickel, and iron, or as arsenic sulfide or oxide. Estuaries are zones between terrestrial and marine ecosystems and play important role in arsenic cycling (Maher 1984; Bone et al. 2006). The features of the estuaries change with the changes in salinity and redox potential (Wang et al. 2012).

However, arsenic (III) oxide is generated due to copper smelting, whereas methylated arsenic compounds are produced due to biological activity. The noxiousness of As in the aquatic system depends on its speciation and concentration. In water, arsenate and arsenite are more dominant than other forms of arsenic. Arsenate is predominant in oxygenated water, whereas arsenite is predominant in a reduced condition. Arsenic is transported from its sources to estuaries and marine system via atmospheric deposition and riverine input. Marine microorganisms are responsible for the transformation of inorganic arsenic into more complex organic compounds such as arsenobetaine, arsenocholine and arsoniumphospholipids.

Aquatic micro-organisms such as phytoplankton and bacteria keep a significant role in arsenic speciation, distribution and cycling in aquatic ecosystems (Howard et al. 1995; Hasegawa et al. 2001; Hellweger and Lall 2004; Sharma and Sohn 2009). Phytoplankton species are responsible for the conversion of inorganic arsenic into methylarsenicals and high order organic arsenic compounds such as arsenosugars, whereas bacteria play an important role for the mineralization of organic arsenic to methylarsenicals (Francesconi and Edmonds 1996; Hanaoka et al. 1995). Aquatic organisms keep and transform arsenic species inside their body after being exposed to arsenic from food or other sources such as water and sediments (Edmonds et al. 1997; Hasegawa et al. 2001). The ability of micro-organisms to accumulate, transform, detoxify, and modify the arsenic speciation depends on several parameters such as the phosphate concentration, pH, redox potential, salinity, temperature, and light intensity (Karadjova et al. 2008).

The average concentration of arsenic in marine water is less fluctuating than in freshwaters (Neff 1997; Smedley and Kinniburgh 2002). The mean concentration of arsenic in marine water is 1.5 mg L^{-1}. The average concentrations of As in Pacific coast near Nakaminato (Ibaraki, Japan) and Onagawa (Miyagi, Japan) were 3.1 μg L^{-1} and 0.6 μg L^{-1}, respectively (Ishikawa et al. 1987). In deep Pacific and Atlantic waters it ranges from 1.0 to 1.8 mg L^{-1} (Cullen and Reimer 1989). However, the concentrations of arsenic in estuaries are much more uniform than in open waters. Arsenic concentration in estuaries might be influenced by effluents from industry and mining activities, bioactivities of aquatic organisms and geothermic water (Smedley and Kinniburgh 2002). The distribution of arsenic is influenced by thermal stratification (Hasegawa 1996). Arsenic was detected uniformly distributed in the water column in Vestfjord estuary in Norway, where the value ranged from 0.75 to 1.05 mg L^{-1} (Abdullah et al. 1995).

Physical mixing of the fresh and seawater masses and salinity may influence the concentration of dissolved arsenic in estuaries and continental shelves. There is a linear relationship between arsenic concentration and salinity. For instance, Seyler and Martin (1991) reported a linear increase in total arsenic concentrations varying from 0.13 mg L^{-1} in freshwater to 1.8 mg L^{-1} in offshore waters, with the increase in salinity in Krka Estuary, Yugoslavia. Redox potential (Eh) and pH are the most important factors controlling arsenic speciation. Under oxidizing conditions, $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst at higher pH, $HAsO_4^{2-}$ becomes dominant. H_3AsO_4 and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively. Under reducing conditions at pH less than about pH 9.2, the uncharged arsenite species $H_3AsO_3^0$ will predominate (Brookins 1988).

Arsenic can be removed from the estuary in several ways. Although As can be scavenged from the water column by the particulate matter, adsorption of As onto iron (and to a lesser extent Mn) oxyhydroxides may be a dominant way of removal (Crecelius et al. 1975; Langston 1983). There is a decreasing trend of arsenic from estuary to ocean due to flocculation of iron oxides with increased pH and salinity (Cullen and Reimer 1989).

2.12.1 Effects of Arsenic on Organisms

Arsenic is included in the priority list of dangerous substances established by ATSDR (2007) as it shows a high ability to accumulate in lipid tissues of organisms and can be transported easily upwards in the trophic chain. It can be found in water bodies as As(V), As(III), As(0), As(III-). Among these ionic forms, As(III) and As (V) are the most toxic ones. Those compounds derive from contaminated water and/or sediments and can be possibly biomagnified within the aquatic food web (Rahman et al. 2012 and references therein). In mammals, the poisoning can be acute (e.g. gastroenteritis) and chronic (e.g. effects on the reproductive – and the immune system) (Norwood et al. 2007). Also in fish, chronic poisoning of As can cause problems in the reproduction process as well as in the development of the young fish at concentrations as low as 1 ppb (Das et al. 1980). Major amounts (85–90 %) of arsenic compounds were found in edible portions of fish, whereas a smaller amount (5–44 %) was detected in lipids of macroalgal species. The concentrations of arsenic differ significantly in phytoplankton and microalgae. Generally, brown algae contain higher amount of total arsenic (around 230 mg g^{-1} d. w.) than green (approximately 23.3 mg g^{-1} d. w.) and red algae (approximately 38 mg g^{-1} d. w.) (Thomson et al. 2007). There are two different assumptions about the degradation of arsenic species: the first one is that As (V) is taken up mainly by phytoplankton and reduced to As (III), while the second one suggests that As(III), taken up by phytoplanktonic organisms, is converted to As(V) and to methylated forms of As which are further eliminated by excretion (Phillips 1990). Those methylated forms are in turn degraded by the action of bacteria, forming again the more bioavailable form As(V) (Rahman et al. 2012).

2.13 Tin and Organotin Compounds (Tributyltin and Triphenyltin)

The environmental significance of tin is mostly related to its organometallic derivatives, namely Organotin compounds (OTs) which are extensively used in the industrial sectors because of their special properties such as PVC stabilizers and catalysts, as biocides in agriculture and as antifouling agents in marine paints to limit the growth of aquatic organisms on ship hulls, fish cages, oil rig supports etc. Even though some natural methylated forms of tin are known, the impact of organotin compounds in marine ecosystems derives mainly from anthropogenic activities (Amouroux et al. 2011). Scientists are globally concerned about organotin due to their ubiquitous presence (at nanomolar concentration in water) and accumulation in aquatic organisms (Atanasov et al. 2005; Hu et al. 2006). Guruge et al. (1996) reported an annual use in 1992 of 50,000 tons, whereas in 1986 it was 35,000 tons. During the last 60 years, significant amounts of organotins have been added into various ecosystems (Hoch 2001). Thirty six organotin compounds are harmful to the natural resources out of 260 known compounds (Eisler 1989). Various factors control the solubility of organotin compounds such as oxidation/reduction potential, pH, temperature, ionic strength, and concentration and composition of the dissolved organic matter (USEPA 2003).

Organotin compounds are persistent in the aquatic environment because of their slow degradation rate and consistent flux (Michel and Averty 1999). Among the organotin compounds, tributyltin (TBT) and triphenyltin (TPT) are the most hazardous and largest discharged compounds into the marine environment. Although triphenyltin (TPT) is mainly used in agriculture such as fungicide and insecticide, it is also used in marine paint formulations. On the contrary, tributyltin (TBT) is widely used in antifouling agent in boat paints, in wood preservation, as an antifungal agent for textile and in industrial water systems (Donard et al. 2001). TBT is more hazardous than TPT and causes chronic and acute toxic effect to aquatic organisms such as zooplankton, algae, molluscs and fishes at larval stage

(Gibbs and Bryan 1996). However, OT compounds are recognized as priority substances in the EU directive on environmental quality standards in the area of the water framework policy (EU 2008). In 2008, the total ban on using harmful organotins in antifouling paints was introduced (EU 2003; IMO 2001).

Tributyltin and triphenyltin are ionizable and make complexes by reacting with different ligands present in the environment (Arnold et al. 1997; Buck et al. 2003). The fate and accumulation of the organotion compounds are determined by the speciation of organotin compounds. In water, tributyltin and triphenyltin exist as various states such as neutral, non-dissociated molecules (triorganotin hydroxide and triorganotin chloride) and/or as organotin cations. Speciation is normally regulated by the pH and salinity of the water. In seawater the hydroxyl-complexes ($>$93 %) are the dominant species, whereas under acidic medium (pH 6), the TBT-cation exists in addition to the neutral TBT-Cl and TBT-OH complexes (Arnold et al. 1997; Burton et al. 2005)

2.13.1 The Behavior and Distribution in the Environment

The biological effects of the TBT and TPT are mainly determined by the distribution of the compounds in the environment, timescale and environmental conditions where they exist. However, the environmental distributions depend on the physical, chemical and biological properties of these compounds and the myriad of the localized conditions.

TBT and TPT are hydrophobic in nature and quickly partition into water-borne particles and their aqueous solubility depend on salinity, pH and temperature (Hoch 2001). After partitioning in water, OTs are trapped in the sediments. These may undergo resuspension into the water column and OTs are returned back into the water. This accumulation acts as a temporary sink and sediments are also a long-term source of dissolved-phase contamination (Hoch 2001; Donard et al. 2001). Organotin compounds can be accumulated at the surface layer of air-water interface due to their hydrophobic characters and may be quickly lost due to volatilization and UV degradation (Adelman et al. 1990).

2.13.2 Bioaccumulation and Biotransformation

Organotin compounds are accumulated significantly by aquatic species while some species degrade or eliminate the effects of bioaccumulation because of having an efficient enzymatic mechanism (Laughlin 1996). Biomethylation is the main process of biotransformation of the organotin compounds, whereas chemical agents such as methylcobalamin (it transfers a methyl group to metals), methyl iodide (it is produced by microalgae and reacts with metals and metal sulfides), humic and fulvic acid (produced due to decomposition of vegetation) and other methyl metals can transmethylate OTs (Hamasaki et al. 1995). Although methylation or biomethylation can engage sediment-or estuary –containing microorganisms,

Table 2.1 Estimated half-lives of TBT in various environmental matrixes

Environmental matrixes	Half-life
Freshwater	6–26 days (light), 4 months (dark)
Estuarine water	1–2 weeks
Sea water	6–127 days
Water/sediment mixture	5 months–5 years
Estuarine sediment	3.8 years
Soil	4–5 months (TPhT)

Adapted from Cima et al. (2003)

sulfate-reducing bacteria and yeasts are predominant in methylating organotins. Organotin compounds are degraded through different processes such as photolysis, biological degradation and chemical cleavage. The degradation rates of organotin compounds can be evaluated from its half-life. Table 2.1 shows the half-life values of TBT at different environmental matrixes.

2.13.3 Effects of Tributyltin (TBT) and Triphenyltin (TPT) on Organisms

Tributyltin and Triphenyltin show adverse effects on the survival, growth and reproduction processes of different aquatic organisms (USEPA 2003; Arizzi Novelli et al. 2002a). Further, (Duft et al. 2003) tested the carcinogenicity of TBT on some organisms. They influence the reproduction process acting as endocrine disrupters causing imposex phenomena in many adult aquatic organisms, e.g. gastropods and daphnids (USEPA 2003 and references therein), sea- and mudsnails and mollusks (Duft et al. 2003; Arizzi Novelli et al. 2002b), *Nassarius nitidus* (Pavoni et al. 2007). The action of tin-compounds alone can introduce those adverse effects in aquatic organisms, but the presence of some other organic or inorganic compounds can improve the effects (Pavoni et al. 2007 and references therein). Further, Arizzi Novelli et al. (2002a, b) tested the toxicity of TBT and TPT on embryos of sea urchin and their sperm cells, with the results of high poisoning symptoms to phenyltin and butyltin, respectively. In fish, TBT inhibits the gonad development and it reduces the thymus as well as the number of lymphocytes. In mammals, the immune system is suffering from a poisoning in TBT and TPT as well as the reproductive one (Sekizawa et al. 2001 and references therein). As organisms of the higher trophic chain have appropriate detoxifying enzymes, TBT and TPT seem to be toxic only for lower organisms (Arizzi Novelli et al. 2002b). Nevertheless, it can have lethal effects on several aquatic organisms, such as crustaceans, algae, echinoderma and fish (Dimitriou et al. 2003 and references therein).

3 The Lagoon of Venice as a Case of Study of Metal Contamination

The international scientific literature offers a large number of studies focusing on the presence, dynamics and cycling of various polluting and harmful elements in both estuarine and coastal environments. Among these, the pollution of the Lagoon of Venice (Northeastern Italy) has received increasing attention from various scientific and socio-economical authorities in the past two decades. The reasons are principally due to its geomorphological complexity and the anthropogenic pressure. This includes the industrial impact and the intensive lagoon use for tourism and fishing purposes. Due to the international significance, Venice and its lagoon were included in the World Cultural Heritage list (UNESCO 1987) and, at present, it hosts 2.5 million tourists per year staying more than six million nights (Comune di Venezia 2012). Scientific studies, have focused on the physical, chemical, biological and ecological aspects of the Lagoon of Venice. Most studies evidenced that it suffers from numerous and worrying environmental and social problems arising from geological features, climate change, economical causes and many kinds of anthropogenic pressures. Among those, the increased frequency and intensity of flooding events, caused by the climate change related sea level rise and land subsidence, certainly represent the main threat for the future of Venice. The debate on this is still far from being conclusive (Fontini et al. 2010; Carbognin et al. 2010). Another controversial issue is related to the high density of anthropogenic pressures, which impacts seriously all the environmental compartments of the lagoon and its ecosystem and cause sediment, water and air pollution, eutrophication phenomena, exploitation of biological resources, degradation of biota, sediment erosion and the consequent salt marsh losses. Since the pollution of the Lagoon of Venice was largely studied in the last decades, it represents an ideal case of study for transitional environments. Various pollutants from different pathways and from both diffuse and point sources have polluted the lagoon. Solidoro et al. (2010) reported a comprehensive overview of the responses of the lagoon ecosystem to both natural and anthropogenic pressures over the last 50 years. Thereafter, some key findings of recent researches are reported and subdivided by pollution sources and environmental issues. This section provides a quick overview of the studies conducted on the lagoon and highlights the major issues addressed in the last 20 years.

3.1 Source of Contamination: Industrial Zone of Porto Marghera

The direct discharges from the industrial zone of Porto Marghera are largely recognized as the main source of the pollution for the Lagoon (e.g., (Pavoni et al. 1988; Frignani et al. 1997; Bernardello et al. 2006; Carrer and Leardi 2006;

Zonta et al. 2007)). Porto Marghera is one of the most important industrial districts of Italy and includes chemical and metallurgical activities, oil-refining and storage, shipbuilding, incineration and thermoelectric power plants burning coal, gas and refuse derived fuel, wastewater treatments, hazardous waste incineration and other factories. It was built on the border of the lagoon starting from 1917 with activities related to oil and coal and largely grew in the following 50 years, reaching a maximum of 31,000 employees and a surface area up to 20 km^2 in the early 1970s. Today, following the reduction of the industrial activity, the employees have decreased to ~12,000, but the area of Porto Marghera probably is still the main source of contamination for the lagoon. In addition to the main industrial zone, the island of Murano hosts small and mid-size glass-making factories having an impact on the lagoon and the atmosphere (Giusti and Polo 2002; Rampazzo et al. 2008). All these inputs resulted in this sediment pollution near the main industrial areas.

A large number of studies, including the older ones, indicated that the industrial zone of Porto Marghera was the main responsible of elevated concentrations of heavy metals in the Lagoon of Venice. For example, Donazzolo et al. (1984) studied the heavy metals pollution of sediments and attributed it to the industrial area. These findings were followed by a large number of more specific studies. For example, Bellucci et al. (2002) reported maximum values of As, Cd, Hg, Pb and Zn in channels of the oldest part of the industrial area. Bernardello et al. (2006) studied the distribution of various heavy metals in the superficial sediments and pointed out the industrial zone of Porto Marghera as the main source of contamination. They also reported maps of pollutant concentrations for the inner part of the lagoon. Coccioni et al. (2009) indicated that the lagoon is affected by trace element pollution (Cd, Cu, Ni, Pb, Zn and Hg) with the highest concentrations in its inner part, which corresponds to the Porto Marghera industrial area, and also revealed a strong relationship between trace elements (in particular Mn, Pb and Hg) and the occurrence of abnormalities in tests with foraminifera. In addition, a study by (Sommerfreund et al. 2010) showed that the current industrial discharges are the main cause of the pollution nearby the industrial area, but they also pointed out the role of tributary loadings as a source of contaminants to the lagoon. Apitz et al. (2009) used statistical methods to separate natural background and anthropogenic concentrations of trace elements in radio-chronologically selected surface sediments of the Venice Lagoon. Han et al. (2011) studied the relocation effects of dredged marine sediments on mercury geochemistry and found that organic matter play a key role in the control of methylation rates via the control of Hg solubility.

Also the role of glass-making factories on the Island of was assessed, but the extent of studies was largely lower. For example, Giusti and Zhang (2002) described the trace element distribution in sediments, marine water and mussels of the Venetian Lagoon around Murano. They found that sediments are contaminated with many elements (Zn, Cu, Ag, As and Pb) with the highest levels in the fine fraction (pelite, <63 μm), which was the main carrier of heavy metals in most sites.

Some studies have also reported on the cycling, transport and the accumulation of many elements in the finest sediments. For example, Martin et al. (1995)

highlighted the significance of colloids in the biogeochemical cycling of some trace metals, whereas Zonta et al. (1994) showed a strong correlation between heavy metals and finer particles content in the sediment ($d < 7.8\ \mu m$) in a study conducted in a salt marsh. Perin et al. (1997) measured the bio-available and non-bio-available phases of some heavy metals in a channel near the industrial zone. They found that the inner canals were very polluted with heavy metals in the form of highly insoluble sulphides.

3.2 Sources: Urban Settlements

The urban agglomerations include the historical part of Venice on the main lagoon island, and the mainland urban settlement of Mestre (a total of 270,000 inhabitants) across the causeway, with the surrounding inland areas. The population dynamics of the historical center had a population peak during the 1950s, before declining to ~$112 \cdot 10^3$ in the early 1970s and to $66 \cdot 10^3$ in the 2000s. The sewer system is normally organized for the mainland, whereas for the islands it is not conventionally structured with some leaks of untreated domestic sewage into the lagoon. There are no more major industries and factories in Venice historical centre and the direct role of sewer systems discharges in heavy metals pollution of the lagoon can be of minor importance. However, a significant indirect effect on the bioavailability of many elements can be supposed.

3.3 Source: Drainage Basin

Rivers, streams and land runoff (Collavini et al. 2005) reach the lagoon. The lagoon has a drainage basin of ~1,850 km^2, which provides a mean yearly freshwater input of 35.5 $m^3\ s^{-1}$ peaking up to 350–600 $m^3\ s^{-1}$ during significant adverse meteorological conditions. The main freshwater tributaries, contributing with more than 50 % of the total annual load (Zonta et al. 2001; Zuliani et al. 2005, 2001), are few small rivers mainly located in the northern lagoon; some of them are partially canalized. The sediment input associated with these river inflows was estimated to be ~33×10^3 tons $year^{-1}$ in the period 1999–2000. This hydrological pattern creates a typical brackish environment with a salinity gradient that ranges from 10 psu near the mainland border to 32–37 psu at the inlets (Molinaroli et al. 2007) with summer peaks over 40 psu in the most confined areas of the northern lagoon (Facca et al. 2011). Some studies were carried out to assess the role of drainage basin in the contamination of the lagoon. Among others, the DRAIN project (Collavini et al. 2005) studied the pollutant loads from the 12 major tributaries of the Venice Lagoon during 1998–2000.

3.4 Source: Air Pollution

The atmospheric wet and dry polluting depositions are principally linked to the industrial emission processes (e.g., Guerzoni et al. 2005; Rampazzo et al. 2008; Rossini et al. 2010). Rossini et al. (2010) and Bettiol et al. (2005) analyzed the atmospheric bulk deposition of Venice and estimated the metal fluxes to the lagoon. They indicate that industrial sources have a quasi-permanent effect in the composition of atmospheric depositions.

3.5 Source: Engineering Works

In addition, the continuous intervention of man with hydraulic works and the excavation of the lagoon canals resulted in continuous changes of geomorphology. Among those, the re-construction of stone jetties at the lagoon inlets (1860–1934), the dredging of deep and large canals for navigation purposes (1926 and 1970) and the mechanical and often illegal clam catching (1990s) had wide impacts on many lagoon areas (Guerzoni and Tagliapietra 2006). Starting from the second half of 2000s, the construction of mobile barriers to safeguard the lagoon from exceptionally high tides (MoSE project) has further altered the structure of the lagoon inlets with likely consequences in hydrodynamics, sediment exchanges with the open sea and the whole ecosystem (Ghezzo et al. 2010). A comprehensive chronology of the most relevant events that affected the lagoon morphology in the last century is summarized in Sarretta et al. (2010).

3.6 Effects of Pollution on Organisms

A number of studies were carried out in both animal and plant species to detect the bioaccumulation and the effects of many pollutants in the Lagoon of Venice. Some studies found high levels of metals in both sediments and target gastropods (Berto et al. 2012). Nesto et al. (2007) evaluate levels and effects of trace metals (Cd, Cr, Cu, Fe, Mn, Pb, Zn), PAHs and PCBs in mussels and fish native of the Lagoon of Venice.

Berto et al. (2006) analyzed the levels of mercury in both sediments and Gastropoda *Nassarius reticulates* in the southern Venice Lagoon and stated that a main cause for mercury pollution might be attributed to the antifouling paints used in great quantity in the recent past near the town of Chioggia. Berto et al. (2007) analyzed the recent contamination of TBT and found high content of organotin compounds in the gastropods sampled near the dockyards, harbors, and marinas.

Among other species, the mollusc *Mytilus galloprovincialis* was used in most studies, probably for being edible and largely available in the lagoon. Zatta et al. (1992) measured the content of heavy metals (Cd, Co, Cu, Cr, Hg, Fe, Mn, Ni, Pb, Zn) and As accumulated in the mollusc *Mytilus galloprovincialis* from the Venetian lagoon. Widdows et al. (1997) studied the effects of pollution on *Mytilus galloprovincialis* and demonstrated that the inhibitory effects of toxicants on the growth of organisms living in the more polluted inner sites. Da Ros et al. (2000) studied the cellular and biochemical response of mussels transplanted from a relatively pristine site to a polluted one and vice versa and evidenced a direct influence in the thinning of the digestive cells and in the increasing number of lysosomes in mussels from the more polluted site. Giusti and Zhang (2002) described the trace element distribution of the *Mytilus galloprovincialis* around the Island of Murano. Their results indicated that the highest trace element concentrations were in the soft tissue of mussels. However, the levels detected were within the recommended Italian and international guidelines for human shellfish consumption, except for arsenic. Irato et al. (2003) sampled a series of different bivalve mollusks: *Mytilus galloprovincialis*, ark clam (*Scapharca inaequivalvis*), and Japanese littleneck (*Tapes philippinarum*) in two sites and analyzed the concentrations of essential and nonessential metals in digestive gland and gills of each bivalve. Results indicated that all the three species accumulated metals to a considerable extent, and also evidenced the *M. galloprovincialis* and *S. inaequivalvis* as sentinel organisms to be used specifically for Zn pollution. Sfriso et al. (2008) investigated the concentration changes of elements (As, Hg, Cd, Cr, Co, Cu, Pb, Mn, Ni, V, Zn, Fe, and Hg) in the soft tissues of *Tapes philippinarum* during its growth. Arsenic was reported higher in clam tissues than in surface sediments and suspended particles, whereas other elements (Cr, Pb, Mn, Ni, and Fe) were found higher in suspended particles and sediments than in *Tapes*.

A large number of studies was also conducted in plant organisms, mainly algal species. Bragato et al. (2006) monitored growth dynamics, nutrient and heavy metal accumulation in the two dominating macrophytes *Phragmites australis* and *Bolboschoenus maritimus,* but they found that the heavy metal concentration in water and soil was not correlated to the plant content. Favero et al. (1996) investigated the metal accumulation of *Ulva rigida* and reported that this specie specifically accumulates Fe. Caliceti et al. (2002) measured the concentrations of heavy metals (Fe, Zn, Cu, Cd, Ni, Pb, Cr, As) in seven seaweeds of environmental and commercial relevance. They found high Pb levels in *Ulva* species and to a lesser extent in *Gracilaria*, whereas Brown seaweeds (*Cystoseira*) were highly contaminated by arsenic. Sfriso et al. (1995) reported that the dominant macroalgal species in the central lagoon, *Ulva rigida,* shows a preferential enrichment of Zn and Mn compared to other metals.

4 A Concluding Remark

After the period of the worst industrial impact and eutrophication, which caused anoxic events till the eighties, the lagoon appeared to enter a phase of progressive improvement of environmental conditions. In this process, in addition to a significant reduction of industrial activity and stricter limits to emissions enforced by law, an important role was played by the water exchange with the sea that ensured a water renewal and enabled a removal of the finest most polluted sediments from inside the lagoon out to the sea. However, as a consequence of the building of the MoSE barriers at the lagoon-sea channels, the water exchange is expected to be significantly limited. More research is in progress.

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Chapter 3
Potentially Harmful Elements in Agricultural Soils

László Simon

Abstract Soil is a very complex and vulnerable system; a living surface soil is a mixture of solid matter, water, air, and biota components. Human activity nowadays involves such high level of environmental interventions which often irreversible damages and destroys the soil. During the past century, as a consequence of industrial, agricultural and urban activities of man, soil and water resources were contaminated with potentially harmful trace elements (metals and metalloids). As a consequence of pollution the fertility of soils, the most important feature of the soil for mankind was changed adversely. Trace element content and status of agricultural soils may influence plant uptake and concentration of the given element in the tissues of food and fodder crops, thus affecting the quality of food and drinking water with potential implications to human health. After demonstrating the sources of potentially harmful trace elements in agroecosystems the characteristics, ecological significance, environmental exposure, behaviour in soil and biological impacts of the seven most commonly occurring potentially harmful trace elements (As, Cd, Cr, Cu, Hg, Pb and Zn) will be presented in this chapter. Focusing on soils and plants, their accumulation is followed up in foods, and their impacts are summarized on human organism. Case studies are presented to demonstrate the presence of potentially harmful trace elements in urban and industrially contaminated soils, their accumulation in plants, and discussing the possibility of phytoremediation.

Keywords Agroecosystems • Plant • Soil • Soil pollution • Trace elements • Arsenic • Cadmium • Chromium • Copper • Mercury • Lead • Zinc • Case studies

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1 Introduction

The *lithosphere* consists of the solid outer mantle of the earth. It is exposed to the atmosphere over one quarter of the earth's surface area. The upper layer of this portion of the lithosphere is widely covered by *soil*. Other parts of the earth's crust are covered with water, and generally the uppermost layer consists of *sediments*. Parent rocks of the soil are disintegrated by physical weathering into rock fragments and minerals, a process that further releases *nutrients for plants*. Residues from organisms return to the weathering mass to be transformed into *humus*. Soils are washed by water to rivers, lakes, and to oceans, where their residues are deposited, and eventually give rise to *rock formation* (Paasivirta 1991; Fig. 3.1). *Soil is created* from the alteration of parent material by the interactions between the lithosphere, hydrosphere, atmosphere, and biosphere (Chesworth 2008).

Soil is the outermost loose fine rock particle covering of the solid earth crust. A living surface soil is a mixture of solid matter, water, air, and biota components. Most important characteristic of the soil is *fertility*, i.e. its ability to supply plants with nutrients and water (Simon 1999; Paasivirta 1991). Soil is not only a part of the ecosystem but also occupies a basic role for humans, because the survival of man is tied to the maintenance of its *productivity* (Kabata-Pendias and Mukherjee 2007).

Land degradation is any human-induced or natural process that *reduces the fertility* (food production) of the soil, deteriorates its quality or limits its functionality, or leads to its complete destruction. Soils are the critical component in land degradation. Beside water and wind erosion, desertification, soil alkalinisation and salinization, soil acidification, soil compaction, soil biological degradation, and other factors *soil pollution* can cause land degradation (Simon 1999).

2 Soil Pollution

Environmental pollution, especially by chemicals, is one of the most effective factors in the destruction of biosphere components (Kabata-Pendias 2011). *Soil pollution* is the process by which the soil physical, chemical, and biological properties formed under natural conditions are significantly and adversely changed. As a consequence of soil pollution the *essential ecological functions of soil* (biomass production, ecological living space and genetic reserve, filtering, buffering, transforming and storing) are damaged (Simon 1999).

Natural and *human* (anthropogenic) *impacts* can cause soil contamination and pollution, which can be *point-like* (covering a small area) or *diffuse* (covering larger areas) (Table 3.1).

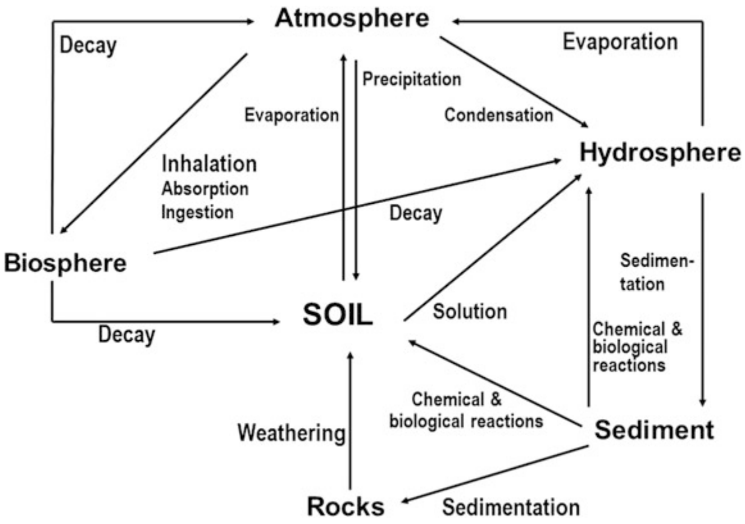

Fig. 3.1 Biogeochemical cycling of metals and metalloids in the environment (Adapted from Paasivirta 1991)

Table 3.1 Most important sources of soil contamination and pollution world-wide

Point-sources	Non-point (diffuse) sources
Natural sources	
Mineral deposits	Wet and dry deposition from the atmosphere derived from natural (e.g. volcanic) sources
Geological formations	Floods, flooding, heavy rains
	Strong winds
	Natural radioactive radiations
Human (anthropogenic) sources	
Sewages	Wet and dry deposition from the atmosphere derived from air pollution
Sewage sludges	Agrochemicals
Animal slurries, manures	Fertilizers
Wastes	Pesticides
Production (industrial) emissions	Transport
	Nuclear explosions

Vermes (1996) in Simon (1999)

Contrary to natural impacts, which cause relatively slow changes, anthropogenic pollutions are modifying the composition, properties and functions of the soils usually *quickly* and *dramatically*. Human activity nowadays involves such high level of environmental interventions which often irreversible damages and destroys the soil. *Anthropogenic pollutants* are present in soil around mines, smelters and foundries, chemical plants, oil refineries, military objects, airports, railway stations, petrol stations, pipelines, containers, liquid and solid waste disposal areas, etc. (Simon 1999).

Soil pollutants includes organic macropollutants (e.g. petroleum and petroleum products), organic micropollutants (e.g. polycyclic aromatic hydrocarbons, pesticides, organohalogen compounds, polychlorinated biphenyls, etc.), inorganic macropollutants (e.g. fertilizing salts and ions as nitrates and phosphates), and *inorganic micropollutants* (e.g. radionuclides, trace metals and metalloids) (Mirsal 2008; Yaron et al. 1996; Simon 1999).

Among all chemical contaminants, *trace elements* (including various metals and metalloids) are believed to be of specific ecological, biological, and/or health significance. *Great risk to environmental health* causes arsenic (As), beryllium (Be), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), selenium (Se), thallium (Tl), vanadium (V), zinc (Zn), and some lanthanides and actinides (Kabata-Pendias 2011). According to McLaughlin et al. (1999) As, Cd, Hg, Pb and Se are the most important to consider in terms of food chain contamination and human health. Where soils are enriched in these elements, it is usually through the agricultural, industrial or urban activities of man, except for Se where high concentrations in soil are often derived from high-Se parent materials.

In Fig. 3.1 a generalized scheme of *biogeochemical cycling* of metals and metalloids in the environment is demonstrated, which occurs there as cations or organic derivatives. Soil plays central role in the *biogeochemical cycling* of metals and metalloids (Paasivirta 1991).

Soil is a very specific component of the biosphere because it is not only a geochemical sink for contaminants but also acts as a *natural buffer* controlling the transport of chemical elements and substances to the atmosphere, hydrosphere, and biota (Kabata-Pendias 2011). *Metals* are a specific group of elements from an environmental point of view. As elements, they *do not degrade in the environment* but accumulate in soils, sediments and seas, and disappear from the biosphere only via geological processes (Fig. 3.1; UNEP 2013).

Metals and *metalloids* are an essential part of our economy as core raw materials for infrastructure and manufacturing products. Demand is expected to remain strong in the future: in developing countries because of rapid industrialization, and in developed countries because modern technologies will require the use of metals. Meanwhile renewable energy technologies – as part of the transition to an inclusive green economy – are generally more metals intensive than fossil fuel ones. Pressures on the environment and human health occur during the whole life cycle of metals. Mining and refining of metals for example, can cause local environmental and health problems due to the release of toxic substances into the ground- and surface water, and into the soil. An increasing share of metal emissions to the environment is coming from non-metal sources such as fossil fuels and phosphate fertilizers. For some metals this is presently the major source. Especially *in agriculture*, *closed loop accumulation* can lead to high concentrations of metals in soils. A sustainable management of metals therefore should include these sources as well (UNEP 2013).

Soil pollution is as old as man's ability to smelt and process ores, and goes back as far as the Bronze Age (2500 BC). Almost all human activities have resulted in increased levels of trace elements in soils, however, this process accelerated after the Industrial Revolution.

Sources of *inorganic micropollutants* (including metals and metalloids) are:

- *industrial activities* (mining and smelting of metalliferous ores, brick and pipe manufacture, cement manufacture, emissions of ceramic, glass and chemical plants),
- *power generation* (burning of fossil fuels, nuclear reactors, incineration of municipal wastes),
- *agricultural practices* (soil amendment with sewage sludge, application of manure, mineral fertilizers, ashes, pesticides, fumigation),
- *transport and urban-derived pollution*,
- *long-range transport of pollutants* (Kabata-Pendias and Mukherjee 2007).

Energy and mineral consumption by man is the main cause of *trace element pollution* in the biosphere (Kabata-Pendias 2011). During the last century as a consequence of mining, metal processing, industrialization, transport, burning of fossil fuels, disposal of wastes, etc. soil and water resources were contaminated with metals and certain metalloids all over the world (Kabata-Pendias and Pendias 2001; Adriano 2001; Alloway 2013). In the industrialized countries trace element contents in agricultural soils have increased significantly over the past century. There is no doubt that trace element content and status of soils may influence plant uptake and concentration of the given element in the tissues of food and fodder crops, thus affecting the quality of food and drinking water with potential implications to human health (Senesi et al. 1999).

Both terms, *contamination* and *pollution*, are used synonymously. According to the definition described by Kabata-Pendias and Mukherjee (2007) *trace element contaminated soils* are not considered to be *polluted* unless a *threshold concentration* exists that begins to affect biochemical and biological processes.

3 Sources of Potentially Harmful Trace Elements in Agroecosystems

Trace elements mean elements present at low concentrations (mg kg^{-1} or less) in *agroecosystems*. Some trace elements, including Cu, Zn, manganese (Mn), iron (Fe), molybdenum (Mo), and boron (B) are essential to plant growth and are called *micronutrients*. Except for B, these elements are also *potentially harmful*, and may be *toxic to plants* at high concentrations. Some trace elements, such as cobalt (Co) and Se, are not essential to plant growth but are required by animals and human beings. Trace elements (metals and metalloids) such as Cd, Pb, Cr, Ni, Hg, and As have *toxic effects on living organisms* and are often considered as contaminants (He et al. 2005).

Soils contain trace elements of various origins:

- *lithogenic* – inherited from the lithosphere (parent material),
- *pedogenic* – from lithogenic sources but forms changed due to soil-forming processes, and
- *anthropogenic* – elements deposited onto and/or into soils as results of human's activities (Kabata-Pendias and Mukherjee 2007).

The *total contents* of *potentially harmful trace elements* – PHTEs (metals and metalloids) in a soil are the sum of the concentrations of elements from lithogenic, pedogenic and anthropogenic sources, minus losses in trace elements removed in crop material, leaching, volatization, erosion or deflation (Alloway 2013; Kabata-Pendias 2011). A wide range of possible anthropogenic (contamination) sources include *atmospheric deposition* of aerosol particles ($<$30 μm diameter), *raindrops* containing metals and metalloids, or gaseous forms of elements, direct applications of *agricultural fertilisers*, *agrochemicals* and various *organic materials* including sewage sludges, livestock manures, food wastes and composts. *Technogenic materials* such as ashes, mine wastes and demolition rubble can be contaminants in existing (pedogenic) soils or can form the parent materials of new, man-made soils (Anthrosols) (Alloway 1990, 2013). The *persistence of contaminants in soil* is much longer than in other compartments of the biosphere, and contamination of soil, especially by trace metals, appears to be virtually permanent. The *input–output balance* of metals in soils shows that trace metal concentrations in surface soils are likely to increase on a global scale, with growing industrial and agricultural activities (Kabata-Pendias 2011).

Common concentrations of PHTEs in uncontaminated agricultural soils are presented in Table 3.2. Although these will have been contaminated to a certain extent by normal agricultural practices they will not have been heavily polluted (Alloway 1990).

Both *deficiency* and *toxicity* of trace elements occur in agroecosystems. Application of trace elements in fertilizers is effective in correcting micronutrient deficiencies (e.g. Zn, Cu, and Mo) for crop production (He et al. 2005).

Soil functions as a filtering, buffering, storage, and transformation system protect against the biological effects of trace element pollution (Kabata-Pendias 2011). Each *soil function* can be associated with *quality features* and *requirements. Guidance values* for PHTEs are used world-wide to regulate exposure to surface soil contamination considering ecotoxicological, biological aspects and primary hazard assessments. The *regulatory guidance values* specify the maximum amount of a pollutant that may be present in the soil without prompting a regulatory response. The eight most frequently regulated PHTEs are Pb, Cd, As, Ni, Cr, Hg, Cu, and Zn (Jennings 2013). The *maximum allowable concentrations* (MAC) for trace metals in soils differ greatly between countries (Jennings 2013; Kabata-Pendias 2011; Nagajyoti et al. 2010). Generally, lower concentrations are for light sandy soils, and for low pH 5–6 range of soils. *Trigger action values* (TAV)

Table 3.2 Total concentrations of potentially harmful trace elements in uncontaminated agricultural soils world-wide

Element	Common value	Range	Element	Common value	Range
	mg kg^{-1} dry weight			mg kg^{-1} dry weight	
As	1–20	0.1–50	Mo	1–2	0.2–5
Cd	0.2–1	0.01–2.4	Ni	50	2–1,000
Co	10	1–40	Pb	10–30 rural	2–300
Cr	70–100	5–1,500		30–100 urban	
Cu	20–30	2–250	Se	0.5	0.01–2
Hg	0.03–0.06	0.01–0.3	Zn	50	10–300

Adapted from Alloway (1990)

are PHTE concentrations above which remedial measures and treatments are necessary. Table 3.3 demonstrates ranges of MACs and TAVs for PHTEs in agricultural soils world-wide.

In several soils of the world *threshold levels have already been exceeded*. Industrial emissions, heavy and repeated applications of sewage sludges, transportation resulted in pollution of garden, orchard and urban soils, and soils near highways with various PHTEs (Kabata-Pendias 2011). Soils of several regions of the world have been and will be in the future subjected to mineral fertilization, pesticide application, waste disposal, and industrial pollution. All these human activities affect both chemical and physical soil properties, and will lead to changes in the behaviour of trace elements in soils. The impact of soil acidification, alkalization, salinity and losses of soil organic matter on the uptake of trace elements by vegetation, particularly by crop plants, have already become serious issues for the environment and for human health (Kabata-Pendias and Mukherjee 2007).

Trace elements originating from various sources may finally reach the *surface soil*, and their further fate depends on *soil chemical and physical properties*, and especially on their speciation (Kabata-Pendias 2011). *Bio(phyto)available* and *mobile fraction* of a given trace element in soil is more important that its total concentration from ecotoxicological point of view (Adriano 2001; Kabata-Pendias 2011). Many *chemical processes* are involved in the transformation of trace elements in soils, but precipitation-dissolution, adsorption-desorption, and complexation are the most important processes controlling *bioavailability* and *mobility* of trace elements there (He et al. 2005). All these processes are governed by several soil properties, of which *soil pH* and *redox potential* are known to be the most important parameters. In most soil conditions the effects of pH on the solubility of trace elements, especially of *microcations*, is more significant than that of redox potential. A steady increase of hydrogen ions in top soils (*acidification*), resulting mainly from emitted sulphur and nitrogen dioxides leads to an imbalance of all nutrients. Acidification may result in destruction of natural buffering properties of soils. Beside soil pH, solubility of trace metals is often the function of the amount and kind of *organic matter* in soil (Kabata-Pendias 2011; Kabata-Pendias and Mukherjee 2007).

Table 3.3 Ranges of maximum allowable concentrations (MAC) and trigger action values (TAV) for potentially harmful trace elements in agricultural soils

Element	MAC	TAV	Element	MAC	TAV
	mg kg^{-1} dry weight			mg kg^{-1} dry weight	
As	15–20	10–60	Hg	0.5–5	1.5–10
Cd	1–5	2–20	Mo	4–10	5–20
Co	20–50	30–100	Ni	20–60	75–150
ΣCr	50–200	50–450	Pb	20–300	50–300
Cr (VI)	–	3–25	Se	–	3–10
Cu	60–150	60–500	Zn	100–300	200–1,500

Adapted from Kabata-Pendias (2011)

The *trace elements from anthropogenic sources* exist mainly on the surfaces of soils as reactive forms and may occur as: water-soluble, exchangeable, associated with organic matter, carbonate, oxides of Fe, Al and Mn and silicates. It has been assumed that the behaviour of trace elements in soils and in consequence their *phytoavailability* differ as to their origin. Several recent reports have indicated that regardless of the forms of the *anthropogenic trace metals*, their availability to plants is significantly higher than those of natural origin (Kabata-Pendias and Mukherjee 2007).

The *atmospheric deposition* of trace elements, mainly trace metals, contributes to contamination of all other components of the biosphere (e.g. waters, soils, and vegetation) (Kabata-Pendias 2011). *Dry* and *wet deposits* contribute variable amounts of metals to the agricultural soil, depending on the nature and distance of point sources. Emissions from large industrial sources, including iron and steel industry, smelters, metal refineries, and metal foundries often have great impact on metal accumulation in the soil (He et al. 2005).

Soil contamination with toxic elements due to *parent materials* (e.g. in serpentine soils, see Sect. 6 on chromium) or point sources often occurs in a limited area and is easy to identify. *Repeated use* of metal-enriched chemicals (pesticides), fertilizers, and organic amendments such as manure or sewage sludge may cause diffuse contamination at a large scale (He et al. 2005). In Table 3.4 typical ranges of PHTEs in biosolids, fertilizers and amendments are summarized.

Sewage sludges (or 'biosolids') are the insoluble residues from the treatment of waste waters at sewage treatment plants. Due to their beneficial contents of nitrogen, phosphorus and organic matter, they are frequently recycled to agricultural land where they have a significant fertiliser value (Alloway 2013; Simon et al. 2000a; Smith 2009). However, the concentrations of PHTEs are a major constraint in the amounts of sludge that can be applied to soils (Alloway 2013; Tsadilas 2011). Sludges from different sewage treatment plants can vary considerably in composition (including trace elements) depending on the sources of discharges in their catchment area (Alloway 2013; Merrington et al. 2003; He et al. 2005; Table 3.4). Long-term regular land application of sewage sludges may lead to excessive accumulation of some potentially harmful trace elements in the arable topsoils (Juste and Mench 1992).

Table 3.4 Typical ranges of potentially harmful trace elements in biosolids, fertilizers and amendments applied to agricultural soils

Elements	Sewage sludge	Sewage sludge*[a]	Phosphate fertilizers	Nitrogen fertilizers	Manure	Limestones
	mg kg^{-1} dry matter					
As	2–26	–	2–1,200	2–120	3–25	0.1–24
Cd	2–1,500	0.4–3.8	0.1–170	0.05–8.5	0.3–0.8	0.04–0.1
Co	2–260	–	1–12	5–12	0.3–24	0.4–3.0
Cr	20–40,600	16–275	66–245	3–19	5.2–55	10–15
Cu	50–3,300	39–641	1–300	1–15	2–60	2–125
Hg	0.1–55	0.3–3	0.01–1.2	0.3–3.0	0.09–0.2	0.05
Mo	1–40	–	0.1–60	1–7	0.05–3	0.1–15
Ni	16–5,300	9–90	7–38	7–34**	7.8–30	10–20
Pb	50–3,000	13–221	7–225	2–27**	6.6–15	20–1,250
Se	2–10	–	0.5–25	–	2.4	0.08–0.1
Zn	700–49,000	142–2,000	50–1,450	1–42	15–250	10–450

Adapted mainly from Kabata-Pendias and Pendias (2001), Alloway (2013)*, and Alloway (1990)**

[a] Range of average metal contents in sewage sludge for individual EU Member States (Alloway 2013)

The European Union (and other developed countries) *regulates the usage of sewage sludge in agriculture* to prevent harmful effects of PHTEs in soil, vegetation, animals and humans. Maximum values are set for concentrations of toxic compounds, and EU countries ban the spreading of sewage sludge when the concentration of certain substances in the soil exceeds these values (Council Directive 86/278/EEC). In concordance with European Union directive, European Commission (2000) recommendations, and EU Member States regulations (Alloway 2013) *regulatory limit values* were set up in Hungary for PHTEs in case of the agricultural utilization of sewage, sewage sludge and sewage sludge compost (Table 3.5).

Beside allowable concentrations of PHTEs in these materials the maximum annual load and maximum allowable concentrations (MAC) of PHTEs in agricultural soils are also regulated in Hungary, and other technologically developed countries. Thanks to the introduction of strict regulations on sewage sludge quality and regulation of environmental emissions of PHTEs, in developed countries Cd, Cr, Hg and Pb levels significantly decreased in municipal sewage sludges (compare the values in first and second column of Table 3.4) during the last two decades (Eriksson 2001; Nicholson et al. 2010; see also next chapters).

Beside sewage sludges regular application of *fertilizers* (primarily phosphates) can considerably enhance the PHTE contents of agricultural soils. MACs for PHTEs in various yield enhancing substances (including artificial, organic and mineral fertilizers, composts, soil ameliorants, liming materials, etc.) were set up therefore in developed countries (see next chapters for MACs of individual trace elements in these materials in Hungary). *Phosphate fertilizers* are considered to be a

Table 3.5 Hungarian regulatory limit values[a] for potentially harmful trace elements (PHTE) in case of the agricultural utilization of sewage, sewage sludge and sewage sludge compost

	Sewage	Sewage sludge	Sewage sludge compost	Maximum load of PHTE[b]	MAC in soil[c]
Element	mg dm^{-3}	mg kg^{-1} dry matter		kg ha^{-1} year^{-1}	mg kg^{-1} dry matter
As	0.2	75	25	0.5	15
Cd	0.02	10	5	0.15	1
Co	0.05	50	50	0.5	30
ΣCr	2.5	1,000	350	10	75
Cr (VI)	0.5	1	1	–	1
Cu	2.0	1,000	750	10	75
Hg	0.01	10	5	0.1	0.5
Mo	0.02	20	10	0.2	7
Ni	1.0	200	100	2.0	40
Pb	1.0	750	400	10	100
Se	–	100	50	1.0	1
Zn	5.0	2,500	2,000	30	200

[a] Hungarian Government Decree 50/2001. (IV.3.) modified by 40/2008 (II.26.)

[b] Maximum allowable annual load of agricultural soils with PHTEs utilizing sewage, sewage sludge and sewage sludge compost

[c] MAC = maximum allowable concentrations in soil according to Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.), and Hungarian 6/2009 (IV. 14.) KvVM-EüM-FVM Joint Decree

serious source of cadmium (see Sect. 5) and other trace metals (e.g. Cr, Zn) (Nziguheba and Smolders 2008; Adriano 2001; Kabata-Pendias 2011; Alloway 2013). At average phosphorus application to soils, the trace metal input via fertilizers is similar to or even larger than the metal input via atmospheric deposition in European agricultural soils for Cd, As and Cr, whereas the reverse is true for Zn, Ni, and Pb (Nziguheba and Smolders 2008).

Livestock manures can be rich in Cu and Zn (see next chapters), since these trace elements are added to animal feeds (Alloway 2013). Manure application to arable lands is therefore of environmental concern similarly to sewage sludge.

Various *pesticides* containing PHTEs (As, Hg, Mn, Pb, Zn) have been used on field and plantation crops. Except copper-based pesticides (see Sect. 7) the use of lead arsenate, phenyl mercuric chloride, ‘Zineb’ (organo-Zn compound), ‘Maneb’ (organo-Mn compound), etc., was banned or restricted world-wide (Alloway 2013; Adriano 2001; Kabata-Pendias 2011).

Besides atmospheric deposition, biosolids, fertilizers, amendments (e.g. lime), livestock manures and pesticides application of *irrigation waters*, *industrial ‘wastes’* (e.g. by-products from the food industry, paper and textile production, tanneries and pharmaceutical/chemical processing, etc.), *water treatment cake*, *dredgings*, *biogas digestates*, *ashes, composts, corrosion* of galvanised structures, *livestock footbaths, lead shots, etc.* can contribute to contamination of agricultural soils with PHTEs (Zn, Cu, Ni, Pb, Cd, Cr, and Hg); (Nicholson et al. 2006, 2010; Eckel et al. 2005).

Urban soils (roadside soils, soils in domestic gardens and allotments) often contain significantly higher concentrations of PHTEs than rural or agricultural soils (Alloway 2004, 2013; Kabata-Pendias 2011). Pb, Zn, Cu, Cd and Cr are the most commonly enriched metals in the soils of many cities, however, elevated concentrations of numerous other PHTEs (including As, Ba, Hg, Ni, Sb, Sn, V, W, etc.) were observed (Dániel et al. 1997; Simon 2001a; Alloway 2004, 2013; Kabata-Pendias and Mukherjee 2007; Wei and Yang 2010; Kabata-Pendias 2011). Detailed information on the sources of PHTEs in urban soils can be found in Chap. 6 and in Alloway (2004). Reasons for lead contamination in urban soils will be detailed in Sect. 9.

Soil microorganisms are the first living organisms subjected to the impacts of PHTEs soil contamination. Being responsive and sensitive, changes in microbial biomass, activity, and community structure as a result of increased metal concentration in soil may be used as *indicators of soil contamination* or soil environmental quality (He et al. 2005; Giller et al. 1998, 2009). The *microbial activities in soil* are associated with uptake or release of a PHTE from a cell, charge alteration of an ion, complexation of an element by various produced compounds, immobilization of a PHTE, or mobilization of an element, often due to the *methylation* (Kabata-Pendias and Mukherjee 2007). *Biological methylation* of some elements such as As, Hg, Se, and Pb may greatly influence their behaviour in soils. Importance of biomethylation in biogeochemical cycling of Hg will be detailed in Sect. 8. *Mycorrhizal fungi* play very specific and important role in the uptake of trace elements by plants. There is evidence that mycorrhiza play a role in the micronutrient supply to plants, and also in immobilization of PHTEs (Kabata-Pendias and Mukherjee 2007; Cuypers et al. 2013; Simon et al. 2006). Plant-associated s*oil bacteria* have been observed to be more resistant to high concentrations of PHTEs than other microbial populations and may have role in PHTE-toxicity alleviation (He et al. 2005; Cuypers et al. 2013; Biró et al. 2007).

Most of the PHTEs accumulate in surface soil (Adriano 2001; Kabata-Pendias 2011) which is netted by *roots of plants*. The biogeochemistry of PHTEs can be substantially influenced by *root activities* and related *rhizosphere processes*. Root and microbial exudations of protons or hydroxyl ions and organic acids are among the major derives of modifications of PHTEs' solubility, speciation, and bioavailability across a large variety of plant-soil systems. In the majority of cases, PHTEs appear to be mobilized by rhizosphere acidification and/or action of organic acids (Wenzel et al. 2011).

As important suppliers of dietary minerals for humans and animals, *plants form a bridge* between the soil elemental composition and the food chain. Plants are intermediate reservoirs through which trace elements from soils, and partly from waters and air, move to man and animals. Plant mineral nutrient uptake is essential for its central role in element cycling, but also for the growth and development of plants (Cuypers et al. 2013; Kabata-Pendias 2011). The *soil-plant transfer* of trace elements is a part of chemical element cycling in nature. It is a very complex process governed by several factors, both natural and affected by humans. Plants *absorb trace elements* by roots from *soil* (or other growth media) and by *above-ground parts* from aerial deposition. *Foliar absorption* is significant in both aerial contamination of plants and foliar applications of fertilizers. With atmospheric pollution, a high proportion of trace metals may enter plant tissues. Elements absorbed by leaves are partly translocated to roots and are also leached from plant foliage, especially by acid rain (Kabata-Pendias and Mukherjee 2007).

Soil is the main source of trace elements for plants both as *micronutrients* and as *pollutants*. In general, plants readily take up trace elements that are in the soil solution in either free ionic or complexed forms (Kabata-Pendias and Mukherjee 2007). Soil physicochemical characteristic may impose limiting factors on the bioavailability of elements (including micronutrients), and *mineral deficiencies* are often experienced in crop production. The uptake and transport mechanisms crucial for essential elements also form an entrance for non-essential metals and metalloids that pose a threat to the plant's fitness, animal and human health (Cuypers et al. 2013). Plants require an *adequate supply of trace elements* or micronutrients for their normal physiological and biochemical functions. Many plants have a narrow concentration range between *deficiency* and *toxicity* for some trace elements (He et al. 2005). It is not easy, therefore, to make a clear division between *sufficient* and *excessive quantities* of trace elements in plants (Kabata-Pendias 2011). In Table 3.6 generalized deficient, normal, toxic and tolerable concentrations of PHTEs are presented in the leaves of plant species.

Plants reveal a great adaptation to the variable composition of growth media, and have developed several *uptake mechanisms* for a given nutrient under deficiency conditions in soils, and can also *exclude an element* at high external concentrations. However, mechanisms involved in the exclusion processes are much weaker than those developed by roots in the absorption of deficient micronutrients. Thus, the excess of trace metals in soils is a stronger stress to plants than their deficiency (Kabata-Pendias 2004). It can be generalized that the *most toxic trace metals* for both higher plants and certain microorganisms are Hg, Cu, Ni, Pb, Co, Cd, Ag, Be, and Sn (Kabata-Pendias and Mukherjee 2007). *General effects of toxicity* on common plant cultivars are stunting and damaged roots, chlorotic, necrotic, brown, and dark green spots, mainly on old leaves, wilting and dying-off of older leaves. Toxicity symptoms are not manifested in all cases of soil contamination. Soils contaminated with trace metals can produce *apparently normal crops* that may be unsafe for human and animal consumption (Kabata-Pendias 2011).

Trace element concentrations in plants reflect, in most cases, their abundance in growth media (soil, nutrient solution, water) and in ambient air. Behavioural properties of PHTEs in soil media influence their availability to plants, are as follows:

- Ag, Cr, Sn, Ti, and Y – very slightly soluble in soil solution and *not easily taken up* by plants (group 1),
- As, Hg, Pb, and F – relatively strongly sorbed to soil particles and *not readily transported* to above-ground parts of plants (group 2),

Table 3.6 Concentrations of potentially harmful trace elements in mature leaf tissue generalized for various plant species

	Deficient[a]	Sufficient or normal	Excessive or toxic	Tolerable in agronomic crops
Element	$\mu g\ g^{-1}$ dry matter			
As	–	1–1.7	5–20	0.2[b]
Cd	–	0.05–0.2	5–30	0.05–0.5
Co	–	0.02–1	15–50	5
Cr	–	0.1–0.5	5–30	2
Cu	2–5	5–30	20–100	5–20
Hg	–	–	1–3	0.2[b]
Mo	0.1–0.3	0.2–5	10–50	–
Ni	–	0.1–5	10–100	1–10
Pb	–	5–10	30–300	0.5–10
Se	–	0.01–2	5–30	–
Zn	10–20	27–150	100–400	50–100

Adapted from Kabata-Pendias (2011)

[a] If less than the stated amounts of essential elements

[b] Fresh weight basis

- B, Co, Cu, Mn, Mo and Ni – mobile in soil and *readily taken up* by plants (group 3),
- Cd, Se and Zn – very mobile in soil and *easily bioaccumulated* by plants (group 4), (Kabata-Pendias 2011).

Elements in *group 1* pose little human risk, because they are not taken up to any extent by plants. Elevated concentrations of elements of *group 1* in foods usually indicate direct contamination by soil or dust. Elements in *group 2* are not readily translocated to edible tissues, and therefore pose minimal risk to human health. Elements in *group 3* are readily taken up by the plants, but are phytotoxic at concentrations that pose little risk to human health. Conceptually, the 'soil-plant barrier' protects the food chain from these elements. Elements in *group 4* pose human or animal health risk at plant tissue concentrations that are not generally phytotoxic (McLaughlin et al. 1999).

Assessment of the likelihood of risks to humans from PHTEs introduced into soil by various anthropogenic activities requires knowledge of the potential for *transfer* of each element from the soil to crops, animals and humans. *Transfer coefficients* (mobility) of selected trace elements in the soil-plant system are summarized in Table 3.7.

Transfer of PHTEs from soils to cops is prevalently a function of the element species, input rate and amount of the element in the soil, soil pH and other soil characteristics, crop species and cultivar grown. Some trace elements can be increased in edible crop tissues when elevated amounts of the element are applied to acidic soil (Cd, Zn, Ni), or alkaline soil (Mo). *Cultivar selection* can be used to reduce food-chain transfer of some elements (Senesi et al. 1999; see example for Cd in Sect. 5). General genotypic variation comparing tendency of the PHTEs accumulation by vegetables is the following: legumes – low, root vegetables – moderate

Table 3.7 Transfer coefficients for selected potentially harmful trace elements in the soil-plant system

Element	Transfer coefficient	Element	Transfer coefficient
As	0.01–0.1	Hg	0.01–0.1
Cd	1–10	Ni	0.1–1
Co	0.01–0.1	Pb	0.001–0.1
Cr	0.01–0.1	Se	0.1–10
Cu	0.1–1	Zn	1–10

Adapted from Senesi et al. (1999)

and leafy vegetables – high. In general, seeds or fruits of cultivated plants are better protected from excessive accumulation of PHTEs than other plant organs (Kabata-Pendias 2011). Grazing livestock may inadvertently ingest soil polluted with trace elements, thus causing a much greater direct exposure than occurring via plant uptake. Estimation of food chain transfer of PHTEs from soil is critical to the valid estimation of the potential for human exposure and human health hazards (Senesi et al. 1999).

In the next sections the characteristics, ecological significance, environmental exposure, behaviour in soil and biological impacts of selected PHTEs (As, Cd, Cr, Cu, Hg, Pb and Zn) will be presented in agroecosystems (focusing on soils and plants), following up their accumulation in foods and summarizing their impacts on human organism. These PHTEs are the most commonly occurring at contaminated sites (Evanko and Dzombak 1997), and their presence in groundwater and soils can pose a significant threat to human health and ecological systems.

4 Arsenic

4.1 Ecological Significance and Utilization of Arsenic

Arsenic (As), the twentieth most abundant element in the earth's crust is a *metalloid*, known for its *toxicity to biota*. In very small concentrations, As appears to be essential in animals and beneficial in plants, however, is most renowned for its toxic effects in the environment. While its high toxic potential has been known and employed since ancient times (e.g. in medicines), it received new and global attention because of the large-scale disaster of As-poisoned drinking and irrigation water at numerous places of the world (Wenzel 2013; Mandal and Suzuki 2002). Arsenic can occur in four oxidation states as arsine (−3 oxidation state), arsenic metal (0 oxidation state), arsenite (+3 oxidation state), and arsenate (+5 oxidation state) in the environment. The *anthropogenic form* of arsenic most frequently released to the environment is As(III) oxide (CCME 2001). Chemically, *arsenic closely resembles phosphorus*, and acts as an analogue in various biological processes such as uptake in plants and microorganism, and in terms of its chemical behaviour in soils (Wenzel 2013; CCME 2001).

Demand for arsenic has fallen sharply since the early 1980s because of concerns about environmental effects (CCME 2001). Until the 1970s, about 80 % of As was used in the manufacturing of pesticides. Due to its toxicity, the use of As in pesticides has decreased. Arsenic compounds can be *utilized* for wood preservation, photoelectric devices, glassware, Pb-acid batteries, feed additives, defoliants, etc. It is also used to improve corrosion resistance and tensile strength in Cu alloys (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias 2011; Adriano 2001).

4.2 Arsenic in Soils

The average concentration of arsenic in the *crust and mantle of the earth* is 1.0–2.5 mg kg^{-1} (Matschullat 2011). The arsenic concentration of the world's *soils* is changing in the range of <0.1–66.5 mg kg^{-1} (Kabata-Pendias 2011), the uncontaminated soils typically contain less than 10 mg kg^{-1}As (Kabata-Pendias 2011; Reimann et al. 2009; Sarkar and Datta 2006; Wenzel 2013). Commonly reported world-average *background As-content* in various *surface soils* is 6.84 mg kg^{-1} (Kabata-Pendias 2011). In Hungary 80 % of uncontaminated soils contain less than 7 mg kg^{-1} of arsenic (Simon 1999).

According to Allard (1995) As concentration in *groundwater* is usually in 0.1–1 μg dm^{-3} concentration level. World baseline for As concentrations in groundwater is in the range of 0.5–0.9 μg dm^{-3} (Wenzel 2013). Allard (1995) reported on 0.01–800 μg dm^{-3} of As in groundwaters of various origin.

Under well-aerated aerobic conditions As^{5+} ($H_2AsO_4^-$) ionic form is dominant in *soils*. It has a strong affinity for iron oxides/hydroxides in soil; thus the concentration of arsenate in soil solution is usually low. In case of reductive conditions and low pH (e.g. in flooded paddy soils) As^{3+} ($H_3AsO_3^\circ$) form is characteristic in soils (Mandal and Suzuki 2002; Zhao et al. 2009; Kabata-Pendias 2011). Reduced forms of arsenic (As^{3+}) are more water-soluble, mobile, bioavailable and toxic for living organisms than oxidised forms (As^{5+}), which accumulates primarily in upper (0–20 cm) layer of soils. In soils with low colloid content, however, the leaching of arsenic compounds to deeper layers was also observed (Adriano 2001). Soil microbes can change the valency of arsenic ions, can *methylate* and *volatize* arsenic; these phenomena can influence the bioavailability, toxicity, migration, and leaching of this element in contaminated soils (Mandal and Suzuki 2002; Kabata-Pendias 2011; Wenzel 2013; Zhao et al. 2009).

The arsenate (AsO_4^{3-}) ions *readily bind to soil constituents* (clay minerals, phosphorus and calcium compounds, carbonates, organic matter), and are most strongly bound to Fe and Al oxides (Mandal and Suzuki 2002; Kabata-Pendias 2011; Adriano 2001; Wenzel 2013).

4.3 Contamination of Soils with Arsenic

In managed *agricultural soils*, As inputs may arise from the application of inorganic and organic *fertilisers*, *lime*, *pesticides* (insecticides, herbicides), *defoliants* (e.g. in potato crops), *desiccants*, *soil sterilants*, *livestock wastes* (where As compounds are used as a fodder additive), and from *biosolids* such as composts or sewage sludge (Wenzel 2013).

The arsenic content of *phosphates* can be relatively high (in average 22.6 mg kg^{-1}), the commonly observed arsenic concentrations in phosphates were in 0.4–188 mg kg^{-1} range (Adriano 2001). The arsenic content of raw phosphates can reach 8 mg kg^{-1} (O'Neill 1990). Kabata-Pendias (2011) reported in average 11.3 mg kg^{-1} (0.5–20.0 mg kg^{-1}) in phosphate fertilizers. As^{5+} ion can substitute for P^{5+} in phosphates such as apatite and may thus become enriched in agricultural lands via fertilizers (Reimann et al. 2009). In most of the artificial N or K fertilizers or in liming materials As is present only in traces (O'Neill 1990; Wenzel 2013; Kabata-Pendias 2011). In Hungary maximum 10 mg kg^{-1} (dry matter) As is allowed in phosphates utilized as artificial fertilizers, similarly to other artificial fertilizers, and organic fertilizers, composts, soil ameliorants, soil conditioners, etc. (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

If arsenic compounds (e.g. roxarsone-(4-hydroxy-3-nitrophenyl)arsonic acid; Arai et al. 2003) are utilized as *feed supplements* for pigs or poultry (10–50 mg kg^{-1} feed As) the excrements can contain up to 30–40 mg kg^{-1} (O'Neill 1990) or 50 mg kg^{-1} (Arai et al. 2003) As on dry matter basis. If these manures were utilized for fertilization of soils, however, the As accumulation in soil ($<$15 mg kg^{-1}) or crops was not considerably enhanced (O'Neill 1990; Arai et al. 2003; Bellows 2005).

In *composts* and *municipal sewage sludges* disposed to arable land relatively low amounts of As were detected (Wenzel 2013; Kabata-Pendias 2011). In sewage sludges 3–30 mg kg^{-1}As was found (Adriano 2001). In sewage 0.2 mg dm^{-3}, in sewage sludge 75 mg kg^{-1} As, while in sewage sludge composts 25 mg kg^{-1} of As can be present in Hungary, if these materials are utilized as fertilizers in agriculture. In soil the total arsenic concentration should not exceed 15 mg kg^{-1} after sewage, sewage sludge or sewage sludge compost application. From sewage, sewage sludge and sewage sludge compost maximum 0.5 kg ha^{-1} arsenic can be transferred annually to agricultural areas (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

Arsenic was 3rd in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). In case of *soil pollution* the As content of soils can exceed 10,000 mg kg^{-1} (Kabata-Pendias 2011). Copper (and other metals) mining and smelting, coal combustion, fly ash application on land, processing of sulphur and phosphorus containing minerals can contribute to the anthropogenic pollution of soils with arsenic (Adriano 2001; Reimann et al. 2009; Kabata-Pendias 2011;

Wenzel 2013). Considerable amount of arsenic was accumulated in soils (mostly in orchards and paddy fields) or in sediments of rivers and lakes from As-containing chemicals. Pesticides: herbicides, fungicides, insecticides; defoliants, and wood preservatives containing As in inorganic (arsenic trioxide, sodium arsenite, calcium arsenate, lead arsenate, chromated Cu arsenate, ammoniacal Cu-Zn arsenate etc.) or organic (mono and disodium methanearsonate etc.) forms were extensively applied for various purposes till the end of 1980s of the last century. Nowadays arsenic containing pesticides and other chemicals were banned or their usage was limited world-wide (Adriano 2001; Wenzel 2013).

Properties of arsenate are similar to phosphates and vanadates. Application of phosphorus containing fertilizers to the soil, therefore, can *reduce the uptake* of As^{5+} ions in plants. In case of special soil features, however, the opposite was also observed. Arsenic accumulation in plants, usually, *cannot be reduced by liming the* acidic As-contaminated soils, since water-soluble (available) calcium arsenate is formed. Application of iron and aluminium salts can enhance the number of binding sites for As in soil, and can *reduce the availability* and plant uptake of arsenic in contaminated soils. Similar effects of zinc and sulphur compounds were also observed (Kabata-Pendias 2011).

4.4 Arsenic in Plants

Arsenic is not an essential trace element for *plants* (Kabata-Pendias 2011; Zhao et al. 2009). At very low concentration, however, arsenic can stimulate the growth of plant roots (Evans et al. 2005). This feature of arsenic may be related to the promotion of phosphorus availability for plants (Nagajyoti et al. 2010). Plants growing in uncontaminated soils contain 0.009–1.7 $\mu g\ g^{-1}$ As; while 1–20 $\mu g\ g^{-1}$ in tissues may be toxic for plants (Pais and Jones 1997; White and Brown 2010). In case of arsenic *phytotoxicity* the weight of roots or shoots is decreasing, roots are discoloured, the young leaves are wilt, the leaf tips and whole leaves are necrotised (Kabata-Pendias 2011; Adriano 2001). Several arsenic accumulator plants (Douglas fir, western hemlock, mountain hemlock, ferns) were identified (Reimann et al. 2009). From polluted soils plant roots accumulate more than 10,000 $\mu g\ g^{-1}$ As, and in shoots several thousand $\mu g\ g^{-1}$ As was detected (Nagajyoti et al. 2010; Kabata-Pendias 2011; Wenzel 2013). Arsenic hyperaccumulation (>20,000 $\mu g\ g^{-1}$ dry matter in fronds) was observed in 12 species belonging to *Pteridaceae* family of ferns (Zhao et al. 2009). The arsenic in common (nonhyperaccumulator) plants is hardly transported (translocated), typically is accumulated in roots (Zhao et al. 2009; Kabata-Pendias 2011). However, in case of application of organic As compounds to soil, As was translocated to shoots or reproductive organs (Tlustoš et al. 2002; Adriano 2001).

4.5 Arsenic in Foods and Humans

Arsenic is not highly mobile and therefore would not be expected to accumulate within the *food chain*. The bioaccumulation index for arsenic is moderate (Pais and Jones 1997). In most of the cases there is not a linear relationship between the As contamination of soil and As content and growth rate of plants (Adriano 2001; Reimann et al. 2009). Usually only the mobile pool of As in soil is related closely to plant uptake of this element (Adriano 2001).

In *human foods* only few hundredths or few tenths mg kg^{-1} arsenic can be found. Consumption of seafoods (seaweeds, marine algae, lobsters, shrimps, oysters, fishes etc.) may enhance dietary intake of As by humans (Adriano 2001; Reimann 2009). Usually, arsenic content of food or fodder plants may not raise enough to threaten human health directly, even if they are cultivated in moderately As-contaminated soils (Adriano 2001). Rice is particularly efficient, however, in As uptake from paddy soil, leading to accumulation in rice grain at concentrations that may pose a health risk to people consuming large amounts of rice in their diet (Zhao et al. 2009).

Serious *health problems* (e.g. skin lesions, skin cancer) of the population can occur if As is present in elevated concentration in *drinking water* or irrigation water. The most extensive As-poisoning occurred in West Bengal (India) and Bangladesh, where population is drinking water from wells drilled into As-rich geologic strata (Adriano 2001). Values of up to 3,200 μg dm^{-3} As have been reported from such wells (Reimann et al. 2009). The current WHO recommended As-level in drinking water is 10 μg dm^{-3} (WHO 2008), which is also a target for the EU, USA and for other developed countries (Adriano 2001; Stollenwerk and Colman 2003).

5 Cadmium

5.1 Ecological Significance and Utilization of Cadmium

Cadmium (Cd) is a naturally occurring metallic element found in soils, waters, plants, and other environmental samples. Cadmium exists in the plus II oxidation state in nature. Cd can affect the ecosystem function at trace levels because of its *pronounced toxicity*. Cadmium is considered as being one of the most ecotoxic metals that exhibit adverse effects on all biological processes of plants, animals and humans. Cadmium is *readily available* for uptake by food crops and food chain contamination with Cd from contaminated soil has led to adverse health effects in humans (Smolders and Mertens 2013; Adriano 2001; Kabata-Pendias 2011). The *toxicity of Cd in soil is persistent*, not only because its residence time exceeds decades but also because its bioavailability does not decrease in the long term (Smolders and Mertens 2013).

The primary *commercial source* of Cd is a by-product from the processing of zinc ores including sphalerite and smithsonite (Martin et al. 2009). The general trend in *global cadmium consumption* over the last two decades has been a steep increase in the use of cadmium for batteries and a decrease in the use for nearly all other applications. In 2005 NiCd batteries accounted for about 82 % of the estimated world consumption. Beside batteries cadmium is used mainly for pigments in plastics, ceramics, and paints, for plating iron and steel, for stabilisers in polymers, and for alloys. These utilizations are restricted in some countries recognizing the toxicity of Cd (UNEP 2010; CCME 1999a).

5.2 Cadmium in Soils

The average abundance of cadmium (Cd) in the *earth's crust* is 0.1 mg kg^{-1}. The average Cd content in various surface soils is changing between 0.2 and 1.1 mg kg^{-1} (except of local anomalies) and the world average in surface soils is estimated as 0.41 mg kg^{-1} (Kabata-Pendias 2011). Uncontaminated light sandy soils or light loamy soils contain less cadmium than heavy loamy soils, since Cd is associated with the finer soil particles (Kabata-Pendias 2011; Smolders and Mertens 2013). The uncontaminated soils typically contain less than 0.5 mg kg^{-1} Cd world-wide, higher cadmium concentrations usually can be attributed to contaminations due to human activity (Adriano 2001; UNEP 2010; Kabata-Pendias 2011; Smolders and Mertens 2013). In great majority of Hungarian soils less than 0.6 mg kg^{-1} of cadmium is present (Simon 1999).

The Cd concentration in uncontaminated *groundwater* is in a range of 0.01–0.1 μg dm^{-3}. In unpolluted groundwater from mineralized areas up to 27 μg dm^{-3} of Cd have been reported due to natural weathering processes of metal-rich phases (Allard 1995).

Divalent cation of cadmium (Cd^{2+}) is prevalent in *soils* (Martin et al. 2009; Kabata-Pendias 2011). Mobility and phytoavailability of cadmium is determined by its chemical forms in soil. The cadmium may be dissolved in the soil solution, can be present bound to inorganic or organic colloids, can be closed in soil minerals, or can also form insoluble precipitates. Soil organic matter, oxyhydroxides of Fe, Al, and Mn and clay minerals are the main Cd adsorbents in soil. In case of soil contamination, in general, the ratio of phytoavailable forms of Cd is significantly increased (Adriano 2001; Kabata-Pendias 2011; UNEP 2010; Smolders and Mertens 2013).

5.3 Contamination of Soils with Cadmium

Beside atmospheric deposition the main reason for *Cd contamination of agricultural soils* is the utilization of phosphate fertilizers and sewage sludges. During the last century the utilization of phosphate fertilizers for agricultural purposes increased cadmium burden of practically all agricultural soils world-wide (Adriano 2001; COWI A/S 2003a; UNEP 2010; Kabata-Pendias 2011; Smolders and Mertens 2013). From 0.15 to 250 mg kg^{-1} Cd was detected in *phosphate fertilizers* (Kabata-Pendias 2011). Application of phosphates, in extreme cases, can enhance the Cd-content of arable soils up to 100 g ha^{-1} annually (Adriano 2001). A considerable fraction of European fertilizers has Cd concentrations >60 mg kg^{-1} P_2O_5 (>137 mg Cd kg^{-1} P; Smolders and Mertens 2013). The European average load of agricultural soils with Pb from P-fertilizers is 1.6 g ha^{-1} annually (Nziguheba and Smolders 2008). In Hungary, in phosphate fertilizers only 20 mg kg^{-1} P_2O_5 cadmium is allowed if they are utilized in agriculture (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

The Cd content in *cattle manure* or processed cattle waste is low (0.14–0.28 mg kg^{-1}), in *poultry waste* 0.42–0.58 mg kg^{-1} Cd was found (Adriano 2001).

From 2 to 1,500 mg kg^{-1} dry weight Cd was detected in various *sewage sludges* (Kabata-Pendias 2011). The Cd content in *municipal sewage sludge* gradually decreased in developed countries during the last 30 years, where nowadays less than 10 mg kg^{-1} Cd is characteristic in this material (Baize 2008). According to Baize (2008) the application of huge quantities of sewage sludges with high Cd content during the 1970s and 1980s has a clear and long-lasting effect on both soil and cereal grain Cd concentrations. In sewage 0.02 mg dm^{-3}, in sewage sludge 10 mg kg^{-1} Cd, while in sewage sludge compost 5 mg kg^{-1} Cd can be present in Hungary, if these materials are utilized as soil amendments in agriculture. Sewage sludge or sewage sludge compost cannot be applied to the soil in which the total Cd concentration exceeds 1 mg kg^{-1}. From sewage, sewage sludge and sewage sludge compost maximum 0.15 kg ha^{-1} cadmium can be transferred annually to agricultural areas [Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)].

Cadmium was 5th in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). In case of massive *pollution* the Cd content of soils can reach several hundred or 1,500 mg kg^{-1} (Kabata-Pendias 2011). Industrial activities (Zn and Pb mining, metallurgy, steel and pigment manufacturing, PVC stabilizers, electroplating, use and disposal of rechargeable Ni-Cd batteries, electronic compounds and photovoltaic cells, oil and coal combustion, waste incineration, etc.), utilization of phosphate fertilizers and sewage sludges in agriculture can contribute to the anthropogenic pollution of soils with cadmium (COWI A/S 2003a; Martin et al. 2009; Kabata-Pendias 2011; Wuana and Okieimen 2011; Smolders and Mertens 2013; Hansen et al. 2013). Anthropogenic sources of Cd are much more significant that natural emissions, and account for its ubiquitous presence in soil. Recognizing the toxicity of cadmium in living systems the global industrial Cd-emission was reduced in developed countries during the last two decades (Martin et al. 2009; Smolders and Mertens 2013). The most significant source of *soil pollution* is the deposition of Cd from the atmosphere (from metallurgical processes, combustion of fossil fuels, waste incineration), and phosphorus fertilization of arable soils (Adriano 2001; UNEP 2010; Kabata-Pendias 2011; Smolders and Mertens 2013).

The *uptake of cadmium in plants* can be affected by soil pH, soil cation exchange capacity, organic matter content, redox conditions, chloride and zinc ion concentration, etc. From acidic soil the plants can accumulate more cadmium, so the *liming of soils* contaminated with cadmium tends to *reduce Cd uptake* of crops. This kind of remediation is not effective, however, for all soils and plants (Adriano 2001; Kabata-Pendias 2011; UNEP 2010). *Amendment of soils* with organic matter, phosphate, industrial by-products (phosphogypsum, red gypsum, and dolomitic residue), and silicon or zinc compounds may have a *remediation effect* decreasing the Cd uptake of plants (Kirkham 2006). If contaminated soil is covered with suitable thickness of uncontaminated soil, the Cd uptake of agricultural crops can be reduced (Kabata-Pendias 2011).

5.4 Cadmium in Plants

The positive *plant physiological effect* of cadmium (which occurs only in very small quantities) is not yet sufficiently confirmed, this element is known on its toxic effects in plants (Smolders 2001; Adriano 2001; Kabata-Pendias 2011; Smolders and Mertens 2013). Grown uncontaminated soils crops are usually contain less than 0.3–0.5 μg g^{-1} of cadmium (Adriano 2001; Kabata-Pendias 2011). From contaminated soils nonhyperaccumulator plants take up several ten μg g^{-1} Cd as a maximum (Martin et al. 1996; Simon 1998; Kirkham 2006). Several plant species were described to hyperaccumulate Cd (i.e. have 100 μg g^{-1} or more Cd in aboveground organs) (Lux et al. 2010). Up to 380 μg g^{-1} Cd was measured in the leaves of penny-cress (*Noccaea caerulescens* [formerly *Thlaspi caerulescens* J&C Presl; Lux et al. 2010], *Brassicaceae*) (Dechamps et al. 2005).

In plants usually 5–10 μg g^{-1} Cd cause *toxic symptoms* (White and Brown 2010); plant growth is inhibited, root system is damaged, roots are bronzed, leaves are chlorotic, the leaf veins and leaf edges has reddish-brown colour, later leaves die and fall off (Simon et al. 1996; Martin et al. 2009; Adriano 2001; Kabata-Pendias 2011). Cadmium in plants inhibits photosynthesis and transpiration, and prevents the uptake and transport of essential micronutrients as Fe, Zn, and Cu (Pais and Jones 1997; Kabata-Pendias 2011).

Zinc is the chemical analogue of cadmium. *Cd-Zn interactions* are commonly observed; both depressing and enhancing effects of each metal have been reported. Increasing soil zinc is known to reduce cadmium availability to plants because Zn inhibits cadmium uptake and cadmium translocation from roots to shoots of plants. In most cases, Zn reduces the uptake of Cd by both root and foliar systems. Zinc deficiency increase Cd uptake by crops (Smolders 2001; Adriano 2001; UNEP 2010; Kabata-Pendias 2011; Smolders and Mertens 2013).

Cadmium in the *soil* does not migrate downwards (its leaching is not characteristic), therefore the topsoil can be enriched with this toxic element to a dangerous level (Martin et al. 2009). *Microorganisms* may have either an inhibitory or a stimulatory effect on the mobility of Cd in soil (CCME 1999a). *Root exudates* can affect Cd absorption by plants through changing the physical and chemical characteristics of rhizosphere (Dong et al. 2007). The presence of Cd in the rhizosphere inhibits root elongation and influences root anatomy. When plant roots are exposed to high Cd concentrations, they increase the production of phytochelatins and sequester Cd entering root cells as Cd-chelates in the vacuole (Lux et al. 2010).

For plants Cd is rather readily *available* and can easily be *transported* within the plant (Adriano 2001). This phenomenon was confirmed in a pot experiment when sunflower plants were grown in a sandy loam brown forest soil artificially contaminated with 0, 1 or 10 mg kg^{-1} of cadmium (Simon 1998). Although Cd was accumulated prevalently in roots, 35 days after 10 mg kg^{-1} Cd-treatment of soil 3.02 μg g^{-1} cadmium was detected in the generative organs (just emerged heads) of sunflower (Fig. 3.2).

Cadmium enters plants from the soil solution (Lux et al. 2010). In general, there is *a linear relationship* between cadmium content of soils and plants (Martin et al. 1996; Simon et al. 1996; Simon 1998; Kabata-Pendias 2011; Smolders and Mertens 2013); however total soil Cd concentration is a poor predictor of Cd risk (Smolders and Mertens 2013). Cd concentrations are greater in roots than is shoots, suggesting that Cd transport to the xylem is restricted in most plants, and is lowest in seeds, fruits, and tubers. This suggests that Cd is not readily translocated in the phloem (Lux et al. 2010; Adriano 2001).

Plants often accumulate considerable amounts of Cd without any visible symptoms of toxicity in their organs. Regular consuming such crops is endangering the health of population. Considering this phenomenon and toxic effects of cadmium on the human body this trace element is considered as one of the most dangerous heavy metals in the food chain (Adriano 2001; Kabata-Pendias 2011; Smolders and Mertens 2013).

5.5 *Cadmium in Foods and Humans*

Cadmium is *highly mobile* and therefore could be expected to accumulate within the *food chain*. The bioaccumulation index for Cd is high (Pais and Jones 1997). Because cadmium is a naturally occurring component of all soils, *all food-stuffs will contain some cadmium*, and therefore all humans are exposed to natural levels of this toxic element (CCME 1999a). If plants are cultivated in contaminated soil, dangerous levels of Cd can be accumulated in their consumable organs. Plants grown in a greenhouse or a container take up more cadmium than same plants grown in soil with the same cadmium levels in the field (UNEP 2010). Plant species and cultivars differ widely in their ability to uptake, accumulate and tolerate cadmium (Martin et al. 2009). In general, the Cd content in leaf vegetables and *Brassica* tops is higher than in storage organs or fruits of other species (Smolders

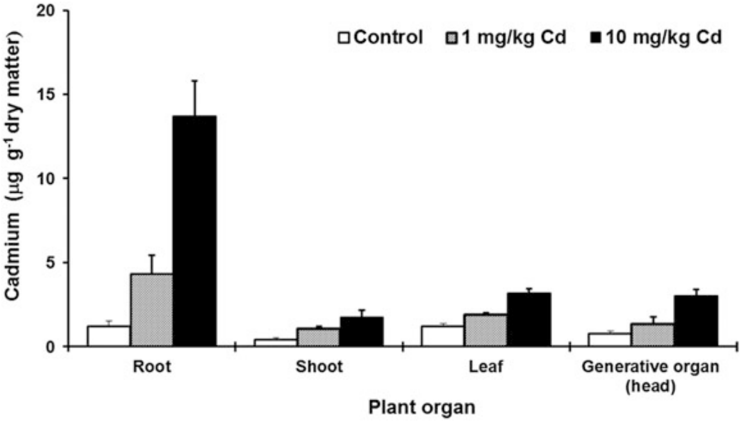

Fig. 3.2 Cadmium accumulation and distribution in sunflower plant (pot experiment, Nyíregyháza, Hungary; Simon 1998)

2001; Kabata-Pendias 2011). Elevated levels of Cd were detected in durum wheat, flax, peanut and soybean seeds, or in sunflower kernels as compared to other consumable seeds (Simon 1998; Smolders 2001; Chaney 2010; Smolders and Mertens 2013). Proper selection of cultivar, in addition to species selection, is very important in managing Cd levels in crops (Adriano 2001). According to Reeves and Chaney (2008) most foods contain low concentrations of Cd that are poorly absorbed, except for rice-Cd. In case of *"itai-itai" disease*, consumption of Cd-polluted was the major source of excessive cadmium intake for local population in Japan (Wuana and Okieimen 2011; Uraguchi and Fujiwara 2012). Molecular engineering and marker-assisted breeding is in progress to develop rice and other cereals which accumulates reduced amounts of Cd in grains during their cultivation (Uraguchi and Fujiwara 2012; Smolders and Mertens 2013).

Cadmium and cadmium compounds are *highly toxic to human health*. Cadmium is classified as a human carcinogen and is highly toxic to kidneys, the skeletal and respiratory systems (COWI A/S 2003a; Kirkham 2006; Martin et al. 2009; UNEP 2010; Smolders and Mertens 2013; Hansen et al. 2013). The safe upper limit for *daily cadmium intake* set by the World Health Organization/Food and Agricultural Organization is 57–71 µg (Pais and Jones 1997). The Joint Food and Agriculture Organization of the United Nations (FAO)/WHO Expert Committee on Food Additives (JECFA) recently (in 2010) established a provisional tolerable monthly intake for cadmium of 25 µg kg^{-1} body weight (Hansen et al. 2013). Cigarette smoking can account for a daily cadmium intake (Pais and Jones 1997; Smolders and Mertens 2013). *Food* is the dominant source of cadmium exposure of humans and accounts for approximately 90 % of the intake for non-smokers. Cadmium in agricultural crops account for most of the intake (UNEP 2010; Hansen et al. 2013). According to Chaney (2010) essentially all human disease from soil Cd has resulted from rice or tobacco consumption. The concentrations of cadmium in most foods range from 0.01 to 0.05 mg kg^{-1}, but higher concentrations may be found in nuts and oil seeds, molluscs. Animal offal (kidney, liver) can exhibit extraordinarily high Cd values, as these are the organs in animals where cadmium concentrates. People with a high intake of meat and other products from marine mammals may have a particularly high intake of cadmium (UNEP 2010; Hansen et al. 2013).

In developed countries the maximum acceptable concentration for Cd in drinking water is 5 μg dm^{-3} (Adriano 2001; UNEP 2010). The cadmium guideline value of World Health Organization for drinking-water is 3 μg dm^{-3} (Hansen et al. 2013).

6 Chromium

6.1 Ecological Significance and Utilization of Chromium

Chromium (Cr) ranks 21st among the elements in crustal abundance, and is omnipresent in the environment (Adriano 2001). The stable forms of Cr are the *trivalent Cr(III)* and the *hexavalent Cr(VI)* species in biological systems. Cr(VI) is considered the most *toxic* and *mobile* form of Cr, which usually occurs associated with oxygen as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) oxyanions. Cr(III) is *less mobile, less toxic* and is mainly found bound to organic matter in soil and aquatic environments. While complexed Cr(III) occurs naturally and is ubiquitous in the environment, the principal source of Cr(VI) in the environment is *anthropogenic pollution*; it rarely occurs naturally (Shanker et al. 2005; CCME 1999b). Chromium(III) is *essential for humans* and animals and Cr deficiency can have detrimental effects on the metabolism of glucose and lipids. *Cr(VI) is toxic to biota* at concentrations in the order of 10–100 times lower than Cr(III) (Gonelli and Renella 2013).

Chromium (produced mainly from chromite ore; Adriano 2001) is *widely used* in the metallurgical industry or in the production of ferrochromium alloys and nonferrous alloys. Cr is also used in the manufacture of refractory bricks, furnace linings, mortars, and castables. Another primary use of chromium is in chemical applications such as metal finishing [Cr(VI)], corrosion control [Cr(III)], leather tanning [Cr(III)] and finishing, wood treatment [Cr(VI)], and the production of pigments [both Cr(VI) and Cr(III)] (CCME 1999b). The *main source of Cr pollution* is considered to be from dyestuffs and leather tanning when wastes are discharged directly into waste streams. Sewage treatment plants from industrial and residential sources discharge substantial amounts of Cr. Chromite-ore processing residue is of the greatest environmental risk in some regions (Kabata-Pendias and Mukherjee 2007).

6.2 Chromium in Soils

In average 100 mg kg^{-1} of chromium can be found in the *earth's crust* (Kabata-Pendias 2011). The chromium content of various soils is changing between 1 and 3,000 mg kg^{-1} (0.02–58 μmol g^{-1}) (Kotaś and Stasicka 2000), the world average is 60 mg kg^{-1} (Kabata-Pendias 2011). The Cr content of Hungarian soils is changing in wide <5–45 mg kg^{-1} range (Simon 1999). Naturally occurring in soil, Cr ranges from 10 to 50 mg kg^{-1} depending on the parental material (Shanker et al. 2005). More than 100–200 mg kg^{-1} in these soils refers to anthropogenic contamination (Adriano 2001; Vodyanitskii 2009; Kabata-Pendias 2011; Iyaka 2012). Chromium concentrations in Californian serpentine soil profiles fluctuate between 1,725 and 4,760 mg kg^{-1} (Oze et al. 2004), and in certain serpentine soils of the world are above 100,000 mg kg^{-1} (Kabata-Pendias 2011).

Cr concentration in uncontaminated *groundwater* in usually in 0.1–1 μg dm^{-3} concentration level (Allard 1995). Rarely exceeding 50 μg dm^{-3}, Cr(III) constitutes a very small percentage of the total chromium found in natural and polluted groundwaters. At a pH >8.5 Cr(VI) is completely mobile and can readily leach out of the soil and into the groundwater system (CCME 1999b).

The fate of Cr *in soils* depends on several factors: redox potential, presence of electron donors or acceptors, oxidation state, pH, soil minerals, competing ions, complexing agents (i.e. low molecular weight organic compounds), water-activity, etc. The two environmentally important oxidation states of Cr, i.e. Cr(VI) and Cr (III), are redox-, and pH-sensitive (Adriano 2001; CCME 1999b). The chromium occurs in soils mainly as Cr^{3+} cation, which precipitates above pH 5.5. The Cr^{6+} cation in the soil is very unstable, readily is reduced to Cr^{3+}. In normal surface soils, reduction of Cr(VI) to Cr(III) is favoured in the presence of reductants such as organic matter, Fe(II), and sulphides. Cr(III) can be oxidized to Cr(VI) in natural environment in the presence of strong oxidants, such as high-valency Mn oxides. Under strongly acidic or strongly basic soil conditions Cr^{6+} ion is very mobile and phytoavailable. This is a very important phenomenon, since Cr^{3+} ion is much less toxic and less available for plants, than the Cr^{6+} ionic form (Adriano 2001; Hörcsik et al. 2006; Kabata-Pendias 2011; Wuana and Okieimen 2011; Shanker et al. 2005; Gonelli and Renella 2013).

A small-plot long-term open-field experiment was set up during 1991 in Nagyhörcsök, Hungary on a calcareous chernozem soil (5 % $CaCO_3$, 3 % humus, pH_{KCl} 7.3). Beside Al, As, Ba, Cd, Cu, Hg, Mo, Ni, Pb, Se, Sr and Zn salts the topsoil was artificially contaminated with 0, 90, 270 and 810 kg ha^{-1} of Cr(VI), in the form of K_2CrO_4. Cr(VI) showed a fast downward migration, after 10 years the largest part of chromium was already leached into the subsoil, reaching layers deeper than 3 m (Kádár and Németh 2011; Kádár 2012).

The sorption of Cr in *soils* is associated primarily with clay contents, and to a lesser extent with iron hydroxides and soil organic matter. The conversion of Cr species in soils can be relatively rapid and significant. Soluble and un-adsorbed Cr complexes can leach from soil into the groundwater (Kabata-Pendias 2011; Wuana and Okieimen 2011). While complexed Cr(III) occurs naturally and is ubiquitous in the environment, the principal source of Cr(VI) in the environment is anthropogenic pollution; it rarely occurs naturally due to its affinity to react with organic matter and other reducing substances (CCME 1999b).

6.3 Contamination of Soils with Chromium

Agricultural soils can be contaminated with chromium through fertilizers, tannery wastes, and sewage sludges. In *phosphate fertilizers* 30–3,000 mg kg^{-1}, in superphosphates 60–250 mg kg^{-1} Cr was detected, where Cr is present probably in less toxic Cr(III) form. In *nitrogen fertilizers* 4–8.5 mg kg^{-1}, in *liming materials* $<$1–200 mg kg^{-1}, and in *organic fertilizers* 6–56 mg kg^{-1} Cr was found (McGrath and Smith 1990; Adriano 2001). Land application of *tannery waste* as organic fertilizer enhanced locally the Cr content of agricultural areas (Bini et al. 2008).

In various yield enhancing substances including artificial, organic and mineral fertilizers, composts, soil ameliorants, soil conditioners, growing media etc., utilized for agricultural purposes chromium concentration is equally limited to 100 mg kg^{-1} (dry matter) in Hungary (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

Chromium concentration in *sewage sludge* is extremely variable, ranging from trace amounts to several thousand mg kg^{-1}, depending on industry of a settlement. It is advantageous that agricultural crops took up limited amounts of Cr from the soils, which were treated with Cr-contaminated sewage sludge or other soil amendments (McGrath and Smith 1990; Adriano 2001; Kabata-Pendias 2011). If sewage in spread to arable soils in Hungary its total chromium concentration is limited to 2.5 mg dm^{-3}, and its Cr(VI) concentration may not exceed 0.5 mg dm^{-3}. In sewage sludge 1,000 mg kg^{-1} (on dry matter basis) and in sewage sludge compost 350 mg kg^{-1} total chromium can be present in Hungary, if these materials are utilized as soil amendments for agricultural purposes. The limit for Cr(VI) present in sewage sludge or sewage sludge compost is equally 1 mg kg^{-1}. Total Cr in soil may not exceed 75 mg kg^{-1}, while Cr(VI) may not exceed 1 mg kg^{-1}, if sewage sludge or sewage sludge compost is applied to arable soils. From sewage, sewage sludge and sewage sludge compost maximum 10 kg ha^{-1} total chromium can be transferred annually to agricultural areas (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

Chromium was 2nd in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). The *soils can be polluted* with chromium during industrial production (e.g. leather tanning, electroplating, paint manufacturing), or by air pollution of steel industry, metallurgy, coal combustion etc. Close to industrial plants, thermal power plants, and along the busy roads the Cr content of the topsoils may be elevated. Dumping of chromite-ore processing residue near Cr-processing plants also led to Cr contamination of soil and groundwater. In case of massive pollution the chromium content of soils usually reached several thousand mg kg^{-1}, or exceeded 10,000 mg kg^{-1} (Adriano 2001; Environment Agency 2002; Su and Ludwig 2005; Bini et al. 2008; Kabata-Pendias 2011; Iyaka 2012; Landrot et al. 2012; Gonelli and Renella 2013).

The main purpose of *remediation* treatments of Cr-contaminated soils is the conversion of easily mobile Cr(VI) to less mobile and less toxic Cr(III) (Kabata-Pendias 2011). There are three main groups of compounds that can be used to reduce Cr in chromite-ore processing residue: (a) reduced sulphur compounds such as hydrogen sulphide, iron sulphide, sodium sulphite, sodium metabisulphite and sodium dithionite; (b) iron based compounds such as zero valent iron, dissolved ferrous iron (Fe^{2+}) or iron-containing minerals hematite, magnetite and biotite; and (c) various organic compounds, including constituents of soil organic matter (Su and Ludwig 2005). Cr(VI) can be reduced to Cr(III) by soil organic matter, S^{2-} and Fe^{2+} ions under anaerobic conditions often encountered in deeper groundwater (Wuana and Okieimen 2011). The Cr(VI)-reducing ability found in some bacteria has raised the possibility of using these microorganisms as a biotechnological tool for remediation of chromate-polluted zones (Cervantes et al. 2001; Zayed and Terry 2003).

Liming, phosphate or organic matter application to soils are known to be effective in *reducing chromate toxicity* in Cr-polluted soils (Kabata-Pendias and Pendias 2001; Pais and Jones 1997). After acidification of the contaminated soil sulphur or leaf litter promoted the reduction of a Cr(VI) to less toxic Cr(III). After the reduction, liming to further precipitate Cr(III) compounds might be advisable (Kabata-Pendias and Pendias 2001). *Immobilization of chromium* with high sorption capacity materials (e.g. smectite clays, coal, bone charcoal), removal of Cr with electrokinetic technique, soil flushing/chromium extraction, reduction of Cr(VI) by ferrous sulphate and/or sulphate-reducing bacterial biofilms, and phytoremediation was proposed to remediate Cr-contaminated sites (Kabata-Pendias 2011; US EPA 2000).

6.4 Chromium in Plants

Chromium is not an essential micronutrient for *plants* (Adriano 2001; Kabata-Pendias 2011; Shanker et al. 2005). Most soils contain significant amounts of Cr, but its availability to plants is highly limited. Usually, plants accumulate low amounts of Cr from soils. The most available to plants is Cr^{6+} ion. Also Cr^{3+} and several complex Cr anions (e.g. CrO_4^{2-}) may be easily available to plants (Kabata-Pendias 2011). Within most of the plant species, Cr(VI) is much more mobile and soluble than Cr(III) (Mei et al. 2002). Root exudates containing organic acids can form complexes with Cr compounds, making them available for plant uptake (Panda and Choudhury 2005). Plant roots can convert Cr(VI) to less toxic Cr(III) (Cervantes et al. 2001; Zayed and Terry 2003). Translocation of Cr from roots to shoots is low; roots accumulate 10–100 times more Cr than shoots or other tissues

(Adriano 2001; Cervantes et al. 2001). Chromium levels in plants growing in 'normal' soils are usually less than 1 μg g^{-1} (dry weight) and rarely exceed 5 μg g^{-1} (Zayed and Terry 2003). Levels in shoots of plants grown on uncontaminated soil usually do not exceed 0.5 μg g^{-1} (dry weight) Cr (CCME 1999b). In general, the Cr content of roots is larger than of shoots (leaves, stems); the minimum quantity of chromium is present in crops or seeds (Kabata-Pendias and Pendias 2001; Cervantes et al. 2001). *Brassicaceae* (turnip, Indian mustard, white mustard, fodder radish, rape) accumulated more chromium in their organs than hemp or amaranth, if these species were grown in a Cr (galvanic mud) contaminated soil (Simon et al. 1998). Similarly, Zayed et al. (1998) detected the highest Cr concentrations in members of *Brassicaceae* family (i.e. cauliflower, kale, cabbage), which are known to be S-loving plants.

Chromium *hyperaccumulator plants* are not known (Brooks 1998; Sarma 2011). *Thlaspi goesingense* Hal., native plant of Ni- and Cr-rich serpentine soils, hyperaccumulated nickel but not chromium, if was grown in a soil artificially contaminated with these metals (Simon and Wenzel 2003). Certain terrestrial or aquatic plants are able to accumulate elevated levels of Cr in their organs if grown in serpentine soil, in chromite-ore processing residue, or in Cr-contaminated soil, sediment or effluent (Kabata-Pendias and Pendias 2001; Keresztúri et al. 2002; Zayed and Terry 2003; Sarma 2011; Kabata-Pendias 2011; Gonelli and Renella 2013).

Besides EDTA the organic chelant picolinic acid was effective to promote phytoavailability of chromium in soil, and enhance *Cr-phytoextraction capacity* of fodder radish and komatsuna plants (both *Brassicaceae*) grown in a soil artificially contaminated with Cr (Simon et al. 2000b, 2001, 2003). In Fig. 3.3 the impact of direct soil application of chromium(III) picolinate is demonstrated on the chromium accumulation in fodder radish shoots and roots.

More than 100 mg kg^{-1} chromium in soils usually is *toxic for plants* (Adriano 2001). Generally, only a very small fraction of the total Cr content in soils is plant available. Only 1–5 mg kg^{-1} Cr present in the soil in the available form, either as Cr (III) or Cr(VI), is considered to be critical for a number of plant species (Zayed and Terry 2003). In plant organs usually 1–10 μg g^{-1} Cr is toxic (Kabata-Pendias and Pendias 2001; White and Brown 2010). In case of chromium phytotoxicity the root development is inhibited, stems wilt, young leaves are chlorotic or have reddish-brown colour, and in the leaves of cereals chlorotic bands are formed. Excess of chromium in plants inhibits the germination and the uptake of essential macro- and micronutrients (e.g. N, P, Ca, Mg, Fe, Mn), induce oxidative stress in plants and affects the activity of antioxidant enzymes (Panda and Choudhury 2005; Shanker et al. 2005; Kabata-Pendias 2011; Adriano 2001; Cervantes et al. 2001; Zayed and Terry 2003).

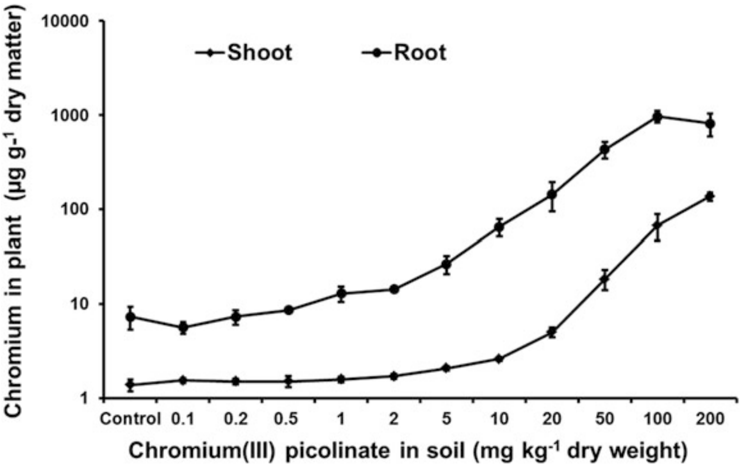

Fig. 3.3 Chromium accumulation in fodder radish grown in soil treated with Cr(III) picolinate (Simon et al. 2001)

6.5 Chromium in Foods and Humans

Chromium has a moderate index of *bioaccumulation* (Pais and Jones 1997). Chromium concentrations in edible plant parts are so low, that they rarely meet the nutritional requirements for human diet (Gonelli and Renella 2013). In common *foods* 0.01–0.16 mg kg^{-1} chromium is present (Kabata-Pendias 2011). Guideline value for Cr in *drinking water* is 50 µg dm^{-3} (Environment Agency 2002). The recommended safe and adequate *dietary intake* of Cr(III) for adults is 50–200 µg (Pais and Jones 1997; Environment Agency 2002).

Trivalent chromium is an *essential micronutrient* for animals and humans, influencing the carbohydrate, lipid and protein metabolism (Pechova and Pavlata 2007). Contents of Cr in plants have recently received much attention due to its importance in human metabolic processes, but also because of toxic and carcinogenic effect of hexavalent chromium. An adequate rate of nutritional Cr has become an important issue (Kabata-Pendias 2011).

7 Copper

7.1 Ecological Significance and Utilization of Copper

Copper (Cu) is 26th in abundance in the lithosphere. Occurs in four oxidation states (Cu^0, Cu^{1+}, Cu^{2+}, and Cu^{3+}) with Cu^{2+} being most common in the environment. Cu^{2+} ion has high affinity for binding to organic matter (Oorts 2013; CCME 1999c).

Copper is an important *essential element* for all living organisms (humans, plants, animals, and microorganisms), and *deficiency* in plants and ruminants occur in soils with low available Cu. Because of the ubiquitous presence of Cu in most foodstuffs the *Cu deficiency in humans* is rare. Elevated soil Cu concentrations cause *toxic effects* in all terrestrial organisms (plants, invertebrates and micro-organisms), and can affect soil ecosystem functioning. *Secondary poisoning* of Cu though the food chain to vertebrates and humans is considered of low risk due to the strong regulation of internal concentrations of this essential element in food plants (Oorts 2013).

Copper is the *third most used metal* in the world, the most important Cu ores are the sulphides, oxides and carbonates (Wuana and Okieimen 2011; Adriano 2001). The long history and widespread use of Cu has resulted in significant *anthropogenic emissions*, which have caused increased environmental Cu concentrations (Oorts 2013). Copper is *mainly used* in electrical applications (65 %), and construction (25 %) (Oorts 2013). Cu is widely used in the manufacture of alloys, textiles, antifouling paints, electrical conductors, plumbing fixtures, pipes, coins, cooking utensils, containers, ammunition, etc. Copper compounds are found in wood preservatives, pesticides, fungicides and algicides as an active ingredient. Copper sulphate may be used as a micronutrient in agricultural fertilizers and as a feed additive (CCME 1999c; Kabata-Pendias and Mukherjee 2007; Adriano 2001).

7.2 Copper in Soils

In average 55 mg kg^{-1} copper occurs in the *earth's crust* (Kabata-Pendias 2011). The copper content of the surface soil varies between 2 and 250 mg kg^{-1} with an average concentration of 30 mg kg^{-1} (Adriano 2001). The range of copper concentration in Hungarian soils is from <10 to 40 mg kg^{-1} (Simon 1999). In uncontaminated agricultural soils usually 1–50 mg kg^{-1} Cu is present. More than 100–200 mg kg^{-1} in these soils refers to anthropogenic contamination (Adriano 2001; Kabata-Pendias 2011; Baker 1990; Oorts 2013).

According to Allard (1995) Cu concentration in *groundwater* in usually in 1–10 μg dm^{-3} concentration level, in uncontaminated groundwater varies between 0.1 and 470 μg dm^{-3}, while Cu concentration in unpolluted groundwater from mineralized areas can reach 850 μg dm^{-3}.

Solubility of copper in *soils*, as most of metals, is greatly dependent on soil pH and will be most readily available at pH values below 6. Cu mobility in soil rich in organic matter can increase, however, at pH values above 7.5 due to the solubilisation of soil organic matter, and formation of copper-soil organic matter complexes (Adriano 2001; Komárek et al. 2010). Depending on soil pH, copper may occur in various ionic forms. Cu hydroxides and carbonates are likely to predominate in most soil. Cu occurs in most soils as the $Cu(H_2O)_6^{2+}$ ion adsorbed on clay minerals or co-precipitated on other minerals and organic soil components. Overall solubility of both cationic and anionic forms of Cu decreases at about pH 7–8. It is supposed that hydrolysis products of copper ($CuOH^+$ and $Cu_2(OH_2)_2{}^{2+}$) are the most significant species below pH 7, while above pH 8 anionic hydroxyl complexes of Cu dominates (Kabata-Pendias 2011).

In general, *copper is accumulated* in the upper few centimetres of soils. However, due to its tendency to be absorbed by soil organic matter, carbonates, clay minerals, and oxyhydroxides of manganese and iron, it may be also accumulated in deeper soil layers. Copper is a rather immobile element in soils and shows relatively little variation in total contents of soil profiles (Kabata-Pendias 2011; Adriano 2001).

Cu deficiency in crop plants most commonly occurs in soils, which are coarse structured and have high pH, were formed from calcareous parent material, and are rich in organic matter. Thus, the deficiency can be a consequence of the low content of total soil Cu, or the condition of the soil reducing the mobility and thus availability of Cu (Kabata-Pendias 2011). Copper deficiency most likely occurs in organic or mineral soils with a pH higher than 7.5 and organic matter content higher than 2 % (Pais and Jones 1997).

7.3 Contamination of Soils with Copper

The main sources of Cu input to *agricultural soils* are *pesticides*, *sewage sludges*, *manures* and *mineral fertilizers* (Oorts 2013). Most important source of Cu contamination is the utilization of copper-based *pesticides* (e.g. Bordeaux mixture: $CuSO_4 + Ca(OH)_2$; copper oxychloride, copper oxides, copper hydroxide etc.) in vineyards, hop, apple, coffee, avocado, citrus, banana, tomato, potato and other plantations (Komárek et al. 2010; Oorts 2013; Romić et al. 2004; Adriano 2001; Kabata-Pendias 2011). Long-term application and subsequent wash-off from the treated plants have resulted in elevated Cu concentrations in vineyard soils. Since Cu is strongly immobilized by soil organic matter and Fe-, Mn-(hydroxides), Cu concentrations in superficial horizons of vineyard soils often exceed 200 mg kg^{-1}. In the topsoils of vineyards the copper concentration can be above 1,000 mg kg^{-1}, and extremely high concentrations (3,200 mg kg^{-1}) were also observed. Such increased Cu concentrations pose a significant risk for groundwater (Komárek et al. 2010; Oorts 2013; Kabata-Pendias 2011; Adriano 2001).

Limited amount of *copper-containing pesticides* can be used even in *organic farming* (Komárek et al. 2010). Copper content was compared in upper layer (0–30 cm) of soils in 28 conventionally or organically cultivated farms located in Northeast Hungary (Simon and Barna 2010). In spite of the excessive using of copper sulphate in organic farms as a fungicide, no significant difference was found between the Cu concentrations of soils in conventionally or organically cultivated farms. In soils of conventionally cultivated farms the total Cu concentration varied between 9.5 and 50.0 mg kg^{-1} (mean 26.1 mg kg^{-1}), while in soils of organically cultivated farms 9.1–75.7 mg kg^{-1} (mean 32.6 mg kg^{-1}) Cu was measured (Simon and Barna 2010). In the leaves of various apple cultivars cultivated in organic farms

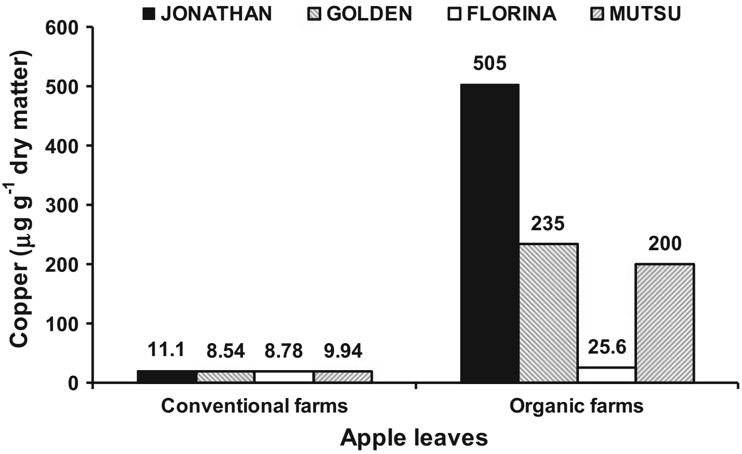

Fig. 3.4 Copper concentrations in the leaves of various apple varieties cultivated during 2010 in conventional or organic farms located in Northeast Hungary (Simon and Barna 2010)

one order of magnitude more copper was detected than in similar cultivars cultivated in conventional farms (Fig. 3.4). In spite of the later fall and decay of leaves, in soils of organic farms the Cu concentration of upper soils was only slightly elevated, as demonstrated above (Simon and Barna 2010).

The copper content of the *sewage sludges* may be considerable (100–1,000 mg kg^{-1}), but in case of their agricultural utilization the Cu accumulation in plants is relatively low (Adriano 2001). In case of sewage sludge application soil microbes can be more sensitive to excess of Cu in soil than plants (Baker 1990). According to Hungarian regulation in sewage 2 mg dm^{-3}, in sewage sludge 750 mg kg^{-1}, while in sewage sludge compost 1,000 mg kg^{-1} of Cu can be present, if these materials are applied to arable soils. These materials cannot be applied to the soil in which the total Cu concentration exceeds 75 mg kg^{-1}. From sewage, sewage sludge and sewage sludge compost maximum 10 kg ha^{-1} copper can be transferred annually to agricultural areas (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

Using copper in *feed supplements* considerably increase the Cu in pig slurry and chicken manure. Therefore, high rates of manure application to croplands are of environmental concern similarly to sewage sludge (Oorts 2013; Baker 1990; Adriano 2001). According to Hungarian regulation (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)) the allowable total copper concentration in organic manures utilized for agricultural purposes can be 100 mg kg^{-1} on dry matter basis.

Copper content of artificial *fertilizers* or *liming materials* rarely exceeds 50 mg kg^{-1}, therefore their regular application only slightly elevates the Cu concentration of soils (Adriano 2001).

In various yield enhancing substances including artificial, organic and mineral fertilizers, composts, soil ameliorants, soil conditioners, growing media etc., utilized for agricultural purposes maximum copper concentration is equally limited to 100 mg kg^{-1} (dry matter) in Hungary (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

Copper was 6th in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). The *pollution* of soils with copper can be caused by *atmospheric deposition* in consequence of mining, metallurgy, or metal processing. Surface soils in the immediate vicinity of copper smelters were found to be heavily contaminated by atmospheric fallout. Often more than 1,000 mg kg^{-1} total Cu concentrations were found there (CCME 1999c). Coal ash generated in thermal power plants may contain significant amounts of Cu, and if is incorporated to the soil may elevate significantly its Cu concentration (Baker 1990). Incineration of wood, fossil fuels and waste, corrosion of electrical wires and pipes, abrasion of car parts, etc. may contribute to the elevation of Cu concentration in urban and roadside soils (Akbar et al. 2006; Wei and Yang 2010; Adriano 2001; Oorts 2013).

Copper equally interacts with the organic and inorganic constituents of the soil and accumulates in the upper soil layers (its leaching is not typical). Since copper mobility decreases with increasing soil pH, the *liming* is reducing the copper uptake of plants. O*rganic substances* (e.g. mixture of compost and woodchips, peat, green waste compost), and phosphate fertilizers have similar Cu immobilizing effects. *Remediation* of Cu-contaminated soil was achieved with application of clays, bentonite, carbonates, and Fe oxides (Kabata-Pendias 2011; Karami et al. 2011; Komárek et al. 2010).

7.4 Copper in Plants

Copper is an *essential trace element* for the *plants*, plays important role in numerous physiological processes (photosynthesis, respiration, carbohydrate and nitrogen metabolism), and is a cofactor of numerous enzymes. Many complex interactions of Cu with other macro- (N, P, Ca) and microelements (e.g. Zn, Fe, Mo, Mn, Se) were observed within plant tissues and also in the external root media, particularly in the uptake and transport processes. Copper is required for plant nutrition only in trace amounts and at higher concentration can be toxic to cells (Marschner 1995; Yruela 2005; Dučić and Polle 2005; Kabata-Pendias 2011). Plants growing in uncontaminated soils contain 5–20 μg g^{-1} (dry matter) of copper.

In case of 2–5 μg g^{-1} Cu in plant organs *deficiency symptoms* can be observed. Typical symptoms of Cu deficiency appear first at the tips of young leaves and then extend downward along leaf margins. The leaves may also be twisted or malformed and show chlorosis or even necrosis. Copper is accumulating prevalently in the roots of plants; aboveground plant organs contain less from this trace element. Usually 150–400 mg kg^{-1} total Cu in soil can be phytotoxic. More than

20–30 μg g^{-1} Cu in plants causes *toxicity symptoms*; rootage is damaged (the number of root branches is reduced, the roots are thickened and coloured), chlorosis develops in leaves, the uptake of essential elements is inhibited (Marschner 1995; Dučić and Polle 2005; Pais and Jones 1997; Kabata-Pendias 2011; Adriano 2001). Copper is normally found only in protein-bound forms in cells, since as a free ion it may generate oxidative stress and cause serious damage to organic molecules. Free copper ions readily oxidize thiol bounds within proteins, causing a disruption of their secondary structure. This means, the reactivity of copper that makes it so useful in redox reactions also makes it toxic (Dučić and Polle 2005).

Plants growing on Cu-polluted areas tend to accumulate increased amounts of this metal, especially near industrial areas, and in soil treated with Cu-bearing pesticides (Kabata-Pendias 2011). Hyperaccumulator plants of Cu exists, and may accumulate several thousand μg g^{-1} (dry matter) Cu in their tissues (Brooks 1998; Sarma 2011).

7.5 Copper in Foods and Humans

Copper content of leafy plants consumed as *food* rarely exceeds 25 μg g^{-1} and usually ranges between 10 and 15 μg g^{-1}. Whole cereal grains normally contain 4–6 μg g^{-1} Cu, and white flour and bread 1–2 μg g^{-1}. Root vegetables, nuts and fruits contain usually less than 10 μg g^{-1} Cu. Certain seafood and organ meats (kidney and liver) contain as high as 200–400 μg g^{-1} Cu, but these foods comprise small portion of the total human diet (Adriano 2001). Alcoholic beverages may contain traces of Cu because of their contact with Cu tanks and containers (EURAR 2008). Copper normally occurs in *drinking water* from Cu pipes, as well as from additives designed to control algal growth (Wuana and Okieimen 2011). Guideline value for Cu in drinking water is 2 mg dm^{-3} (WHO 2008).

Similarly to plants, copper is also an *essential micronutrient for animals*, but in high concentration may be toxic for aquatic life (Adriano 2001). World-wide, copper deficiency in *humans* is rare; it is usually associated with long-term consumption of cow's milk or with severe malnutrition in infants and young children. *Daily dietary intake* of $\leq$2 mg Cu per day for adults may suffice. Unlike some man-made materials, copper is not magnified in the human body; *copper toxicity* in humans is very rare (EURAR 2008; Wuana and Okieimen 2011; Adriano 2001).

8 Mercury

8.1 Ecological Significance and Utilization of Mercury

Mercury (Hg) is considered as *global pollutant* (Kabata-Pendias 2011). Mercury is a persistent environmental pollutant with bioaccumulation ability in fish, animals, and human beings. Mercury salts and organomercury compounds are among the most poisonous substances in our environment. The mechanism and extent of toxicity depend strongly on the type of compound and the redox state of mercury (Tangahu et al. 2011).

Mercury can *cycle in the environment* as part of both natural and anthropogenic activities. Results indicate that the amount of Hg mobilized and released into the biosphere has increased since the beginning of industrial age (Adriano 2001). According to Boening (2000) global reservoir of atmospheric mercury has increased by a factor of 2–5 since the beginning of industrialized period. The major natural sources of atmospheric mercury are degassing of the lithosphere and the oceans, and emissions from volcanoes. Man-made sources (see detailed below) probably contribute rather less on a global scale, but may be important locally (Hopkins and Hosford 2009). Once in air, Hg can be widely dispersed and transported thousands of kilometres from emission sources. Mercury undergoes a series of complex chemical and physical transformations as it cycles among the atmosphere, land, sediment and water (Adriano 2001; Selin 2009) (Fig. 3.5).

Mercury can be utilized for the production of chlorine (gas) and sodium hydroxide (chlor-alkali process), vinyl chloride monomer production, for production of measuring and control instruments, electrical apparatus, energy-saving fluorescent lamps, alkaline batteries, for the recovery of gold and silver from ores, for the manufacture of fulminate (explosive salt), vermillion (red pigment), agricultural chemicals, wood impregnation, dental fillings, paints, pharmaceuticals, thermometers, etc. Considering the toxic properties of mercury many of these applications have now been phased out world-wide or in developed countries (Steinnes 1990, 2013a; Kabata-Pendias 2011; Morgan et al. 2009; Tangahu et al. 2011).

8.2 Mercury in Soils

The average concentration of mercury (Hg) is 0.04 mg kg^{-1} in the *earth's crust* (Steinnes 2013a). The average content of Hg in *soils* all over the world is estimated 0.07 mg kg^{-1} (Kabata-Pendias 2011). In 70 % of Hungarian soils 0.01–0.05 mg kg^{-1} of Hg can be found (Simon 1999). According to Adriano (2001) in normal, uncontaminated soils only 0.06–0.20 mg kg^{-1} Hg is present. The background levels of Hg in soils are not easy to estimate due to widespread Hg pollution. Data reported for various soils on a world-wide basis show that mean concentrations of Hg in surface soils do not exceed 1.5 mg kg^{-1} (Kabata-Pendias 2011).

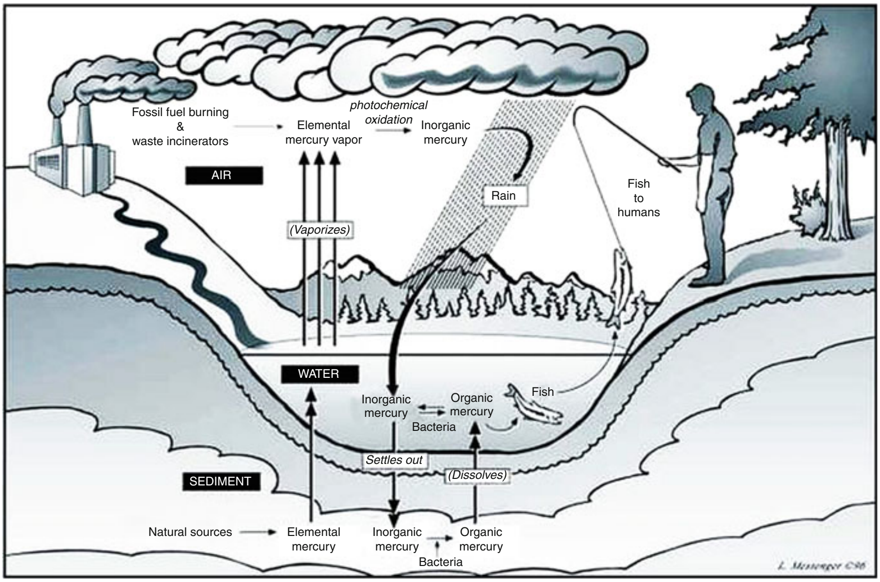

Fig. 3.5 Biogeochemical cycling of mercury in the environment (Source: http://www.mercury.utah.gov/atmospheric_transport.htm)

The very low Hg concentration level in *groundwater* systems is in 0.01–0.1 μg dm^{-3} range. In average 0.05 μg dm^{-3} Hg is present in normal, uncontaminated groundwater (Allard 1995; Adriano 2001).

Mercury can be equally bound to inorganic and organic components of *soil particles*. Chemical, biological, photochemical processes can convert mercury to various compounds, among these the most toxic is the volatile Hg vapour and methyl mercury. The major *soil factors* that determine the fate and behaviour of mercury are pH, organic matter and clay content, redox potential, cation exchange capacity (CEC), aeration, and texture. The major processes that determine the mobility and distribution of mercury in the terrestrial environment are adsorption, chemical reactions, leaching, volatilization, photolysis, and biodegradation (CCME 1999d). In soils, the migration processes involving Hg are rather limited; therefore, the Hg content of surface soils is slowly built up, even under a low input of this metal. The Hg accumulation in soil is controlled mainly by a formation of organic complex and precipitation. Thus, the Hg mobility requires dissolution processes and biological and chemical degradation of organomercury compounds (Kabata-Pendias 2011).

There are three soluble forms of Hg in the *soil environment*. The most reduced is Hg^0 metal with the other two forms being ionic of mercurous ion Hg_2^{2+} and mercuric ion Hg^{2+}, in oxidizing conditions especially at low pH (Tangahu et al. 2011). Elemental mercury has low water solubility and is easily volatilised from soil to air. This is a significant component in the geochemical cycle of mercury (Hopkins and Hosford 2009). Under natural conditions, most of the Hg^{2+} ion in the soil is either bound in the soil minerals or adsorbed onto organic or inorganic solids, with only a very small portion present in the soil solution (CCME 1999d). The Hg^+ ion is not stable under environmental conditions since it dismutates into Hg^0 and Hg^{2+}. A second potential route for the conversion of mercury in the soil is *methylation* to monomethyl or dimethyl mercury by aerobic and anaerobic (e.g. *Clostridium* sp.) bacteria (Brooks 1998; Tangahu et al. 2011; CCME 1999d). Methylation of Hg is generally most likely occur in water-saturated soils where anaerobic conditions prevail. Hg(II) in the soil solution appears to be more available for methylation than soil bound Hg(II) (Steinnes 2013a). According to general calculation, about 1–3 % of total Hg in surface soils is in the methylated Hg forms, and the rest may be considered as Hg(II)·complexes (Kabata-Pendias 2011). The transformation of organomercury compounds, especially methylation of elemental Hg, plays the most important role in Hg cycle in the environment. The methylated Hg is readily mobile and easily taken up by living organisms, including several higher plants (Kabata-Pendias 2011; CCME 1999d).

The following properties are characteristic for *Hg species in soils*:

- easy volatilization: Hg^0 and $(CH_3)_2Hg$,
- easy solubilisation: $HgCl_2$, $Hg(OH)Cl$ and $Hg(OH)_2$,
- low mobility: CH_3Hg^+ and CH_3HgS^-,
- non-reactive species: HgS, Hg(CN), and Hg^{2+} bound to organic matter (Kabata-Pendias 2011).

8.3 Contamination of Soils with Mercury

Traces of Hg can be transferred to *agricultural soils* from commercial *fertilizers* (50 μg kg^{-1}), *organic manures* (<100 μg kg^{-1}; Adriano 2001) and *liming materials* (20 μg kg^{-1}) (Steinnes 1990). Kabata-Pendias (2011) reported 10–120 μg kg^{-1} Hg in phosphate fertilizers. In artificial fertilizers, organic fertilizers, mineral fertilizers, composts, soil ameliorants, and soil conditioners equally less than 1 mg kg^{-1} (on dry matter basis) of Hg can be present in Hungary, if these materials are utilized for agricultural purposes (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

Utilization of Hg-containing *fungicides* and seed disinfectants was restricted or banned world-wide. Supply of Hg to the soil by seed dressing was as high as 1 mg m^{-2}, and in cereal-producing soils achieved 100–200 mg m^{-2} year^{-1} (Steinnes 1990).

In the *sewage sludge* generally 5–10 mg kg^{-1} Hg was present, and occasionally values of 100 mg kg^{-1} were reported during the end of last century (Steinnes 1990). Fortunately, general efforts to reduce water pollution have led to a significant reduction of the Hg level in sludges in developed countries (Steinnes 2013a). At the end of 1990s' from 0.6 to 3.0 mg kg^{-1} (dry weight) Hg was present in sewage sludge of seven European Union countries (Mukherjee et al. 2004). According to

Hungarian regulation in sewage 0.01 mg dm^{-3}, in sewage sludge 10 mg kg^{-1}, while in sewage sludge compost 5 mg kg^{-1} Hg can be present, if these materials are applied to arable soils. These materials cannot be applied to the soil in which the total Hg concentration exceeds 0.5 mg kg^{-1}. From sewage, sewage sludge and sewage sludge compost maximum 0.1 kg ha^{-1} mercury can be transferred annually to agricultural areas (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

The original Hg sources common to all soils are the minerals constituting the rock forming the soil parent material. In surface soils *atmospheric deposition* is also a very significant Hg source. It is estimated that half of the global mercury pollution over the past few decades was *accumulated in soils* (Steinnes 1990, 2013a). Mining and smelting of ores (in particular Cu and Zn smelting; Steinnes 1990), combustion of fossil fuels (primarily coal, in which 10 mg kg^{-1} Hg can be present; Kabata-Pendias 2011), incineration of wastes, and industrial production (Hg cell chlor-alkali process for production of Cl and caustic soda) can contribute to *Hg pollution of soils* (Steinnes 1990, 2013a; Chen and Yang 2012). Mercury was 7th in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). The highest Hg accumulation (several thousand mg kg^{-1}) is reported for soils in the vicinities of gold and mercury mining or ore deposits and chlor-alkali plants. Increased levels of Hg are also observed around coal power stations, metallurgic plants, and battery recycling facilities (Kabata-Pendias 2011; Steinnes 2013a). The mercury content of *contaminated soils* can reach several ten mg kg^{-1}, while in the vicinity of mercury mines values of the order of 100 mg kg^{-1} were detected (Steinnes 1990, 2013a; Adriano 2001; Kabata-Pendias 2011). Mercury concentration in urban soils can be higher than background values of soils in rural areas (Wei and Yang 2010).

Considering the unique behaviour of Hg, *remediation* of Hg contaminated sites can be complicated and costly. Physical separation, thermal treatment, use of leaching agents and permeable reactive walls, stabilization and other techniques may be effective for polluted soil remediation (Hinton and Veiga 2001). Phytoremediation of Hg-contaminated soil is in experimental phase, phytovolatization of mercury by transgenic plants is promising (Tangahu et al. 2011; Kabata-Pendias 2011). Mercury accumulation in crops can be *reduced* by soil application of liming materials, sulphur containing compounds or rock phosphates (Kabata-Pendias 2011; Azevedo and Rodriguez 2012).

8.4 Mercury in Plants

For *plants* mercury is not an essential trace element, its positive biological functions are not known. Usually 2–10 mg kg^{-1} of Hg in the soil is phytotoxic. In soils Hg^{2+} is a predominant and bioavailable form for plants. Hg^{2+} is one of the metal ions that are the most toxic to soil biota. The plants accumulates mercury primarily in their roots, in most of the cases its transfer to aboveground organs is low. However, translocation within the plant to other parts including shoots and seeds occurs (Adriano 2001; Kabata-Pendias 2011; Chen and Yang 2012; Steinnes 2013a; Azevedo and Rodriguez 2012). In addition to Hg uptake from roots, the aerial part of plants, particularly leaf is another important way for accumulation of Hg, due to the industrial emission of Hg to the air and microorganism-mediated Hg emission from soils (Chen and Yang 2012). Plants are known to directly absorb Hg vapour. The soluble Hg forms in aerosols are easily adsorbed by leaves, needles or shoots of plants, and are transported inside plants (Kabata-Pendias 2011).

According to Adriano (2001) total Hg concentrations in *common agronomic plants* and products prepared from these plants range from <0.001 to 0.3 μg g^{-1}. Kabata-Pendias (2011) reported that the background levels of Hg in vegetables and fruits vary from 0.0026 to 0.086 and from 0.0006 to 0.070 μg g^{-1} (fresh weight). In contaminated areas the mercury concentration of food or feed plants may rise considerably, the highest values were measured in mushrooms (Kabata-Pendias 2011).

The Hg affinity to sulfhydryl groups apparently is the key reaction in disrupting metabolic processes of plants (Kabata-Pendias 2011; Azevedo and Rodriguez 2012). Common symptoms of *mercury toxicity to plants* are inhibition of photosynthesis, stunted roots and stunted seedlings, all with consequent reductions in yield. In susceptible plant species 0.5–1 μg g^{-1}, while in less sensitive plants 1–8 μg g^{-1} of mercury is reducing the yield. *Mercury poisoning* stops the growth of plants, protein synthesis is inhibited, the water management of plants is disturbed (Macnicol and Beckett 1985; Kabata-Pendias 2011; Boening 2000; Azevedo and Rodriguez 2012). Excess of Hg in plants can *disturb the uptake* of K, Mg, Mn and Fe (Boening 2000).

Mercury *hyperaccumulator* plants are not known (Sarma 2011), although transgenic plants (*Arabidopsis thaliana*) with the genes for mercury ion reductase (reduction of toxic Hg^{2+} ion to relatively inert Hg^0) are supposed to resistant to high Hg concentration, and may be useful in Hg phytoextraction (Brooks 1998; Kabata-Pendias 2011).

8.5 Mercury in Foods and Humans

Food is the main source of mercury in non-occupationally exposed populations; the mean dietary intake of mercury in various countries ranges from 2 to 20 μg per day per person (WHO 2008). According to Hopkins and Hosford (2009) the adult oral mean daily intake of total mercury from food and water combined is estimated to be 1.5 μg day^{-1}, of which 0.5 μg day^{-1} is methyl mercury and about 1.0 μg day^{-1} is inorganic mercury. Some of the methyl mercury formed in the environment reaches terrestrial and aquatic *food chains*, where bioaccumulation occurs. The highest concentrations are found in predatory fish at the top of the food chain. *Fish and fish products* are the major source of mercury in the human diet. Regular consumption of Hg contaminated fish and shellfish led to Minamata disease (a neurological syndrome caused by severe mercury poisoning) in Japan during late 1950s (Adriano 2001; Hopkins and Hosford 2009; Boening 2000; Azevedo and Rodriguez 2012). According to Adriano (2001) in meat 1–50 μg kg^{-1}, while in fish 30–1,500 μg kg^{-1} Hg is present.

Guideline value for Hg in *drinking water* is 1 μg dm^{-3} in the European Union (Council Directive 98/83/EC). Almost all mercury in uncontaminated drinking water is thought to be in the form of Hg^{2+}. Thus, it is unlikely that there is any direct risk of the intake of organic mercury compounds, especially of alkyl mercurials, as a result of the ingestion of drinking water. However, there is a possibility that methyl mercury will be converted into inorganic mercury. Guideline value of World Health Organization is 6 μg dm^{-3} for inorganic mercury in drinking-water (WHO 2008).

Mercury is among the most toxic elements to many *higher animals* and *man*. All chemical forms of Hg are *toxic to humans*. Methyl mercury shows strong teratogenic effects. Its carcinogenic and mutagenic activity has also been implied (Steinnes 2013a).

9 Lead

9.1 Ecological Significance and Utilization of Lead

Lead (Pb) is the most common *metallic pollutant* of the biosphere, and is best known for its toxic effects for the population. As a result of human activity water, air and soil are equally contaminated with lead world-wide. The steadily increasing amounts of Pb in arable or uncultivated surface soils have been reported for various terrestrial ecosystems. Although is not very mobile in soil, lead may enter surface waters as a result of the erosion of lead-containing soil particles and the dumping of waste containing lead products. Emissions to the air as well as to water on an international scale seem to be decreasing due to a phase out of leaded petrol in developed regions, improved flue gas cleaning and waste water treatment (UNEP 2010; COWI A/S 2003b; Kabata-Pendias 2011). According to Reimann et al. (2012) the atmospheric contamination of the northern hemisphere contributes nowadays little to the total Pb inventory of European agricultural soils. However, contamination of soils with lead is very irreversible and therefore, a cumulative process in surface soils will continue even if its inputs are low (Kabata-Pendias 2011).

Lead ranks fifth behind Fe, Cu, Al, and Zn in industrial production of metals (Wuana and Okieimen 2011). *Lead is used* primarily for the production of acid batteries. Other uses include solders, bearings, cable covers, ammunition, plumbing, pigments, caulking, plastics, fishing tools, lead crystal glass, ceramics, cathode ray tubes, lead balancing weights for vehicles, alloys (e.g. type-metal in typography), radioactive radiation protective vests, and other products. Lead is utilized for production of sulphuric acid (UNEP 2010; COWI A/S 2003b; CCME 1999e; Wuana and Okieimen 2011). To avoid uneven combustion in the engine cylinders (i.e. knocking or pinking) Pb alkyls (tetraethyl and tetramethyl) were added to petrol from 1923 (Davies 1990). Leaded petrol in most of the countries was phased out during the last decades because of excessive air, water and soil pollution from automobile exhaust (UNEP 2010).

9.2 Lead in Soils

In average 15 mg kg^{-1} lead is present in the *earth's crust* (Steinnes 2013b; Kabata-Pendias 2011). The Pb concentration of *surface soils* is changing between 3 and 90 mg kg^{-1}, being the highest in Cambisols and Histosols. The background Pb content of soil is inherited from parent rocks. However, due to the widespread Pb pollution, most soils are likely to be enriched in this metal, especially in the top horizon (Kabata-Pendias 2011). The mean content of Pb in *uncontaminated soils* world-wide has been estimated to be 17 mg kg^{-1} (Steinnes 2013b). In European agricultural soils (0–20 cm) lead concentrations vary from 1.6 to 1,309 mg kg^{-1}, with median of 16 mg kg^{-1}. Majority of Pb concentration anomalies coincide with known Pb mineral belts or deposits and anthropogenic pollution (Reimann et al. 2012). In Hungary 80 % of soils contain less than 25 mg kg^{-1} Pb (Simon 1999).

Lead concentration in *groundwater* systems is usually in 0.1–1 μg dm^{-3} concentration range. However, Pb concentration in unpolluted groundwater from mineralized areas can reach 390 μg dm^{-3} (Allard 1995).

Lead *in soils* is strongly bound to colloids and organic matter, or is present as an insoluble precipitate. Only a very small portion of Pb in soil is present in solution. Mainly due to sorption by soil organic matter Pb accumulates primarily in the upper layers (top few centimetres) of the soil; its concentration gradually decreases with depth (Adriano 2001; Kabata-Pendias 2011; Steinnes 2013b). In general, Pb is not very mobile in soil. The downward movement of elemental Pb and inorganic Pb compounds from soil to groundwater by leaching is very slow under most natural conditions. Soil pH, content of humic acids and amount of organic matter influences the content and mobility of lead in soils. Acidic conditions (lower pH) and formation of organic complexes increase the solubility of Pb. In the absence of appreciable humic matter, lead is strongly adsorbed on clay minerals and iron oxides. Clays, silts, iron and manganese oxides, and soil organic matter can bind lead and other metals electrostatically (cation exchange) as well as chemically (specific adsorption). Pb is present in *soil* predominantly in the +2 oxidation state. Lead occurs in the soil solution as cationic Pb^{2+}, $PbCl^{+}$, $PbOH^{+}$ and anionic $PbCl_3^{-}$, $Pb(CO_3)_2^{2-}$ species (UNEP 2010; Steinnes 2013b; Kabata-Pendias 2011; Adriano 2001).

9.3 Contamination of Soils with Lead

The *fertilizers* and *liming materials* contain Pb from traces to several hundred mg kg^{-1} (Adriano 2001), but they do not contribute significantly to the Pb contamination of the food chain, considering the extremely low mobility of lead in soils. According to Kabata-Pendias (2011) in phosphate fertilizers from 1 to 200 mg kg^{-1} Pb is present, with the mean of 12.2 mg kg^{-1}. The European average load of agricultural soils with Pb from P-fertilizers is 1.0 g ha^{-1} annually, and the average Pb concentration in European inorganic fertilizers was only 2.9 mg kg^{-1} dry weight (Nziguheba and Smolders 2008). In various yield enhancing substances (artificial, organic and mineral fertilizers, composts, soil ameliorants, soil conditioners, growing media etc.) utilized for agricultural purposes equally less than 100 mg kg^{-1} (dry matter) of Pb can be present in Hungary (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

The wide utilization of *lead arsenate insecticide* in agriculture was banned world-wide during the last century (see the Sect. 4 Arsenic).

Sewage sludge utilized in agriculture lands loads soils with lead. Concentrations of lead in sewage sludge were high (820–1,832 mg kg^{-1} dry weight, Adriano 2001) until the end of 1980s. The introduction of strict regulations on sewage sludge quality in developed countries has led to reduced Pb levels in sludge, hence by 2000 concentrations in most EU Member States had fallen to <200 mg Pb kg^{-1} dry weight (Eriksson 2001; Eckel et al. 2005; Nicholson et al. 2010). From the sewage sludges relatively *low amount of Pb is transferred to the crops or fruits* of agricultural plants, since most of the plants are not able to transport lead from their roots to the above-ground organs (McBride 2003). In sewage 1 mg dm^{-3}, in sewage sludge 750 mg kg^{-1} (dry matter) and in sewage sludge compost 400 mg kg^{-1} (dry matter) lead can be present in Hungary, if these materials are utilized in agricultural lands. Sewage sludge or sewage sludge compost cannot be applied to the soil in which the total Pb concentration exceeds 100 mg kg^{-1}. From sewage, sewage sludge and sewage sludge compost maximum 10 kg ha^{-1} $year^{-1}$ lead can be transferred to agricultural areas (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

Soil pollution with Pb can be attributed to industrial activity (mining, smelting, metallurgy) and operation of coal-fired power plants. Production, utilization, recycling and disposal of Pb-containing products, lead acid batteries, lead-based paints or pigments, abrasion of tires, combustion of plastics also contributed to contamination of soils with Pb. Lead was 1st in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997). In heavily polluted areas (e.g. in the vicinity of industrial plants) the total lead concentration of soils can reach several thousand, sometimes several tens of thousands mg kg^{-1} (Davies 1990; Adriano 2001; Kabata-Pendias 2011; Steinnes 2013b; UNEP 2010; CCME 1999e). Soils of hunting and clay pigeon shooting areas, military shooting ranges are reported to be highly contaminated with Pb (Kabata-Pendias 2011; Nicholson et al. 2010; Steinnes 2013b; Czira et al. 2013).

Concentrations of Pb found in *urban soil* are influenced by anthropogenic activity and are therefore likely to be much greater than those found in soil from rural areas (Markus and McBratney 2001). For urban soils 30–100 mg kg^{-1}, while for rural soils 10–30 mg kg^{-1} Pb concentration is characteristic (Table 3.2; Alloway 1990). Coal and wood burning, plastics and rubber production, runoff from metal surfaces, car batteries, transport, particles of paints etc. contributed to elevated levels of Pb in urban soils (Alloway 2004; Steinnes 2013b). Along busy roads and highways is an increase in soil lead content (up to 7,000 mg kg^{-1}; Kabata-Pendias 2011) from automobile exhausts, which is gradually decreasing moving away from roadside (Markus and McBratney 2001; Wei and Yang 2010; Simon 2001a).

Lead contamination was studied in *roadside topsoils* of Nyíregyháza city, and in wild and cultivated chicory (*Cichorium intybus* L.) indicator plants from 1994 to 1996, when cars were operated with leaded petrol in Hungary (Simon 2001a). In roadside urban topsoils the total Pb concentrations reached 607 mg kg^{-1}, and were significantly higher than in uncontaminated topsoils (with maximum 9 mg kg^{-1} Pb) located in meadows or gardens far from traffic. Elevated levels of Pb were found in wild chicory organs, or in cultivated chicory leaves alongside the roads, as compared to uncontaminated sites. With increasing distance from a busy highway gradually decreasing levels of Pb were found in the leaves of chicory indicator plant exposed to effects of traffic for 30 days or 60 days (Fig. 3.6).

Beside increased motorization *Pb-containing paints* contributed to lead contamination of urban soils, mostly in garden topsoils close to the houses with painted walls or other structures (Alloway 2004; Adriano 2001; Kabata-Pendias 2011; Steinnes 2013b). Lead as pigment in paints has been discontinued in developed countries but is still used in some developing countries, specifically in industrial settings (UNEP 2010).

The *lead accumulation in plants can be reduced* by soil liming or soil application of phosphates, sulphates, clay minerals, iron or manganese oxides and organic materials (biosolids, manures). Besides liming, phosphorus compounds (e.g. H_3PO_4; KH_2PO_4, triple superphosphate, apatite/rock phosphate, bone meal, fish bones) are very effective in reducing the Pb bioavailability. In soils heavily polluted with Pb, the formation of insoluble pyromorphite, $Pb_5Cl(PO_4)_3$ is observed (Kabata-Pendias 2011; Hettiarachchi and Pierzynski 2004; Tang et al. 2012). However, application of a phosphorus compound is not the best for stabilization of Pb-contaminated media in all cases. In a *phytostabilization* study, treatment of limed mine spoil (containing 2,154 mg kg^{-1} Pb) with potassium phosphate (0.5 % KH_2PO_4) retarded the Pb accumulation in red fescue roots or shoots to least extent as compared to municipal sewage sludge compost, peat or natural zeolite application (Simon 2005).

Because Pb is very strongly bound in almost all soil types, its *phytoextraction* is rather limited (Cunningham and Berti 2000; Kabata-Pendias 2011). Several plant species (mostly the members of *Brassicaceae* family) could accumulate in their tissues more than 50 mg g^{-1} dry weight of lead (Tangahu et al. 2011). Since most of

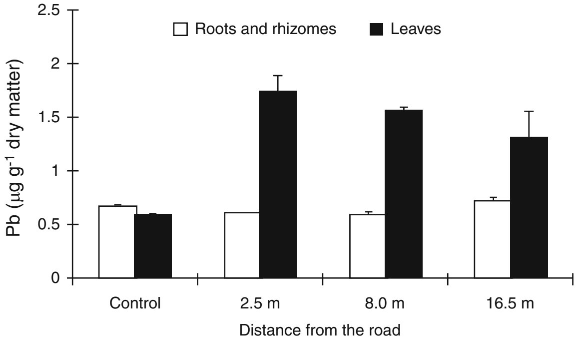

Fig. 3.6 Lead accumulation in cultivated chicory (*Cichorium intybus* var. *foliosum*) placed to control area (far from traffic) and placed at increasing distance from the highway E573 near Nyíregyháza (Hungary) after 30 days of exposure (Simon 2001a)

the lead is accumulated in the roots of these plants, direct *phytoextraction* of contaminated soils seems to be unrealistic, since the Pb concentration in easily harvestable shoots is low. Application of various chelants to Pb-contaminated soils, however, can promote the lead accumulation in plants (Huang et al. 1997; Cunningham and Berti 2000). This phenomenon is called *chelate induced phytoextraction* (Schmidt 2003). In shooting-range and ammunition destruction site located in Hungary 900 mg kg^{-1} total Pb concentration was detected in a sandy soil (Czira et al. 2013). Based on the results of a pot experiment with maize it was observed that soil application of the chelant EDTA can change the phytoavailability and mobility of Pb in this contaminated soil. In roots of maize the lead concentration was enhanced eight times (reaching 4,611 µg g^{-1} dry matter), and in shoots was doubled (reaching 302 µg g^{-1}) after EDTA application, as compared to untreated cultures (Czira et al. 2013).

9.4 Lead in Plants

Lead is not essential element for the *plants* (Sharma and Dubey 2005; Kabata-Pendias 2011). In plants growing in uncontaminated soils from 0.5 to 10 µg g^{-1} of lead is present; the average value is 2 µg g^{-1}. In case of lead uptake from soil the roots accumulates much more lead than the above-ground organs of plants. Since very small portion of the lead in soil is present in solution (which is the immediate source for lead in plant roots) the direct lead uptake of plants from soil usually is low. Soil acidification (and low soil organic matter content), however is associated with increased mobility and bioavailability of lead (Kabata-Pendias 2011; Adriano 2001; UNEP 2010).

Lead compared to the other potentially toxic metals is moderately *phytotoxic*, however in heavily contaminated soils the microbial and enzyme activity is reduced (Adriano 2001; Davies 1990; Kabata-Pendias 2011). Generally, 100–500 mg kg^{-1} Pb in soils and 30–300 µg g^{-1} Pb in plants generate phytotoxicity symptoms (Kabata-Pendias 2011; CCME 1999e). Critical leaf concentration of lead causing toxicity is 10–20 μg g^{-1} according to White and Brown (2010). In case of Pb toxicity the development of the plant slows down, the photosynthesis, cell division, water uptake, and the activity of key enzymes is inhibited. Leaves are dark green and stunted, older leaves wither, roots are brownish, short and thickened (Kabata-Pendias 2011; Nagajyoti et al. 2010; Sharma and Dubey 2005). Mechanisms of Pb-detoxification include sequestration of Pb in the vacuole by the formation of complexes, phytochelatin synthesis and binding to glutathione and amino acids (Sharma and Dubey 2005).

Lead *interacts* with Ca, P, S, and Zn uptake and metabolism in plants (Kabata-Pendias 2011).

Studies have shown that lead does not readily *accumulate* in the fruits or crops of agricultural plants. Lead accumulates to the greatest extent in leafy vegetables (especially in lettuce) in the neighbourhood of polluted areas. Higher concentrations are more likely to be found also on the surface of root crops (e.g. carrots) (Wuana and Okieimen 2011; Kabata-Pendias 2011; Adriano 2001). Generally, it has been considered safe to use garden produce grown in soils with total lead levels less than 300 mg kg^{-1}. The risk of lead poisoning through the food chain increases as the soil lead level rises above this concentration. Even at soil levels above 300 mg kg^{-1}, most of the risk is from lead contaminated soil or dust deposits on the plants rather than from direct uptake of lead by the plant (Wuana and Okieimen 2011).

9.5 Lead in Foods and Humans

Lead enters to the *human body* through inhalation of lead-contaminated dust, through consuming of Pb-contaminated *foods*, consuming soil (pica), or drinking water. Pb soldered cans were phased out, because interacted with foods. Most lead in *drinking-water* arises from plumbing in buildings (WHO 2008; Wuana and Okieimen 2011; Adriano 2001). In the drinking water 10 μg dm^{-3} can be present in the European Union (Council Directive 98/83/EC), this value is identical with the guideline value of WHO (2008). The *provisional tolerable weekly intake* for lead is 3.5 mg kg^{-1} of body weight per day to all age groups (WHO 2008). In the European Union fruits, vegetables, cereals, bakery wares and beverages are the major sources of dietary lead, together accounting for most of the intake. The daily intake of lead per person was estimated at 26.8 μg in Japan, and 17 μg in Finland from foods and drinks (UNEP 2010).

Lead is not essential, but in very small amounts may have stimulative effects in some animal species. In the animal and human body high concentration of lead is carcinogen and can cause genetic anomalies. Lead is a cumulative poison, which initially accumulates in the liver and kidney, then is deposited in bones. Lead damages the nervous system, blood, liver and kidney function, the hormonal regulation, and the cardiovascular system. Lead may have adverse impact on the intellectual development of children (WHO 2008; UNEP 2010; Wuana and Okieimen 2011).

10 Zinc

10.1 Ecological Significance and Utilization of Zinc

All life on earth has evolved in the presence of natural levels of *zinc* (Zn). Due to its general availability to organisms (bioavailability) and its characteristics, zinc plays a specific role in various biological reactions. Zinc is an *essential element* for all life, from man to the smallest microorganism, including plants and animals (IZA 1997; Mertens and Smolders 2013). Zinc is *essential* for the normal healthy growth and reproduction of plants, and when the supply of plant-available zinc is inadequate, crop yields are reduced and the quality of crop products is frequently impaired (Alloway 2008).

Zinc metal is *produced* both from ores (typically from sphalerite; ZnS) and from recycled zinc products. Zinc is a recyclable material, at present about 30 % of the world's zinc supply comes from recycled zinc (IZA 1997). *Zinc is utilized* in brass, bronze and other zinc-based alloys, in galvanized products, metal coatings, in building and construction, automotive and medical equipment, household appliances, batteries, televisions, tools, fittings, copying papers, parchment papers, cosmetics, pharmaceuticals, rubber goods, tires, toys, glasses, paints and in agricultural micronutrient fertilisers and animal feeds (Mulligan et al. 2001; IZA 1997; Adriano 2001). The *primary* and fastest growing *use* of zinc is for *galvanizing*. It is anticipated that zinc demand will continue to increase due to increasing demand for galvanized products for automobiles and for structural components in the construction industry. The *second* most important *use* of zinc is in the manufacture of brass and bronze for plumbing components and for heating and cooling system components (CCME 1999f; Mertens and Smolders 2013).

Sources of *anthropogenic zinc* in the environment include electroplaters, smelting and ore processors, mine drainage, domestic and industrial sewage, combustion of solid wastes and fossil fuels, road surface runoff, corrosion of zinc alloys and galvanized surfaces, and erosion of agricultural soils (CCME 1999f). The industrial extraction and refining of zinc began in Europe in the late eighteenth century. This *industrial activity* has resulted in *anthropogenic* (man-made) *input* of zinc to the environment (including soils). From the 1970s on, however, growing attention to the environment has led to a *progressive reduction in zinc emissions* to air and water, and the zinc industry has achieved a major reduction in emissions during recent decades (IZA 1997).

10.2 Zinc in Soils

The abundance of zinc in the *earth's crust* is between 52 and 80 mg kg^{-1} (dry weight), (Kabata-Pendias and Mukherjee 2007); the average Zn content is estimated at 70 mg kg^{-1} (Kabata-Pendias 2011). Zinc is naturally present in all soils

(Mertens and Smolders 2013). The range of Zn background concentration in normal *soils* is between 10 and 300 mg kg^{-1} (Adriano 2001). In soils with various *texture* 31–100 mg kg^{-1} zinc was reported; the lowest background values were found in light sandy soils, while the highest in calcareous and organic soils. Mean Zn for world-wide soils are calculated as 64 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007). In European soils the median Zn concentration was found at 52 mg kg^{-1}, with 4 mg kg^{-1} of minimum and 2,832 mg kg^{-1} of maximum (Lado et al. 2008). In Hungary 80 % of soils contain <25–75 mg kg^{-1} Zn (Simon 1999).

Zinc concentration in *groundwater* systems is usually in 10–100 μg dm^{-3} range. Zn concentration in unpolluted groundwater from *mineralized areas* can reach 2.6 mg dm^{-3} (Allard 1995).

Soil texture, pH, nature of the parent rocks, clay and organic content all affect the natural content of *zinc in the soil* (Mulligan et al. 2001; Adriano 2001). Zinc is present in the +2 oxidation state in soil (Mertens and Smolders 2013). The most common and mobile Zn in soil is in forms of free and complexed ions in soil solution. In the *soil solution*, Zn occurs in forms of cations: Zn^{2+}, $ZnCl^{+}$, $ZnOH^{+}$, $ZnHCO_3^{+}$, anions: ZnO_2^{2-}, $Zn(OH)_3^{-}$, $ZnCl_3^{-}$ and Zn-organic species (Kabata-Pendias and Mukherjee 2007; Kabata-Pendias 2011). Under acidic conditions, zinc is usually divalent (primarily present as free Zn^{2+} cation) and quite mobile. At high pH, zinc is bioavailable due to the solubility of its organic and mineral colloids. Zinc hydrolyses at pH 7.0–7.5, forming $Zn(OH)_2$ at pH values higher than 8. Under anoxic conditions, ZnS can form upon precipitation, whereas the unprecipitated zinc can form $ZnOH^{+}$, $ZnCO_3$, and $ZnCl^{+}$ (Mulligan et al. 2001). Zinc becomes more *soluble* as pH decreases; therefore zinc is more mobile and increasingly *available* to organisms in low pH environments, especially below pH 5. Leaching of zinc occurs more readily from acid soils (CCME 1999f). Although *Zn is very mobile in most soils*, clay fractions and soil organic matter are capable of holding Zn quite strongly, especially at neutral and alkaline pH regimes. There are two different mechanisms of Zn *sorption*: one in acid media related to cation exchange sites, and the other in alkaline media that is considered to be the chemisorption and is highly influenced by organic ligands. Also hydroxides of Al, Fe, and Mn appear to be of importance in binding Zn in some soils. Silicates, carbonates, phosphates, oxides and organic matter may contribute to the metal retention of zinc in soils (Kabata-Pendias and Mukherjee 2007). In general, total zinc was found to be evenly distributed throughout *soil profiles*. However, extractable zinc was reported to decrease with depth in the profile (Adriano 2001).

Zinc deficiency in soils is more common world-wide in both tropical and temperate climates than deficiency of any other micronutrient (Adriano 2001). It was estimated that about 30 % of the agricultural soils are Zn deficient. Zn deficiency is mainly attributed to the *low Zn bioavailability* in soil. Critical thresholds are typically 0.1–1 mg DTPA-extractable Zn in one kg of soil (Mertens and Smolders 2013). Zinc deficiency in crop plants *most commonly occurs in soils* with low total zinc concentrations (such as sandy soils), low pH, highly weathered parent materials with low total zinc contents (e.g. tropical soils), high calcium carbonate content (calcareous soils), neutral or alkaline pH (as in heavily limed soils or calcareous soils), high salt concentrations (saline soils), peat and muck (organic soils), high phosphate status, with prolonged waterlogging or flooding (paddy rice soils), and with high magnesium and/or bicarbonate concentrations in soils or irrigation water (Alloway 2008). Overliming, heavy phosphorus fertilization and organic matter amendment can contribute to Zn-deficiency of plants (Kabata-Pendias 2011). Many plant species are affected by zinc deficiency on a wide range of soil types in most agricultural regions of the world. The major staple cereal crops: rice, wheat and maize are all affected by zinc deficiency, together with many different fruit, vegetable and other types of crops including cotton and flax (Alloway 2008). There is a strong relationship between Zn concentration in tissues with the growth and yield of crops. The *critical limits of Zn in plants* indicating deficiency are: <10 µg g^{-1} *definite* Zn deficiency, 10–15 µg g^{-1} *very likely*, 15–20 µg g^{-1} *likely* and >20 µg g^{-1} *unlikely* (sufficient) (Hafeez et al. 2013). Once identified, zinc-deficient soils can be easily treated with *zinc fertilisers* (e.g. 20–30 kg ha^{-1} zinc sulphate). Foliar sprays of zinc sulphate, zinc nitrate or chelated forms of zinc are mainly used on fruit trees and plantation crops (Alloway 2008).

10.3 Contamination of Soils with Zinc

Agricultural practices are known to increase Zn contents of surface soils (Kabata-Pendias 2011). Application of *livestock manures, fertilizers, sewage sludge, agrochemicals* and *industrial waste products* (e.g. food processing wastes, slaughterhouse wastes, sludges from paper manufacturing, etc.) may contribute to Zn content of soils or crops (Alloway 2008; Nicholson et al. 2006, 2010; Mertens and Smolders 2013). Crop Zn toxicity can occur in Zn-contaminated soils (Broadley et al. 2007).

All *livestock manures* contain zinc derived from the original animal diet (e.g. grass, hay, cereals, etc.), but additional amounts of zinc may have been intentionally added to livestock diets. In areas with intensive livestock production, zinc (together with copper) is often fed to the animals for health and welfare reasons, or as growth promoters. Zinc is added, for example, to the feed of young pigs to control post-weaning diarrhoea, and to feed of poultry for nutritional reasons (Nicholson et al. 2006; Alloway 2008; Alloway 2013). The excreted Zn appears in livestock manures, which may load agricultural soils with this metal. In average 919, 580 and 495 mg kg^{-1}·dry matter zinc was found in pig, cow or poultry slurry, respectively, in six EU countries (Kabata-Pendias and Mukherjee 2007). Nicholson et al. (2010) found in average 630 mg kg^{-1} dry matter Zn in pig farmyard manure, and 360 mg kg^{-1} in broiler litter, originating from farms in England and Wales. From 2003 the maximum permitted levels of Zn in animal feeds of pig, poultry, cattle or sheep are equally 150 mg kg^{-1} in European Union to limit zinc accumulation in livestock manures (Nicholson et al. 2010).

In *inorganic fertilizers* (excluding Zn fertilizers), Zn is only present as an impurity in very low doses (Mertens and Smolders 2013). The average Zn concentration in European inorganic fertilizers was 166 mg kg^{-1} dry weight (Nziguheba and Smolders 2008). Kabata-Pendias and Mukherjee (2007) reported 61–200 mg Zn kg^{-1} in NPK fertilizers, <2 mg Zn kg^{-1} in ammonium nitrate, and 141–625 mg Zn kg^{-1} in triple superphosphate fertilizers. Among inorganic fertilizers in superphosphates were found the highest concentrations of zinc (<600 mg kg^{-1}), but their use is declining due to its replacement by higher purity compounds as monoammonium phosphate and diammonium phosphate (Alloway 2008). In average 43 g ha^{-1} zinc is added to the European agricultural soils annually through the application of phosphate fertilizers (Nziguheba and Smolders 2008).

According to Adriano (2001) Zn is present in *lime* only in traces (<5–8 mg kg^{-1}). Alloway (2013) indicated 10–450 mg kg^{-1} of Zn as a world range in lime fertilizers (Table 3.4), and 22 mg kg^{-1} as an EU median.

In various *yield enhancing substances* including artificial, organic and mineral fertilizers, composts, soil ameliorants, soil conditioners, growing media etc., utilized for agricultural purposes zinc concentration is not limited in Hungary (Hungarian Agricultural and Rural Development Ministry Decree 36/2006 (V.18.)).

Sewage sludge (biosolid) utilized in agriculture lands as a fertilizer loads soils with zinc (Juste and Mench 1992). Similarly to other PHTEs, former high concentrations of zinc present in sewage sludges (e.g. 560–6,890 mg kg^{-1} dry weight in the United States, 700–49,000 mg kg^{-1} dry weigh in the United Kingdom, Adriano 2001; see also data in Table 3.4) gradually decreased during the last 25 years in technologically advanced countries (Eriksson 2001; Merrington et al. 2003; Nicholson et al. 2010). Weighted mean of Zn concentration in sewage sludges of European Union member states was fallen to 811 mg kg^{-1} dry weight (Alloway 2013). Industry accounts for more than 50 % of the Zn load in sewage sludge, and the use of body care products is the main source of domestic Zn in municipal sewage sludges (Mertens and Smolders 2013). Although the amount of zinc applied at a particular site with sewage sludge could be significant, it would take many years for the total concentrations in soils to reach the regulatory limits (e.g. 200 mg kg^{-1} in Hungary, see Table 3.5) (Alloway 2008; Nicholson et al. 2010; Juste and Mench 1992).

In sewage 5 mg dm^{-3}, in sewage sludge 2,500 mg kg^{-1} (dry matter) and in sewage sludge compost 2,000 mg kg^{-1} (dry matter) *zinc can be present* in Hungary, if these materials are applied to agricultural soils. From sewage, sewage sludge and sewage sludge compost maximum 30 kg ha^{-1} $year^{-1}$ zinc can be transferred to agricultural lands. Sewage sludge or sewage sludge compost cannot be applied to the soil in which the total Zn concentration exceeds 200 mg kg^{-1} (Table 3.5) (Hungarian Government Decree 50/2001 (IV.3.) modified by Hungarian Government Decree 40/2008 (II.26.)).

Among Zn-containing *agrochemicals* the foliar-applied fungicide '*Zineb*' (zinc ethane-1,2-diylbis(dithiocarbamate); $C_4H_6N_2S_4Zn$) is used to control downy mildews, rusts and redfire disease in fruits and vegetables (Alloway 2013). In developed countries its utilization was recently banned. *Zinc sulphate* solution can be used in *fungicidal footbaths* against foot lameness of cattle or sheep. Dispersion of footbath solutions can contaminate the agricultural soils around the area of footbaths with zinc. Used footbaths should be emptied into slurry stores, and contribute to zinc concentrations in the slurries when they are spread to land (Nicholson et al. 2010).

It has been estimated that in most European ecosystems, and in particular in agricultural soils, the *annual input of Zn exceeds* its removal through leaching or biomass production (Eckel et al. 2005; Kabata-Pendias 2011; Mertens and Smolders 2013).

Beside agricultural production zinc can enter the soils, air and water from galvanizing plant effluents, coal, oil and waste burning, leachates from galvanized structures, natural ores and municipal waste treatment discharge. Zinc is commonly found in wastes as zinc chloride, zinc oxide, zinc sulphate and zinc sulphide. Since ZnO is used for the manufacturing of automobile tires, zinc could be present in road surface runoff, contributing to Zn contamination of roadside soils. Beside general urban and industrial emissions industrial processes (mining and smelting of non-ferrous metals) can also contribute to *soil pollution* with Zn (Mulligan et al. 2001; Alloway 2008). Corrosion of galvanized (Zn-coated) structures, such as fences and roofs adds significant amounts of Zn to soils, receiving runoff or suspended particles (Alloway 2013). Corrosion of exposed zinc surfaces, however, has decreased markedly during the last two decades, as a result of stringent control of sulphur dioxide emissions in the industrialised world, decreasing the acidity of atmosphere and rainfall (IZA 1997). In 1999/2000 the European average of atmospheric deposition of zinc into arable soils was estimated to 227 g ha^{-1} annually (Nziguheba and Smolders 2008). The relatively small amounts of zinc deposited on the soil are unlikely to provide enough zinc to overcome deficiency problems in soils (Alloway 2008). The *Zn-contaminated topsoils* contain several hundred or several thousand mg kg^{-1} Zn world-wide, while in *heavily polluted soils* near old mining areas and metal processing industry Zn concentration can reach several ten thousand mg kg^{-1} (Kabata-Pendias 2011). Zinc was 4th in the order of occurrence among metal pollutants found in the Superfund Sites (where remediation is necessary) located in the United States (Evanko and Dzombak 1997).

Amelioration of Zn-contaminated soils is commonly based on controlling its availability by addition of lime or organic matter, or their combination (Kabata-Pendias 2011). For *in situ remediation* of Zn-contaminated soils solidification/stabilization, vitrification, electrokinetic treatment, flushing and chemical stabilization can be effective (Martin and Ruby 2004; Mulligan et al. 2001). In chemical stabilization phosphate-based amendments added to the contaminated soil can be effective immobilization of Zn in soil. Beside phosphates lime, red mud, beringite (an alkaline aluminosilicate), iron and manganese compounds, lime-stabilized biosolid, and zeolite mixed into a contaminated soil can reduce zinc bioavailability (Mertens and Smolders 2013; Martin and Ruby 2004).

In an allotment garden located nearby a former galvanization plant (Nyíregyháza, Hungary) a slightly acidic brown forest soil with loamy sand texture was contaminated with Cd, Cr, Cu, Ni and zinc (139.7 mg kg^{-1} Zn in cc. HNO_3–H_2O_2 extract and 77.7 mg kg^{-1} Zn in Lakenen-Erviö [H_4EDTA in ammonium acetate buffer] extract). In a control uncontaminated brown forest soil with similar characteristics 56.0 and 14.7 mg kg^{-1} Zn was found (Simon 2001b). *Natural*

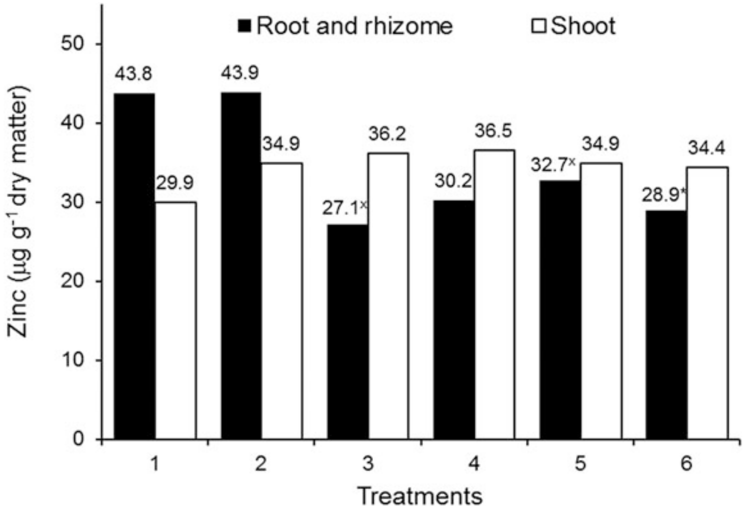

Fig. 3.7 Zinc accumulation in chicory (*Cichorium intybus* var. *foliosum*) grown in galvanic mud contaminated soil treated with various zeolites and a bentonite (pot experiment, Nyíregyháza Hungary, 1996; Simon 2001b). Treatments: *1* control uncontaminated soil, *2* contaminated soil, *3* 2 and 5 % clinoptilolite, *4* 2 and 5 % mordenite, *5* 2 and 5 % clinoptilolite with H-montmorillonite; *6* 2 and 5 % montmorillonite (bentonite). Student's *t*-test. Data are means of three replications. Statistically significant at $^{x}P < 0.1$; $^{*}P < 0.05$ level as compared to treatment 2

zeolites (clinoptilolitic rhyolite tuff, mordenite rhyolite tuff, and clinoptilolite altogether with H-montmorillonite), and a *bentonite* (montmorillonite) mined in Zemplén Hills (Hungary) were mixed to this contaminated soil. Chicory (*Cichorium intybus* var. *foliosum*) indicator plant grown in contaminated soil accumulated elevated levels of Cd, Zn, Cu and Cr in its shoots, as compared to uncontaminated soil. Natural zeolites and bentonite application reduced the accumulation of Zn in chicory roots and rhizomes (Fig. 3.7), and a slight decrease was also detected in Ni, Cr and Cu uptake of the test plants. It was found that the decrease of Zn uptake in chicory roots and rhizomes is related to decrease in exchangeable (bioavailable) form of zinc in contaminated soil after zeolite or bentonite application (Simon 2001b).

10.4 Zinc in Plants

Zinc is an essential element for the *plants* (Marschner 1995). Zn plays important role in plant metabolism by influencing the activities of key enzymes, stabilization of ribosomal fractions and synthesis of cytochrome. Plant enzymes activated by Zn are involved in carbohydrate metabolism, maintenance of the integrity of cellular membranes, protein synthesis, regulation of auxin synthesis and pollen formation. The regulation and maintenance of the gene expression required for the tolerance of environmental stresses in plants are Zn dependent. Zinc seems to affect the capacity for water uptake and transport in plants and also reduce the adverse effects of short periods of heat and salt stress (Hafeez et al. 2013; Kabata-Pendias and Mukherjee 2007; Alloway 2008).

Soluble forms of Zn are readily available for plants, and usually the uptake of Zn is linear with its concentration in soils (Kabata-Pendias 2011). Zinc is acquired from the soil solution primarily as Zn^{2+} ion, but also potentially complexed with organic ligands, by roots which feed the shoots via the xylem (Broadley et al. 2007). Within the plants zinc was reported to have high or intermediate mobility (Kabata-Pendias 2011). In plants zinc antagonistically interacts with macro- and micronutrients as phosphorus, nitrogen, copper, and iron (Hafeez et al. 2013; Kabata-Pendias 2011; Alloway 2008). The ratio of Cd to Zn in plant media controls the occurrence of synergism or antagonism between these two cations (Kabata-Pendias 2011).

In most crops, the typical leaf Zn concentration required for *adequate growth* approximates 15–20 μg Zn g^{-1} dry weight (Marschner 1995). Severe *Zn deficiency* is characterized by root apex necrosis (‘dieback’), whilst sublethal Zn deficiency induces spatially heterogeneous or interveinal chlorosis (‘mottle leaf’), the development of reddish-brown or bronze tints (‘bronzing’), and a range of auxin deficiency-like responses such as internode shortening (‘rosetting’), epinasty, inward curling of leaf lamina (‘goblet’ leaves) and reductions in leaf size (‘little leaf’) (Broadley et al. 2007).

Zinc toxicity in crops is far less widespread than Zn deficiency. However, Zn toxicity occurs in soils contaminated by mining and smelting activities, in agricultural soils treated with high doses of sewage sludge, and in urban and peri-urban soils enriched by anthropogenic inputs of Zn, especially in low-pH soils. Flooding of alluvial soils with Zn-polluted river water and sediments may also cause Zn-toxicity in plants. Macnicol and Beckett (1985) indicated 100–200 mg kg^{-1} acetic acid soluble Zn in soils toxic for plants. In general, very high concentrations of zinc, such as >500 mg Zn kg^{-1} could cause yield reduction, but it is unlikely that agricultural crops would be grown on significant areas of soils with such high concentrations (Alloway 2008). Toxicity symptoms usually become visible at >300 μg Zn g^{-1} dry weight in leaves, although some crops show toxicity symptoms at <100 μg Zn g^{-1} leaf dry weight (Marschner 1995; Broadley et al. 2007; Alloway 2008). *Zinc toxicity symptoms* include reduced yields and stunted growth, Fe-deficiency-induced chlorosis through reductions in chlorophyll synthesis and chloroplast degradation, and interference with phosphorus, magnesium and manganese uptake. Crops differ markedly in their susceptibility to Zn toxicity. There is also genetic variation in sensitivity to Zn toxicity within species, including soybean and rice (Broadley et al. 2007).

Numerous plant species (including *Noccaea caerulescens* [formerly *Thlaspi caerulescens* J&C. Presl.], *Cardaminopsis hallerii* L., *Viola calaminaria* (Gingins) Lej.) were described to *hyperaccumulate* Zn (have more than 10,000 μg g^{-1} dry matter Zn in aboveground organs) (McGrath 1998; Lasat and Kochian 2000; Broadley et al. 2007). Despite the ability to accumulate high levels if zinc and other metals in the shoot of these plant their use for soil phytoremediation is severely limited by their small size and slow growth (Lasat and Kochian 2000).

10.5 Zinc in Foods and Humans

Food is the primary source of zinc for man, with only a small part coming from drinking water. The major sources of zinc in the diet are red meat, poultry, fish, seafood, whole cereals and dairy products. The *recommended daily zinc intake* is 12 mg day^{-1} for adult women and 15 mg day^{-1} for adult men. Daily intake is not only dependent on food, but also on sex, age and general health status. Growing infants, children, adolescents, women in pregnancy and the elderly have a higher zinc requirement (IZA 1997).

Drinking-water usually makes a negligible contribution to zinc intake, unless high concentrations of zinc occur as a result of corrosion of pipings and fittings. Under certain circumstances, tap water can provide up to 10 % of the daily intake (WHO 2003). Zinc is not of health concern at concentrations normally observed in drinking water (seldom exceeding 0.1 mg Zn dm^{-3}), therefore guideline values have not been established by WHO (2008).

Zinc is an *essential trace element* required for proper growth, development, and function of *animals* and *humans*. In humans zinc is vital for the proper functioning of enzymes, for the stabilisation of DNA and the expression of genes, and for the transfer of nervous signals. The human body contains 2–3 g of zinc (compared with 7 g of iron) which is found everywhere in the body, with the highest levels in muscles, liver, kidneys, bones and prostate (IZA 1997; Alloway 2008; Kabata-Pendias and Mukherjee 2007).

Around 30 % of the world's human population has *diets deficient in zinc*. Zinc deficiency in humans affects physical growth, the functioning of the immune system, reproductive health and neuro-behavioural development, etc. Therefore the zinc content of staple foods, such as rice and wheat, is of major importance (Alloway 2008). Zinc deficient soils produce food products that are low in Zn and human Zn deficiency may occur. For example, bread wheat grain Zn typically contains 30 mg kg^{-1} of zinc that decreases to below 15 mg Zn kg^{-1} in deficient crops (Alloway 2008; Mertens and Smolders 2013). *Biofortification* of plant foods with zinc involves both the breeding of new varieties of crops with the genetic potential to accumulate a high density of zinc in cereal grains (genetic biofortification), and the use of zinc fertilizers to increase zinc density (agronomic biofortification).

11 The Behavior of Potentially Harmful Trace Elements in Soil-Plant System: Examples from Open-Field Case Studies

Pavel Tlustoš, Jiřina Száková, and Daniela Pavlíková

The first step leading to the complex assessment of the potential risk in soil-plant transport of the potentially harmful trace elements (PHTEs) at the contaminated sites should be detailed monitoring of PHTE contents and their mobility in soils as well as element uptake by plants.

As frequently published, PHTE contents in top layer of soils in *urban areas* can be a good indicator of *atmospheric deposition*. Elevated contents of PHTE such as Cd, Cu, Pb, and Zn were determined in soils affected by intensive traffic (Li et al. 2001; Garcia and Millán 1998). Simultaneously, statistical analyses proved the effect of traffic on Cd, Pb, and Zn contents in grass species in the vicinity of the roadway (Garcia and Millán 1998). The potential effect of intensive traffic on detrimental element contents in soil and vegetation was investigated in the vicinity of a selected section (1 km) of a highly frequented highway, as affected by the distance from the roadway (1, 35, and 70 m) (Modlingerová et al. 2012). *Aqua regia* and 0.11 mol dm^{-3} acetic acid soluble contents of As, Cd, Cr, Cu, Mo, Ni, Pb, and Zn in soils and total contents of these elements in aboveground biomass of *Achillea millefolium* L. (*Asteraceae*) and *Vicia cracca* L. (*Fabaceae*) were determined. The element contents did not exceed the maximum permissible limits for both soils and plants (evaluated as fodder crops). Moreover, high variability of element contents in soils and plants, and soil characteristics did not allow us to estimate the rate of potential effect of road traffic. Some of the elements, however, tightly related to atmospheric deposition caused by traffic such as Pb and Zn tended to decrease in soils with increasing distance from the roadway. However, long-term changes (in this case more than 100 year long period) in soil chemistry, resulting in significant changes in potential plant-availability of elements due to atmospheric deposition were reported by Blake and Goulding (2002). The results presented by them were based on precise *long-term experiment* documenting the suitability of such as experiments for an assessment of long-term impact of soil contamination on the mobility and plant-availability of PHTE in soils.

Short-term open-field experiments can result in substantial improvement of the knowledge concerning potential risk of PHTE uptake by plants in the contaminated areas. Surroundings of Kutná Hora city (Czech Republic) are areas characterized by former silver mining activity. Therefore, a high level of PHTEs was reported in soil close to the historical mines and potential environmental impact of these element levels was monitored by Králová et al. (2010). The *aqua regia extractable* element

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values in soils exceeded the Czech threshold values representing 30 mg kg^{-1} As, 1.0 mg kg^{-1} Cd, 200 mg kg^{-1} Cr, 80 mg kg^{-1} Ni, 140 mg kg^{-1} Pb and 200 mg kg^{-1} Zn, by up to 15-fold for zinc, 30-fold for cadmium and even 80-fold for arsenic. Mobile portions of elements determined in 0.11 mol dm^{-3} CH_3COOH solution did not exceed 1 % of the 'pseudototal' element content for As, Cr, and Pb. Plant species growing in these soils represented an ordinary ruderal plant community of 29 species without occurrence of metallophytes. Moreover, the element concentrations in aboveground biomass of plants were low. *Transfer factors*, given as a ratio of element content in plant and its 'pseudototal' content in soil, varied from 0.0003 to 0.003 for As, from 0.001 to 0.174 for Cd, and from 0.016 to 0.169 for Zn. Evidently, the analysed plant species are characterized by low ability to take up the PHTEs and by low translocation of them to aboveground biomass and the potential risk for animals consuming this biomass is negligible.

Moreover, possible remediation of these soils must be taken into account and phytoremediation suggest itself environmental friendly method leading to decrease of soil contamination level (McGrath et al. 2001; Pulford and Watson 2002). Baroni et al. (2004) monitored arsenic levels in soil and in 64 plant species in the area contaminated by former *mining activity*, and observed also low arsenic concentrations in plants regardless of the contamination level at the particular site. Higher arsenic concentrations in aboveground biomass were determined exclusively in the sample of *Mentha aquatica* L. Therefore, a *field study* was conducted in the former mining area close to Kutná Hora to compare (i) the growth potential and arsenic uptake by commercially available plants of *M. aquatica* and arsenic-tolerant plants originating from the arsenic contaminated site; (ii) to compare the arsenic compound transformations within aboveground biomass of both experimental plants, and (iii) to assess potential phytoremediation ability of both plants in field conditions (Száková et al. 2011). The total arsenic, cadmium, and zinc contents in aboveground biomass of *M. aquatica* as affected by season, location, and plant origin are summarized in Fig. 3.8.

The experiment, however, showed that although *M. aquatica* seems to be able to grow in contaminated soils without symptoms of phytotoxicity, its efficiency to remove arsenic from the soil is limited, as can be demonstrated by total removal of arsenic from 1 m^2 of the plot after three vegetation periods representing only 21.5 mg. Only *arsenite* and *arsenate*, but no organoarsenic compounds were identified in both stems and leaves. Among the arsenic compounds in the aboveground biomass, arsenate was the predominant arsenic compound and reached up to 80 % regardless of the origin of the mint plants. Although not suitable for phytoextraction, the plants are able to create thick and permanent vegetation cover capable of surviving more subsequent vegetation periods, and may be applied towards the *stabilization* of the extremely contaminated sites. Moreover, the vegetation cover is stable for several vegetation periods without intensive fertilizers and/or pesticide application. However, potential environmental risks arise from elevated plant biomass arsenic content which exceeds the maximum permissible limits for feedstuffs. If applied towards the stabilization of contaminated land,

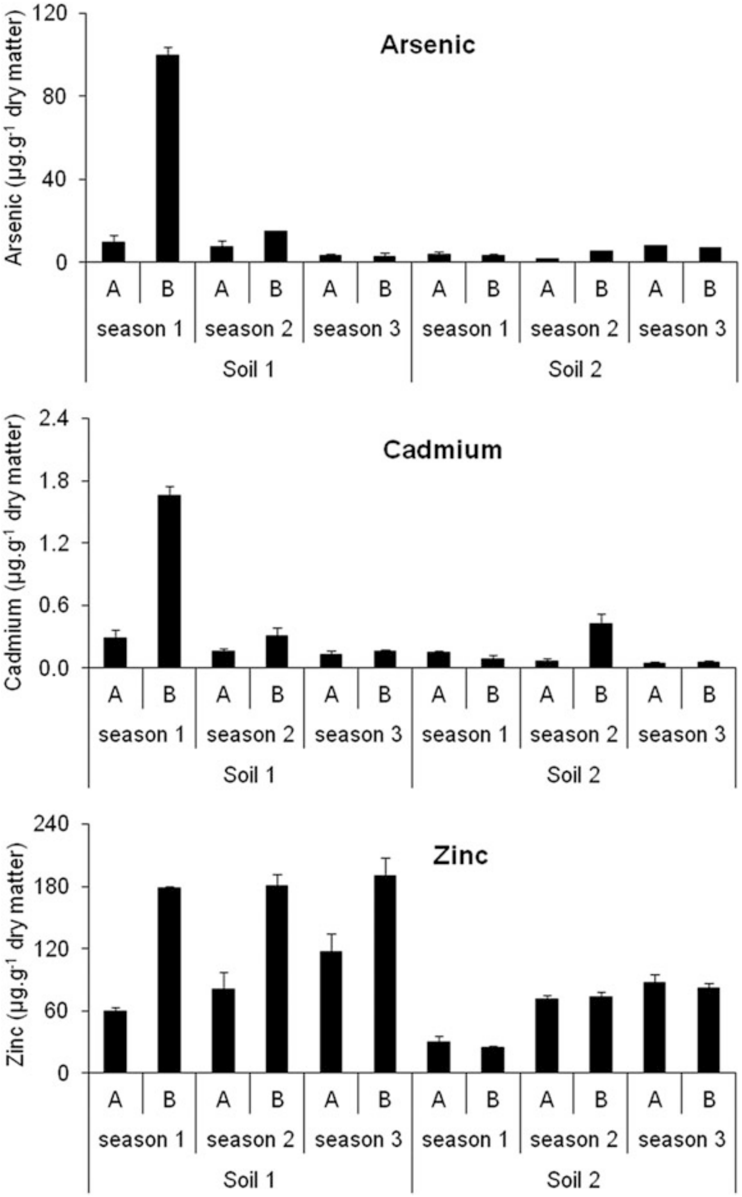

Fig. 3.8 Total arsenic, cadmium, and zinc contents (μg g^{-1} dry matter) in aboveground plant biomass of *M. aquatica* (Field experiment, Kutná Hora, Czech Republic, 2007–2009; Száková et al. 2011). Data are presented as mean ± standard deviation, n = 3. *A* commercial plants, *B* plants originating from the contaminated site

protection against herbivorous animals as well as suitable disposal of the contaminated biomass should be achieved (Száková et al. 2011).

Similarly, *small scale field experiment* was carried out on soil contaminated with chemicals from the *waste incineration plant* in Hradec Králové (Czech Republic). Screening of this allotment showed very different contamination of all observed PHTEs on places where the material intended to be burnt without safety of leakage into soil (Kacálková et al. 2009). At this site, the heavy metals (Cd, Cu, Hg and Zn) phytoextraction potential of maize (*Zea mays* L.), willow (*Salix x smithiana* Willd.) and poplar (*Populus nigra* × *P. maximowiczii*) in soils contaminated with these elements was compared and assessed. Grown plants showed the different accumulation of observed elements in plant tissues as well as the influence of total content of the PHTEs in soil. All the investigated PHTEs (Cd, Zn, Cu, Hg) concentrations in particular maize parts decreased in the order roots > leaves > seeds. Comparable results were also presented by Nigam et al. (2001). The highest Cd and Zn concentrations were found in willow-tree biomass, mainly in the leaves. Cu and Hg were mostly accumulated by maize roots and lower amount was found out in willow-tree leaves again. In reference to total production of each plant the maximum Cd and Zn total uptake by aboveground biomass was found by poplars (201 mg Cd m^{-2} and 38,200 mg Zn m^{-2}) and maize, which showed only high Zn uptake. The biggest amount of copper (2,563 mg Cu m^{-2}) was accumulated by aboveground maize biomass and by poplar (2,394 mg Cu m^{-2}). The highest Hg uptake differs in reference to total Hg content in soil; willow-tree has the highest uptake on the place with lower Hg content in soil (44.6 mg Hg m^{-2}) and surprisingly maize has the highest uptake (92 mg Hg m^{-2}) on the site with higher Hg content in soil. Summarizing the results the most suitable plant for uptake of all observed PHTEs (Cd, Hg, Cu and Zn) was in this case poplar. The better result would be achieved by growing of maize only on soils contaminated with mercury (Kacálková et al. 2009).

As evident from the mentioned results, the effective *phytoremediation* is hampered by limited number of species able to accumulate the PHTEs, as well as by the limited element mobility in soil (Salt et al. 1995). In this context, *enhanced phytoextraction* using ethylenediaminetetraacetic acid (EDTA) and its salts for the remediation of an agricultural soil contaminated with less mobile PHTEs as Cd, and mainly Pb originating from smelting activities in Příbram (Czech Republic) was assessed on the field scale (Neugschwandtner et al. 2012). EDTA was applied to the first year's crop of maize (*Zea mays* L). Metal mobilization and metal uptake by the plants in the soil were monitored for two additional years when wheat (*Triticum aestivum* L.) was planted. The application of EDTA effectively increased water-soluble Cd and Pb concentrations in the soil. However, *phytoextraction efficiency* and phytoextraction potential were too low for Cd and Pb phytoextraction in the field in a reasonable time frame (as less than one-tenth of a percent of total Cd and Pb could be removed). This strongly indicates that EDTA-enhanced phytoextraction as implemented in this study is not a suitable remediation technique for PHTE contaminated soils. Alternatively, natural low molecular weight organic acids or their salts, that are exuded by plants into the soil has positive effects on the phytoextraction of PHTEs from soil (Evangelou et al. 2006). Opposite approach to suppress the potential soil-plant transfer is represented by different countermeasures to reduce the transfer of PHTEs to edible parts of crops are tested to allow the crop production in the contaminated areas (Puschenreiter et al. 2005). As reviewed by the authors, the application of soil amendments is very effective measure to reduce the concentration of heavy metals in crops. Both organic (e.g. farmyard manure) and inorganic amendments (e.g. lime, zeolites, and iron oxides) were found to decrease the metal accumulation. Further effective methods to *reduce metal transfer* into food chain include crop rotation and cultivation of industrial or bioenergy crops. It is concluded that the methods presented here comprise several tools, which are easy to apply, and are effective to allow safe agriculture on moderately contaminated soils (Puschenreiter et al. 2005).

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Chapter 4
Potentially Harmful Elements in Forest Soils

A Pedological Viewpoint

Denis Baize and Folkert van Oort

Abstract Forest ecosystems differ from agroecosystems, in the first place by the established vegetation cover of deciduous or needle trees, associated with a specific biochemical cycling of forest organic matter. The presence of a forest floor (litter O and humus-rich A horizons) introduces additional pathways of biogeochemical cycling of potential harmful major and trace elements (PHTE), with respect to soils under agricultural land use. Moreover, unlike agroecosystems, forest soils are predominantly affected by only one way of PHTEs inputs, deriving from atmospheric deposition. Aged and established forests are generally in a state of equilibrium with respect to elemental cycling. In such forest soils, especially in their deep horizons which are most often little affected by any contamination, PHTE contents are fairly close to the initial natural pedo-geochemical background concentrations. Consequently, they can be used as a reference for other soils developed in the same parent material, but under agricultural land use and affected by anthropogenic contaminations. Exceptions are forest soils located in the proximity of industrial or mining areas, which are more exposed to short-range industrial atmospheric fallout.

Forest soils often have a lower buffering capacity against acidification than agricultural soils due to the adding of acid-neutralizing amendments (fertilization, liming, and compost) to the latter. In strongly acid forest soils, the risks of mobility of PHTEs are well-established and migration may occur in soluble, pseudo-soluble or particulate forms. Soil acidity may lead to high levels of Al and Mn, representing additional risks of aluminium or manganese toxicity. The forest floor represents a particular metal trapping medium in soils. When a mor-type humus layer is present

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at the surface of forest soils, exogenous pollutants accumulate, as a first step, in a fully organic surface horizon. But the fate of contaminants in terms of permanent retention, or subsequent partial or even full release, and times of retention are items that are still under debate. In the particular case of podzols with strongly acidified soil conditions, PHTEs are susceptible to migrate to depth and to a part intercepted (long-term, permanently?) in the B horizons whereas another part may leach out of the soils and possibly transferred to the groundwater.

For a good understanding and a relevant interpretation of PTHE concentrations through the soil profile, in terms of accumulation or impoverishment, the limits of the morphological horizons must be respected during sampling. Such horizons may be of small thickness (for instance Bh horizons in podzols), but they can demonstrate substantially contrasted concentrations, for instance in the case of strongly differentiated soils (cf Table 4.3). Taking into consideration the characteristic processes involved in the formation of soil horizons, is essential for a better insight into mechanisms and pathways of cycling of PTHEs. Hence, for a valid assessment of the presence, distribution and fate of PTHEs in forest soils, and in order to allow an appropriate comparison with anthropogenic contaminated agricultural soils, it is crucial to take account of different soil parameters, such as the nature of the parent material, pedological characteristics and specific physico-chemical conditions. Moreover, and surely, it is essential to adopt a soil sampling strategy that is adapted to the aims and/or different parts of multidisciplinary study programs.

Keywords Forest soils • PTHEs • Geochemical background • Soil forming processes • Biogeochemical cycles

1 Introduction

Almost any chemical element, trace as well as major elements may become harmful in soils at high concentrations, with respect to ecological components and human health, regardless from its origin, geogenic or anthropogenic (Adriano 2001). But more than its total concentration, harmful effects of elements depend on its chemical form (speciation) that governs its bioavailability. Chemical speciation of elements in soils is complex, it varies according to different environmental conditions. The soil pH, as well as the soil's nature, and mineral, organic and biological composition, and land use are important parameters to consider for environmental risk assessment. In this chapter we will evoke different elements: a major (Al) and several trace metals (Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn).

1.1 Specific Characteristics of Forest Soils

Forest soils have physicochemical properties that may considerably differ from those in soils under agricultural land use. To a part, these differences are due to the fact that the occurrence of large forest areas is nowadays often restricted to situations which are considered as little or non-suitable for agronomic purposes, because too poorly drained, too steep, too stony, too shallow, or too poor. But forest soils also differ by some unique properties: the deep rooting of trees, the role of microorganisms associated with the forest vegetation, and a specific cycling of organic carbon. Often, at high latitudes and altitudes, there is formation of a forest floor, the O horizon composed of more or less decomposed organic debris (leaves, needles, bark, fruits and lignified materials). Then, decaying of litter produces organic acids that promote eluviation and lixiviation processes (Binkley and Fisher 2012). The occurrence of a litter layer exerts a great influence on the soil's physical, chemical and biological properties. Such specific characteristics of forest soils are associated with a distinct soil profile development and macro- and micromorphological features. Forest soils will become more acidified if the acid neutralising capacity of the parent material is small (van Breemen and Finzi 1998). When developed on comparable parent material, forest soils often, but not always, demonstrate a lower soil pH (Ugolini and Edmonds 1983; Hesterberg 1998; Bacon and Hewitt 2005) than those observed in agricultural soils. Such a difference is often related to the application of chemical and/or organic fertilization, or soil amendments with acid-neutralizing treatments in agricultural soils (Blum et al. 1997; Goulding and Blake 1998; Andersen et al. 2002). Soil acidification enhances the liberation of major metal elements, such as Al, Fe and Mn, which at low pH become more mobile and potentially toxic. An additional major difference between forest and agricultural soils is the annual ploughing and other tillage operations in the latter ones.

1.2 Origin of Trace Metal Contamination

In comparison with open agricultural land, forest soils are quasi-exclusively affected by atmospheric deposition. Forest soils have been frequently mentioned to accumulate more trace metals in the surface horizons than is observed for soils under agricultural land use (Blum et al. 1997; Adriano 2001). Abundant literature is available for the accumulation of airborne lead (e.g. Jensen and Svensmark 1989; Hanschmann and Opp 1993; Keller and Védy 1994; Johnson and Petras 1998; Hernandez et al. 2003; Bacon and Hewitt 2005; Steinnes and Friedland 2006). Forest ecosystems represent an efficient filter for toxic substances (Schlesinger and Reiners 1974; Binkley and Fischer 2012), due to the height and density of the tree canopies that intercept atmospheric dust by dry and wet deposition (Bergkvist et al. 1989). Consequently, although many large forest areas are often considered as natural ecosystems and only little impacted by anthropogenic contamination, forest soils may demonstrate surprisingly high surface concentrations of trace elements. The origin of such accumulations is to a large extent ascribed to long-range atmospheric deposition (Jensen and Svensmark 1989; Wang et al. 1995; Adriano 2001; Steinnes and Friedland 2006) deriving from human activity such as coal combustion, metal smelting, waste disposal etc. (Nriagu and Pacyna 1988; Ragsdale and Berish 1988). But besides interception of long-range pollution, forest soils may also be the receptor of short-range pollution, i.e. industrial atmospheric deposition, for instance for situations close to industrial metallurgical complexes (Ruan et al. 2008). Both in cases of long-range and short range atmospheric deposition, the amounts of anthropogenic (exogenous) trace elements may widely dominate the natural (endogenous) trace element concentrations (Semlali et al. 2001a, b; Fernandez et al. 2008; van Oort et al. 2009).

1.3 Fate of Trace Metals

Particularly under prevailing acid conditions in many forest soils, the pH to a large extent determines whether one will observe a net accumulation or loss of a given metal element in the humus-bearing upper horizons, and hence, the time of its residence at the soil's surface (Steinnes and Friedland 2006). Metals predominantly present in a free, or exchangeable form (Zn, Cd) are susceptible to pH fluctuations (McBride 1989; McBride et al. 1997; Sauvé et al. 2000). With a decrease of the soil pH, they will easily migrate in the soil solution toward depth. Downward moving trace metals may be either partly intercepted and sorbed on negatively charged soil constituents such as clays and iron and manganese oxides (van Oort et al. 2006, 2008) or leach out of the soil toward the water table. Other trace elements, with a less mobile character and a great affinity for organic matter, such as Pb and Cu are less susceptible to soil pH or become mobile at lower pH values than Zn and Cd. Yet they may migrate in colloidal form (Erel et al. 1997; Citeau et al. 2003; Semlali et al. 2004), associated with organic matter (or oxides) and either precipitate in the upper B horizon or may leach even to greater depths (van Oort et al. 2006).

1.4 Forest Stands Sometimes Mask Ancient Cultivation or Industrial Activity

Several authors have noted that large areas nowadays under forest have been cultivated several centuries ago, sometimes as early as the Roman Empire period, as was shown by work of Dupouey et al. (2002) and Dambrine et al. (2007) for large areas in north-eastern France. Such more or less ancient cultivation probably had only small impacts as far as the trace metals are concerned. By contrast, extended forest areas may include, and mask, numerous sites affected by historical mining activities, as it was demonstrated for instance in the Harz region (Germany) and Morvan area (France) (Monna et al. 2000, 2004). Therefore, the widely spread idea that forest soils represent long-lasting natural ecosystems only little affected by human activity, always needs careful checking.

1.5 Objectives

In this chapter, we do not intend making an exhaustive overview of the fate and behaviour for the different trace elements in soils, since excellent references exist on that topic (e.g. Alloway 1995; Adriano 2001). The aim of this chapter is to present from a pedological point of view the key factors for a valid understanding of the distribution and fate of some major and trace elements in forest soils in comparison to soils under agricultural land use. It is clear that many soils occurring under forest are still calcium-saturated, or even calcareous, but these soils were not much studied because considered as presenting fewer risks towards human health or our environment. Therefore, our contribution will focus on the occurrence and dynamics of trace metals in more or less acidified forest soils of temperate climate in Western Europe. Note that the case of poplar stands or short-term rotation woodlands will not be discussed, because they can be considered as lignified monocultures and so are little different from usual agricultural soils (Binkley and Fischer 2012).

In this chapter, we emphasize items about (1) the key factors for interpreting concentrations of different trace metals in soils, (2) how to distinguish natural from anthropogenic trace elements, (3) specific behaviour of some trace metals in forest soils in comparison with soils under agricultural land use. In Sect. 5 we illustrate these items with examples from case studies on trace metal (Zn, Pb, Cd) accumulations, distributions and movements in forest systems located in France.

2 Concentrations of Trace Elements in Soils: The Three Keys

2.1 The Initial Inheritance: The Geochemical Background

Under any climate, the **number one key** which from the outset determines the concentrations in potentially harmful trace elements (PHTEs) found in soils today is the chemical composition **inherited** from the parent material, usually called "geochemical background". This corresponds to the mineralogical composition of the rock whether originally-formed (in the case of extrusive and igneous rocks) or

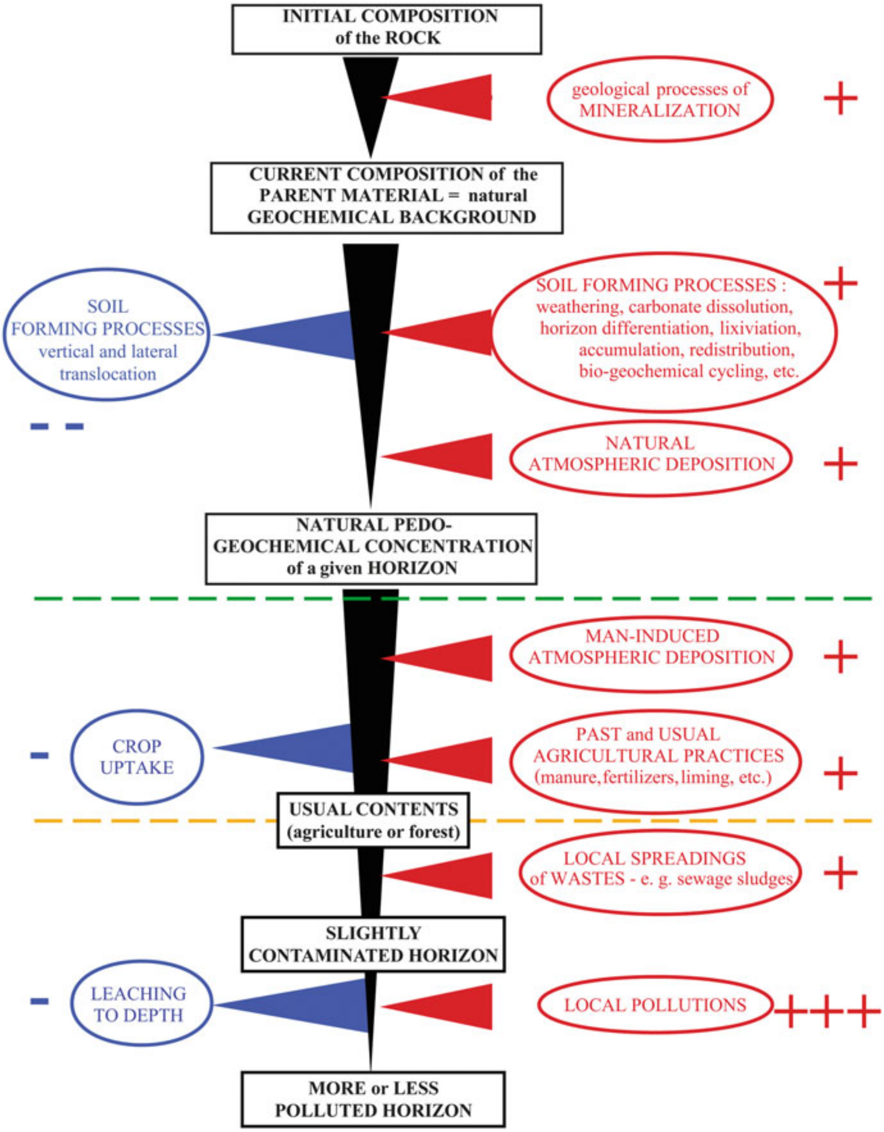

Fig. 4.1 Progressive acquisition of trace element composition of a soil horizon: from the initially-formed rock to the ploughed surface horizon (Ap horizon). On the *right*, in *red*: factors increasing the trace element contents. On the *left*, in *blue*: factors decreasing them

initially deposited (in the case of marine sediments, moraines, loess and alluvium), which have sometimes been modified by subsequent mineralization (Fig. 4.1).

A first example is given by still weakly differentiated soils, which are abnormally rich in nickel and chromium, because they developed from rocks containing

Table 4.1 Strong anomalies of nickel and chromium due to ferromagnesian primary minerals (olivine, pyroxenes, and amphiboles)

				Cr	Ni	Fe	Mg
Horizon	Depth (cm)	pH in water	Total C (g kg^{-1})	(mg kg^{-1})		(g kg^{-1})	
Davos – # 1							
A	4–6	5.1	102	2,600	411	68	40
Bw1	8–15	6.0	30	2,800	587	91	52
Bw2	20–30	6.4	12	1,650	1,115	64	166
BC	50–60	6.6	4	2,300	1,702	62	207
C	80–90	6.8	2	1,750	1,996	59	215
Mauriac							
A1	4–7	5.2		293	168	75.6	8.4
A2	8–24	5.2		376	213	94.5	10.9
R	24–55			371	214	78.4	53.7
Bassin plat							
	0–20	5.4	22	930	1,040	209	
	20–60	5.2	17	780	980	194	
	60–85	6.2	7	880	896	207	
	85–130	6.6	5	1,110	989	219	

Davos: Soil developed in serpentinic rock slide material. Swiss Alps, under subalpine climatic conditions, near **Davos** (Gasser et al. 1995); **Mauriac**: Mountain grassland; altitude 700 m; mean annual rainfall 1,300 mm; the parent material is a slightly weathered basaltic flagstone of the Tertiary era. Trace metals are determined by alkali fusion (Soubrand-Colin et al. 2007); **Bassin plat**: Réunion Island. Andic cambisol developed in volcanic ash (Doelsch et al. 2006)

large amounts of olivine, pyroxenes, chromite, spinels, etc., which are all minerals bearing Ni and Cr. This is the case, for example, of the basalts and basanites of the French Massif Central (Soubrand et al. 2007) or of the Réunion Island (Doelsch et al. 2006) and the serpentinites in the Swiss Alps (Gasser et al. 1995). See Table 4.1.

Another example comes from soils developed in alluvium showing abnormally high contents of some PHTEs. As a general rule, alluvium display extremely variable particle-size (from heavy clays to large boulders), but above all, their composition is totally dependent on the lithology of materials abraded upstream. So, some alluvial soils of little streams flowing down the Vosges or the Cévennes (France), exhibit high concentrations of Pb, Zn, and Cu, simply because these alluvium are located downstream of strongly mineralized rocks.

The case of moraines is different, being deposited by Alpine glaciers (Switzerland – the canton of Geneva and France – the Savoy region). The glacial tills deposited by the ancient Rhone glacier contain numerous little fragments of “green stones”. That is the reason why the still weakly differentiated soils developed in them are heavily loaded in nickel (40–220 mg kg^{-1}) and chromium (78–226 mg kg^{-1}), whereas they are poor in iron and of medium texture (see Table 4.2, Fig. 4.2). No similar findings are observed in the case of the Jura glaciers.

Table 4.2 Soil composition mirrors that of their parent material (Buatier and Wiart 1997)

			Cr	Ni	Co	Cu
Depth (cm)	Clay (g kg^{-1})	pH in water	(mg kg^{-1})			
0–30	245	6.1	164	117	16.9	26.3
30–60	216	6.7	175	126	18.4	25.9
60–90	327	7.7	226	188	23.3	34.1

Calcium-saturated soil developed in a calcareous moraine (Pays de Gex, France). Natural anomalies in Cr and Ni are due to little fragments of "green stones" in the parent material. This table also illustrates the interest of the vertical comparison

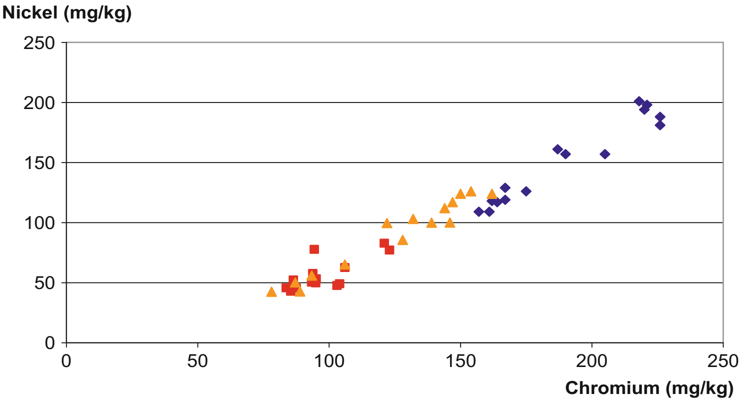

Fig. 4.2 Soils developed in alpine moraines (*Pays de Gex*, France). Relationship between nickel and chromium; N = 45 (3 different plots × 5 replicates × 3 sampling depths), r = 0.98 (Buatier and Wiart 1997)

These examples show the importance of considering the initial geochemical composition of the parent material for understanding and a correct interpreting of observed PHTE concentration (Blaser et al. 2000; Baize and Sterckeman 2001).

2.2 The Second Key: Soil Processes Leading to Natural PedoGeochemical Concentration (NPGC)

In regions with temperate climates and in those with cold climates, the **soil forming processes which can markedly change this inheritance** in upper soil horizons are few. These are:

(a) Partial or total dissolution of carbonates, resulting in a relative accumulation of non-lixiviated PHTEs; the total dissolution of limestone causes huge changes since the calcite may represent between 90 and 99 % of the dissolved rock. Thus, the constituents that have not been evacuated out of the soil (clay

Table 4.3 Total PHTE concentrations in a forested planosol developed in glauconitic "green sands" (Albian – Champagne humide, France) (Baize 1997a)

Horiz.	Depth (cm)	Clay	Org. Carbon	Total Cu	Total Cr	Total Cd	Total Pb	Total Zn	Total Ni	Total Fe
		(g kg^{-1})		(mg kg^{-1})						(g kg^{-1})
A	0–5	169	81.1	5.3	26.6	0.19	22.5	37	6.4	14.1
E	10–20	107	15.2	4.7	31.5	0.03	12.8	14	3.9	12.8
Eg	25–40	115	7.3	3.8	35.9	0.03	14.7	10	4.3	17.0
Bg	43–48	490	6.1	6.4	130.0	0.03	18.7	53	25.8	78.6
B	60–75	523	3.3	7.3	127.0	0.02	18.0	56	31.2	74.0
B/C	90–110	375	2.4	6.6	115.0	0.01	17.8	46	30.1	62.5
C	140–155	400	1.5	6.8	121.0	0.03	16.1	51	37.9	67.4

A marked contrast can be observed between upper horizons with a low Fe, Cr, Ni, Zn content and the deeper ones with a much higher content. Lead is more abundant in the surface humus-bearing horizon and remains unrelated with iron and clay contents, because of the global long-range atmospheric deposition

minerals, iron oxides, cadmium, and zinc) may reach very high concentrations in residual soils (Baize 1997b; Dubois et al. 2002; Prudente et al. 2002).

(b) Translocation of clay particles (vertical or lateral illuviation – *e.g.* case of Luvisols and Planosols) leading, over the long-term, to the formation of upper soil horizons with markedly lower PHTE content than deeper soil horizons (McKeague and Wolynetz 1980) (see Table 4.3). Large losses of TEs associated with clay particles or iron oxides can also occur in very old residual clayey soil mantles, leached down into the karst network (Baize 2012);

(c) Direct and total weathering of clay minerals by acidolysis, ferrolysis, etc. leading to the development of upper soil horizons very poor in major (Al, Fe) and trace elements (e.g. Petersen 1976; Brinkman 1979; Semlali 2000);

(d) Podzolization, where iron, aluminium and most trace metals form organo-metallic complexes, that are able to move down from the upper A and E layers and accumulate at depth in "spodic" B horizons. This translocation can affect natural substances as well as anthropogenic ones (Tables 4.4 and 4.8) (Delas 1966; Saur and Juste 1994; Filipe 1999; Semlali et al. 2000, 2001b; Brännvall et al. 2001; Kaste et al. 2003; Steinnes and Friedland 2005). Such an extreme soil forming process remains rather uncommon under temperate climates but represents a more common soil type in Scandinavia as well as in the vast territory of boreal forests covering large parts of North America and Russia. Podzols preferentially develop in very acid and permeable parent materials with little amounts of reactive soil components, able to develop strong chemical bonds with metals such as clay minerals and hydrous oxides.

(e) Dilution by very abundant organic matter (in the case of Umbrisols with humose topsoils);

(f) In soils with redoximorphic features, trace metals tend to accumulate associated with Fe and Mn oxyhydroxides acting as adsorbers (Latrille et al. 2001). These natural accumulations may display a wide variety of sizes and shapes but

Table 4.4 Evidence of vertical translocation of natural or anthropogenic metals through podzols

Horizon	Depth (cm)	pH in water	Org. matter[a] (g kg^{-1})	Total Pb (mg kg^{-1})	Total Cu (mg kg^{-1})
Sore					
O	0–4	4.0	262	17.5	
A	4–37	3.8	32.7	10.1	
E	37–67	4.3	3.7	5.8	
Bh	67–97	4.8	28.7	13.2	
Bs	97–127	4.5	6.7	8.9	
C	127–160	5.0	5.0	7.5	
Cestas			**Total carbon (g kg^{-1})**		
	0–20		29.5		1,880
	20–37		23.2		3,131
	37–55		4.9		350
	55–70		3.7		137

These two soils have in common to be thick podzols developed in quartzose aeolian sands *("sables des Landes de Gascogne",* France). **Sore**: Dry moor. An iron pan is visible at 67 cm (Saur and Juste 1994). **Cestas**: Pollution by copper salts in a site of pine timber treatment (Delas 1966); See also Table 4.8

[a] Organic matter determined by ashing 6 h at 800 °C

Table 4.5 Mineralization of a rock transmitted to the soil

Depth	Clay (g kg^{-1})	Carb. (g kg^{-1})	pH in water	Cd (mg kg^{-1})	Pb	Zn	Ni	Fe (g kg^{-1})	Mn (mg kg^{-1})
0–26	247	12.3	5.9	1.20	134	436	64.5	41.7	5,833
26–40	531	6.4	7.0	2.50	192	783	78.6	60.4	7,385
40–58	524	5.7	7.2	3.40	218	968	97.1	65.1	9,200
58–90	592	5.4	7.4	4.30	245	1,138	101.0	69.4	9,045
90–95	603	4.2	7.7	n.d.	n.d.	1,999	n.d.	85.5	24,975

This soil is developed in the total carbonate dissolution residue of a strongly mineralized marly limestone (Sinemurian platform, Burgundy; Baize and Chrétien 1994; Mench et al. 1997; Baize 1997b). The black deeper horizon (90–95 cm) exhibits particularly high iron, manganese and zinc concentrations. This table also demonstrates the interest of the vertical comparison when the surface horizon shows abnormally high PHTE contents which do not result from anthropogenic pollution but are a natural anomaly

generally remain in the soil horizon with heterogeneous distributions in relation with the mottled colour pattern. More often in deeper horizons, a strong absolute accumulation of iron, manganese and a suite of associated trace metals can occur, leading to singular soil horizons with a blackish hue (see Table 4.5**,** the deepest layer).

A good example of the above-mentioned process in ***a*** is provided by soils formed in the clayey residue resulting from the total carbonate dissolution of Jurassic limestone with an unusually high cadmium content (i.e. with 0.40–8 mg kg^{-1} rock – France, Swiss Jura). A large part of the freed cadmium is immobilized *in* *situ*, sorbed onto iron and manganese oxy-hydroxides, giving rise to soil horizons with natural concentrations that may exceed 2 mg kg^{-1}, sometimes reaching values as high as 22 mg kg^{-1} (Baize and Sterckeman 2001; Dubois et al. 2002; Prudente et al. 2002; Rambeau et al. 2010). See also Box 4.1.

Box 4.1: Cadmium in Soils of Haut Jura (Prudente 1999; Prudente et al. 2002)

The site thoroughly studied is a large fir forest (common forest of Les Fourgs – France), very close to the Swiss border, located at an altitude of about 1,150 m above sea level. 93 soil samples taken in 31 soil pits were analysed after dissolution by HNO_3 (according to Swiss regulation). These samples come from surface A horizons as well as from deeper ones, in contact with the underlying, limestone which was also analysed at 23 sites. After crushing, the rock samples were dissolved by acetic acid in a solution buffered at pH 5. As a result, Cd determined in this way corresponds solely to that linked with the carbonate phase.

In soils, Cd concentrations range from 0.10 to 22.3 mg kg^{-1} with a median of 1.0 mg kg^{-1}. Fifty six samples exceed the "indicative value" of the Swiss regulation fixed at 0.80 and only 6 show Cd contents higher than 7.0 mg kg^{-1}. In addition, there is a strong variability in space, vertically (from one horizon to another) as well as laterally (from place to place). As a general rule, it can be observed rather low values in the upper layers and much higher values at depth, in the horizons in contact with the limestone.

Cadmium concentrations in the underlying rocks range from 0.05 to 3.59 mg kg^{-1} regardless of their lithofacies. During the soil formation by calcite dissolution, the freed cadmium may be lixiviated or, conversely, be fixed onto iron and manganese oxy-hydroxides.

Another illustrative case is that of "chestnut-coloured" soils of the Sinemurian "back slope" in Burgundy (Table 4.5, Fig. 4.3). The locally mineralized marine limestone included a wide variety of trace elements (As, Cd, Cu, Co, Ni, Pb, Zn, Tl). These PHTEs originate from hydrothermal venting along a network of faults delimiting an old Hercynian horst. Soils have developed in the residual clay resulting from the limestone dissolution, which provoked a further PHTE concentration process in soils. These soils consequently have much higher contents than the underlying rock (Baize and Chrétien 1994).

In very old strongly and deeply weathered soils of the inter-tropical areas with a perhumid climate, many elements are lixiviated (e.g. Mg, Ca, Si), but others accumulate *in situ* (*e.g*. Cr, Ni, Cu, Mn, Ti, V, Zn, Pb) and combine with the diverse iron oxide forms (e.g. Nalovic and Quantin 1972; Anand and Gilkes 1987; Becquer et al. 1995; Trolard et al. 1995; Lang Burak et al. 2013).

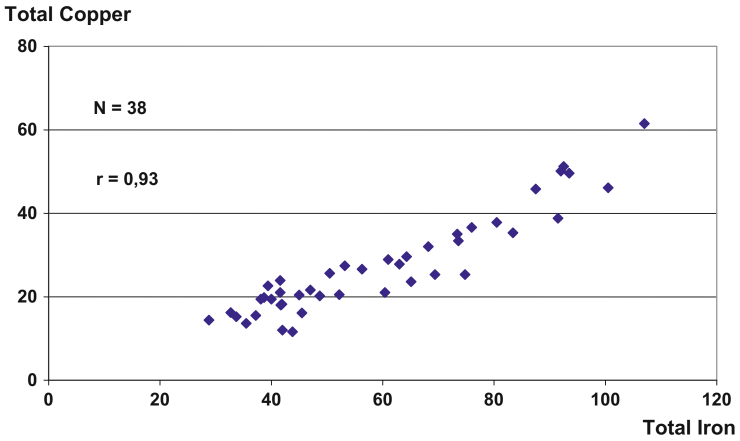

Fig. 4.3 "Chestnut-coloured soils" over Sinemurian marly limestone (Burgundy, France – Baize and Chrétien 1994) showing a broad range of unusual large values; 38 samples taken at different depths at 14 sites; Cu concentrations are expressed as mg kg^{-1}; Fe as g kg^{-1}

2.3 The Third Key: Contamination Induced by Human Activities

Diverse anthropogenic contributions have much more recently been added to the pre-existing natural stocks: (i) atmospheric fallout from long-range of short-range origins; (ii) trace elements added unwittingly by fertilizer, sewage sludge or waste spreading. The level of the latter type of contamination and its chemical nature primarily are of great concern for agricultural soils.

3 Distinguishing the Natural from the Anthropogenic

3.1 Relevance

An excellent summary of this question was given by Mol et al. (2009): "*For environmental risk assessment the question of reactivity is of even greater relevance than the question of total concentration because it determines the mobility, human exposure and ecotoxicological importance of the elements. For proper environmental soil management it is of vital importance to be able to distinguish between natural pedogeochemical concentrations and anthropogenically elevated levels of trace elements*". By making this distinction, it is possible to obtain an initial assessment of possible dangers to human health, especially through phytoavailability of metals to cultivated plants. Trace metals of anthropogenic origin are generally much more reactive species than those of natural origin, even when in abnormal abundance. In fact, the latter have been strongly adsorbed for millennia onto various solid phases or are co-precipitated with Fe or/and Mn oxy-hydroxides. The determination of local natural pedogeochemical concentrations (NPGC) and subsequently of the local level of contamination allows us not to declare as being "polluted" (with the serious socio-economic or financial consequences which may ensue) a plot of ground in a context of strong natural anomalies. If necessary, it allows us to fix realistic and relevant target values for pollution cleanup, suited to the geological and pedological context.

3.2 Sampling Strategy

The distinction between trace metals originating from atmospheric and non-atmospheric (recycling by root uptake in the soil) origin in the upper part of soils is complicated. Different approached can be used. Some of them are rather easy to implement, but others are fairly laborious and imply expansive analyses**.**

Three simple approaches have been proposed for assessing the overall level of trace element contamination of soil horizons (Baize 1997b): the vertical comparison, the lateral comparison and the typological approach. For a correct application, it is essential to use chemical dissolution methods such as hydrofluoric acid or alkaline fusion, that extract the "total" amounts of elements, including those present in the crystal structure of silicate minerals.

3.2.1 Vertical Comparison

Principle: the trace element contents of the surface plough layer (coded as Ap horizon in the FAO classification – IUSS Working Group WRB 2006) are compared with those of the underlying soil horizons. Basically, there is no reason that these concentrations should be much higher in the surface horizons. On the contrary, under climates of Western Europe, soils show often lower contents of clay, iron and associated PHTEs in upper horizons than at depth (case of Luvisols and Planosols).

Examples are given in Tables 4.2 and 4.5: when examining the PHTEs only in the Ap horizons, one might consider that these two soils are markedly contaminated. Yet, their concentrations continuously increase toward depth, the hypothesis of a strong natural geochemical anomaly is imperative. This approach is very simple: only three or four samples have to be collected at different depths at each site and it does not require much knowledge in soil science or pedology. For interpreting values, one must consider possible carbon, clay or iron gradients in the soil under study. This approach can be used only for estimating the level of contamination of surface Ap horizons. Its use is more problematical for Pb and Cd that frequently show values higher in the surface layer than in deeper soil horizons. This approach is based on the assumption that the pollutants have remained

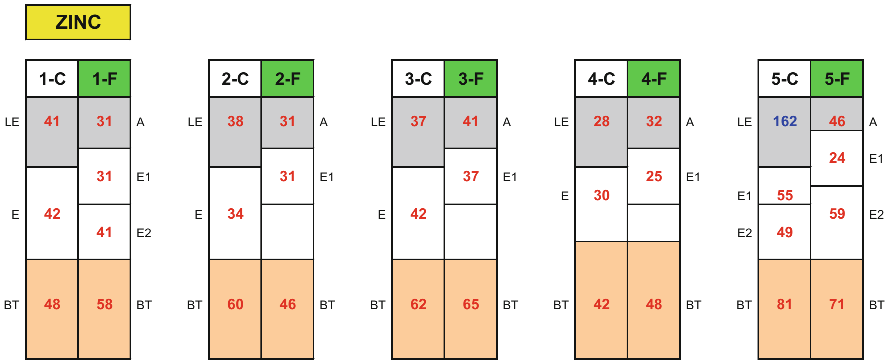

Fig. 4.4 Lateral comparison. Five couples of forested (*F*) versus cultivated (*C*) Albeluvisols (south-east of the Paris basin – Baize 1997b). Zinc concentrations are expressed as mg kg^{-1}. The site 5-C received heavy sewage sludge spreading during the 1970s and, as a consequence, has been markedly contaminated

predominantly in the surface layer. In the case of downward migrations, an accurate interpretation becomes impossible.

3.2.2 Lateral Comparison with a Forest Soil

Principle: the PHTEs concentrations in soil horizon samples from cultivated soils are compared with those measured in the equivalent horizon of the same soil series, located closely **under forest**. An analogical reasoning is used, very similar to that used in agricultural experiments.

This second approach implies simple superposed samplings both at the studied site and the forest soil used as a “reference”, and offers the possibility to deal with any horizon of the profile, not only the Ap horizon (see Fig. 4.4).

Forest soils do not always occur at short distance and/or do not have the same pedological characteristics. Besides, the forest soil may sometimes have been contaminated (recently or in ancient times) without clear evidence. Finally this approach requires pedological knowledge for recognizing the similarity between the paired soil profiles and the lateral equivalence of horizons.

3.2.3 Typological Approach

Principle: the analytical results of a given soil horizon are compared with data previously collected on similar horizons from the same soil series. This approach is more reliable and more sensitive, and represents the best among the three cited sampling strategy approaches. Moreover, it considers any type of soil horizon.

Basically, for a particular soil series, strong natural geochemical relationships exist which are used as a base for assessing accumulations or losses of trace

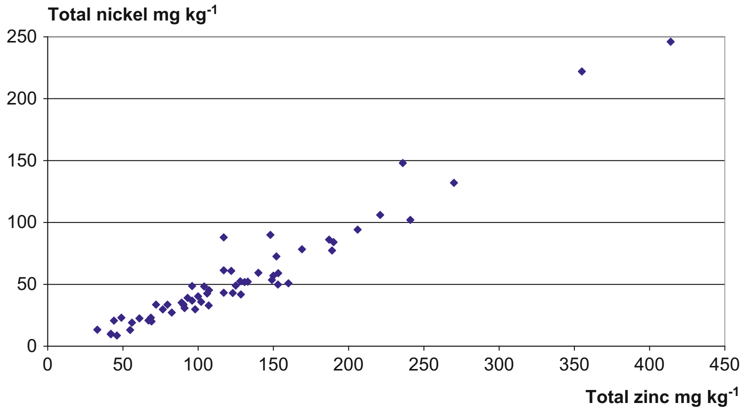

Fig. 4.5 Strongly differentiated soils developed in "clay with cherts" (Burgundy, France). The Ni – Zn relationship (total concentrations) is practically perfect (r = 0.96). The very broad range of values can be noticed; 59 samples were taken (most of them from forested soils) at different depths

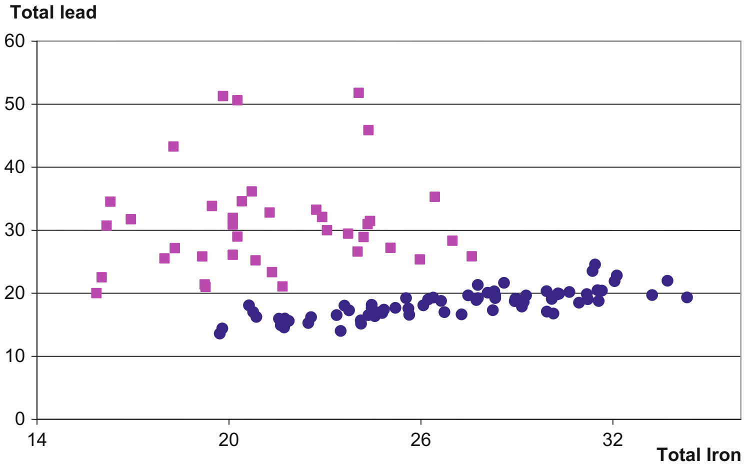

Fig. 4.6 Cultivated soils developed from loess in the Northern France: relationship between total lead and total iron (Sterckeman et al. 2006); *pink squares* for Ap horizons, *blue circles* for all other deep horizons. The natural geochemical relationship between Pb and Fe is strong for all deep horizons indicating the absence of anthropogenic additions. In the surface horizons, no Pb –Zn correlation is observed and that underlines a more or less strong lead contamination. Pb concentrations are expressed as mg kg^{-1}; Fe as g kg^{-1}

elements. For instance, such relationships may link iron contents to trace metal contents (see Fig. 4.3) or one trace metal with another (see Figs. 4.2 and 4.5). Consequently, in case of soil contamination, even minor, it is easy to detect it (Figs. 4.6 and 4.7 Bézu). The deviation of values with respect to the correlation base

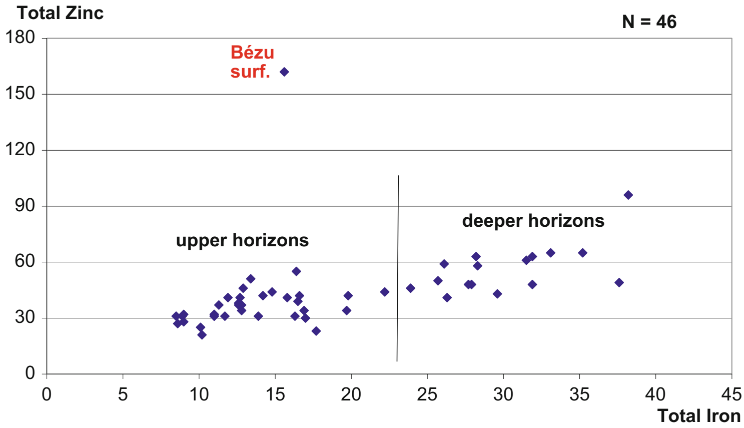

Fig. 4.7 Albeluvisols developed in a loamy aeolian deposit (South-east of the Paris basin). Fourty-six samples were taken at different depths from forest and cultivated soils. Strong correlation between total concentrations of Zn and Fe is observed. One sample, outside this correlation comes from an experimental plot amended with sewage sludge at high rates (Ap horizon – site Bézu). See also Fig. 4.4; Zn concentrations are expressed as mg kg^{-1}, Fe as g kg^{-1}

line, representing the pedogeochemical background level of the soil series, gives an estimation of the amount of contamination for each trace metal (Lamy et al. 2006; Fernandez et al. 2007).

The determination of the natural pedogeochemical concentrations of PHTEs for a given soil series demands field experience and insight in the historic and ways of dissemination of contaminants. Between 25 and 50 soil samples, as little contaminated as possible, must be analysed for each soil series. Therefore, the sampling strategy must be organized by giving priority to (i) soils for a long time **under forest** which may have received some atmospheric deposition but are free of agriculture derived contamination; (ii) deep horizons of cultivated soils, assumed to be uncontaminated. This approach requires consistent previous geological and pedological knowledge relative to the soil series under consideration: good morphological and analytical definition of the series and the determination of PHTE concentrations for several dozens of soil samples. Consequently, this approach is rather time and finance demanding, needing intervention of scientists skilled with soil science. In this approach also, the forest soils are used as reference systems. Some restriction in its application may arise: (1) in case of acid physicochemical conditions in forest soils favouring a partial lixiviation of some metal elements toward depth or even out of the soil, (2) for soils in the proximity of mining or industrial metallurgical sites, where surrounding areas have diversely been contaminated over several kilometres distance (Sterckeman et al. 2000), including forest land. Examples of such situations are discussed and illustrated hereafter (Sect. 5.1).

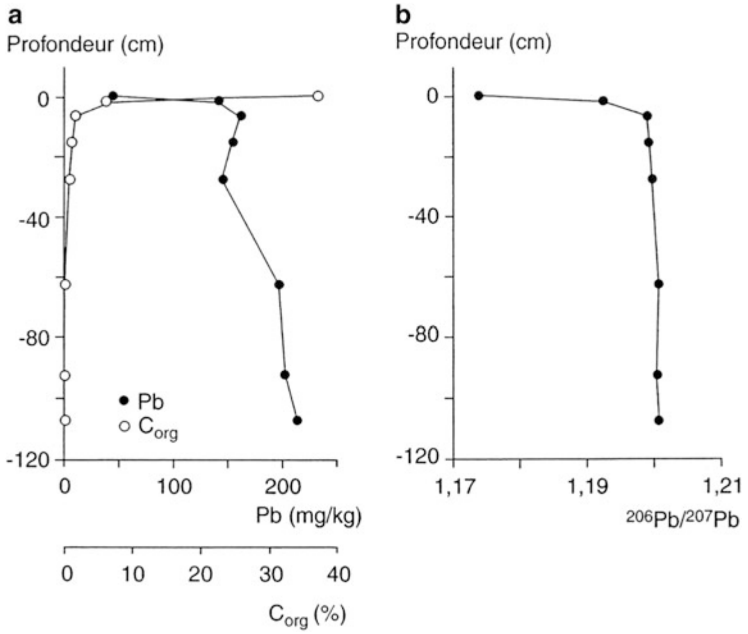

Fig. 4.8 Soil profile "*Bois de Belle Verne*" (Northern Morvan, France) (Lévêque et al. 2002); (**a**) distribution profile of organic carbon and Pb concentrations, (**b**) vertical distribution of lead isotopic ratio $^{206}Pb/^{207}Pb$

3.2.4 Use of Stable or Radioactive Isotopic Ratios

For some decennia, the isotopic ratio approach was widely used for lead to trace Pb sources in the environment. The use of stable lead isotope ratios is a very powerful tool that in most cases allows a definite distinction between the natural, geogenic lead in soils and the amount added by air pollution (Bacon et al. 1992; Erel et al. 1997; Monna et al. 2000; Lévèque et al. 2002; Semlali et al. 2000, 2001a, 2004; Bacon and Hewitt 2005; Steinnes and Friedland 2005; Fernandez et al. 2008) (see Figs. 4.8, 4.13 and 4.15).

"*Pb naturally present in a soil generally shows a different isotopic composition to that of Pb from anthropogenic sources* (excepted in the case of mining activities). *So, the isotopic signature of Pb constitutes a useful additional recorder of contamination*". In addition, "*stable isotopic signature of the Pb can be studied associated with the different fractions giving valuable information about soil processes when applied to partitioning studies*" (Emmanuel and Erel 2002).

More recently, such isotopic ratio approaches have been applied also to distinguish different pools of cadmium and zinc (Cloquet et al. 2006; Weiss et al. 2008; Juillot et al. 2011).

3.2.5 Enrichment Factors (EF) Assessment

This approach considers the abundance of the metal of interest, relative to the abundance of a conservative lithologic element (such as Zr, Sc, Ti or Al) with no significant anthropogenic source (Blaser et al. 2000; Semlali et al. 2001a; Shotyk et al. 2001). This ratio can then be normalized to the corresponding ratio in the upper continental crust (e.g. Sterckeman et al. 2006) and such an EF is known as "crustal enrichment". Therefore, it seems more reasonable that the assessment of enrichment factors for topsoils would be made by comparison with the deeper horizons or parent material of each individual soil profile (Blaser et al. 2000; Bourenanne et al. 2010).

Note that the very principle of this method is contested by Sucharovà et al. (2012). These authors argued by comparing O horizons with the correspondent B horizons in forest soils of the Czech Republic but, in our opinion, B horizons were sampled at too shallow depth and, therefore, cannot represent the unweathered parent material.

The two latter approaches (isotopic ratios and EF) are quite elaborate methods and need precautions, funds and time (for sampling, pre-treatments, and analyses).

4 Special Features of Forest Soils in Regard to Soils Under Agricultural Land Use

4.1 A Lower Impact of Anthropogenic Contaminations

Forest soils generally are exempt of anthropogenic inputs related to agronomical practices (fertilisers, organic amendments, liming, sewage sludge, waste water, etc.), all of them possibly containing unwilled substances, including PHTEs. In forest soils, the only inputs of anthropogenic origin are nearby or remote air-borne deposition.

For a long time it has been well-recognized that long-range transport of pollutants in the atmosphere affects both remote rural as well as industrial or urban areas and that forest ecosystems and regions with high precipitation are most strongly influenced by atmospheric deposition (e.g. Heinrichs and Mayer 1980). These authors concluded that there is probably no land surface in central Europe where the local balance for most heavy metals on the ecosystem level is not strongly influenced, or dominated, by atmospheric deposition pollution. The bulk of the atmospheric input measured nowadays would be of anthropogenic origin as far as heavy metals are concerned.

Bergkvist et al. (1989) gave us a good insight of what is atmospheric deposition. "*Metals are deposited to the tree canopy as wet and dry deposition. Wet deposition includes precipitation in the form of rain and snow as well as fog and cloud droplets. Dry deposition comprises particle deposition and gas sorption. Bulk* *deposition is commonly defined as the total wet and dry fallout collected in a continuously open vessel placed in an open field*". The dry deposition to a forest is much greater than to a grass-cover or otherwise open area (see Sect. 5.1). Due to aerodynamic properties and the greater leaf area, conifers are much more efficient in trapping aerosols than are deciduous trees. The dry deposition to deciduous trees is greater when they are foliated than during the winter. However, the higher pollution load of metals commonly occurring during the winter may well increase the deposition.

Another specificity of forests with high trees is that there are interactions of rainwater with foliage or needles (not forgetting the stemflow). As a result, the solution which reaches the « forest floor » has not exactly the same composition than the deposition at the top of the canopy (Gandois et al. 2010).

4.2 Fluxes of Atmospheric Deposition (Present or Past)

These fluxes considerably vary from a place to another and, at least, three main types of air-borne deposition can be distinguished:

- **local point-sourced deposition** close to a well-identified source, located at a distance less than 4–6 km. A typical case is that of industrial activities (e.g. Godin et al. 1985; van Oort et al. 2001, 2009), where a rapid and generally exponential decrease of the total concentrations measured in the surface horizon can be observed with increasing distance from the emitting source, until reaching the local background UAC or UFC (see Box 4.2.).
- **long-range diffuse air-borne deposition**: numerous sources merge, including mobile ones, the impacts spread as far as about 30–300 km (e.g. Saur and Juste 1994; Blaser et al. 2000; Steinnes et al. 1989, 1997, 2005; Kaste et al. 2003; Berg et al. 2006);
- **global diffuse deposition** which affects the entire surface of the Earth, even if the fluxes remain very small (e.g. Hong et al. 1994; Boutron 1995; Shotyk et al. 1998).

As far as lead is concerned, figures found in the literature broadly vary from 1 to 85 g ha^{-1} year^{-1} for remote rural areas far from any big city and from 100 to 400 g ha^{-1} year^{-1} in rural areas of Poland, Germany, Wallonia and Great Britain (Galloway et al. 1982; Navarre et al. 1980; Alloway et al. 1999). Some studies on the evolution of lead contents in soils in France gave the following values for the Paris suburban region: 930 g ha^{-1} year^{-1} at Versailles between 1929 and 1984 (Juste and Tauzin 1986); 650 g ha^{-1} year^{-1} between 1938 and 1999 at Grignon (Baize and Bourgeois 2005); 50–300 g ha^{-1} year^{-1} at Versailles between 1990 and 2000 (Semlali et al. 2004).

Box 4.2: NPGC and UAC

The natural pedo-geochemical concentration (NPGC) is the concentration of any substance resulting from natural geological and soil forming processes, without any man-induced addition (Adriano et al. 1997; Baize 1997b). From one place to another, this natural content is greatly variable, according to the parent material composition and the soil type (Fig. 4.1).

It is always essential to specify for what territory the NPGC is defined: for instance a country, a watershed, a county, a land plot, the area where spreads a particular typological soil unit.

The most interesting, the local NPGC, can be defined for a precise soil horizon, one soil profile or a specific soil-series. These values can be determined by using peculiar approaches, methods of analysis, and analogical thought processes (see text).

The usual agricultural contents (UAC) are the most frequent range of concentrations measured in the ploughed horizons under "normal" agriculture (i.e. without waste application or local industrial pollution). Commonly, the range of values contained between 10th and 90th percentiles is used, known as "frequent values range". Once again, the territory under consideration must be defined. These usual agricultural contents can be determined for any soil series. They result from the addition of:

- the effects of past agricultural practices,
- plus the atmospheric deposition,
- less the losses due to an open biogeochemical cycle (export in crops) or to lixiviation and lessivage. . . . . .to the natural NPGC (Fig. 4.1).

Usual forest contents (UFC) can also be defined in the same way, taking into account the different nature of organic and organo-mineral layers.

Establishing a nationwide budget of atmospheric Hg in Norway, Berg et al. (2006) reported that "*the current mercury levels in sediments. . .are substantially affected by long-range atmospheric transport. Compared to the pre-industrial lake sediments the surface sediments had significantly elevated Hg concentrations, usually by a factor of 2–4 in the country as a whole.*" For the period 1990–2002, the mean annual Hg deposition has varied between 21 and 9 µg m^{-2} $year^{-1}$.

Current rates of atmospheric trace metal deposition were in southern Norway (in 1992) about 9 mg m^{-2} Zn, 4 mg m^{-2} Pb and 0.1 mg m^{-2} Cd. Total deposition of these metals in this region from 1976 to 1992 averaged roughly 310 mg m^{-2} Zn, 170 mg m^{-2}, and 5 mg m^{-2} Cd (Berthelsen and Steinnes 1995).

Besides their great variability in space, these fluxes have broadly varied in the course of time. From the antiquity, several periods of mining and industrial activities were followed by periods of interruption. Such variations were recorded in sediments, peat-bogs, or glaciers (Sugden et al. 1991; Jensen 1997; Steinnes

1997; Monna et al. 2004). In modern times, a strong increase of lead atmospheric deposition was observed corresponding first with the development of the industrial revolution in Europe, and then with the introduction of lead in petrol as anti-knock additive. Currently a marked decreasing input of Pb can be observed due to the withdrawal of the leaded fuel (e.g. Miller and Friedland 1994; Candelone and Hong 1995; Azimi et al. 2003; Steinnes and Friedland 2005).

The works of Shotyk and colleagues achieved on peat-bogs in Switzerland have shown that antique mining and metallurgical works have been recorded and could be still recognized today some thousand years later. These activities were located far from Switzerland and fluxes recorded highly varied with time (Shotyk and Blaser 1999; Shotyk et al. 1998, 2000).

The PHTEs mainly involved in medium- and long-range air-borne contaminations are Pb, Cd, Hg, Zn, and Cu. In soils, Ni, Cr and Co most often have a geogenic origin (with the exception of areas located close to smelters such as these in the Kola peninsula – Reimann et al. 2001).

4.3 Strong Acidity

Very often, forest soils show a strong acidity but that is not a general rule: numerous soils under forest are calcium-saturated or even calcareous.

Many studies on impacts of trace metal deposition on natural forest ecosystems have been conducted in Scandinavia, Northern Russia or North America because the soils are to a large extent chemically very poor and acid. Hence, great concern has risen for the ecosystems, in particular related to forest decline and acid rains. Yet, most of studied soils are podzols[1] with a particular type of pedogenesis characterised by eluviation/illuviation of humus-metal complexes (see Sect. 4.3.4). There are three main consequences of strong soil acidity (the particular case of podzols will be dealt with apart, see Sect. 5).

4.3.1 Possible Vertical Mobility of Zn and Cd

For all soils, a main pattern of leachability is associated with soil acidity (Bergkvist et al. 1989). In the literature, field studies under forests are quite rare and most often limited to the “purely organic mor horizons” (e.g. Tyler 1978) or “A horizons” (e.g. Tyler 1981). Most of the research is dedicated to polluted agricultural soils (e.g. Degryse et al. 2001) and often carried out in the laboratory conditions on soil samples in columns.

A good means of studying the matter translocating through the soil profile is the use of lysimeters. These are not easy to implement (Keller and Védy 1994) but the

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[1] *Spodosols according to the USDA Soil Taxonomy.*

composition of the waters collected in this way gives useful information. Fluxes of trace metals as well as major elements are usually measured in the soil solution after filtration through a 0.45 μm membrane and mass balance calculation are then based on soluble compounds (Ugolini and Dahlgren 1987; Bourg and Védy 1986). This size limit is arbitrary but conventional. In some cases (especially that of podzols or heavily polluted sites), it is necessary to take into account the whole content of the gravitational water because transported matter can be in particulate or colloidal forms also (Guillet et al. 1981; Keller and Domergue 1996; Citeau et al. 2003, 2006, 2009).

Römkens and Salomons (1998) gathered *in situ* soil solution samples at 6 depths in 30 Dutch forest and arable sandy soils. Their conclusions were as follows. "*The solubility of trace metals under field conditions is linked strongly to soil parameters such as pH, soil organic matter and dissolved organic carbon. In very acid soils (pH $<$ 4.5) 80 % of all Zn and Cd concentrations exceeded current ground water quality standards as a result of the high metal solubility at this low pH. Taking into account the low acid buffering capacities in these sandy soils, continuous acidification may cause further increase of metal concentrations in soil solution*". In case of conversion of these poorly productive soils to forest or wetlands, remobilization of Cd and Zn, therefore, is likely to occur in the topsoil after afforestation.

4.3.2 Risk of Aluminium and Manganese Toxicity

In soils with pH in water $>$ 5.0, aluminium is chiefly in the form of insoluble oxyhydroxides. When soils are obviously acid (i.e. pH $<$ 5.0), the exchangeable aluminium becomes abundant on the adsorbing complex and may become phytotoxic, in particular for seedlings. At lower pH the oxyhydroxides forms evolve to ionic forms $Al(OH)_2^+$ or $Al(OH)^{2+}$, and finally to Al^{3+}, if the soil pH decreases under 4.5. These ionic forms can provoke an inhibition of root growth (Bonneau 1995). This kind of toxicity has been revealed since a long time for *Pinus maritimus* (Juste 1966). Toxicity features appear at about 50 mg Al L^{-1} in the soil solution and is clearly marked for concentrations of 200 mg L^{-1}. Sugar maple (*Acer saccharum*) would be particularly sensible to Al-toxicity (from a concentration of 4 mg Al L^{-1}). Even in acid soils, concentrations of ionic Al rarely exceed 5 mg Al L^{-1} in the soil solution. So, a real toxicity would not be reached under temperate climates for the common species with a moderate resistance (such as *Picea abies, Abies alba, Fagus sylvatica*). Rather than toxicity, the competition of Al with Ca and Mg may lead to problems to forest stand health even if the root growth (criterion often chosen for assessing the toxicity) is not hindered (Bonneau 1995).

Contrarily to the case of Al^{3+} which chemical form primarily depends on the soil pH, the phytoavailability of manganese is mainly function of the present oxidation-reduction and moisture conditions. Only the most reduced forms of Mn (Mn^{2+} and Mn^{3+}) are easily available to plant roots. Therefore, manganese toxicity can occur both in the case of strongly acid soils and of poor drainage conditions.

Accumulation of these reduced forms in uppermost humose horizons can affect adversely seedlings of conifers.

4.3.3 A Much Higher Phyto-Availability of Trace Elements to Plants Through Roots Absorption

In forest ecosystems, PHTEs incorporated in trunks, branches, and leaves will represent virtually no risk with respect to human health. By contrast, a strong pollution of the surface horizons can contaminate the edible parts of mushrooms and forest berries (blueberries, raspberries, strawberries, or brambles) giving rise to potential hazards for consumers (e.g. Michelot et al. 1998; Kalac and Svoboda 2000; Benbrahim et al. 2006).

One approach is widely adopted to characterize metal behaviour in soil and sediments with the aim of estimating their potential bioavailability. It consists in partitioning the metals in the solid phase into various operationally-defined fractions by using chemical extractants of increasing strengths (Tessier et al. 1979). Very usual for polluted agricultural soils, this method is less often used for forested ones (e.g. Chlopecka and Hutchinson 1997).

In literature, we did not find references presenting toxicities to plants in a forested environment due to natural trace elements. The main processes reported are involving aluminium and manganese (see above Sect. 4.3.2).

4.3.4 The Special Case of Podzols

Podzols are very acid, highly permeable soils, with low clay contents, where the occurrence of high amounts of reactive organic compounds favours the downward movement of trace elements in the form of humus-metal complexes. In podzols, migration of pseudo-soluble forms (i.e. cheluviation) is responsible for the formation of podzolic B illuvial horizons after migration through the E horizon (e.g. Duchaufour 1982; Driessen and Dudal 1991; Keller and Domergue 1996). Such conditions lead to increased risks of translocation of pollutants introduced at the surface toward depth and *in fine* to the water table (Delas 1966; Saur and Juste 1994). Some selected literature quotations illustrate the special lixiviation character of acid podzols for trace metals, even for the low-mobile lead.

Steinnes et al. (2005) in a quantification work of pollutant lead in podzols in Norway note: "*It is apparent from the present data that the vertical transport of Pb differs considerably between the sites. Whereas some sites show little or no pollution-derived Pb in the B horizon, around 70 % of the Pb in the upper B horizon at the three southernmost sites comes from atmospheric deposition. This means that, in the south of Norway, a major part of the pollutant Pb is no longer in the O horizon but has moved down to the E and B horizons. Similar conclusions were reached in the corresponding Swedish study (*Brännvall et al. 2001*). Possible reasons for the more extensive transfer in the south include higher total input of Pb* *and possibly a greater turnover of humic matter at higher mean annual temperatures. The most important factor, however, is likely to be the significantly higher atmospheric deposition of acidifying substances in the south, which may, to a great extent, release Pb from exchange sites in the humus layer and promote downward leaching"*.

Berthelsen and Steinnes (1995) carried out an investigation of the vertical distribution of Zn, Pb, Cd and Cu in podzol profiles, comparing 12 forested sites and 9 clear-cut areas. According to these authors, "*Clear-cutting of forests leads to drastic changes in the underlying soil, both concerning direct effects on the humus layer and soil solution chemistry. The lack of trees reduces the evapotranspiration, thus giving higher water content in the soil and increased water percolation through the soil in clear-cut areas."* With respect to the movement of low-mobile elements such as Pb in acid soil conditions of podzols, these authors note: *"The total content of Pb in the L + F + H horizons was significantly lower in clear-cut than in forested areas attributable to distinctly lower Pb contents in the H horizons of clear-cut areas soils. This fact combined with significantly thinner humus layers in clear-cut areas compared to forested areas presents evidence for increased losses of Pb from the humus layer after clear-cutting. Higher Pb contents in the Ae and B horizons of the clear-cut area soils than in forest area soils, show that at least parts of the Pb lost from the H horizon in clear-cut areas were re-adsorbed or re-precipitated in the Ae and B horizons."*

4.4 Impact of Waterlogging

Some forest soils show temporary or quasi-permanent waterlogging, and they are most often not reclaimed by drainage as it is frequently the case for agricultural areas. What are the consequences on the dynamic of PHTEs of these temporary but frequent phases of reduction followed by phases of re-oxidation? Their association with Fe and Mn hydrous oxides leads to their reversible adsorption, a subsequent desorption is possible according to the physico-chemical conditions (e.g. Alloway 1995; Strawn et al. 2012). As Mn oxides are more easily reducible than Fe oxides, they often control trace elements availability and so their mobility in the environment. The chemical and bacterial dissolution of Mn oxides favour the release of associated trace metals under reductive conditions (Quantin et al. 2002).

Charlatchka and Cambier (2000) implemented artificial waterlogging experiments on undisturbed soil blocks. They concluded: "*pH variations definitively influence trace metal solubility, whatever they are induced by reductive dissolution, organic acid formation or other processes and that strong acidification can be obtained with well buffered soil when about 1 % of the available carbon is anaerobically transformed into organic acids. … Given a steady pH, reducing conditions enhance the mobility of trace metals, at first by dissolution of Mn and Fe oxides; Pb appeared more sensitive to these processes than Zn, and finally Cd. As a general rule, hydromorphy in a well buffered contaminated soil at a first step should increase the mobility of divalent trace metals, by decreasing pH and* *reducing Mn and Fe oxides, but prolonged flooding can lead to fix trace metals again, rather by re-adsorption or precipitation phenomena than by formation of insoluble sulphides"*.

4.5 The Bio-geochemical Cycling of Elements

Elements (nutrients as well as PHTEs) are more or less absorbed by roots in surface A and deeper soil horizons, and then partially transferred up to the surface organic layers by means of the fallout of dead aerial organs (leaves, needles, stems and twigs). If this cycle remains closed, the fluxes are small but as it is a long-lasting process (several thousands of years) the amounts of elements involved in that cycle may be sizeable. If there is removal of wood by yielding of timbers and branches or harvesting of the litter, then the cycle is broken. The soil, particularly its uppermost layers, becomes increasingly impoverished in nutrients as well as in PHTEs.

For quite some time, a warm controversy about the biological cycling of lead is under discussion. For some authors, the processes of "plant-pumping" and then that of "organic binding" must be preferred for explaining the accumulation of lead in the forest floor of Scandinavian and Northern Russia forest soils (Rasmussen 1998; Reimann et al. 2001). The possible return from the depth to the soil surface, due to the absorption by roots and the natural cycle, have also been envisaged by Denaeyer-De Smet 1974; Bruckert et al. 1979; Guillet et al. 1980. Conversely, most authors (such as Heinrichs and Mayer 1980; Blaser et al. 2000; Kaste et al. 2003; Steinnes et al. 2005; and many others) explain this uppermost accumulation of PHTEs solely by long-range deposition from urban and industrial areas.

Another way of presenting the debate is to ask the question: is lead abiotic? For some authors, the answer is positive (Heinrichs and Mayer 1980; Craig et al. 1991). Bergkvist et al. (1989) state: "*The first sink for Cu and Pb is the litter and mor layers*". And these authors add: "*The organic topsoil is often regarded as an almost permanent sink for Pb*" (in contradiction with findings in Sect. 4.3.4: this is not true in the case of podzols).

4.6 Accumulation of Air-Borne Pollutants

Air-borne pollutants as well as recycled geogenic trace metals can accumulate in the organic litter (coded O) and organo-mineral horizons (coded A). The metals incorporated in the ligneous tissues are withdrawn from the geochemical cycle for the lifetime of the forest, and will be partially exported from the ecosystem when the forest is harvested.

A thorough field study carried out in Central Germany (Heinrichs and Mayer 1977, 1980) has clearly shown that the metals bound in the cycling fraction reach the soil together with litterfall within a short time i.e. after <1year in a beech forest, after <7 years in a spruce forest. Very often, there is a strong binding in organic matter and the metals are accumulated in the organic topsoil or humus fraction again being withheld from further cycling. According to the same study, lead is strongly accumulated in the organic surface layer which retains 80–100 times the amount of Pb found in annual litterfall. The Pb concentrations are clearly decreasing from the top to the deeper soil horizons.

Bourg and Védy (1986) studied the dissolved trace metals in gravitational water of two acid sandy soils of the Vosges Mountains (France), both developed in weathered sandstones and located under forests. One was a Dystric Cambisol with a mull type humus form and the second an Orthic Podzol with a mor type humus layer. In conclusion, they established that: "*the fate of the trace metals associated with the dissolved organic matter should follow the dynamics and evolution of their organic vectors. The free metal fraction whose size depends on the organic complexation constants, is available for either biological uptake (including upward recycling, a significant phenomenon in acid brown soils) or for further downward migration.*" Besides, this study illustrates a major difference of trace metal cycling in "acid brown" soils and podzols.

4.7 Organic Matter Gradients

As a consequence of the previous point, **organic matter (OM) gradients** with depth can be observed under forests, different from OM gradients characteristic for agricultural cultivated or grassland soils. Very often, under forest vegetation, there is a thick accumulation of humified organic matter and most of the PHTEs are tightly linked with organic matter whatever its forms! Considering the differences in bulk density of organic, organo-mineral or mineral horizons, we must be careful in using concentrations of PHTEs. A better approach is to reason with metal stocks and consequently, different pedogenetic layers must be sampled separately (cf. Sect. 5.1).

4.8 Impacts of High Concentrations of PHTEs on Ecosystems

If these PHTEs are of natural (geogenic) origin, no impact will be seen on the forest ecosystem because:

1. the local microbial and arthropod populations are adapted for a long time to such conditions;
2. the easy-labile chemical forms are less abundant than the little or non-labile forms because more mobile species have leached in the course of time.

On the contrary, if these **high concentrations** are the result of **pollution**, a chronic exposure to the solid and liquid phase can give rise to toxicity to indigenous soil microbial communities, resulting in a weakening or a strong reduction of biologic activity, a decreasing rate of degradation of the soil OM, a decrease of incorporation of OM to deeper soil horizons by bioturbation and an abnormal accumulation of PHTE-rich organic matter at the surface, as was demonstrated for metallophyte grassland under sparse poplar/birch vegetation in northern France (Balabane et al. 1999; Dahmani-Muller et al. 2000; van Oort et al. 2002a, 2009).

Moreover, a study by Bringmark and Bringmark (2001) has shown an inverse correlation between microbial respiration and Pb and Hg concentrations in the mor layers of soils in southern Sweden. This observation was readily explained by toxic metal effects. An alternative explanation, that metals and microbial respiration both co-vary with degree of decomposition in the humus layer, has been convincingly shown for a few sites but cannot explain why the respiration/metal correlations were strongest for all sites with high loads of Pb or Hg.

5 Importance of Soil Forming Processes and Land Use on the Distribution and Fate of Trace Elements – Two Case Studies

One major difference between forest and agricultural soils lies in the nature and dynamics of organic matter. Extended forest covers occupy land areas for long periods and large amount of organic materials are returned to soils as fallen litter and decaying roots (Binkley and Fisher 2012). The role of soil organic matter (SOM) as a metal sorbing agent has been frequently stressed (McBride 1989; Krosshavn et al. 1993), and the stability of SOM-metal interactions is recognized to be a crucial factor governing the fate of metals in soils (McBride et al. 1997; Sauvé et al. 2000; Labanowski et al. 2007). Therefore, the distribution and biochemical cycling of organic matter in soils under different land use is essential to consider when assessing trace element concentrations in forest soils, in comparison to agricultural land (Blum et al. 1997; van Oort et al. 2002b, 2009).

Hereafter, a first case study highlights the importance of land use on the fate (deposition, incorporation, redistributions) of air-borne trace metals, derived from past industrial activity in northern France in soils under different land use. The example illustrates some difficulties which may arise when assessing ‘soil contamination’ of fairly comparable metal pollutant inputs in soils that evolve differently due to influences of human activity (soil tillage, fertilization and amendments in arable land soils), biological perturbation (earthworm activity in grassland soils) and soil acidification (promoting eluviation/lixiviation processes of trace metals in forest soils).

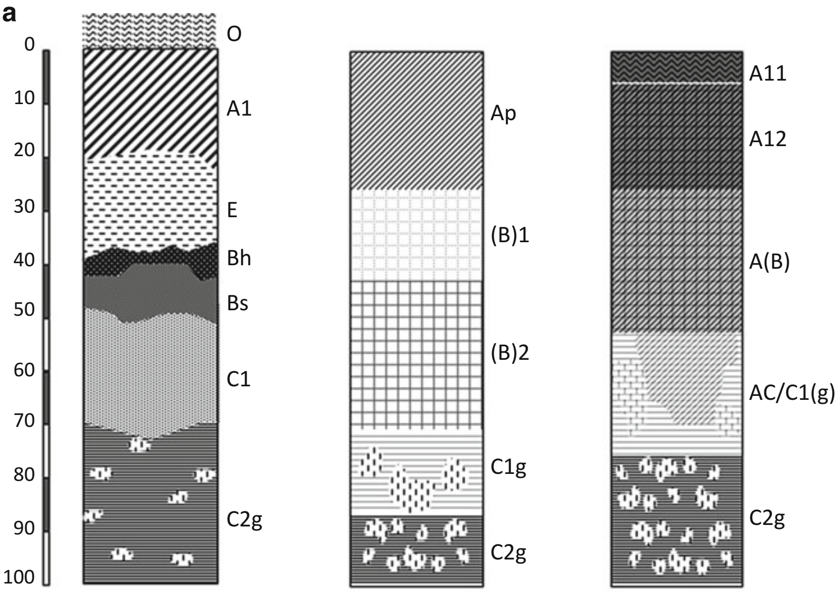
The second case study gives evidence for the migration of lead, widely considered as a low or non-mobile metal in soils, in two forest ecosystems in France. The first is an andosol developed on volcanic basaltic scoria in the Massif Central, the second is a podzol developed in sandy textured sediments in the "Landes de Gascogne". These two sites are affected by medium- and long-range atmospheric deposition, respectively. The migration dynamics of Pb are discussed in relation to specific features of pedogenesis in these two different forest systems.

5.1 Relevance of an Adapted Sampling Strategy for Survey of Spatial Airborne Metal Contamination

Inputs, incorporation dynamics and biochemical cycling of organic matter in soils widely diverge under different land use and lead to clear different macro-morphological soil characteristics (Fig. 4.9). Moreover, forest topsoils frequently contain higher trace metal contents than arable land and grassland soils, ascribed by many authors to diffuse atmospheric deposition favoured by a greater filter action of forest canopies (e.g. Schlesinger and Reiners 1974; Heinrichs and Mayer 1980; Jensen and Svensmark 1989; Hanschmann and Opp 1993; Hernandez et al. 2003; Steinnes and Friedland 2005). Under different land use, the concentration profiles of trace metals were mentioned to be related, to a large extent, to the distribution of organic matter concentrations (Blum et al. 1997). With time, the distribution of trace elements added to soils by atmospheric deposition will change according to soil nature, soil behaviour and human practices. Consequently, for assessing soil contamination in soils under different land use, an adapted sampling strategy must be used that considers both soil morphology and the incorporation dynamics of trace elements, as well as the type of contamination. Taking into account of these aspects is a *sine qua non* for "comparing the comparable" (Thiry and van Oort 1999; van Oort et al. 2007).

The comprehension of metal dynamics in soils in relation to land use requires knowledge on related soil development characteristics and behaviour. Consequently, the use of a sampling strategy that considers metal concentrations in genetic soil horizons is essential (Cf. Sect. 3.2.3). Differences in profile development under different land use, but on similar parent material (Fig. 4.9a), mainly result from of a combination of factors: specific biochemical cycling of organic matter, vegetation, faunal activity, and agronomic practices.

The examples presented in Fig. 4.9 correspond to (i) a soil under pine-beech forest, (ii) a soil used for cereal crop production and (iii) a soil under permanent grassland, un-ploughed for one century. The arable and permanent grassland soils are developed in aeolian cover sands, under the same topographic, climatic and pedological conditions and differ mainly by their agronomical land use, remaining unchanged during the twentieth century (Fernandez et al. 2007). The forest stands occur on the same parent material, but at an altitude of about 5 m higher. These varying land use and environmental conditions have led to widely diverging physicochemical soil properties. Fairly similar airborne metal loads arriving at the surface of the three soils are incorporated differently according to processes



Acid forest soil
Haplic Podzol. OM accumulation (O) and eluviation (E) / illuviation (Bh, Bs) horizons

Arable land soil
Luvic Cambisol. Mixing of OM by annual plowing over the Ap horizon

Permanent grassland soil
Eutric Cambisol. Incorporation to depth of OM by earthworm activity

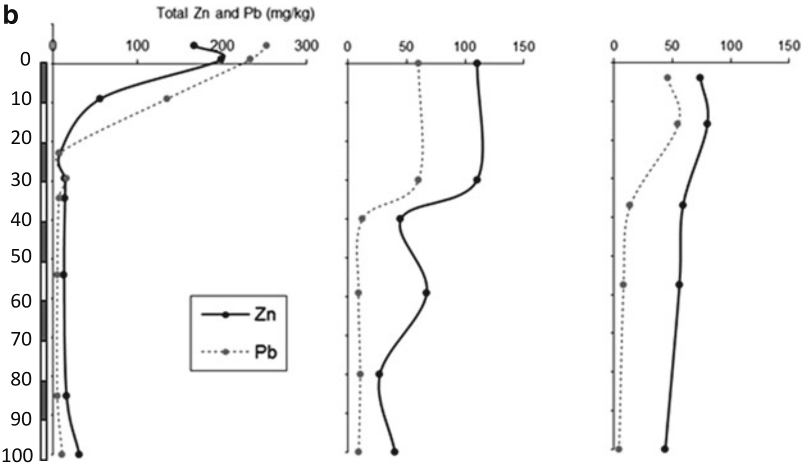


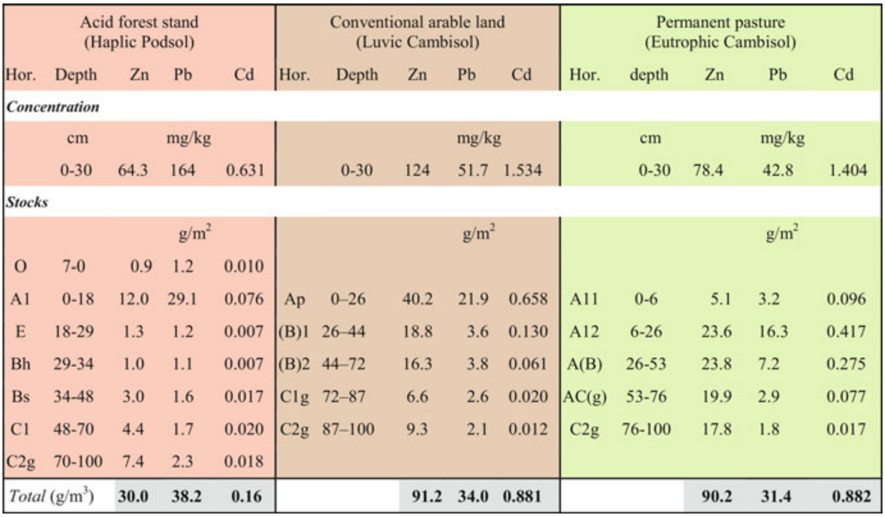
Fig. 4.9 Soil profiles and metal distribution to depth in soils under different land use. (**a**) Macromorphology of soils under forest, arable and grassland developed in aeolian cover sands in northern France, affected by industrial atmospheric metal deposition from a zinc smelter plant active between 1901 and 1962. All three sites are located windward with regard to the former industrial complex, at distances of 3,500, 3,250 and 3,100 m, respectively; (**b**) corresponding depth profiles of Zn and Pb concentrations (Adapted from van Oort et al. 2009). Soil classification according to IUSS Working Group WRB (2006)

specific of each type of land use. In Fig. 4.9b, metal concentrations in the genetic horizons of the three soils are presented. The metal contamination derives from short-range atmospheric fallout deposition emitted during the first half of the twentieth century by a zinc smelter complex in northern France (Thiry et al. 2002), disseminating large amounts of Zn, Pb, and Cd in the environment (van Oort et al. 2009). When focussing on the distribution of concentrations with depth for a mobile (such as zinc and cadmium) and a little or no-mobile trace metal (such as lead), 50 years after cessation of metallurgical activity, great differences of Zn and Pb concentration distributions are observed, both between the soils, but also between the two metals. In the O horizon of the forest soil, large Pb concentrations are observed, more than five times higher than in adjacent agricultural soils (Fig. 4.9b). Moreover, in the upper 20 cm of the forest soil, in the O and A1 horizons, the Pb concentrations are much larger than for Zn, and remain about equal in the E and Bh horizons until about 40 cm depth. This is contrarily to what is observed in the arable land and grassland soils where concentrations of Zn are larger than of Pb.

This example clearly illustrates the importance of considering land use and soil morphology when performing sampling for geochemical survey in an area to assess soil pollution. The analysis of metal concentrations on samples collected at arbitrary depths (but frequently referred to as representing 'the soil's surface layer') may lead to substantial over- or underestimation of metal concentrations, because soil horizon thickness, physicochemical and physical soil conditions usually greatly vary from one soil to another:

– *under acid forest stands*, where organic matter frequently is the predominant metal sorbing soil constituent, largest concentrations are found in the litter layer (Keller and Védy 1994) containing large amounts of decaying organic fragments, also designates as 'particulate organic matter (POM)', very efficient metal binding compounds in soils (Wang et al. 1995; Balabane and van Oort 2002; Labanowski et al. 2007). Yet, being composed of solely organic matter, the O horizon has a very low bulk density, and despite its often large metal concentrations, the contribution of this horizon to the total metal stock in the soil is only minor. Moreover, in forest soils with often more acid soil conditions, metals are generally more mobile (McBride 1989) and more or less transferred downward, partly in dissolved form (Zn) or associated with colloids (Pb) (Citeau et al. 2003).
– *under arable land*, atmospheric deposition is incorporated by annual ploughing, the metal concentrations are homogenized over a depth of about 30 cm and fertilization and liming practices favour metal retention in the plough layer (Adriano 2001; Fernandez et al. 2007),
– *under permanent grassland*, soil homogenization is to large extent due to roots and faunal activity, notably earthworms (Nahmani et al. 2003). Consequently, a part of the metal contaminants, both mobile Zn as well as the immobile Pb, is mechanically incorporated and transferred to depth by worm activity (Fernandez et al. 2010).

Table 4.6 Surface concentrations (0–30 cm) and calculated amounts (stocks) of Zn and Pb stored in each soil horizon (in g m^{-2}) for soils under forest, arable and permanent grassland and cumulated stocks for 1 m^3



Acid forest stand (Haplic Podsol)					Conventional arable land (Luvic Cambisol)					Permanent pasture (Eutrophic Cambisol)				
Hor.	Depth	Zn	Pb	Cd	Hor.	Depth	Zn	Pb	Cd	Hor.	depth	Zn	Pb	Cd
Concentration														
	cm		mg/kg					mg/kg			cm		mg/kg	
	0-30	64.3	164	0.631		0-30	124	51.7	1.534		0-30	78.4	42.8	1.404
Stocks														
			g/m^2					g/m^2					g/m^2	
O	7-0	0.9	1.2	0.010										
A1	0-18	12.0	29.1	0.076	Ap	0–26	40.2	21.9	0.658	A11	0-6	5.1	3.2	0.096
E	18-29	1.3	1.2	0.007	(B)1	26–44	18.8	3.6	0.130	A12	6-26	23.6	16.3	0.417
Bh	29-34	1.0	1.1	0.007	(B)2	44–72	16.3	3.8	0.061	A(B)	26-53	23.8	7.2	0.275
Bs	34-48	3.0	1.6	0.017	C1g	72–87	6.6	2.6	0.020	AC(g)	53-76	19.9	2.9	0.077
C1	48-70	4.4	1.7	0.020	C2g	87–100	9.3	2.1	0.012	C2g	76-100	17.8	1.8	0.017
C2g	70-100	7.4	2.3	0.018										
Total (g/m^3)		**30.0**	**38.2**	**0.16**			**91.2**	**34.0**	**0.881**			**90.2**	**31.4**	**0.882**

Data compiled from Fernandez et al. (2007); van Oort et al. (2009)

For more valid assessment of the importance of metal contamination in an area including forest and agricultural soils, for instance with the aim of producing spatial distribution maps of total metal contents in soils, a better sampling strategy consists in comparing metal concentrations in the soil's surface layer with comparable thickness of the plough layer where the atmospheric deposited metal loads are annually homogenized, i.e. 30 cm (Table 4.6). Collecting such samples also in soils under grassland and forest signifies that the atmospherically added metal loads are artificially homogenized over a depth of 25–30 cm in order to obtain comparable soil volume with respect to the samples collected in the ploughed layer of the arable soil. Such approach is illustrated in Fig. 4.10, presenting the mean concentrations of Zn, Cd and Pb from samples of 0–30 cm depth, collected in different soil transects across agricultural and forest land.

Such an approach gives quite another view of metal accumulations in the surface layer: Pb concentrations are still largest in the forest soil (Fig. 4.10b), but largest Zn and Cd values are found in surface horizons under arable land, whilst smallest in the soils under forest (Fig. 4.10a, c). Moreover, the variability of total metal concentration is large, as shown by the error bars, particularly for Zn and Cd in agricultural land soils. This is mainly ascribed to variable pH values in the latter (pH: 5.5–7.5) in comparison to the acidified forest soils (pH: 3.5–4.5) but also to phenomena of temporary waterlogging in soils close around the forest edge occurring in lower topographic positions, inducing increased mobility of Pb (cf. Sect. 4.4) The forest soils (Haplic Podzols) located at 850 m from the forest edge, have developed in well-drained conditions.

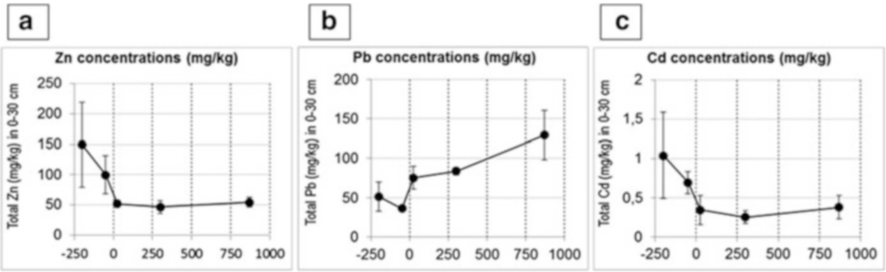


Fig. 4.10 Total concentrations of (**a**) Zn, (**b**) Pb, and (**c**) Cd in the 0–30 cm layer (average plough depth of Ap horizons of arable soils) of soils under cultivation, permanent grassland and forest stand in an area located approximately 3–4 km from a former zinc smelter in northern France. Average values calculated for three transects with five sampling sites located in agricultural land 200, 50 m before the forest edge (0 m), and 25, 300 and 850 m inside the forest (Modified and completed after van Oort et al. 2001)

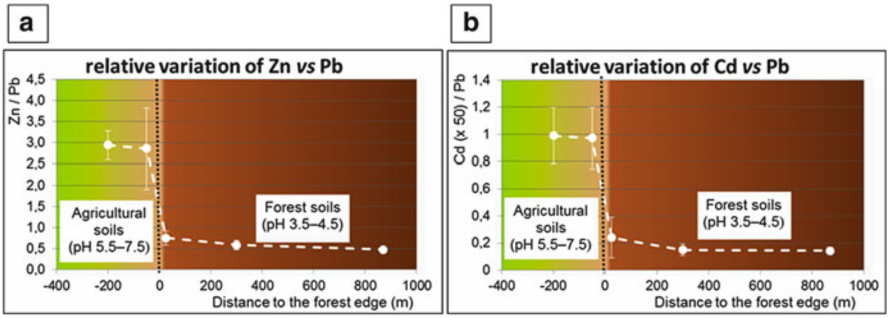


Fig. 4.11 Total metal concentration ratios between more mobile (Zn, Cd) and a little or non-mobile trace element (Pb) in agricultural and adjacent forest soils, affected by past industrial metal fallout. (**a**) Zn/Pb ratios, (**b**) Cd/Pb ratios (Cd concentrations × 50). Average metal concentrations measured on bulk samples from the 0–30 cm layer of soils under arable land, permanent grassland and forest land, located between 3 and 4 km from the former zinc smelter complex (Modified and completed after van Oort et al. 2001, 2009; Fernandez et al. 2007)

When presenting these same data as the concentration ratio of mobile (Zn, Cd) and little or non-mobile (Pb) metals, better insight is obtained in the dynamics of these elements in soils under different land use (Fig. 4.11). Such expression of total trace metal concentrations in surface horizons by using metal concentration ratios clearly reveals the behaviour of mobile metals (Zn, Cd) in acid conditions of the forest soils, where the major part of Zn and Cd contaminants has been leached to depth during the twentieth century.

In the view of such an important migration of mobile trace metals in soils, particularly in forest soils with low pH, a well-adapted approach for studying the fate of metal contamination under different land use consist in comparing the metal stocks over the depth of the profiles. Reasoning in metal stocks, instead of metal concentrations gives better insight in the incorporation and redistributions of metal elements as well as in possible outputs of trace metals to the water table. This approach is illustrated in Table 4.6 for the three soils presented in Fig. 4.9, under forest, arable land and permanent grassland.

These data were calculated by multiplying the average trace metal concentrations in the horizon ([M], expressed as g kg^{-1}), the mean thickness of each horizon (E, m), and the bulk density (Da, $kg.m^{-3}$) of each horizon. When cumulating the amounts of metals for 1 m soil depth, total metal stocks in the soil profiles are obtained, presented as g m^{-3} in Table 4.6. These data illustrates very well that in the two agricultural soils, total stocks cumulated over 1-m depth are very similar, both for mobile and non-mobile elements, indicating that, although differently incorporated in the soils under arable land use or permanent grassland, little or no metal have leached out of these soils, as confirmed by validating and prospective modelling work (Mallmann et al. 2012; Rheinheimer et al. 2013).

In the forest soil, the total stock of Pb is in the same order with respect to those observed in the agricultural soils, even larger, illustrating the capacity of tree canopies to intercept more atmospheric metal-bearing dust than cultivated plants. By contrast, the Zn and Cd stocks in forest soils are much smaller than under agriculture, and that demonstrates the important leaching of mobile trace elements in the podzolic conditions. In the permanent grassland soil, Pb stocks at 50–60-cm depth are larger than at comparable depth in the arable land soil, and due to biomechanical incorporation by earthworms (Fernandez et al. 2010). When considering the fairly constant average Zn/Pb ratio of about 3.5–4 found in surface horizon under cultivation, and after subtracting the estimated local pedogeochemical concentrations for Zn, Pb, and Cd (Fernandez et al. 2007; van Oort et al. 2009), the total nowadays observed Zn stock (30 g m^{-3}) only represents 1/5th of what would have been the global Zn deposition stock ($\approx$ 130–150 g m^{-3}). Consequently, about 80 % of airborne Zn has leached out of the first metre of the forest soil profile. For Cd, the findings are similar.

These findings have great implications for some general ideas about the metal mobility and bio availability often considered to increase in acid soil conditions. But in the case of past atmospheric metal contaminations of acid forest systems, where with time a large proportion of more mobile elements such as Zn and Cd have been leached out of the soil profile, their remaining pools may be nowadays more strongly retained by reactive soil constituents. This fact is illustrated in Table 4.7 by data from EDTA extractions of Zn, Pb and Cd in acid forest soils and adjacent agricultural soils. The proportions of $\underline{\text{non}}$-extractable Zn and Cd in the 0–30 layer acid forest soils are noticeably larger (1.5–2 times) than the $\underline{\text{non}}$-extractable pools in agricultural soils, whereas for Pb these pools are similar. Such a hypothesis of very large non-EDTA extractable pools of Zn and Cd in acid soil conditions was recently put forward in work of Camizulli et al. (2013) in the case of large forested areas in the Morvan (France), where soils have been contaminated by historical mining activities.

Table 4.7 Proportions of Zn, Pb, and Cd, **non-extractable** by EDTA in forest soils and in soils under agricultural land use in northern France, affected by past metallurgical atmospheric fallout

		Zn	Pb	Cd
Soil reference	pH (water)	mg/kg		
Forest soils				
MN-F 19	4.5	75	34	82
MN-F 21	4.2	86	56	68
MN-F 26	4.3	84	21	75
MN-F 29	4.2	71	28	63
	Mean	79	35	72
Agricultural soils				
MN-CA 1	6	40	10	15
MN-CA 10	6	58	30	48
MN-PP 2	5.5	54	50	31
	Mean	51	30	31

Determinations carried out on bulk samples collected in the 0–30-cm surface layers

5.2 Evidence for Migration of Metal Trace Elements in Forest Soils: The Case of Pb

Trace metals occurring in the soil solution predominantly in a free or exchangeable form and pH susceptible, such as Zn and Cd, will easily migrate in acid soil conditions (e.g. McBride 1989; Adriano 2001, cf. Table 4.6)**.** For less mobile elements, such as Cu and Pb, with strong affinity for organic complexes, findings diverge. For instance, Wang et al. (1995) conclude for a full retention of atmospheric lead in podzols of the northern Hardwood forested ecosystems (New Hampshire, USA). Andersen et al. (2002) showed that after afforestation, no increase of higher solubility of Pb was observed despite soil acidification. In a review paper, Steinnes and Friedland (2006), mention a general consensus for "*a slow movement of Pb out of the mineral soil, but that the loss of any significant lead from the mineral soil will take a century or more*". They underlined the need for field monitoring studies. Moreover, Steinnes et al. (2005) note that vertical movement of pollution-derived Pb in forest soil from Norway greatly differed between the study-sites and that in the south of Norway, about 70 % of Pb in the Bh horizon derived from atmospheric deposition. Such a vertical distribution of low-mobile metals is often ascribed to colloidal transport (Kretzschmar et al. 1999; Citeau et al. 2003, 2006), notably by organic complexes or iron oxi-hydroxide compounds. Citeau and collaborators performed field monitoring between 2000 and 2002 on metal fluxes in gravitational water collected at the base of genetic horizons of soils under different land use. They demonstrated that for the acid forest soil, Zn occurred mainly in a free, dissolved form, whereas Pb was predominantly associated with organic substances, either as labile or stable complexes (Fig. 4.12).

For some trace elements, in particular for Pb, the use of isotopic ratios offers the possibility to distinguish the lead pools of anthropogenic (or exogenous) and natural (or endogenous) origin in soils (e.g. Bacon et al. 1992; Erel et al. 1997; Bacon and

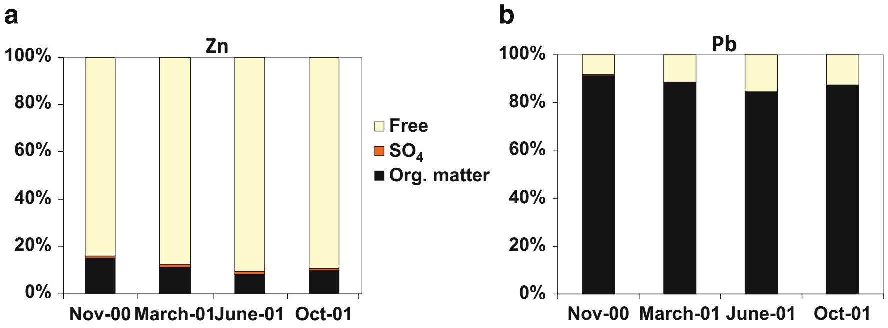


Fig. 4.12 Theoretical speciation of Zn (**a**) and Pb (**b**), calculated by Soilchem (Sposito and Coves 1988) on gravitational soil water collected at the base of the O horizon of the Haplic Podzol of Fig. 4.9 (From Citeau et al. 2009), during different seasons between November 2000 and October 2001. Metals in the soil solution occur either as free, dissolved elements (frequently the case for Zn), in a complexed form with inorganic ligands (sulfate) or associated with organic compounds (frequently the case for Pb)

Hewitt 2005); and to demonstrate the incorporation and distribution of anthropogenic lead at depth in soils (Semlali et al. 2001a, 2004). To illustrate the usefulness of this isotopic tool for unraveling the incorporation dynamics of a low mobile element such as Pb in soils, we compare the distributions of exogenous and endogenous Pb in two forest soils: an andosol developed on volcanic basaltic scoria, with neoformation of short-range order aluminosilicates (allophane), highly reactive toward heavy metals, and therefore acting as an trace metal-accumulating medium, and a podzol developed in a quartzose sandy sediment which is a highly lixiviating medium. For the first site, lead accumulation in the surface horizon was ascribed to former mining activities, located several tens of kilometres away, but large Pb concentrations in rains with heavy storms occurring annually, have been reported nowadays (Négrel and Roy 1998). In sandy podzols of the “Landes de Gascogne” and receiving dominantly western winds from the Atlantic Ocean, noticeable lead concentrations in the surface horizons have been mentioned by Saur and Juste (1994) and ascribed to long-range aerosol transport. Some selected characteristic pedo- and geochemical data of the andosol and podzol are presented in Table 4.8.

Both soils show substantial Pb concentrations in the organic litter horizons, reaching up to 62.7 mg kg^{-1} in the Oa horizon of the Andosol and 25.5 mg kg^{-1} in the O layer of the podzol. In the andosol, the Pb concentrations decrease progressively from the A1 horizon to the C horizon, whereas in the podzol a noticeable Pb increase occurs in the illuvial Bh and Bs horizons, almost twofold the Pb concentrations of the overlying A1 and E horizons.

When analyzing lead isotopic ratios for the soil horizons of the andosol forest site (Fig. 4.13), the variation of ^{206}Pb/^{207}Pb *vs* ^{206}Pb/^{204}Pb is linear and progressive from the surface to depth, with highest ratios in the C and R horizons, and lowest in the uppermost Oi horizon (Fig. 4.13a). In the podzol (Fig. 4.13d), the lowest signal

Table 4.8 Selected pedogeochemical data of a young andosol in the Massif Central and a podzol in the "Landes de Gascogne", France

Haplic andosol under *Pinus sylvestris*, Puy de la Vache (St Gènes – Champanelle, France); altitude: 1,000 m, ann. Precip. 700–1,000 mm					Haplic podzol under *Pinus pinaster*, Les Landes (Marquèze, France); altitude: 75 m, ann. Precip. 1,100 mm				
Hor	Depth	pH	Org. C	Pb	Hor	Depth	pH	Org. C	Pb
	cm		g/kg	mg/kg		cm		g/kg	mg/kg
Oi	7.5–2.5	–	521	19.1					
Oa	2.5–0	–	278	62.7	O	7.5–0	–	394	25.5
A1	0–14	5.5	68	19.6	A1	0–45	3.8	33	4.7
A2	14–40	5.9	59	12.5	E	45–100	4.2	2.7	4.0
Bw	40–55	6.3	32	6.6	Bh	100–155	4.1	28	9.2
C	55–60	6.7	7.5	4.1	Bs	155–210	4.3	8	8.5
R	> 60	8.5	0.8	4.3	C	> 210	4.5	1.2	5.7

Data from Semlali et al. (2001a)

is also found in the O horizon, but within organo-mineral soil horizons, the $^{206}Pb/^{207}Pb$ ratio is highest in the A horizon, followed by the E, C, Bs, and Bh horizon. Such a sequence suggests that in the podzol, exogenous Pb migrated to depth and is preferentially accumulated in illuvial horizons.

Relations between metal distributions and specific pedogenetic processes can be interpreted from their distribution patterns among specific particle-size fractions. Physical fractionation in water represents an original approach for isolating soil fractions in size classes that may express differences in mineralogical composition, nature of organic matter (Christensen 1992) and reactivity toward heavy metals (Ducaroir and Lamy 1995; Labanowski et al. 2007; Lang Burak et al. 2013). When applying the isotopic ratio chemistry on such soil fractions of the andosol, the $^{206}Pb/^{207}Pb$ ratio increases in the A horizon from the finest <2 µm fraction to the coarse >2 mm fractions (Fig. 4.13b), similar to the organic carbon distributions (Semlali et al. 2001a). In the Bw horizon, the lowest $^{206}Pb/^{207}Pb$ ratio is for the 200–2000-µm fraction (Fig. 4.13c), ascribed to preferential retention of Pb on thin neoformed mineral coatings of smectite and amorphous allophanic compounds, a first stage of mineral weathering at depth in the andosol (Jongmans et al. 1998).

In the Bh horizon of the podzol, the lowest $^{206}Pb/^{207}Pb$ ratio among the size fractions is obtained for the 100–200-µm fraction (Fig. 4.13e). This fraction is quasi-exclusively composed of quartz grains with amorphous humus-illuviation coatings (Fig. 4.14a). These results indicate that Pb in such humus coatings is mainly of an exogenous origin (Semlali et al. 2001a) and suggest either the interception of dissolved Pb^{2+} by the organic compounds of the humus coating or the illuviation and precipitation of colloidal 'Pb-organic substances' in the Bh horizon.

Additional evidence for the migration of Pb in podzols and its significant accumulation in the humus-illuviation coatings on quartz grains can be visualized by using synchrotron-facilitated micro X-ray fluorescence (µ-SXRF). In Fig. 4.14, a small 50 × 325 µm surface of a soil thin section, including thin humus coatings

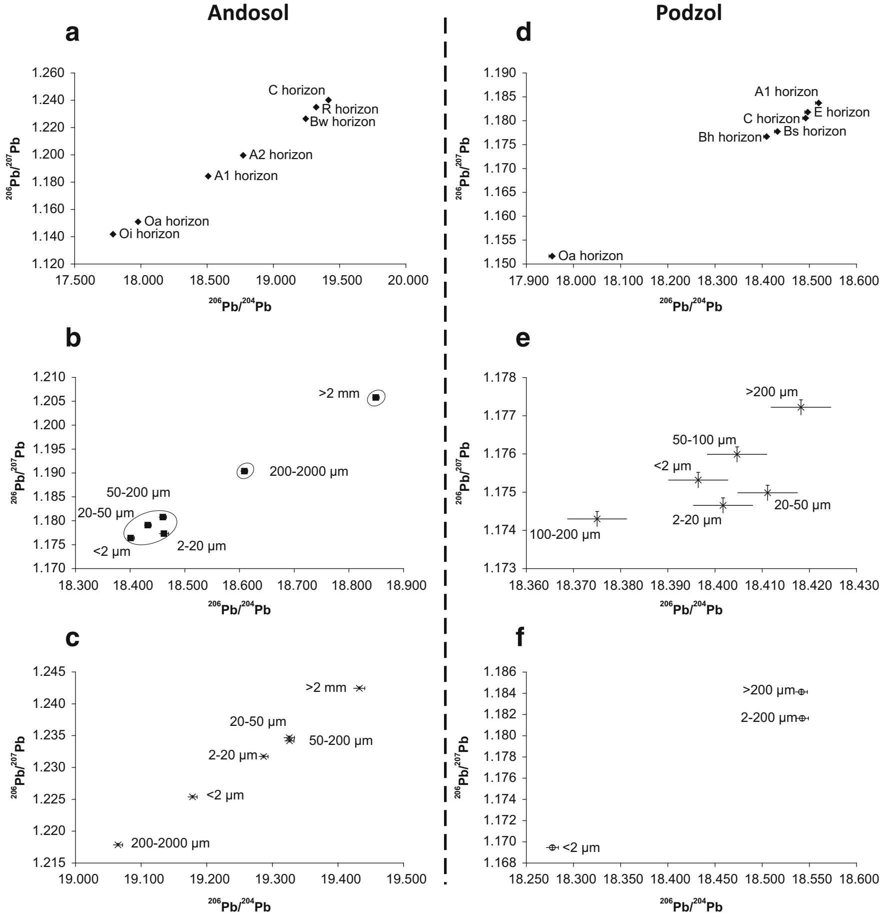


Fig. 4.13 Isotopic lead composition in soil horizons and in particle-size fractions in selected soil horizons, (**a**) in all andosol horizons, (**b**) in size fractions of the andosol A horizon, (**c**) in size fractions of the andosol Bw horizon, (**d**) in all podzol horizons, (**e**) in size fractions of the podzol Bh horizon, (**f**) in size fractions of the podzol C horizon (From Semlali 2000)

covering quartz grains (Fig. 4.14a) was analyzed by µ-SXRF using a beam spot of 25 × 25 µm and a dwell time of 1,000 s (modified after Semlali 2000). Chemical distribution maps of Si, Mn, Fe and Pb are thus obtained (Fig. 4.14b). These maps clearly demonstrate a simultaneous occurrence of lead, iron and manganese in the humus coatings, corroborated by strong correlation coefficients (Fig. 4.14c) and their absence in the quartz grains (negative correlation of trace metal with Si).

The 100–200 µm fraction in this illuvial Bh horizon contains only 6.8 g kg^{-1} of organic carbon and has a Pb concentration of 12.9 mg kg^{-1} (Semlali et al. 2001a), whereas in the bulk Bh horizon, the total Pb concentration reached 9.2 mg kg^{-1} (Table 4.8). When attributing the Pb concentration in this 100–200-µm fraction to

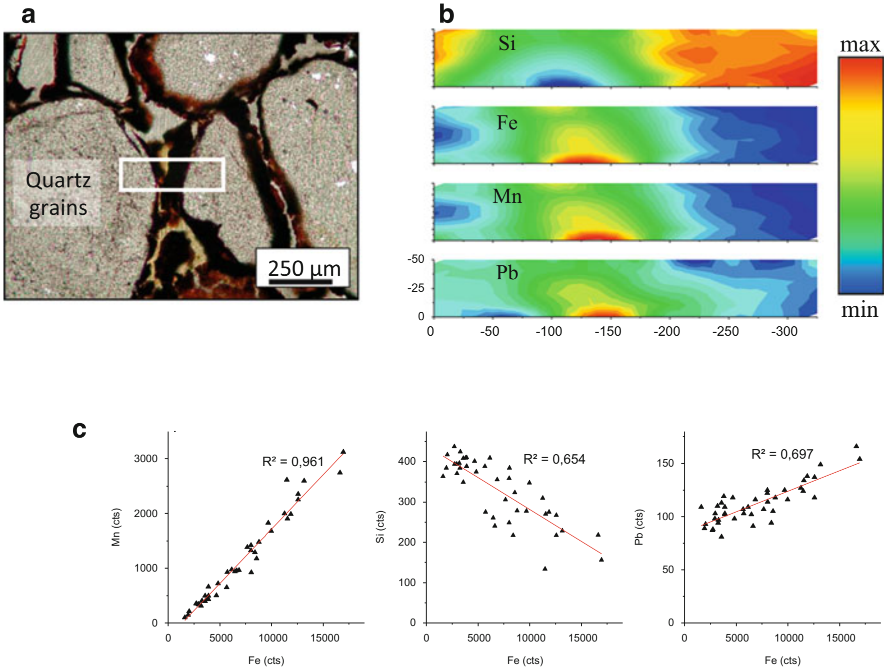


Fig. 4.14 Elemental distribution maps obtained by synchrotron facilitated micro X-ray fluorescence on a soil thin section of the podzol Bh horizon. (**a**) Optical microscopy photograph of the studied area showing *dark brown* humus coatings of about 50–100-µm thickness; (**b**) elemental distribution maps of Si, Fe, Mn and Pb of a 50 × 325 µm area (beam spot of 25 × 25 µm; number of analyzed points: 42; dwell time 1,000 s). The maps show that Fe, Mn, Pb are located in the humus coatings; (**c**) selected elemental correlations for Mn/Fe with $R^2 = 0.961$, for Si/Fe with $R^2 = 0.65$ and for Pb/Fe with $R^2 = 0.697$ ($n = 42$, $p < 0.001$) (Modified and completed after Semlali 2000)

its organic matter content, by considering the OM as the exclusive metal-intercepting soil phase, the Pb concentration of the organic carbon of the humus coatings would reach almost 200 mg Pb kg^{-1} Org C, much higher than when attributing the global horizon Pb concentration to its global organic carbon content, only 30 mg Pb kg^{-1} Org C. Moreover, in the C horizon, at more than 2-m depth, the $^{206}Pb/^{207}Pb$ ratio in the <2-µm fraction is much lower than in coarser fractions (Fig. 4.13f), indicating that exogenous lead has been transferred to great depth.

From these isotopic ratio data, a distinction can be made, at the scale of the total soil profile as well as at the scale of soil fractions, between natural and anthropogenic lead, by using scandium (Sc) as a conservative endogenous element to estimate the endogenous lead pools in the soil horizons (Semlali et al. 2001a). Scandium is known to have no significant anthropogenic source (Shotyk et al. 2001) and is low or non-mobile in soils. In Fig. 4.15, the distribution of endo- and exogenous lead is presented for the two forest soils. In the andosol (Fig. 4.15a), exogenous lead widely dominates in the surface horizons and decreases with depth

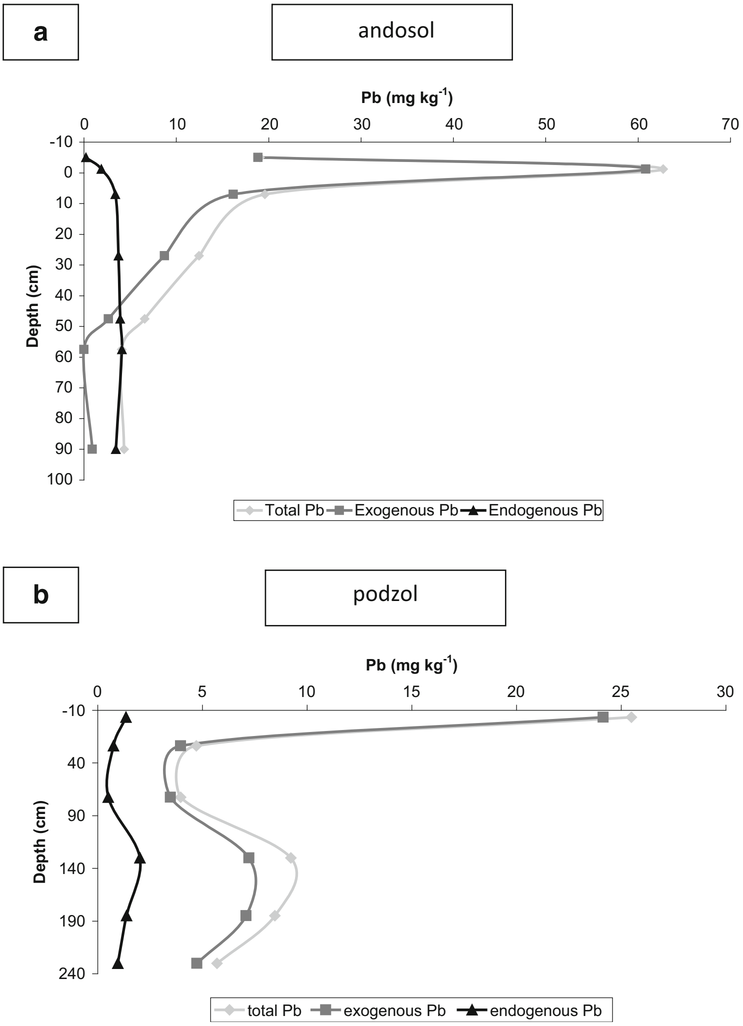


Fig. 4.15 Distributions at the scale of the soil profile of total, endogenous and exogenous lead concentrations (**a**) in an andosol of the Massif Central, (**b**) in a podzol of the Landes de Gascogne (From Semlali 2000)

suggesting that exogenous lead is strongly associated with organic matter and amorphous secondary soil constituent such as allophane. Considering that little exogenous Pb is currently present in gravitational water and in throughfall, in comparison to other elements such as Zn and Cu (Semlali et al. 2001b), the incorporation of exogenous lead as deep as in the Bw horizon probably illustrates its migration in the past, during intensive mining activities. Endogenous Pb is still predominantly located in unweathered primary minerals, such as feldspar. The distribution of exogenous lead preferentially occurring in the finest fractions, its general decrease with depth, as well as an endogenous Pb pool fully representing the total Pb content in C and R horizons (Fig. 4.15a) illustrate the highly metal-sorbing properties of the soil constituents, and are in full agreement with specific character of andosol pedogenesis.

In the podzol, the distributions of endo- and exogenous lead are strongly different (Fig. 4.15b). Exogenous lead is the dominant metal pool in the O, A, and E horizons. In the A horizon, the coarse sand fraction is *virtually* free of exogenous lead, indicating that the organic matter, sole lead bearing soil phase, and mineral compounds occur as juxtaposed constituents. In deeper Bh and Bs horizons, the exogenous Pb pool still represents an important proportion of the total lead content and is dominantly present in humus and iron coatings, respectively. In the C horizon, the total Pb concentration of 5.7 mg kg^{-1} (Table 4.8), mainly located in the < 2-μm fraction, is composed predominantly of exogenous Pb (more than 80 %). Considering the quasi exclusive coarse sand texture (99 %, less than 1 % of clay) in the C horizon, these findings strongly suggest that in this well drained, acid forest soil, exogenous lead has leached out of the soil profile. As seen for the andosol, the Pb distribution patterns at a micro and macro-scale in the podzol are concordant with its typical soil-forming processes.

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Chapter 5
Potentially Harmful Elements in Abandoned Mine Waste

Mohammad Wahsha and Mamoon M.D. Al-Rshaidat

Abstract Soils are essential components of the environment therefore; soil quality must be controlled and preserved. However, the increased concentration and distribution of potentially toxic elements (PTE) in soils by anthropogenic activities of industrial and mining resources are causing worldwide concern. The anomalous concentration of PTE may affect the soil's environment, reducing it's quality and therefore pollution which can be followed by an eventual accumulation through the food chain. This implies a serious risk for crops, livestock and human health. There is an increasing need to apply innovative technologies of prevention, monitoring, risk assessment and remediation, more sustainable and economical, in the context of mining site soils.

In this chapter, the impact of PHEs from abandoned mine sites on the environment is discussed through case studies from Europe (NE Italy). The environmental effects recognized for these specific sites could be valid other mining sites worldwide. Some case studies highlight the toxicity assessment of contaminated soils from abandoned mining areas; others focus on the metal uptake and translocation ability in plants that can produce adverse effects on plant morphology and health and biological soil quality evaluation of abandoned mining site.

Keywords Potentially toxic elements • Mine waste • Spolic Technosols • Accumulator plants • Phytoremediation • Soil quality

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1 Introduction

Soil is a key resource for the life of organisms in terrestrial environments; it is the basis of the ecosystem and of our farming system of food production (Chesworth 2008). It is imperative to acknowledge that current and future exploitation of mineral resources will produce even more wastes and impose more threats on Earth. Pollution of soil with Potentially Harmful Elements (PHEs) is a major concern worldwide since it can cause the transfer of contaminants to other environmental compartments, such as surface water, groundwater and biota, with a consequent spread of pollution over a wider area than the initial one (Lal 2006). PHEs in the soil can be partly absorbed by the plants that derive nutrients from that soil, with the risk of accumulation and toxic effects along the food chain and also to humans (Markert et al. 2003).

Mining is only one of the pathways by which metals enter the environment. Mining itself affects relatively small areas, and this could not pose severe environmental problems. The environmental impact arises when ores are mined, milled and smelted, and a certain amount of metals is released in the surrounding areas and to waterways. Depending on the nature of the waste rock and tailings deposits, a wide dispersion of the metals both in solution and in particulate form is possible. A consequence of the high content of toxic heavy metals, in combination with reduced soil thickness, leads to discontinuous vegetation coverage that is composed mainly of crust lichens, mosses, fescue and wild vegetation genetically tolerant to high metal concentrations (Wahsha et al. 2012b).

Plants may be classified into three groups on the basis of their ability to accumulate metals in their aerial parts (Baker and Brooks 1989) Excluders are those plants whose metal concentrations remain unaffected by metal contents in soils up to a critical level, when toxic symptoms appear; Indicator plants are those whose metal concentrations reflect those the related soil; Accumulator plants have the ability to take up and concentrate metals from soils, independently on levels of metal concentrations. Among the species that may tolerate high metal concentrations in their tissues, plants presenting exceptional accumulating ability are referred to as hyperaccumulators.

2 PHEs Contamination in Soil

Soils are presently contaminated with PHEs, which are originated from different sources in particular by heavy metals, which can negatively affect soil's chemical, physical and biological properties worldwide. In this context, heavy metals can be added to the soil through diverse natural or/and anthropogenic sources. The major natural sources of heavy metals in soils are: weathering (such as soil erosion and deposition of windblown dust and running water); volcanic eruptions and bushfire.

The major anthropogenic input of heavy metals to soils mainly occurs by: Atmospheric deposition, result from energy production, power generation emissions, metal mining, smelting of metalliferous ores and manufacturing, waste and wood burning; sewage sludge, municipal and organic wastes and co-products from agriculture and food industries; Land disposal of industrial waste; Fertilizer and pesticide (insecticides, herbicides, fungicides) and soil heavy metal pollution through chemical and biological warfare (Wahsha et al. 2012d; Alloway 1995).

The environment is rather strongly influenced by manmade activities through heavy mining, especially in areas where low-grade metal ores are being extracted, which produces higher quantities of soil wastes (e.g. Heavy metals).

Heavy metals found in soils are originated from different sources. In some places we can find natural forms of contamination, due to the presence of particular rock types, such as serpentinites (Ghaderian et al. 2007). In other places, anthropogenic metal accumulation is recorded (Zhang et al. 2009). Indeed, human activity is considered to be the major source of pollution by heavy metals in soils. Among the various causes of this type of contamination we can mention mining and processing of metals, which are linked to generate several environmental problems (e.g. acid mine drainage, impacts on the landscape, pollution of water, soil removal and pollution). The ever-increasing demand for metals lead to more mining and, therefore, to larger amounts of waste production. Accessing mined produces is always accompanied by excavation of range volumes of waste rocks, whose disposal is another important problem of mining. However, little attention has been paid to processing and disposal of mining waste, which have been generally dumped on the ground, to become a potential source of pollution (Lottermoser 2010; Lal 2006; Selim and Sparks 2001).

Dispersal pattern of mine spoils can be recognised by mining activity. The effect of these irregular anthropogenic deposits is the development of a new soil material that covers the original one. Immature Entisols (Lithic Spolic Xerorthents and Spolic Xerorthents,) are formed on mine spoils <100 year old. These soils are characterized by a thin solum (<30 cm), little organic matter accumulation (mean 14 g/kg organic carbon, range 1–33 g/kg), dark brown (10YR3/3) to reddish (5YR4/6) colour, coarse texture (sandy loam to loamy), and subalkaline pH (mean 7.4, range 6.9–7.8). Detailed descriptions of soil properties of a selected profile on mine waste are given in Table 5.1.

Soils developed on old mine dumps or in the proximal parts (<0.5 km) of the dumps, have a >50 cm thick solum, sandy loam to loam texture, blocky structure, slightly acidic pH (mean value 6.3, range 4.9–7.7), humus accumulation (up to 14 % organic matter in the A horizon), moderate to low cation exchange capacity (CEC) (mean 20 $\text{cmol}_c\ \text{kg}^{-1}$), with significant desaturation (base saturation <60 %). As a rule, they have distinct A-B-C horizonation and a well formed cambic horizon. Thus, they are Inceptisols *Spolic Haploxerepts* or *Spolic Dystroxerepts*, (Table 5.2). Frequently, a discontinuity occurs between the upper and the lower portions of the profile, which developed from the underlying bedrock. Data (not reported) indicate relevant differences and a remarkable polycyclic evolution, due to the superposition of mine spoil over the normal soil. Colour,

Table 5.1 Selected properties of the Spolic Technosols

	Particle size distribution %				Organic carbon	Cation exchange capacity (CEC)
Horizon	Silt	Clay	Sand	pH	g/kg	($\mathrm{cmol_c\ kg^{-1}}$)
A1	47	10	43	7.6	8	11.0
A2	46	9	45	7.4	4	9.0
B1	50	8	42	7.5	2	7.1
B2	48	9	43	7.7	–	9.0
2BC	57	8	35	7.8	–	17.7

texture, reaction, and CEC are the most prominent features that present important differences in soils. Soil horizons show dark brown (7.5YR3/2) to dark reddish brown (5YR 3/3) colour, well individualized structure, from crumby to fine blocky beds. Texture is coarse (sandy loam to loam) in surface horizons of mine spoils and loamy to clayey underneath. Values of pH around 6.3 at the surface indicate a soil reaction that is slightly acidic; this is slightly subalkaline (pH 7.4) and base-saturated at the bottom. Cation exchange capacity increases with depth, from 15 to 25 cmol (+)/kg (Bini 2010).

Shrubby vegetation with shallow trees (i.e. holm-oak, strawberry tree, heath, etc.) is the typical flora of these sites, where rock-rose is the dominant plant.

Far from the mine dumps (>0.5 km) the soil samples show little evidence of mine spoil in the profile. Sulphide minerals are found especially at the surface, as revealed by mineralogical and chemical investigation (Bini 2012). An abrupt textural change (Table 5.3) indicates a marked discontinuity between the upper and lower part of the soil profile. The upper part (A and E horizons) has dark brown (10YR2/2) to yellowish brown (7.5YR3/4) colours, loam to sandy loam texture, crumby structure, high organic carbon content (mean 21 g/kg), and subalkaline pH. The lower part (Bt horizon) presents reddish colours (5YR3/4–2.5YR3/4), a strong clay content increase (clay loam to clayey texture), organic carbon decreases; pH is subalkaline with traces of carbonate. Therefore, they are classified as Alfisols. Since there is evidence for mine waste in the profile, these soils should be classified as *Spolic Rhodoxeralfs or Spolic Haploxeralfs*. However, considering the net discontinuity already mentioned, these soils could be classified as *Spolic Xerorthent over Typic Rhodoxeralf* (or *Haploxeralf*) (Bini 2012).

3 Mine Soils Pollution

The availability of resources from mining sites is not an easy task, where some products are existing in almost in 100 % of the excavated sites, such as the production of sand, clay and gravel, while other products such as gold are barely reaching few parts per million of the raw material, therefore generating large volumes of wastes. Copper, zinc, and gold mining goes through several processes; such as grinding, washing, and sizes of the raw material of rocks, which generates

Table 5.2 Selected properties of the Spolic Dystroxerept

	Depth	Particle size distribution %				Organic carbon	Organic matter	CEC	Base saturation
Horizon	cm	Silt	Clay	Sand	pH	g/kg	g/kg	cmol(+)/kg	%
A1	0–47	34.7	15.3	50	6.4	27	46	25.5	62
A2	47–70	33.3	15.1	51.6	6.3	21	36	15.4	47
Bw	70–90	30.8	11.1	58.1	6.2	8	13	13.0	58

Table 5.3 Selected properties of the Spolic Haploxeralf

	Depth	Particle size distribution %				Carbonate	O. C.	Organic matter	CEC
Horizon	cm	Silt	Clay	Sand	pH	g/kg	g/kg	g/kg	cmol(+)/Kg
A1	0–3	23.9	9.5	66.6	7.6	0	23	40	29.5
A2	3–15	29.8	13.7	56.5	7.7	0	19	33	37
E	15–40	35.7	9.9	54.4	7.9	0	6	11	33
Bt_1	40–110	40.7	40.3	19	8.0	4.1	7	12	19
Bt_2	110–120	39.9	30	30.7	8.0	58	11	19	23

some byproducts such as dust and other fine-grained material, the later could be used as natural fertilizers. In general, forma mining is always producing volumes of waste material known as “gangue”. Of the processes with such large volumes of mining wastes, ranked from high waste to low are coal, non-ferrous ores, ferrous ones, and industrial minerals. The type and magnitude of the released contaminants from mining sites is controlled by many factors, such as the geology, topology and climate of the mined sites, and the techniques applied for mining and processing of the mined resources. Understanding all these factors should be deemed critically important for better control of waste discharge from mining areas. Improper operations of mining activities have been facing increasingly strong criticism by environmentalists (Lottermoser 2010).

Both physical and chemical processes work during rock alteration. Physical processes appear to be a leading role during the initial stages. Steep morphology areas, where most mining districts are located, are the most affected by these processes. Loose and coarse-grained material forms as a consequence of rock fragmentation. Rock fragments migration on instable slopes, erosion of fine particles by wind plus runoff, all these processes contribute to land modelling.

The rock transformations also occur by chemical processes such as oxidation potential (Eh >250 mV), acidification (pH <7), hydrolysis, metal leaching, precipitation of oxy-hydroxides and sulphates, argillogenesis. Wet and high temperature climatic conditions increase the role of chemical processes and stimulate mine waste reactivity. Thus, the physical and chemical processes of soils developed from mine soils lead to new soils with a different set of physical and chemical features.

The formation of a biologically active substrate may occur as the parent material is finely subdivided and weathered, and this permits the development of a pioneer vegetation (lichens, mosses). Litter accumulation (OL horizon) is the process that characterizes the early stage of soil formation. Subsequently, organic matter decomposition (OF horizon), humus formation (OH horizon), mineralisation (A horizon) constitute a first pedogenetic phase (Bini 2012, 2010). According to Jabiol et al. (2007), this phase may bring to the differentiation of several types of humus as a function of litter composition, microflora and microfauna activity, pH and climate conditions.

A second pedogenetic phase is determined by *in situ* mineral transformations (e.g. acid hydrolysis), oxyhydroxides and clay formation (stage of *cambic* horizon formation). In this phase, colour varies from very dark brown (10YR 3/3) to dark brown (7,5YR 3/3), reddish brown (2,5YR 3/2), dark yellowish brown (10YR 4/5), or blackish (5YR 2, 5/5), in relation to the nature of the bedrock, and/or to the amount of mine waste.

A third pedogenetic phase is consistent with solute leaching and particles migration towards bottom (stage of *argillic* horizon formation); precipitation of new minerals (e.g. carbonate, sulphate) is also likely to occur. However, this third phase is difficult to assess in mine waste materials. Since the time elapsed from mining operations in most cases is not sufficient for Bt formation, considering that the landscape morphology is generally undulated, with slopes ranging from 15 to 45 %, which makes erosion a dominant process. However, soils developed from waste dumps are generally shallow (20–100 cm), skeletal, coarse-textured (sandy loam to loamy sand), little developed, with limited horizonation (Bini 2007, 2012).

Mine waste production varies between countries, depending on intensity of mining activities in each country, and on methods of mining and processing (Table 5.4).

Earth’s crust is noticeably enriched with different metallic and mineral compounds accumulated over time due to various geological processes. Geological processes leads to the formation of different deposits according to the amount and type of mineral enrichment in each deposit. Mineral deposits formation and differentiation is an important aspect in understanding the environment. Deposits geology (included rock composition, geomorphology etc.) may influence the characteristics of soil chemistry, surface and ground water properties leading to the natural enrichment of soils, waters, and sediments with metals and metalloids (Lottermoser 2010).

Natural enrichment of metals and metalloids varies between sites, leading to the adaptation of the covering vegetation to specific soil contaminants. For example, *serpentine flora* is the type of vegetation highly adapted to lands with overlying soils highly enriched with iron, nickel, chromium and magnesium. Soils enriched with boron favor the growth of cereal and legume crops. Soils enriched in selenium have tolerant vegetation covering, although animals grazing on such plants will suffers acute toxicity.

Accordingly, elemental enrichment in ores and rocks could cause unfavorable effects on local and regional ecosystems due to the signature of such elemental

Table 5.4 Mining waste production compared to municipal waste in different countries of the world

Country	Mining waste (Mt)	Tailing waste (Mt)	Municipal waste (Mt)
European Union	4,700	1,200	218
United States	2,000	–	200
South Africa	1,100	–	421
Australia	1,750	–	1,300
China	700	300	–

Source: Lottermoser (2010)

enrichment to surrounding water bodies, soils and sediments. Such adverse effects could result from geological processes or artificially imposed due to the improper mining practices and mine wastes disposal and management (Lottermoser 2010).

4 Environmental Impacts of Abandoned Mines, Scientific Issues and Case Studies

The impact of PHEs from abandoned mine sites on the environment will be discussed through case studies from Europe (NE Italy). The environmental effects recognised for these specific sites could be valid other mining sites worldwide.

The area we are considering is an abandoned mine site in North-East Italy called “Imperina Valley”, at an altitude ranging between 543 and 990 m above sea level. The geological substrate consists of rocks of the metamorphic basement (Pre-Permian), in tectonic contact with dolomite rocks (Dolomia Principale, Upper Triassic).

The Imperina stream crosses the valley; even if no settlements can be found in this area, many buildings and tunnel outlets still witness the past mining activity. Part of the area (right side and a portion of the bottom) lies within the National Park of the Belluno Dolomites. The mined area, located along the tectonic contact between basement and dolomites, consists of a deposit of mixed sulfides, composed primarily of cupriferous pyrite, pyrite and chalcopyrite, with minor amounts of other metallic minerals (Frizzo and Ferrara 1994). Copper and sulphur were the main products extracted. Until the beginning of the twentieth century, copper was extracted and processed directly in situ through roasting, a method with a severe impact on the area due to acid rains formation and intensive wood cutting. Today, the vegetation cover is mainly constituted of mixed forests (*Abies alba* Mill., *Picea abies* (L.) H. Karst., 1881, *Fagus sylvatica* L. and *Ostrya carpinifolia* Scop.), with clearances where herbaceous and shrubby vegetation prevails over the arboreal one (Dissegna et al. 1997).

The first certain historical records indicate that mining in the Valle Imperina dates back to the first years of the fourteenth century, thanks to research funded by the Republic of Venice into the mining of copper. Very probably, the extraction of minerals had already commenced in pre-Roman times, considering the particular condition and position of the rocks and the proximity of the Agordo valley; this theory is also backed up by the large amount of items made from bronze and copper found in archaeological excavations in the whole of the Belluno valley.

A notable increase in the production of copper derives from the passage of the property rights of the mines from private hands to the Republic of Venice; in fact, initially the mine was subdivided in tunnels and "mints" owned by private individuals with obvious management problems and lack of efficiency of the mining. This passage started gradually at the end of 1,600, but it was only in 1,835 that these mines formally become public property, in the hands of the Austro-Hungarian Empire.

During the first years of the last century, the whole process was electrified, and in 1925 the new standard-gauge electric railway line allowed for the loading of the materials which had been extracted from the mine and taken to the situation by cableway.

After the First World War, production stabilised at around 50,000 tonnes a year up to the period 1940–1944. Following this period, after a first attempt to modernise the mine in the early 1950s, the condition of the mineral deposit and its exhaustion led initially to staff reductions and, finally, to the complete closure of the mine on 8 September 1962 (Wahsha et al. 2011).

4.1 Case Study 1

4.1.1 PHEs Contamination in Soils and Plants of an Abandoned Mine

Over the past decades, human activities such as metal mining and milling operations have been recognized as one of the most important sources of contamination in the environment, along with mine and mill waste water (Jung 2001; Navarro et al. 2008). Heavy metal contamination has been a serious problem in the vicinity of abandoned mine sites due to the discharge and dispersion of mine-waste materials into the ecosystem (Jung and Thornton 1996). These heavy metals have a potential to contaminate soil and water (Haque et al. 2008; Lim et al. 2008). Extraction of metals from sulphide minerals usually results in large amounts of waste materials that often contain elevated concentrations of potentially harmful metals such as Cu, Zn, Cd, and Pb (Jian-Min et al. 2007; Lee et al. 2001). The degree of heavy metal contamination around mines varies depending upon geochemical characteristics of elements and degree of mineralization of the tailing (Navarro et al. 2008). Yun-Guo et al. (2006) reported that abandoned mining sites represent significant sources of metal pollutants in water and soils and a threat to the ecosystem. These metals can be transported, dispersed and accumulated in plants and then passed through the food chain to human beings as the final consumer.

The restoration of metal-contaminated sites is one of the most important environmental issues. Soil pollution by chemicals poses serious hazards to surface and ground waters, plants and humans, and presents relevant social, sanitary and economic costs (only in the U.S. up to 250$ m^{-3} soil; Adriano et al. 1995; Bini 2010). Metal accumulation in soil diminishes soil fertility, microbial activity and plant growth (Lehoczky et al. 1996). Moreover, trace elements are very persistent, can interact with plant roots by adsorption or release from the soil particles, and therefore increase the risk of long-term soil pollution and of toxic effects on organisms (Rosselli et al. 2006).

The assessment of soil contamination by metals has been extensively carried out through plant analysis (Blaylock et al. 2003; Brooks 1998; Ernst 1996; Wenzel et al. 1993); both wild and cultivated plant species have been frequently used as (passive accumulative) bioindicators for large scale and local soil contamination (Baker 1981; Baker and Brooks 1989; Bargagli 1993; Zupan et al. 1995; Zupan et al. 2003).

In the last decades, attention has been deserved to plants as tools to clean up metal-contaminated soils by the low cost and environmental friendly technique of phytoremediation (Adriano et al. 1995; Baker et al. 2000). This technology is focused on the ability of plants to accumulate high heavy metal concentrations (up to 100 times the normal concentration) in their aerial parts (i.e. they are hyperaccumulator plants as defined by Baker 1981). The plant ability to uptake metals was firstly applied in phytomining projects (Brooks and Robinson 1998; Ernst 1993; Helios-Rybicka 1996; Mc Grath 1998; Vergnano Gambi 1992), and only successively, when environmental contamination became a global concern, it was recognized as an useful tool for remediation projects (Adriano et al. 1995; Bini 2010, 2005; Bini et al. 2000b; Mc Grath 1998; Salt et al. 1995). Indeed, tolerant or accumulator populations of higher plants may colonize naturally or even anthropogenic metal-enriched areas, accompanying the disappearance of sensitive plants. Therefore, they may be utilized in restoration of such areas. The choice of plants is a crucial aspect for the remediation techniques. Up to now, more than 400 plants that accumulate metals are reported, Brassicaceae being the family with the largest number of accumulator species (Bini 2010; Marchiol et al. 2004; Mc Grath 1998).

Heavy metal accumulation is known to produce significant physiological and biochemical responses in vascular plants (Mangabeira et al. 2001). As stated by Preeti and Tripathi (2011), there is a direct relationship between chemical characteristics of soil, heavy metals concentration and morphological and biochemical responses of plants. Yet, metabolic and physiological responses of plants to heavy metal concentration can be viewed as potentially adaptive changes of the plants during stress.

Plants growing on abandoned mine sites and naturally metal-enriched soils (e.g. serpentine soils) are of particular interest in this perspective, since they are genetically tolerant to high metal concentrations, as reported by several authors (Bini 2005; Giuliani et al. 2008; Maleci et al. 1999; Brooks 1998; Pandolfini et al. 1997; Vergnano Gambi 1992), who studied endemic serpentine flora (*Alyssum bertoloni*, *A. murale*, *Silene paradoxa*, *Stachys serpentini*, *Thymus ophioliticus*) at various sites in the world. All these authors agree that morphological, physiological and phytochemical characters of serpentine plants are strongly dependent on the substrate composition (what Jenny, in 1989, called "the serpentine syndrome"), and that they are likely metal accumulator or tolerant ecotypes.

Understanding the mechanisms of metal bioaccumulation by plants species and of metal bioreduction by microorganisms is a clue to the efficiency of phytoremediation techniques. The localization and the chemical form of metals in cells are key information for this purpose (Kidd et al. 2009; Sarret et al. 2001). After their assimilation by plants, heavy metals could interfere with metabolic processes and are potentially toxic (Lopareva-Pohu et al. 2011); phytotoxicity results in chlorosis, weak plant growth, yield depression, and may be accompanied by disorders in plant metabolism such as reduction of the meristematic zone (Maleci et al. 2001), plasmolysis and reduced chlorophyll and carotenoids production (Corradi et al. 1993). Mangabeira et al. (2001) studied the ultrastructure of different organs of tomato plants (root, stem, leaf) which showed visible symptoms of Cr toxicity, and argued that CrVI induces changes in the ultrastructure of these organs. Similar findings were reported by Vasquez et al. (1991) for Cd in vacuoles and nuclei of bean roots. Since both these metals are known to be inessential to plant nutrition, it is suggested that they are likely confined in roots by a barrier-effect as defense strategy during stress. Conversely, essential metals such as Zn and Cu are easily conveyed to the aerial parts, as reported by Fontana et al. (2010).

Among wild plants, the common dandelion (*Taraxacum officinale* Web) has received attention (Bini et al. 2000a; Królak 2003; Zupan et al. 2003; Simon et al. 1996) as bioindicator plant, and has been also suggested in remediation projects (Turuga et al. 2008), given its ability to uptake and store heavy metals in the aerial tissues. *T. officinale* is a very common species, widely diffused in Central and Southern Europe, easy to identify and greatly adaptable to every substrate (Keane et al. 2001; Malawska and Wilkomirski 2001). Moreover, this species is commonly collected to be used in cooking as fresh salad or boiled vegetable, and is used also in ethnobotany and traditional pharmacopoeia (Rosselli et al. 2006). Therefore, when grown on heavily contaminated soils, it may be potentially harmful if introduced in dietary food, as it occurs in many countries.

Previous studies of our research group (Bini et al. 2000a; Fontana et al. 2010) investigated the heavy metal concentration of soils developed from mine waste material, and the wild plants (*Plantago major, Silene dioica, Stachys alopecuros, Stellaria nemorum, Taraxacum officinale, Vaccinium myrtillus, Gymnocarpium dryopteris, Gymnocarpium robertianum, Salix caprea, Salix eleagnos, Salix purpurea*) growing on those contaminated soils, in order to determine the extent of heavy metal dispersion, and the uptake by both known and unreported metal-tolerant plant species.

In the last few years many studies have focused on the potential use of trees as a suitable vegetation cover for phytoremediation (French et al. 2006; Jensen et al. 2009). A very suitable tree for use in phytoremediation is willow (Landberg and Greger 2002). Pulford and Watson (2003) detailed the phytoremediation potential of willow in heavy metal contaminated areas. Willows have not been included in the group of hyperaccumulators of heavy metals, but on the other hand they provide potential bioindicator of pollution (Mleczek et al. 2009). However,

Table 5.5 Average concentration of PHEs in soils and plants of interest expressed as mg kg^{-1}

	Cd	Cr	Cu	Pb	Zn	Fe	
PHEs in selected soils	2.41	65.16	1,378	4,811	1,051	256,308	
Italian average	0.53	100	51	21	89	–	
International average	0.30	200	20	10	50	–	
Excessive values	5	100	100	100	250	–	
Residential limits	–	150	120	100	150	1,000	
S. purpurea	Root	5.75	2.98	23	11.3	96	250
	Leaves	2.85	3.48	28	26	231	475
S. eleagnos	Root	3.16	4	61	46	248	394
	Leaves	3.4	3.8	31	36	495	523
S. caprea	Root	4.15	3	40	519	180	621
	Leaves	1.75	2.4	33	152	300	901
T. officinale	Root	0.51	1.2	57.5	102	67	213
	Leaves	0.86	3.5	65	134	133	662

metal concentrations in willows depend on species, growth performance, root density, distribution within the soil profile and sampling period (Chehregani et al. 2009). Moreover, willow has been recently recognized as a good accumulator of heavy metals (Meers et al. 2007).

Our aim was to assess total concentration of six potentially toxic metals (Cd, Cr, Cu, Pb, Zn and Fe) in the soil and plant samples of *T. officinale* and three dominant willow species (*Salix purpurea* L., *Salix caprea* L. and *Salix eleagnos* Scop.) collected from abandoned mixed sulphide mine dumps of Imperina Valley, in order to propose these plants for phytoremediation plans (Table 5.5).

Comparing the values found with those of control levels of Angelone and Bini (1992), the total concentrations of most of the investigated metals (Cd, Cu, Pb, Zn and Fe) in the soil samples were significantly higher ($p < 0.05$), and almost above the toxicity threshold according to the Italian legislation (D.L. 152/2006).

The area is almost not contaminated by Cr, whereas there are a contamination by Zn, Cu, Pb and Fe that show high concentrations, particularly at sites affected by mining activities and ore processing.

There is a linear positive correlation between Pb, Cu, Zn and Fe (Cu/Pb 0.867; Pb/Zn 0.616; Cu/Zn 0.688; Cu/Fe 0.933). This is consistent with their calcophile geochemical behaviour, since these metals tend to form compounds with sulfur, as chalcopyrite ($CuFeS2$), sphalerite (ZnS) and galena (PbS), commonly found in the Imperina Valley ore deposits (Frizzo and Ferrara 1994). Cr is negatively correlated with Cu (−0.847), Pb (−0.816), Zn (−0.604) and Fe (−.0754). Conversely, Fe indicates a significant positive correlation with Pb (Fe/Pb 0.734). Furthermore, Fe it is not significantly correlated with Cd. Therefore, it is likely that most of iron in soils of the study area derives from the alteration of pyrite and chalcopyrite mineralization. For all elements, it might be that the same type of elements combination occurring in the mineralization of Imperina Valley is found in soil. This means that no element of the mineralization has been removed in a special way, since the factors of pedogenesis have acted for a some decades in the areas affected by ore processing, and thus the soil chemical characteristics still seem to be close to those of the parent material, as it was found by Bini (2005) in mine soils of Tuscany.

It is noteworthy to point out, however, that willows ability to accumulate heavy metals in different parts is independent of the species; rather, it depends on local factors as soil and pedoclimate (particularly temperature, aeration and water content) and on plant physiology and aging (Wahsha et al. 2012b). Moreover, a counteracting behavior of essential and toxic heavy metals is likely to occur as a barrier effect of the roots (Fontana et al. 2011).

The calculation of translocation factors (TF) highlights that willows translocate and accumulate metals in the aerial parts, in particular Cu (*S. purpurea* TFCu = 4.72), Pb (*S. purpurea* TFPb = 3.42), Zn (*S. caprea* TFZn = 3.48), Fe (*S. purpurea* TFFe = 1.44), and Cr (*S. purpurea* TFCr = 1.24). Most of the plant species had BCF less than one and TF more than one, although the concentration of heavy metals remained below 1,000 mg kg^{-1}. In general, metal concentrations in plants vary with plant species; plant uptake of heavy metals from soil may occur either passively with the mass flow of water into the roots, or through active transport from root cells (Kabata-Pendias 2004; Mun et al. 2008).

In this case study, the metal translocation ability, combined with rapid growth and a higher biomass than herbaceous plants, qualifies willows as good candidates for phytoremediation of polluted soils (Bini 2007). Since most of the studied willows were capable to uptake and translocate more than one metal from roots to shoots and, based on high TF values, they can be used for phytoextraction. On the other hand, Cd shows very low translocation factors in all investigated plants, and proved to be blocked in the roots, since it is known to be unessential to plants, thereby suggesting some exclusion strategy by plants (Vandecasteele et al. 2002).

Anthropic influence related to mining activity in soils of the studied area is evident. Soils in the mining site are highly contaminated by heavy metals, mainly Cu, Zn, Pb and Fe. The metal content in willows show relatively high concentrations of these elements. The results of this study indicated that there is an increasing need for further research on the mechanisms whereby such plants are able to survive in contaminated soils. Furthermore, studies should aim to determine the growth performance, biomass production and metal accumulation of these species in metal contaminated soils for their better management and conservation.

Concerning *Taraxacum* (plants), data show that this species is tolerant to high metal concentrations, which supports the use as a bioindicator plant. Metals accumulated preferentially in roots, but also leaves proved accumulator organs, being able to store up to 200 mg kg^{-1} Pb and 160 mg kg^{-1} Zn, with only little damages (e.g. reduced foliar surface, reduced plant development).

Soil analysis of the studied area (data not reported) showed low pH, low cation exchange capacity, percentage of sand higher than 50 %, absence of structure and low capacity of the soil to retain water and metals. High heavy metal (Cd, Cr, Cu, Pb, Zn, Fe) concentrations were recorded in both soils and selected plants (*T. officinale*) growing on mine tailings. There is a relationship between metal content in soils and plants, which qualifies *T. officinale* as an indicator plant, rather than accumulator.

The ability of *T. officinale* to uptake and translocate heavy metals, particularly the essential micronutrients Zn and Fe, from soil to plant was ascertained.

Plants proved to accumulate heavy metals in their shoots more than in roots. This is an effective and cheap option for phytoremediation of contaminated areas and also to decrease erosion risk. The accumulation of metals in plants, however, affects the normal processes of plant metabolism. The study shows that there is a relationship between high metal contents in plants and their modified morphology: strong reduction of leaf thickness, modified parenchyma structure, and decreased mitochondria organization were ascertained, although toxic symptoms were apparently absent.

The evaluation of metal uptake by plants, combined with geobotanical observations, proved a useful tool to find tolerant plant populations to be used in revegetation programs aimed at reducing the environmental impact of contaminated areas. The selection of new genotypes from metal-tolerant species will bring large advances in phytoremediation of contaminated sites. Further investigations may help understanding if dandelion could be a metal-tolerant plant to grow on slightly metal-contaminated soils for restoration purposes (Maleci et al. 2013; Wahsha et al. 2011).

4.2 Case Study 2

4.2.1 Environmental Impact of PHEs on Native Flora Growing on Mine Dumps

Bioavailable heavy metals can enter the food chain through primary producers, reducing growth cycle and altering some biochemical pathways in plants (Loureiro et al. 2006). Moreover, heavy metals induce oxidative stress by generation of hydrogen peroxide, superoxide radical, hydroxyl radical and singlet oxygen, collectively termed reactive oxygen species (ROS) (Wahsha et al. 2012c; Verma and Dubey 2003). Many organic molecules are exposed to severe damage by free radicals after high accumulation of heavy metals in plants (Alfonso and Puppo 2009; Joshi et al. 2005). Formation of ROS in cells is associated with the development of many pathological states (e. g. reduced root elongation, seed germination, signaling imbalance) (Bini et al. 2008; Wahsha and Al-Jassabi 2009). This has contributed to the creation of the oxidative stress concept; in this view, ROS are unavoidable toxic products of O_2 metabolism, and aerobic organisms have evolved antioxidant defenses to protect against this toxicity (Alfonso and Puppo 2009). Oxidative stress can increase sharply in cells either due to the decrease in the activity of the antioxidant defense systems or to the overproduction of ROS (Wahsha et al. 2012d; Mukherjee et al. 2007; Soffler 2007). The most harmful effect induced by ROS in plants is the oxidative degradation of lipids, especially polyunsaturated fatty acids (PUFA) in cell membranes known as lipid peroxidation, which can directly cause biomembrane disorganization (Gobert et al. 2010; Wahsha et al. 2010; Timbrell 2009). Several studies reported that ROS can initiate lipid peroxidation through the action of hydroxyl radicals (Armstrong 2008; Katoch and Begum 2003). Lipid peroxidation reactions are usually free radical-driven chain reactions in which one radical can induce the oxidation of PUFA (Abuja and Albertini 2001). The lipid peroxide Malondialdehyde (MDA) is one of the major end-product of lipid peroxidation process (Yadav 2010). In this case, membrane destabilization and fusion are directly correlated with MDA production (Wahsha and Al-Jassabi 2009; Wahsha et al. 2010). The determination of MDA content is widely used as a reliable tool to detect the oxidative stress hazard by estimating the formation of lipid peroxides in biological material (Loureiro et al. 2006; Taulavuori et al. 2001; Zielinska et al. 2001). Furthermore, the formation of ROS and an increased MDA production were observed in plants exposed to different heavy metals as Cr, Pb, Cu and Zn under laboratory conditions (Aravind and Prasad 2003; Baryla et al. 2000; Sinha et al. 2005; Verma and Dubey 2003).

The LPO levels (expressed as MDA contents) in the common dandelion (*Taraxacum officinale* Weber ex F.H. Wigg. 1780), and different willows (*Salix purpurea* L., *Salix caprea* L., and *Salix elaeagnos* Scop.) vary proportionally with the level of heavy metals in soils of the corresponding site indicating a close relationship between MDA and metals, thus confirming the LPO test to be effective in environmental contamination assessment (see Table 5.6).

The control plants of *T. officinale* exhibited normal levels of LPO, and it was 0.2063 μM in leaves and 0.1450 μM in roots. There was a dramatic increase in MDA level in leaves and root homogenate from *T. officinale* collected from Imperina Valley. In agreement with previous results by Savinov et al. (2007), the increase of MDA production in *T. officinale* was expected because when heavy metal levels increase in soil their absorption by roots will increase, and the lipid peroxidation through the possible excessive generation of free radicals will be incremented. *T. officinale* responds to the increased heavy metal contents by intensification of LPO processes, which are related to the concentrations of Cu, Zn, Pb and Fe in the soil, as a result of an imbalance in the homeostasis of the antioxidant defence system (Alfonso and Puppo 2009).

Lipid peroxidation in leaves and roots of willows, measured as MDA content, are given in Table 5.6. Compared to control, heavy metals induced oxidative stress in willows was evident from the increased lipid peroxidation in roots, stems and leaves, indicating an enhanced MDA production, with MDA increasing in leaves in comparison to roots and stems. This is in agreement with data reported by Kuzovkina et al. (2004) and Ali et al. (2003). Generally, in both parts of the plant, the MDA contents were found to be positively correlated with metal accumulation ($p < 0.05$). The high level of MDA observed in investigated plants under metal stress might be attributed to the peroxidation of membrane lipids caused by ROS due to metal stress indicating a concentration-dependent free radical generation (Bini 2010; Ali et al. 2003).

Table 5.6 The contents of MDA of dandelion and willows

Plant	MDA concentration (μM)	
	Leaves	Roots
T. officinale	7.0	7.7
S. purpurea	34.4	28.8
S. eleagnos	32.9	25.3
S. caprea	29.6	24.9

The soils in the mining area are highly contaminated by trace elements, mainly Cu, Zn, Pb and Fe. The observed ability of *Salix* species and *T. officinale* to continue growth in the presence of heavy metals and to accumulate metals in their tissues, and particularly in leaves, demonstrated their tolerance to moderate to high levels of metals (has this already been states?). Therefore, they have good potential to be used in phytoremediation projects. Our results show that *T. officinale, S. purpurea, S. caprea* and *S. elaeagnos* exposed to great metal concentrations in soils result in an increment in LPO in their tissues, suggesting an important role of oxidative stress in the pathogenesis of heavy metal-induced cellular toxicity, and they can be a promising bioindicator for such research. The LPO process proved to be a useful tool for health assessment of wild-growing plant species, as it reflects the anthropic heavy metal pollution in ecosystems.

4.3 Case Study 3

4.3.1 Biological Soil Quality Evaluation of Mine Dumps

Heavy metals have been reported to disturb the ecosystem structure and functioning for long time, and the results of this study largely agree with published data (Wahsha et al. 2012a). Soil health is the continued capacity of the soil to function as a vital living system, providing essential ecosystem services. Within soils, all bio-geo-chemical processes of the different ecosystem components are combined. These processes are able to sustain biological productivity of soil, to maintain the quality of surrounding air and water environments, as well as to promote plant, animal, and human health (Karlen et al. 2001). A common criterion to evaluate long term sustainability of ecosystems is to assess the quality of soil. Recently, several bioindicators of soil quality and health have been reviewed (Chauvat et al. 2003; Parisi et al. 2005). Among them, microarthropods, due to their high sensitivity to respond to environmental changes, play a fundamental role in the dynamics of organic matter and in the fragmentation of soils, at different scales of time and space (Loranger-Merciris et al. 2007). Thus, they can also contribute to metal translocation through the ecosystem in polluted environments. The Soil Biological Quality index (QBS-ar), which is based on microarthropod groups present in the soil (Parisi et al. 2005), may be applied to assess its biological quality: the higher is the number of microarthropod groups adapted to soil habitats, the higher is soil quality.

In soil samples collected from abandoned mixed sulphide mine dumps of Imperina Valley, the QBS-ar values appeared to decrease significantly ($p < 0.05$) with respect to soil pollution by heavy metals. QBS-ar values appeared to decrease significantly ($p < 0.05$) with respect to soil pollution by heavy metals. The correlation matrix (R^2) between heavy metals in soil and QBS-ar values showed that QBS-ar values were negatively correlated with Fe (−0.102), Pb (−0.384), Cu (−0.405) and Zn (−0.702). Conversely, our QBS-ar values indicate a significant positive correlation with Cr (0.298) and Cd (0.55). The presence of Acarina, Symphyla, Protura and Collembola is important, being considered metal-tolerant (Migliorini et al. 2004): for example, Symphyla seem to be quite affected by high lead concentrations and our results show a decrease in their abundance in areas with high concentrations of Pb, Zn and Cu.

Former activities proved to affect the microarthropods community altering both quantity and quality of litter and the chemical-physical structure of the microhabitats. We found in the study area a moderate soil health status of the surface horizons due to the ecological success of secondary recolonization after abandonment, although affected by heavy metal contamination. Even if we could not find a statistical difference between QBS-ar and humus forms/ecosystem type, there seem to be different structures of microarthropods communities in terms of richness and evenness.

In this case we hypothesize that 50 years of biological restoration of the mine site could have improved the microarthropods biodiversity, driving humus development towards a better ecosystem functional stability. QBS-ar index proved a useful tool to evaluate soil biological health. However, there is an increasing need for further research focusing on soil health restoration assessment, combining QBS-ar index with soil bio-physical-chemical indicators.

5 Conclusion

It is imperative to acknowledge that current and future exploitation of mineral resources will produce even more wastes and impose more threats on Earth. Therefore, management and utilization of once unwanted mine wastes should be seriously considered through implementation of proper waste disposal management plans which focus on the utilization of wastes rather than considering it as unwanted.

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Chapter 6
Potentially Harmful Elements in Urban Soils

Massimo Angelone and Metka Udovic

Abstract Throughout the human history, the anthropic activity inevitably leads to a legacy of increased PHE concentration in the environment. Nowadays the urban environment can be considered the main habitat for humans. Therefore, the acknowledgment and the understanding of the impact of PHEs in urban soils and dusts is imperative in order to develop a plan for the sustainable management of urban areas, which should limit this impact on human and environmental health. A historical background regarding urban soil contamination is presented, along with an overview of the PHEs and PGEs found in urban soils. As humans are daily exposed to PHEs present in air, water and soil, studies are focusing on their long-term effects and on the toxicological impact of PHE (PHEs') combinations, rather that of single elements. The importance of a comprehensive assessment of PHEs in urban soils and dusts, including their bioavailability, is discussed.

Keywords PHE • PGE • Urban geochemistry • Urban pollution • Urban soils • Anthrosols

1 Introduction

Potentially harmful elements (PHEs), in natural condition, can be considered rather immobile in soil. However their continuous release by anthropic activities gives rise to the increase of their concentration level in all the environmental matrices and, in particular, on top soils, as consequence of the presence of organic matter and clay materials. Industrial and urban areas are the most polluted settings, so the

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Table 6.1 Factors affecting natural and anthropic soil formation

Natural soil	Anthropic soil
Parent material	(1) Mixing soil from other areas
	(2) Mixing material of various origin
	(3) Removed and/or excavation material
Time	(1) Frequent land use variations
	(2) Landscape isolation
Climate	(1) Urban areas result wormer than rural or natural
	(2) Differences in drainage and in rainwater runoff mechanical effect
Morphology	(1) Presence of manmade structures and barriers
	(2) Presence of water flow barriers
Living organisms	(1) High productivity
	(2) Presence of exotic species

population is continuously exposed to high levels of PHEs even though their adverse health effects have been recognized their adverse health effects as daily reported in the news (Järup 2003).

Urban soils are particular ecosystems influenced by human activity that alters their pedochemical characters acquired through the natural dynamics of the soil. Human activity, over time, has refined and changed the landscape adapting to its own needs, reworking the original materials, adding new ones: exotic, alien or from technological origin. These soils have thus become accumulation and storage areas for anthropogenic materials released into the environment in such quantities as to change (sometime up to 10–100 times) the natural background. The factors affecting natural and anthropic soil formation and the source of PHE in urban environment are reported in Tables 6.1 and 6.2. Table 6.3 contains some information on the technological substrate present in urban areas and related wastes.

Bockheim (1974) stated that urban soils are material having a non-agricultural man made surface layer more than 50 cm thick that has been produced by mixing, filling or land surface contamination. In such areas soils can be further divided in natural soils, if developed on natural materials, and anthropogenic soils if developed on manmade materials employed to modify urban morphology and for specific activity (Bullock and Gregory 1991; Scheleuß et al. 1998; USDA 2005).

2 History

Studies on urban stratigraphy showed the long-term human influence witnessed, as an example, by Pb variation in wood from nineteenth century to nowadays in old American beech trees, following the industrialization trend and the utilization of leaded and, from 1990, unleaded gasoline (Pierzynski et al. 2005).

Archaeological studies date back evidence of urbanization from 7500 B.C. as for the case of the town of Hacilar, Turkey. From 2500 B.C proof have been reported for Gerico (Palestine) and for the civilizations developed along the course of Nile,

Table 6.2 Sources of potentially harmful pollutants in the urban environment

Sources	Pollutants
Cars (exhaust, fuel, oil,)	Ba, Cd, Pb, Cr, Cu, Pd, Pt, Rh, Zn, V, NO_x, C_6H_6, PAH, CO, SO_2, Pb, Phenols, Hydrocarbons, Halogenated hydrocarbons
Tires	Cr, Cd, Cu, Ni, Zn
Brakes wear	Cu, Zn
Road and urban surface weathering	PAH (asphalt), metals (concrete)
Road and urban surface winter management	Detergents, salts, Cd, Cu, Fe, Ni, Zn
Corrosion of construction materials	Cd, Zn
Domestic heating systems	Co, Mn, Ni, V
Garbage incineration, fire releasing from various materials	Cu, Zn, Ba

Table 6.3 Technological substrates and related wastes commonly present in urban areas

Source	Waste material
Construction and housing	Brick, concrete, mortar, plaster
Road work	Bitumen asphalt, tar asphalt
Ironwork, Steelworks, Foundries, Heavy metal works	Steel and furnace slag, sand of foundry, pumice
Incinerator	Fly and bottom ash
Household	Glass, metal, paper, plastic, ceramic, organic garbage, wood, bulky refuse

Indo, Tigris, Euphrates and Tiber rivers, as the case of Rome that can be considered one of the best sites to study urban soil being continually inhabited from the Bronze Age as testified by archaeological relics in soil profiles (Carandini 2012; Anguillano 2013). More recently studies on the city of Greater Angkor, Cambodia, evidenced that, from 1000 to 1200 B.C., this city represented the most extensive currently known preindustrial urban complex in the world (Simon 2008).

In medieval urban areas garbage deposits containing iron mixed with ceramic and other materials were found. The industrial revolution is witnessed by the increased presence of coal and iron and of the secondary products related to their use and processing. In more recent times the diffusion of the tertiary sector and the introduction of new living standards, continuous and relentless use of land with the increase of anthropic surface extention, results in a serious detriment of natural and agricultural lands. Trends on recent population distribution in the world areas are reported in Table 6.4.

Modern investigation on the geochemistry of urban soils started in the late 1960s. Studies on urban garden evidenced that the levels of some elements such as Cu or Pb, were higher in urban areas than in rural areas, which are strongly influenced by land use. (Purves 1966; Purves and Mackenzie 1969; Thornton et al. 1985; Thornton 1991, Kelly et al. 1996; Ajmone-Marsan and Biasioli 2010).

Table 6.4 Distribution of the population (% of the total) in the world from 1950 to 2011

	Urban	Rural	Urban growth 1972–2001	Annual growth (AG)
Europe	75	25	0.3	Expected AG until 2015: + 0.3 %
Africa	38	62	4.0	+ 3.5 %
Latin America Caribbean	75	25	6.0	AG in 1972: + 58.9 %
North America	77	23	0.1	AG in 1978: 73.8 %
OCEANIA[a]	71.7	28.3	72.7	AG + 1.51 %

[a] Period 1975–2000

Owing to their origin, urban soils show a high spatial and vertical heterogeneity characterized by abrupt lithological and physical-chemical changes, great porosity, bulk density and texture variability. Notwithstanding these soils are subject to drastic change and degradation, soil properties remain rather similar to those of natural performing ones, some ecological functions such as pollutant absorption and plant growth sustainability. However, in large cities or complex urban environment, the ecological function, such as providing habitat to insects and microorganisms can be greatly reduced. The relation among some soil properties and urban soil contamination is reported in Table 6.5.

While the major inputs of PHEs into soil are atmospheric deposition, application of manure, inorganic fertilizers and sewage sludge, mining and smelting activities, or alluvial deposition, in the urban environment the main sources of trace elements are the emissions from vehicular traffic. Until now, the most studied PHEs were Pb, Cd, Cu, Cr, Fe, Mn, Ni, Pb and Zn. Previous studies have shown that their concentration levels and distribution are related to traffic intensity, to the distance from roads and to roads pattern, local topography and building effects. Pb is, for example, ubiquitous in the urban environment as a result of industrial emissions, and its extensive past use in alkyl-Pb compounds as antiknock additives in gasoline, and Pb-based paints and pipes (Callender and Rice 2000). Until the nineties it was estimated that around 11–15 % of the total refined Pb world consumption was utilized for petrol additives and that the average Pb concentration in petrol was 0.7 g L^{-1}, while in the car exhaust it reached 0.4 g L^{-1} of consumed fuel. Industrial emissions also contributed to the environment release of elements such Cd, Cu, Fe, Cr, Hg, Pb, and Zn.

3 PHEs' Impact on Human Health

Humans are daily exposed to PHEs present in water, air and soil at different concentration levels. Their intake however depends on the chemical characteristics of the PHEs as well as on the population patterns and behaviour. The intake of PHEs can occur either directly via ingestion, inhalation and, to a lesser extent, via dermal contact absorption, or indirectly with the consumption of food grown in contaminated areas (Sharma and Agrawal 2005; Dean 2007). There is a growing

Table 6.5 Influence of some soil properties on soil contamination in the urban environment

Action		Positive effects	Negative effects
Soil sealing	60–65 % of urban areas and 20–30 % of sub-urban areas result sealed	In highly contaminated soils, sealing reduces risk to human health. Soils covered with asphalt limit water percolation	Microclimate alteration: influence of the wind speed, increase temperature and humidity. Soil vegetation and biotopes habitat alteration Water infiltration reduction. Evapotranspiration and runoff alteration; polluted litter accumulation. Alteration of subsoil gaseous circulation
Erosion	Related to construction, building demolition, soil excavation, back-filling and soil handling operation, truncating		Reducing bottom soil protection; degradation of parks, playgrounds and vegetation Increase damages related to heavy rain
Compaction	Differences arise in case of sandy or loamy-clay. Increase of soil density	In case of dry condition loamy and clayey soils result to be resistant to compaction processes	Loamy and clayey soils in case of wet condition evidence high compaction. Aggregates tend to break down, increase of bulk density and sand particles packing. Reduction of vegetation and biological activity, earthworm population habitat restriction, reduction of water infiltration and gas diffusion owing to pore space limitation
Soil pH	Building materials raise the soil pH		Ca release in dry conditions produces top soil cementation and impermeable surface

tendency to promote urban agriculture for the improvement of gardeners' economic and social status, to make more available locally produced food and to improve the social wellbeing of the urban population (Brown and Jameton 2000). However, food production in urban areas implies a through overview and understanding of the presence of PHEs in urban soils. Soil ingestion is generally considered to be the most important exposure route and it is usually associated with eating of dirt in children (pica) and with occupational exposure in adults (Davis and Mirick 2006; ISO/TS 2007). Soil consumption can also occur deliberately (i.e. geophagy), for example for medical purposes or as part of a regular diet (Abrahams 2005). Geophagists usually consume only certain soils with specific properties, usually with the purpose to compensate a mineral nutrient imbalance, leading thus to a discriminatory intake of soil constituents (Certini and Scalenghe 2007). However, along with the mineral nutrients, PHEs can also be ingested, potentially causing adverse health effects (Abrahams 2012). Several reports have been published concerning this particular topic. For example, the study of Abrahams et al. (2013) on the bioavailability of PHEs in two African geophagical materials, Calabash chalk and Undongo, which are commonly used in Nigeria and among the emigrants in different parts of the world, showed that the consumption of these clay soil material does not substantially contribute to PHEs' intake, nor to a better Fe uptake, one of the primary reasons for the geophagy. Conversely, Al-Rmalli et al. (2010) showed that a type of clay, sikor, commonly consumed by Bangladeshi women in Bangladesh and in the United Kingdom, especially during pregnancy, may be an important source of As, Cd and Pb intake. The average daily consumption of sikor would thus contribute up to 370 and 1,236 mg kg^{-1} of As and Pb to the diet, respectively. However, different factors affect the actual oral uptake of PHEs into the system.

For a correct estimation of PHEs' oral intake, it is very important to consider the size of the ingested soil particles, as smaller particles have larger surfaces, on which PHEs can be adsorbed. In their study on the size distribution of soil particles adhered to children's hands, Yamamoto et al. (2006), for example, pointed out that the cut-off diameter of 2 mm defined by the Japanese Ministry of the Environment is too permissive and may lead to an underestimation of the risk posed by contaminated soil intake. A considerable percentage of PHEs is released into the environment in the particulate forms, which are highly mobile and can easily interact with other chemicals. The size of the particulate matter (PM) varies, e.g. $PM_{2.5}$ and PM_{10} for particles with diameter smaller than 2.5 μm and 10 μm, respectively, which are further divided into narrow classes (Kampa and Castanas 2008). Small particles can enter the human body also via inhalation, leading to a significant PHE absorption in the respiratory tract, in addition to the gastrointestinal absorption due to the ingestion of soil particles and to the consumption of vegetables and water contaminated with airborne particles. In a study on the relationship between soil particle-size fractions and Cr, Cu, Ni, Pb and Zn content in five European cities, Ajmone-Marsan et al. (2008) reported that all the PHEs were concentrated in the <10 μm fraction. Interestingly, the accumulation factors in the finest fractions were higher where the overall soil contamination was lower, indicating, that relying on PHEs' concentration values in the soil solely may lead to an underestimation of the health risk for humans. Similarly, Cai et al. (2013) reported about significantly higher mean PHE concentration in urban dusts than in urban soils. While 89 % of investigated park soil and all residential areas were classified as lowly-moderately polluted, and 86 % of roadside soils and 91 % of sport ground soils were described as moderately polluted, all dusts were classified as highly polluted.

PHEs are known to have significant negative effects on human health at different levels, ranging from acute reactions due to the exposure to increased levels of PHEs, to chronic illness, including cancer (Kampa and Castanas 2008). Exposure to mercury due to the industrial activity, for example, has been found to be correlated to the increased kidney disease mortality among the population in the nearby residential zone (Hodgson et al. 2007). Similarly, epidemiological studies have reported an elevated incidence of beryllium sensitization (BeS) among workers occupationally exposed to Be-bearing dust particles, which may develop into the potentially fatal lung disease, the chronic Be disease (CBD) (Virji et al. 2011). Long-time exposure to PHEs may also impair fertility. Louis et al. (2012) found the Pb and Cd blood levels to be significantly associated with reduced couple fecundity, prolonging thus the conceiving time. It should be also highlighted that maternal exposure to PHEs, in particular to Pb, resulting in maternal blood levels >1 μL L^{-1}, can have severe negative effects on the developing fetus, impairing the cognitive and motor abilities of the child, or even inducing spontaneous abortion (Bellinger 2005; Schell et al. 2006).

Many studies have focused on children, since they represent the most vulnerable group of people. Children are exposed to soil PHEs by dust and/or soil tracked into homes on shoes or family pets (Hunt et al. 2006), by dust deposition in closed spaces (Laidlaw and Filipelli 2008), by their mouthing behavior and during their recreational outdoor activities (Ko et al. 2007; Abrahams 2012). In addition, children stature usually coincides with the lower airborne mixing layer produced by vehicular traffic vibrations. The suggested values of daily ingested soil are different, with values up to 137 mg d^{-1}, or even 1,432 mg d^{-1}, when pica behavior is present (Moya et al. 2004). The ingestion values proposed by the US EPA differ in relation to the routes of intake and are of 50 mg d^{-1} for soil solely, 100 mg d^{-1} for soil and dust and 1 g d^{-1} for soil pica behavior (US EPA 2008). So far, much attention has been given especially to Pb, which remains one of the major public health problems in the United States (Todd et al. 1996). As reported by Mielke et al. (2010) in a study on the Pb legacy from vehicle traffic in Californian urban areas, about 5.4 million tons of Pb additives were used in the USA in the period between 1927 and 1994. Another important source of soil pollution in urban areas is the Pb-based painting, which can substantially contribute to the overall Pb dust emissions, e.g. by power sanding and paint scraping (Mielke et al. 2001). Pb has a high uptake percentage into the children's organism; 50 % of the ingested Pb is retained into the organism, compared to the 5 % in adults (Laidlaw and Filipelli 2008). As Pb accumulates in the developing neural system and in bones, it may lead to permanent neural deficiencies, such as impaired intellectual performance, learning disorders and attention-deficit/hyperactivity disorder (ADHD) (Oskarsson et al. 1995; Nigg et al. 2008). An extensive overview of the existing studies concerning the soil/dust Pb in urbanized areas within the United States and the blood Pb in children can be found in Mielke et al. (2010). Similarly, in a study on children Pb-blood levels in New York City, Billick et al. (1980) reported a significant relationship between Pb-blood levels and gasoline Pb content.

Not only Pb, but also Zn, Cr, Cu, Cd and Ni are largely present in urban soils and dusts (Mielke et al. 2000; Wei and Yang 2010). Some PHEs, such as Cu, are harmless in small quantities, whereas some other PHEs, including Pb and Cd, may have neurotoxic effects. No homeostasis mechanisms are known so far for many PHEs, and exposure to high levels of PHEs could have serious negative effects on humans, e.g. accumulation in fatty tissues, negative effects on central nervous system and internal organs (Dockery and Pope 1996). Long-term exposure to PHEs may lead to several diseases, among them a high potential to develop cancer (Nriagu 1988; Kurt-Karakus 2012). Hubbard et al. (1996), for example, reported about significant exposure-response effects regarding the cryptogenic fibrose alveolitis among subjects occupationally exposed to metal or wood dust. Willis et al. (2010) have studied the connection between the incidence of Parkinson disease and PHE (Cu, Pb and Mn) emission in urban areas. The results showed that a significant increase of Parkinson disease (PD) risk was statistically significantly associated to the long-term residence of the observed subjects in U.S. counties with high cumulative industrial Cu or Mn release. Also worksite conditions implying exposure to Fe, Cu, Mn, Hg, Zn and Pb showed a significant association with the PD (Gorell et al. 1997). Interestingly, the more than 20 years' exposure to combinations of Pb-Cu, Pb-Fe and Fe-Cu showed a greater association with PD than with any of these metals alone. It has been reported that significant correlations can be found among different PHEs in soil or dust, e.g. between Pb and Cd, Zn and Cd, Pb and Zn, Cd and Zn, Cu and Pb, Pb and Zn, respectively (Cai et al. 2013). Such correlations indicate the source of PHEs: the significant correlations (at 99 %) between Pb and Zn in soil ($r = 0.381$) and dust ($r = 0.363$) indicate a traffic source coupled with industrial emissions. Further, significant correlations (at 95 %) between Zn and Cu in soil ($r = 0.351$) and dust ($r = 0.341$) indicate a possible origin in mechanical abrasions of vehicles (Jiries et al. 2001). However, the toxicological impact of PHE mixtures on human health still remains poorly understood.

4 Assessment of PHEs in Soils

Total PHE concentration in soil is the most common measure of soil contamination, and further, of environmental and human exposure. One of the most used standard analytical methods for the determination of elemental concentrations is the *aqua regia* leaching followed by AAS, ICP-MS, or similar analysis. The *aqua regia* leaching is a partial (pseudototal) extraction, where carbonates, mostly sulphide minerals, some silicates, clay minerals, salts and hydroxides are dissolved in a mixture of nitric and hydrochloric acid (ISO 11466 1995). However, different extraction methods may be preferred, according to the physical and chemical characteristics of the soil sample. In a study on selected PHEs in top soils of the main urban areas in Campania, Albanese (2008) reported that anthropogenic elements are easily extractable owing to their weak association with the crystalline lattice of the soil minerals and, as a consequence, can be dangerous to human health. The ammonium acetate–EDTA extraction method (AA-EDTA) could be a more suitable method for the risk assessment purpose. In a comparative study on the suitability of three methods of PHE determination in soil samples, Sastre et al. (2002) proposed a decision chart for the selection of the most appropriate digestion procedure considering the sample nature and the purpose of the analysis. In addition to the *aqua regia* leaching, the microwave-assisted digestion (US EPA 2007) and the nitric acid extraction (Tam and Yao 1999) were tested by the authors. Recently, also the non-destructive XRF spectrometry has gained attention for its simple use for quick PHE screening in soils and other materials (US EPA 1998; Bachofer 2004). Additionally, several studies have tested simpler extraction procedures to be used as predictors of the total PHE content in soil. Wharton et al. (2012), for example, compared three commonly used screening tests, i.e. the modified Morgan, Mechlich 3 1-M HNO_3 extraction with the standard total Pb testing method (US EPA 2007). In their study, the 1-M HNO_3 extraction test resulted to be the best predictor of the total Pb content in soil.

The derivation methods for screening values used to regulate land contamination are widely variable among countries, due to different geographical, biological, sociological, regulatory and political needs (Carlon 2007). Although the total concentrations of PHEs in soil are still largely used as direct measures of maximum PHE intake, the urge of considering the complexity and heterogeneity of soil for the assessment of health risks for humans is gaining attention (Wragg and Cave 2002; Latawiec et al. 2010). PHEs are present in soil bound to soil fractions with different solubility and chemical characteristics. Consequently, they may have different toxic effects on organisms (Rieuwerts et al. 1998; Rodriguez et al. 1999; Oomen et al. 2000; Arnold et al. 2003; Geebelen et al. 2003; Krishnamurti and Naidu 2008; Buccolieri et al. 2010). The risk posed by contaminated soils to human health depends on the potential of the PHEs to leave the soil and enter the human bloodstream (Wragg and Cave 2002). The fraction of PHEs that can be absorbed by the body in the central blood compartment through the gastrointestinal system, the pulmonary system and the skin is defined as bioavailability (Ruby et al. 1996; Paustenbach 2000). Since bioavailability can be measured only in time consuming and expensive *in vivo* animal studies subject also to ethical considerations, *in vitro* bioaccessibility tests are preferred for the evaluation of the risk posed by PHEs to human and environmental health (Whitford 2006). Here bioaccessibility is defined as the fraction of PHEs, which is available for absorption. Innovative physiologically based extraction tests are the most comprehensive existing methods for the assessment of PHE bioaccessibility in soil. They aim to simulate human physiological processes, which affect the uptake of PHEs into the human body (Wragg and Cave 2002; Dean 2007; Peijnenburg et al. 2007). So far, most of the attention was given to the development of a unified *in vitro* method for the simulation of the human uptake of metals through the digestive system, especially by children (Wragg and Cave 2002; Oomen et al. 2003). For the implementation of the EU Soil Thematic Strategy, which dictates to the EU state members to identify areas where pollution has adverse effects on human and environmental health, a unified methodology is needed. For this propose the standardization of the novel UBM (Unified BARGE Bioaccessibility Method) (Wragg et al. 2011) is very important. A first step was made by Denys et al. (2012), which validated the UBM procedure with an *in vivo* animal (swine) model.

PHE uptake into the human body through dust particle inhalation is less known. After dust particles enter into the lungs, the PHEs are affected by three chemically different environments: the extracellular lung solution, the cytoplasm of the alveolar macrophages and the lyzosom (Collier et al. 1992). Currently only a few existing methods are available providing an approximate simulation of only one of the three environments, either by simulating the PHE solubility in the artificial extracellular lung solution (Ansoborlo et al. 1999; Twining et al. 2005), or with *in vivo* tests using primate lung macrophages (Poncy et al. 1992). It is therefore needed to develop a unified method for the assessment of PHE uptake through the respiratory system, which should comprise all the three mentioned environments.

The assessment of the lability of PHEs using diffusive gradients in thin films (DGT) is another innovative in situ method for the evaluation of the dynamics of PHEs between the solid soil and the liquid soil phases (Zhang et al. 1998; Peijnenburg et al. 2007). The DGT method is very suitable for the assessment of PHE uptake into plants (Tandy et al. 2011) and in soil organisms (Koster et al. 2005), which allows us to evaluate the human uptake of PHEs from the consumption of food produced on polluted soils.

Literature data reference levels on some PHE in world rocks and soils are reported in Table 6.6, while a data collection from some selected urban areas are displayed in Table 6.7.

5 Platinum Group Elements (PGEs)

In relation to economic and living standard conditions changes and with the introduction and development of new technologies, new chemical species and related pollutants have been continuously released into the environment. Among these we can mention PGEs (Platinum Group Elements) and REEs (Rare Earth Elements), both present in many industrial processes and in particular in car catalysts, to reduce traffic emissions of Pb, NOx etc. (Morrison and Rauch 2007; Zereini and Alt 2006). The strong development of electronics and computer industry has required the use of large amounts of tantalum, gallium and REEs such as cerium, lantanium, etc.; in fact, their chemical and physical properties are essential for the operation of televisions, computers and mobile phones.

Recently PGEs, mainly Pt, Pd, and Rh gained attention as possible threat for human and environmental health. These heavy metals are considered to be mostly inert and non-mobile, but there is evidence of their spread and bioaccumulation in the environment. Occurring in airborne particulate matter PGEs accumulate in organisms with time, as shown in studies reporting their enhanced levels in humans working in certain occupational environment (e.g. refineries and catalyst

Table 6.6 Reference levels of some PHEs in rocks and soils (mg/kg)

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	Zn	Reference
UCC[a]	2.0	0.10	11.6	35	14.3	0.056	18.6	17	0.31	52	Wedepohl (1995)
UCC	4.8	0.09	17.3	92	28	0.050	47	17	0.40	67	Rudnick and Gao (2003)
European soils		0.79		53	19.5		27	39		68	Angelone and Bini (1992)
World soils		0.30		200	20		40	10		50	Angelone and Bini (1992)
		0.06		68	22		22	30		66	Kabata-Pendias (2000)
	6.0	0.35	8.0	70	30	0.06	50	35		90	Adriano (2001)
Excessive levels		5.00		100	100		100	200		250	Kabata-Pendias (2000)
Pre industrial levels		0.55		48	34		40	22			Callender (2003)

[a]Upper continental crust

productions). Even if elemental (metallic) PGEs have generally no biological effect, some of their salts, such as hexachloro platinate and tetrachloro palatinate, may have severe allergic and sensitivization effects (Merget and Rosner 2001). Moreover, their accumulation in humans have been associated with long-term effects, e.g. asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis etc. (Ravindra et al. 2004).

Conspicuous is the literature available on PGEs. For evident space limitation all information can't be thoroughly presented in the present work. However, more information may be found in the following papers and in the enclosed references: Barefoot (1999), Ravindra et al. (2004), Morrison and Rauch (2007), Rauch et al. (2005), Angelone et al. (2006), Zereini and Alt (2000, 2006), Kalavrouziotis and Koukoulakis (2009).

As previously mentioned, PGEs are present in car catalysts which convert dangerous compounds, such as NOx, carbon monoxide (CO) and the unburned hydrocarbons (HC) into less dangerous compounds, such as CO_2, N_2 and H_2O. Despite these evident advantages, their use gives rise to new environmental concerns. As an example, the continuous thermal and mechanical wearing out of the catalyst causes the release of PGE wash-coat particles. These particles are emitted in the order of few ng km^{-1} in a wide range of sizes. i.e. <3.1 μm (~13 %), from 3.1 to 10 μm (~21 %) and >10 μm (~66 %) (Artelt et al. 1999). A data collection of PGEs released from various catalysts in different operative conditions is reported in Table 6.8, while the levels of Pt, Pd and Rh in two different European catalysts are reported in Table 6.9.

Even though PGEs have long been considered to be non-reactive (inert) elements, it has been recently observed that the effect of PGEs on human health depends on the degree of their bioavailability and that the proportion of soluble and hence quite reactive PGEs chemical forms may reach levels up to 10 % (Klaassen 1996). Literature data show evidence that PGE compounds are toxic,

Table 6.7 Potentially harmful element concentration in urban top soils in some world cities (mg/kg) n/a, information not available. Where available, the information on soil usage is specified

Location	Soil usage	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	V	Zn	Reference
Warsaw, Poland	n/a		0.73	5.1	32	31		12	57			166	Czarnowska (1980)
Glasgow, UK	n/a		0.53			97			216			207	Gibson and Farmer (1986)
Brussel, Belgium	Urban gardens				42			55	55				Albasel and Cottenie (1985)
Glasgow, UK	n/a		0.53			97			216			207	Gibson and Farmer (1986)
Hamburg, Germany	n/a		2.0		95	146		62	218			516	Lux (1986)
London, UK	n/a		1.0			73			294			183	Thornton (1991)
Hamburg, Germany	n/a	23	1.2		52	81	0.60	31	168			381	Lux (1993)
Rome, Italy	Urban area		0.31						331				Angelone et al. (1995)
Prague, Czech Rep.	Urban parks		1.07			47		8	67			91	Scharova and Suchara (1995)
Richmond, UK	n/a		<0.2			30			158			108	Kelly et al. (1996)
Wolverhampton, UK	n/a		0.80			62			106			231	Kelly et al. (1996)
Aberdeen, UK	Park soils			6.4	23.9	27		14.9	94.4			58.4	Paterson et al. (1996)
	Road soils			6.2	22.9	44.6		15.9	173			113	
Florence, Italy	Urban parks				104	71		71	102			138	Bini et al. (1995)
Madrid, Spain	n/a			6	75	72		14	161		30	210	De Miguel et al. (1998)
Bangkok, Thailand	n/a		0.29		26	42		25	48			118	Wilcke et al. (1998)
Manila, Philippines	n/a		0.57		114	99		21	214			440	Pfeiffer et al. (1988)
Berlin, Germany	City limits	5.1	0.92		35	79	0.42	11	119			243	Birke and Rauch (2000)
Tallinn, Estonia	n/a			5.2	39.9	45		16	75.3		31.7	156	Bityukova et al. (2000)
Danang-Hoian, Vietnam	n/a		0.8	34	92.2	76		22.6	3.6		95.3	141.8	Thuy et al. (2000)
	Soil particle <63 μm		0.4	17.4	103.7	55.9		14.6	1.8		100.7	81.3	
Coruña, Spain	n/a		0.3	11	39	60		28	309	3		206	Cal-Prieto et al. (2001)
Hong Kong	n/a		2.18			25			93			168	Li et al. (2001)
Oslo, Norway	n/a	5.48	0.41	9.98	32.5	31.7	0.13	28.4	55.6		51.3	160	Tijhuis et al. (2002)
Palermo, Italy	Urban areas		0.68	5.2	34	63	0.68	17.8	202	3.0	138	54	Salvagio Manta et al. (2002)
Aviles, Spain	n/a	15	2.4		18	20		11	107			477	Gallego et al. (2002)
Nanjing, China	n/a				85	66			107			163	Lu et al. (2003)

Jakobstad, Finland	n/a	2.7	0.25		23	22		7.9	59			82	Peltola and Aström (2003)
Naples, Italy	Urban soils				11	74			262			251	Imperato et al. (2003)
Beijing, China	n/a					71.2		22.2	66.2			87.6	Chen et al. (2005)
Miami, USA	Residential areas								161				Chirenje et al. (2004)
	Commercial areas								223				
	Public parks								107				
Gainesville, USA	Residential areas								67				
	Commercial areas								37				
	Public parks								22				
Damascus, Syria	Agricultural soils			13	57	34		39	17			103	Moller et al. (2005)
Hong Kong	Urban areas		0.36	3.55	17.8	16.2		4.08	88.1			103	Lee et al., (2006a)
Naples, Italy	n/a		0.56		28.2	97.5			158		111	181	Maisto et al. (2006a)
Tuscany, Italy	n/a					85		59	219			128	Bretzel and Calderisi (2006)
Torino, Italy	Urban soils				191	90		209	149			183	Biasioli et al. (2006)
Torino, Italy	Urban soils	11	1.30	27	233	94	0.90	164	124	2.8	86	170	Biasioli and Ajmone-Marsan (2007)
Ibadan, Nigeria	n/a	3	0.15		56	32		17	47			94	Odewande and Abimbola (2008)
Baltimore, USA	n/a		1.1	15	72	45		27	231			141	Yesilonis et al. (2008)
Shanghai, China	n/a		0.52		108	59.3		31.1	70.4			301	Shi et al. (2008)
Aveiro (Portugal)	Parks, road sides, gardens				7	46		12	72			86	Ajmone-Marsan et al. (2008)
Glasgow (UK)					52	62		41	195			178	
Ljubljana (Slovenia)					43	48		22	102			177	
Sevilla (Spain)					32	55		31	223			157	
Torino (Italy)					303	107		260	277			235	
Kavala, Greece	n/a	38	0.2		240	48	0.1	77	571			175	Christoforidis and Stamatis (2009)
Moscow, Russia	n/a		2.0	4.3	79	59		19	37			208	Plyaskima and Ladonin (2009)
Mexico City, Mexico	n/a				117	101		40	140			307	Morton-Bermea et al. (2009)
Chicago, USA	n/a	20		11	71	150	0.64	36	395			397	Cannon and Horton (2009)
Izmit, Turkey	n/a		0.23	17	34	37		39	35			72	Canbay et al. (2010)
Trondheim, Norway	(Survey 2004)	4	0.19		65	39	0.15	45	81			112	Anderson et al. (2010)

(continued)

Table 6.7 (continued)

Location	Soil usage	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Sb	V	Zn	Reference
	(Survey 1994)	3	0.24		73	42	0.21	48	52			151	
Sialkot, Pakistan	n/a		46	36	107	19		83	122			78	Malik et al. (2010)
Islamabd, Pakistan	n/a		3.5	17		18		91	208			1643	Ali and Malik (2011)
Torino, Italy	parks				116	57		127	57			106	Sialelli et al. (2011)
	road soils				464	202		415	454			275	
China, 21 cities	n/a	12	0.39	14	69	40	0.31	25	55			109	Luo et al. (2012)
Estarreja, Portugal	n/a	10	0.26		15	28			35			59	Cachada et al. (2012)
Rome	Parks					107		48	417			220	Calace et al. (2012)
Ghaziabad, India	n/a		0.40		288	122		147	147			187	Chabukdhara and Nema (2013)
Tianjin, China	n/a		1.01		96.4	41.7		34.0	30.8				Wu et al. (2013)
Las Tunas, Cuba	n/a			14	97	94		35	42			199	Diaz Rizzo et al. (2013)
Guangzhou, China	n/a		0.23		22.4	41.6		11.1	65.4			277	Quan et al. (2013)

Table 6.8 PGEs released from various catalysts in different operative conditions

Catalyst model	Operative condition test	Emissions rate	References
Pellet type	48 km h^{-1} 96 km h^{-1}	Pt: 1.2 μg km^{-1} Pt: 1.9 μg km^{-1}	Hill e Mayer (1977)
Monolith type	Engine at the lowest r.p.m.	Pt :67 ng m^{-3}	Rosner and Hertel (1986)
Monolith type	80 km h^{-1} (new catalyst) 80 km h^{-1} (old catalyst) 130 km h^{-1} (new catalyst) 130 km h^{-1} (old catalyst)	Pt: 12 ng km^{-1} Pt: 9 ng km^{-1} Pt: 90 ng km^{-1} Pt: 18 ng km^{-1}	Artlet et al. (1999)
Pt/Pd/Rh, Pd/Rh catalysers (18,000 km)	Test at constant speed (80 km h^{-1})	Pt: 6.3–7.5 ng km^{-1} Pd: 1.2–1.9 ng km^{-1} Rh: 0.6–1.2 ng km^{-1}	Moldovan et al. (1999)
	Standard test drive	Pt: 11–58 ng km^{-1} Pd: 2–24 ng km^{-1} Rh: 1.5–7 ng km^{-1}	
Pt/Pd/Rh catalysers Pd/Rh	Gasoline	Pt: 27–313 ng km^{-1} Pd: 6–108 ng km^{-1} Rh: 8–60 ng km^{-1}	
	Diesel	Pt: 47–170 ng km^{-1}	
Monolith type	Gasoline	Pt: 10.2 ng km^{-1} Pd: 14.2 ng km^{-1} Rh: 2.6 ng km^{-1}	Rauch et al. (2002)
	Diesel	Pt: 223 ng km^{-1} Pd: 75.8 ng km^{-1} Rh: 33.7 ng km^{-1}	

Table 6.9 PGEs levels in two European auto catalysts adopted before 2004

Catalyst type	Pt μg g^{-1}	Pd μg g^{-1}	Rh μg g^{-1}
Ceramic-based	990 ± 21	307 ± 3	218 ± 2
Metallic-based	2,424 ± 89	16 ± 1	567 ± 2

while Pd and Rh are also potentially carcinogenic elements (Leikin and Paloucek 1995). However, Pt has been used as an anti-cancer drug, while Pd chloride has been employed for the treatment of tuberculosis without too many side effects.

PGEs released in the environment are mostly deposited on the roadsides. Available data on PGEs concentrations in urban environment in some world cities are reported in Table 6.10.

Since the size of a large amount of catalyst particles is <10 μm (referred to as PM10) health problems can arise from their direct inhalation of dust particles. The size fraction between 2.5 and 10 μm can easily reach the nose-pharynx region, while the size fraction <2.5 μm can reach the alveolar region.

The chemical transformations of PGEs, which can occur after their release in the environment, may increase their bioavailability, as for Pt^{+6} which is known to be a powerful oxidizing agent (Barefoot 1999).

Table 6.10 PGEs concentration levels in urban environment from some world cities (ng g^{-1})

Location	Pt	Pd	Rh	Matrix	Reference
San Diego, USA	100–600	38–280		Suburban road dust (high traffic)	Hodge and Stallard (1986)
	300	15–24		Road dust (residential area)	
Germany	1,000	100	110	Road dust (high traffic)	Shäfer et al. (1996)
Rome, Italy	14.4–62.2	102–504	1.9–11.1	Urban road dust	Petrucci et al. (2000)
Austria	55–81	4–5.5	10–12	Tunnel dust from airshaft	Schramel et al. (2000)
Frankfurt, Germany	72	6	18	Highway soil	Zereini and Alt (2000)
	46	4	9	Urban soil	
Rome, Italy	0.8–6.3			Urban soil (1992)	Cinti et al. (2002)
	7.0–23.7			Urban soil (2001)	
Madrid, Spain	144–339		44–64	Road dust (<63 μm)	Gómez et al. (2002)
Honolulu, USA	15–160			Road dust	Sutherland (2003)
	2–160			Soil	
Accra, Ghana	39 ± 24			Road dust	Kylander et al. (2003)
	15 ± 5.3			Road side soil	
Perth, Australia	8.8–91	58–440	53–419	Road dust	Whiteley and Murray (2003)
	3.5–27	13.8–108	31–107	Road side soil	
Naples, Italy	4.2 ± 6.5	12.7 ± 13.2		Urban soil	Cicchella et al. (2003)
London, UK	4.6–356.2			Road dust (<75 μm)	Ward and Dudding (2004)
Austria	1–134	0.79–21.2	.17–13.2	Soil	Fritsche and Meisel (2004)
Białystok, Poland	111 ± 13	42 ± 1	19.7 ± 2.7	Road dust (<75 μm)	Lesniewska et al. (2004)
	23.3 ± 3.8	23.9 ± 1.2	6.76 ± 1.3	Tunnel dust	
Perth, Australia	20.5–419	19.8–440	3.7–91.4	Road dust (<63 μm)	Whiteley (2005)
	13.9–153	9.4–100	1.2–26.6	Soil	
São Paulo, Brasil	0.3–17	1.1–58	0.07–8.2	Road soil (high traffic)	Morcelli et al. (2005)
Seoul, Korea	0.4÷444			Soil and Road dust	Lee et al. (2006b)
Athens, Greece	127÷54.5	112÷52.8		Road side soil	Riga-Karandinos et al. (2006)
Sheffield, UK	8–606	8–1,050		Road side soil	Jackson et al. (2007)
	27–408	26–453		Road dust	
Beijing, China	4–356	0.1–125	2.7–97	Road dust	Wang et al. (2007)
Germany	50.4	43.3	10.7	Road side soil	Wichmann et al. (2007)
Beijing, China	7.60–126	3.38–57.5	.97–31.4	Urban soil	Pan et al. (2009)
	6.56 90.9	6.68–120	1.99–31.7		

(continued)

Table 6.10 (continued)

Location	Pt	Pd	Rh	Matrix	Reference
Guangzhou, China					
Hong Kong	15.4–160	6.93–107	1.61–34.5		
Macao, China	3.58–21.9	2.01–27.3	0.44–5.63		
Qingdao, China	3.72–9.72	3.26–13.4	1.00–2.88		
Mumbai, India	3.20–9.40	1.32–42.4	0.24–1.36		
Calcutta, India	2.59–9.43	1.31–4.07	0.40–2.27		
Hyderabad, India	1.5–43	1.2–58	0.2–14.2	Road dust	Mathur et al. (2011)
Palermo, Italy	0.6–2,240			Upper urban soil	Orecchio and Amorello (2011)
	0.3–16			Lower urban soil	
Prague-Ostrava, Czech Rep.	<0.7–7.7	<0.45–50.0	<0.08–3.86	Urban park	Mihaljevič et al. (2013)

Data on body fluids among the occupationally exposed population, e.g. PGE manufacturing workers, or among the population exposed to road traffic, show levels of Pt ranging between 150 and 450 mg L^{-1} (Kalavrouziotis and Koukoulakis 2009), while the normal levels fall in the range from 0.1 to 2.8 μg L^{-1}. Merget and Rosner (2001) reported that halogenated platinum salts act as sensitizing substances causing asthma, rhinoconjuctivitis and contact urticaria in the exposed population.

Recent studies on the effects of PGE-graded salts on the human health suggest that these compounds foster lymphocyte proliferation and cytokine release while, in addition, speciation influences their immune capacity. Chemical and biological interactions among trace elements and PGEs may affect their absorption and metabolism resulting in modified toxic effects. Correlations between Pt and Pd blood and serum concentrations suggest this kind of interaction (Barany et al. 2002).

It is generally accepted that, similarly to Cd and Cr, also Pt^{2+}, Pt^{5+} and Pd^{2+} give rise to toxic effects on cellular level, but with much worse damages than in the case of Cd. A lower toxic potential is reported for Rh (Krug et al. 2006; Nel et al. 2006).

According to Boscolo et al. 2004, in vitro activity of Pd compounds is higher than that of other PGE salts. This experimental result agrees with the increment of sensitization and allergenic contact dermatitis in relation to the increase of Pd levels in the urban population. In addition, as reported by Paolucci et al. (2007), PGEs can amplify the immune response to allergens while Linnett and Hughes (1999) report that PGE risk assessment could be based on the results of respiratory sensitizing potential of halogenated Pt salts.

6 Pt and PGE in Italian Urban Environment: A Case Study

With the aim to determine Pt background levels and the Pt time dependent accumulation factor in Italian urban and 'natural' soils, since 1992 a sampling campaign was carried out in some Italian cities. Globally, two hundred eight soil samples were collected from selected sites in the urban areas of Rome, Naples, Palermo and Padua, taking into account traffic intensity, pollution source distance, green areas extension, number of inhabitants and morphology. Soil parent materials were selected in order to be really representative of Italian geological setting and variability.

Preliminary results evidence that Pt concentration levels in urban soils are, in some cases, slightly higher than the average level in Italian "natural" soils. Moreover, a comparison between data from samples collected in 1992 and data from 2001 campaign, shows a slight but analytically significant increase of Pt, paralleling a Pb level decrease, clearly related to the large introduction of unleaded fuel.

In some cases, Pt in urban soils resulted to be slightly higher than the background concentration of Italian 'natural soils' (3.1 ± 2.1 ng g^{-1}), developed mainly on sedimentary and volcanic rocks. As a general consideration, soils deriving from limestone rocks evidence a wide concentration range for Pt (<1–6 ng g^{-1}), reflecting the variable contents of insoluble residue of these rocks.

No data on Pd and Rh levels in natural soils and related parent materials are reported for Latium (central Italy) because all concentrations were below the detection limit.

The Pt levels in various soil materials from Latium are plotted in Fig. 6.1 while the variation of the Pt levels in different environmental condition in Latium and Rome are reported in Fig. 6.2.

As a general consideration, Pt concentrations in the studied samples are higher in the dumped soils collected close to the main traffic roads (mean 10, max 13.8 ng g^{-1}), compared to the relatively undisturbed soils. Top soils are enriched in Pt, compared to bottom soils, confirming the explanation of a recent deposition of atmospheric particulate matter containing Pt particles emitted from vehicle exhaust.

While grain-size distribution generally affects PHEs (generally the Pb, Zn, Cd and Hg content increases with decreasing soil grain size), no significant relation was observed for Pt. This could be related to the low Pt concentration in soils which, at the present time, does not allow a clear discrimination between the background Pt levels and the contribution of Pt particles of size 5–10 μm released by vehicle catalysts. Moreover, it has been observed that Pt associated to particular matter is generally not readily mobilized, but redistributed in the various grain size fractions of soils (Fig. 6.3).

Similar data on Pt in urban soils have been reported by Cicchella et al. (2003, 2008) in a study on PGEs in soils from urban areas of the Campania region, southern Italy, along with data on Pd and Rh. The authors also discuss on the relationship between high population density and traffic, and PGE levels in soils. Data on Pt distribution in Palermo urban soils (Sicily) have been discussed by

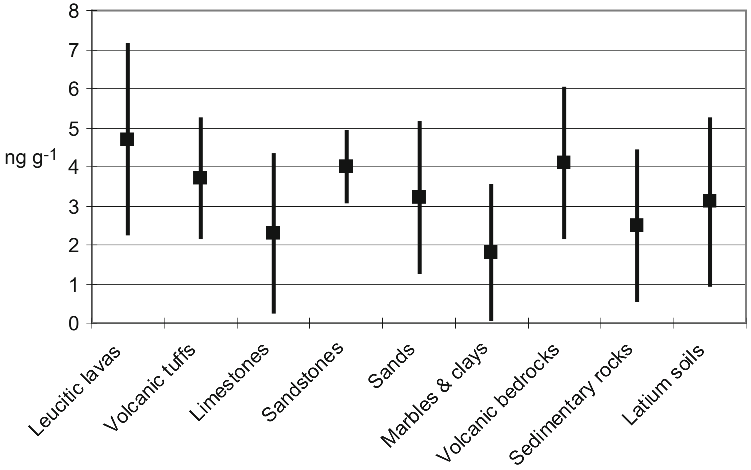

Fig. 6.1 Platinum in different soil parent materials from Latium, Central Italy

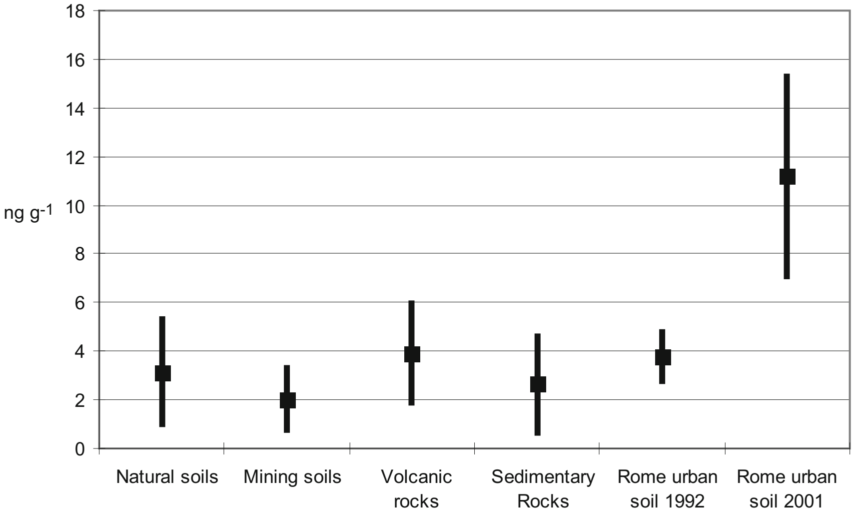

Fig. 6.2 Comparison of Pt levels in different matrices in the Latium Region and Rome (Italy)

Orecchio and Amorello (2010, 2011), while interesting data on Pt and Pd in pine needles from Palermo urban area have beer reported by Dongarra et al. 2003. A data collection of PGE in urban soils from some Italian cities is reported in Table 6.11.

Among the various particulate fractions emitted, the most abundant fraction (>10 μm) falls down and settle on the road-side within a few hours. The smaller particles (<10 μm) can remain in suspension even for several days while the smallest may be transported over long distances. As a consequence PGE accumulation in soils alters their natural geochemical background, which is very low,

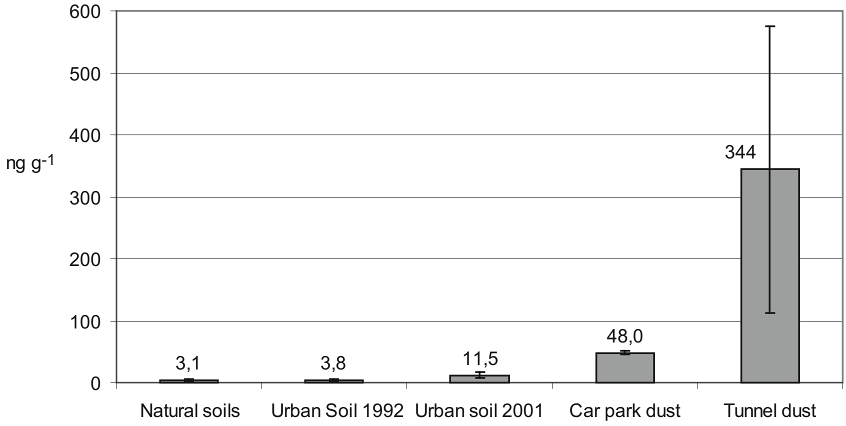

Fig. 6.3 Differences in Pt concentration in urban matrices in Rome, Italy

Table 6.11 PGEs in urban soils in some Italian cities (ng g^{-1})

City	Element	Mean	Median	Min.	Max.	Reference
Padova	**Pt**	1.4 ± 1.3	0.9	0.1	5.7	Cinti et al. (2002)
Rome	**Pt**	11.5 ± 4.7	10.6	7.0	19.4	
Viterbo	**Pt**	10.3 ± 3.6	9.6	4.9	20.0	
Naples	**Pt**	8.5 ± 2.5	8.4	4.7	14.3	
Palermo	**Pt**	1.0 ± 0.9	0.7	0.2	3.9	
Latium natural soils	**Pt**	3.1 ± 2.1	2.9	<1.0	5.0	Cinti et al. (2002)
Avellino	**Pt**	2.4 ± 1	2.1	1	6.1	Cicchella et al. (2008)
	Pd	2.2 ± 6.4	1.0 <0.05	<.5	38	
	Rh	<.06 ± .13		<.05	0.61	
Benevento	**Pt**	2 ± 3.3	1.0	0.4	18.4	
	Pd	1.5 ± 1.8	0.9	<0.5		
	Rh	<.05 ± .09	< 0.05	<0.05	8.7	
					0.6	
Salerno	**Pt**	13.1	2.1	<0.1	278	
	Pd	15.3	2.4		432	
	Rh	1.79	0.28	<0.5	47	
				0.07		
Palermo	**Pt** (range)			0.3	2,240	Orecchio and Amorello (2011)

usually in the order of few ng g^{-1} (Cinti et al. 2002). Winds and run-off waters can disperse and redistribute the top soil and dust PGE enriched particles at a considerable distance from their original source. (Barbante et al. 2001; Rauch et al. 2005).

Owing to transport modality in urban environment, road dusts are particularly enriched in PGEs, in fact their concentrations reach levels of one or more orders of magnitude higher compared to the levels of urban soils. As a consequence, dust is

Table 6.12 PGEs in tunnel and road dusts in some Italian cities (ng g^{-1})

City	Matrix	Pt	Rh	Pd	Reference
Naples	Tunnel dust	533 ± 564	73 ± 39	n/a	Angelone et al. (2007)
	Road dust	133 ± 106	23 ± 10,3	n/a	
Rome	Tunnel dust	344 ± 232	69 ± 49	563 ± 244	
	Road dust	44.3 ± 6,3	n/a	n/a	
Viterbo	Road dust	110 ± 26	n/a	n/a	

n/a, data non available

the most polluted matrix in the urban areas. Data on PGEs in urban soils and dusts from some Italian cities are reported in Tables 6.11 and 6.12.

The large standard deviation shows a great lack of homogeneity for the analyzed samples, which may be related to traffic conditions, roads morphology, wind direction, and presence of barriers. However, the data are generally in agreement with those reported in the literature (Ravindra et al. 2004).

7 Conclusions

Since ancient times, human activities have poured large amounts of hazardous substances into the environment, but issues related to urban environment pollution have started to gain attention only in the 60s. In the last 25 years we have witnessed a rapid expansion of urban and industrial areas without any control of the sources of contamination and with absolute lack of policies or regulations.

In natural conditions most of the PHEs are present at low concentration levels in soil. However, pollutant emissions due to human activity have become predominant compared to natural emissions. This fact is particularly evident when we consider the releases of some PHEs into the atmosphere due to, for example, mining activities or fossil material combustion. In addition to the consequences concerning strictly the environment, increased PHE levels have also affected the population health, especially in urban areas, where higher incidence of diseases related to an excessive presence of PHEs (e.g. Pb, Cd, Ni, As and Hg) is recorded. Moreover, until the mid-90s of the last century, the long-term negative effects of urban pollution on biota have been neglected. Nowadays, toxicological studies help us understand the potential effects of PHEs on the human and environmental health. The role of relatively recent industrial components, such as PGEs and REEs, is also considered, since there is a high concern about their impact on human health.

From the geological point of view, the research approach has hanged lately in order to better understand the complexity of the urban environment. While geochemical early studies involved only individual elements, a gradual tendency towards a multi-element approach can be now observed. This includes studies on the spatial distribution and interaction among different environments, which were made possible by the availability of recent technological innovations in the field of environmental analysis.

It is evident that, in urban environment, the vehicular traffic is still one of the most significant sources of contamination. Although the replacement of the gasoline Pb with alternative additives in new catalytic devices, which use high quantity of REEs, PGEs and Mn, has caused a substantial reduction of Pb in urban areas, it has also led to the introduction of previously unknown compounds and particles into the environment. The PHE potential hazard to humans is mainly related to their very fine dimensions and their consequent chemical-physical properties. Besides, their interactions with the biota are yet to be understood fully. The increasing frequency of respiratory diseases in the urban population, in particular among children and workers, is a clear evidence of the effect of the exposure to PHEs in urban road dusts.

Because the urban environment is the preeminent habitat for humans at the present time, a comprehensive assessment of urban soil resources and quality planning should be considered as a priority, in order to balance the effects of anthropic pollution. An harmonized assessment and comprehensive understanding of the legacy of PHEs in urban environment is the next challenge in order to create a sound platform for a sustainable management of urban areas along with the constraint of negative health consequences.

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Chapter 7
Remediation of Potentially Toxic Elements in Contaminated Soils

Jaume Bech, Maria Manuela Abreu, Hyo-Taek Chon, and Núria Roca

Abstract This chapter aims to offer an overview of the main remediation methods of potentially toxic elements in contaminated soils, mainly heavy metals, metalloids and radionuclides, focusing on their essential characteristics, advantages and limitations. It consists of two main groups of technologies: the first group dealing with containment and confinement, minimizing their toxicity, mobility and bioavailability. Containment measures include covering, sealing, encapsulation and immobilization through solidification (cement-based, polyethylene and resine binders, bituminization or asphalt batching and vitrification or glassification) and stabilization with inorganic and organic amendments. The second group, remediation with decontamination is based on the remotion, clean up and/or destruction of contaminants. This group includes mechanical procedures (excavation, transport and disposal to landfills), physical separations, chemical technologies such as soil washing with leaching or precipitation of potentially toxic elements, soil flushing, thermal treatments (desorption, pyrometallurgical processes and incineration) and electrokinetic technologies (electromigration, electroosmosis, electrophoresis and combinations of electrokinetics with other techniques). There are also two approaches of biological nature: bioremediation (biosorption, bioreduction, biomineralization and bioleaching-with some examples from Korea) and phytoremediation (phytoextraction, including chelate-assisted phytoextraction, phytostabilization, phytoremediation in mining activities -with examples from

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Portugal, Spain, Ecuador, Peru and Chile mainly-, phytovolatilisation and phytomining).

Keywords Soil remediation • PTEs • Soil containment • Bioremediation • Phytoremediation

1 Introduction

Soils are essential components of the environment, the basis of terrestrial ecosystems and a crossroad for biogeochemical cycles at the litosphere-hydrosphere-biosphere-atmosphere interface. Therefore, soils are a limited precious and fragile resource, the quality of which should be preserved. The concentration, chemical form and distribution of potentially toxic elements in soils depends on parent rocks, weathering, soil type and soil use. However, their concentration can be altered by mismanagement of industrial and mining activites, energy generation, traffic increase, overuse of agrochemicals, sewage sludge and waste disposal, causing contamination, environmental problems and health concerns.

In contaminated soils metals such as Pb, Cr, Zn, Cd, Cu, Hg and Ni are frequent. Metals such as Ba, Be, Al, V, Ag, Mo and Tl are less frequent. Metalloides such as As, Se and Sb and radionuclides such as U, Th, Pu, Am, Ra, ^{137}Cs, ^{90}Sr, and Po may also be present.

In general, heavy metals and some metalloids such as As and Sb as well as certain radionuclides are more persistent in the environment than organic pollutants; only Hg and Se can be easily bioremediated. This persistence of the potentially toxic elements hampers the cost/time/efficiency of remediation technologies making them very expensive and difficult. The choice of the most appropriate soil remediation techniques depends on the concentration, nature and distribution (local or diffuse contamination) of the potentially toxic elements, the site characteristics, soil type and soil properties, mainly texture, organic matter, pH and rH values (Wong et al. 1997; Mulligan et al. 2001). Obviously, the optimal election of the remediation technology needs the identification of the soil pollution problem, an applicable site, the end use of the remediated soil, risk assessment, baseline, regulatory limits, threshold and intervention values. Therefore, in the remediation technology for a specific site, not only cost, time and efficiency should be considered, but also the soil protection factor. The remediation process should be as soil protective as possible (Meuser 2013).

This chapter aims to offer an overview of the main remediation methods of potentially toxic elements in contaminated soils, mainly heavy metals, metalloids and radionuclides, focusing on their essential characteristics, advantages and limitations. It consists of two main groups of technologies: the first group dealing with containment and confinement minimizing their toxicity, mobility and bioavailability (Page 1997; FRTR 2002; Khan et al. 2004; Marques et al. 2011). Containment measures include covering, sealing, encapsulation and immobilization through solidification and stabilization (Sharma 2004). The second group, remediation with decontamination, is based on the remotion, clean up and/or destruction of contaminants. This group includes mechanical procedures, physicochemical technologies such as soil washing with leaching or precipitation of potentially toxic elements, soil flushing and thermal and electrokinetic treatments. There are also two approaches of biological nature: bioremediation and phytoremediation.

2 Remediation by Containment and Immobilization Measures of Potentially Toxic Elements in Soils

2.1 Soil Containment

This is a remediation approach of contaminated soils, impeding their contact with people and the environment and attempts to prevent their migration. It is not a final remediation procedure, but it is adopted to prevent actual exposure of diffusion of contaminants from the site, especially in groundwater under the polluted area. Containment is adopted when remediation is not feasible due to adverse effects of the cleanup (such as the handling of soils and the management of process residuals that may pose hazards i.e. radiation exposure in the case of cleanup of radionuclide contamination) or to excessive costs. The choice of containment is common in cases when a fast response measure is necessary as with radionuclide-contaminated soils. The most used methods in soil containment are: surface cover, side barriers and encapsulation.

2.1.1 Surface Cover

A surface cover or cap is a layer of uncontaminated soil or of synthetic liners such geomembranes, clays, asphalt, concrete and others, placed over the contaminated soil or landfilled waste. The complexity of the surface cover depends on the hazardousness and concentration of the potentially toxic elements present, soil properties (mainly texture, organic matter and pH value), topography and climatology of the contaminated area.

The goal of surface cover is to keep people and ecosystems from coming into contact with the potentially toxic elements of a contaminated site. Furthermore, the cover stops rain and snow, avoiding harmful elements from being carried to the groundwater. Moreover, it prevents running water from running off and wind erosion that could spread contaminants offsite or into rivers and lakes.

There are three main types of soil cover processes: topsoiling, soil covering or soil capping and sealing.

- Topsoiling or toposil cover is the most common reclamation method, and uses the natural topsoil cover or a ‘vegetative layer’ that is a top soil layer planted with grass. This method, which is the most natural and the simplest, consists of using unpolluted or ‘clean’ soil of the non-contaminated surrounding area. If topsoiling is not possible, there are other similar technologies of ‘covering’ or ‘capping’.
- Soil covering or soil capping: uses a single layer or composite or complex cover with several layers or multilayers. The thickness of the surface cover depends on the nature and concentration of the potentially toxic elements on the site that must be reclaimed, the future use of the area concerned (agricultural, forests, parks, gardens, playgrounds, sport fields, industrial, etc.) and the type of topsoil. It is therefore difficult to recommend a thickness, because this value must correspond to the specific characteristics of the contaminated site. Opinions for different cases differ. Delschen (2000) recommends a thickness of 40 cm and ideally a surface cover of 70 cm to avoid the transfer from soil-plant for certain crops and metals. Monitoring of the topsoil cap is necessary to ensure its protection. A disadvantage is that supplies of topsoil are not available locally. Another disadvantage is that the structure of the original ‘clean’ soil ‘in situ’ has deteriorated in its excavation and transport to the contaminated site. The unfavourable changes of the soil’s physical properties due to the vulnerability of aggregates can cause soil compaction. Other frequent problems are due to bioturbation created by the activities of earthworms, moles, mice and other edaphofauna species. Their dynamics can mix the clean or uncontaminated soils with the contaminated soils. For these reasons it can be necessary to install complementary groundwater monitoring wells around the covered site and periodical checking of the water composition to determine the possible leaking. Future excavations through the soil cap or mixing of clean and contaminated soil is not allowed. Topsoiling with a natural topsoil or with other materials in a single cover is appropriate for lightly contaminated soils, especially for insoluble contaminants. In case of ‘hot spots’ of more highly contaminated soils or landfill waste or for soluble potential toxic elements such as Cr^{6+}, it is recommended to use complex, composite or multilayer caps (Fig. 7.1).
- Sealing: for highly contaminated areas the complete sealing of the surface with asphalt or concrete can be recommended. In fact, the soil’s nature and properties (structure, porosity, edaphon, microbial activity, etc.) are lost. The new artificial surface is a hard slab or pavement layer only useful for roadway paving, parking lots or building slab foundations. Usually the sealed cover structures have a thickness of 10–20 cm. This cap surface must be graded and provided of a drainage system to avoid water ponding.

2.1.2 Side Barriers

The soil cover or soil cap only treats the surface of the polluted area which prevents the vertical entry of the rain water into the waste and the possible contact of the

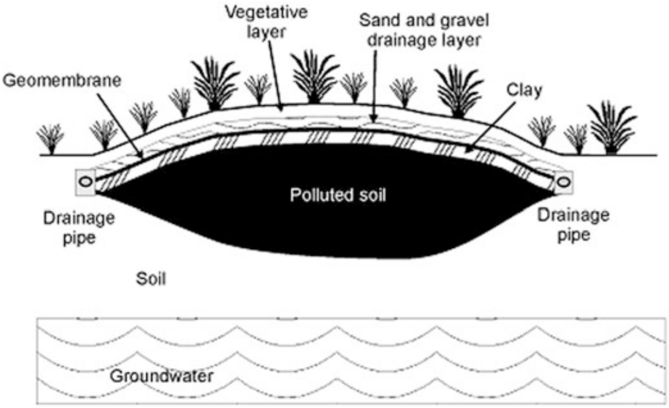


Fig. 7.1 Example of a cover with several layers (Drawing by N. Roca)

potentially harmful elements with people and the ecosystem. It cannot prevent the horizontal flow of ground water through the contaminated soil. For this reason subsurface barriers, especially vertical barriers are focused on the lateral migration of potentially toxic elements. The name used by some authors such as Wuana and Okieimen (2011) is 'vertical engineered barriers' (VEB). These barriers are made with slurry walls, grout walls or geomembrane curtains. Steel, cement and bentonite are also used. In acidic soils (pH 2–3) extreme caution is necessary because the steel can suffer corrosion. Furthermore, sheet pile walls of steel, bored pile walls and rounded piles or soilcrete columns are used. Also slurry trenches, cut-off walls are used as barriers, filled with slurry materials such as cement-water-bentonite mixtures. Horizontal barriers within the soil (trenches or wells) can restrict downward movement of potentially toxic elements by acting as underlying liners without the requirement for excavation. This is frequent in grout injections. Meuser (2013) offers detailed civil engineering methodologies of the subsurface barriers, pp. 175–184 of *Soil Remediation and Rehabilitation.* There have been problems with soil compaction and vertical boreholes that can increase the likelihood of contaminant migration (Mulligan et al. 2001).

2.1.3 Encapsulation

Encapsulation or isolation includes soil cover, side barriers as well as bottom sealing. The barrier system in this approach means a complete sealing of the contaminated site. Encapsulation is used when the bottom of the contaminated soil is located underneath the groundwater table or when the distance between the bottom of the contaminated soil and the groundwater is short. The advantage over the other approach of containment is a safer protection. The disadvantages are that it is an expensive technique and it is problematic to verify a complete sealing of the bottom. Moreover, this technique needs a long term monitoring using observation wells upstream and downstream. Furthermore, although the possibility of gas generation is scarce, it is not impossible (e.g. radon from radionuclides, As, Se and Hg volatilization from organometallic pollutants). Therefore, a gas drainage system is needed to avoid slow gas migration through the walls damaging buildings and posing a threat to humans.

2.2 Solidification

Solidification is a containment method for stopping the migration and the bioavailability of potentially toxic elements in contaminated soil by trapping them in a compacted solid mass. The soil nature changes in a monolitic block by means of treatment processes of cementation, using water and binding agents such as Portland cement, puzzolanic materials, fly ash, blast furnace slag, cement kilns, bitumen and polyethylene or thermal energy to melt the soil in the vitrification technique. The solidification is applied mostly to soils contaminated with cationic metals, and is only recommended to a limited extent for soils containing elements forming oxyanions such as Sb, As, Be, Cr, Se and V (Meuser 2013). Mulligan et al. (2001) thought that As, Cr^{6+} and Hg were not suitable for this type of treatment. Soils can be treated in situ or ex situ.

2.2.1 Cement-Based Solidification

Cement-based solidification reduces the mobility of metals thanks to the formation of immobile hidroxides and carbonates and due to the fixation of the metals into the mineral structure, especially in the lattice of a new hydrous calcium aluminium sulphate format named ettringite. The cement and Portland cement consist of Ca silicates and Ca aluminates, which with the water added during the procedure lead to hidrated Ca aluminosilicates and Ca $(OH)_2$, raising the pH value that favours the precipitation of some heavy metal contaminants (Marques et al. 2011; FRTR 2002). Moreover, the above mentioned Ca $(OH)_2$ reacts with CO_2 and originates $CaCO_3$, which increases the strength of the solidified product (Meuser 2013). The cement-based solidification improves in the presence of fly ash, which is cheaper than Portland cement. It can also be used like fly ash, volcanic tuff, kild dust and blast furnace slag. The potentially toxic elements contaminated soils is mixed with water, alkali additives like cement or CaO and the pozzolanic-based materials. One example of the application of this technology is the Colmix process (Mulligan et al. 2001) that uses slurry including cement, slag-based grout and lime, used to immobilize heavy metals and ammonium in a landfill in Scotland. Guo et al. (2006) used alkaline elements for immobilization of: Cd, Cr, Cu, Pb and Zn; Bhat et al. (2002), cement based solidification to Be contaminated soils. Some disadvantages of this technology are that the fly ash increases the volume of treated soil, that in the long term there is a disintegration of cements with a possible quick metal leaching (La Grega et al. 2001), and that consequently long term monitoring is necessary.

2.2.2 Solidification with Polyethylene and Resine Binders

Authors such as Marques et al. (2011) and Meuser (2013) reported this approach over the use of polyethylene binders for solidification of contaminated soils. The thermoplastic binders are heated previously, applied over dry soil, and then cool and solidify. Different resines are also used for solidification of contaminated soils, such as epoxide, polyester resin an urea resin. They need organic solvents, sometimes with toxic properties for human inhalation. These binders produce a strong solidified product. The period of time necessary to solidify the soil is relatively long. With time, one disadvantage of some of mentioned binders is their potential biodegradation, so a long monitoring period is necessary.

2.2.3 Bituminization or Asphalt Batching

Bitumen, derived from oil or asphalt from coal are used heated at 130–230 °C and molten and mixed with the contaminated soil, producing a mixture of extruded soils and bitumen. This mixture cools down and solidifies. This process can be improved by the addition of stabilising agents such fly ash or cement. Bitumen is the cheapest and most common thermoplastic binder (USEPA 1989). The solidified material can be used for roadway paving and car park construction purposes. The potentially toxic elements usually treated are: As, Cd, Cr, Hg, Pb and radionuclides.

2.2.4 Vitrification or Glassification

This is usually a in situ technology that uses electric power to heat and melt the contaminated soil and other earthen materials such as dewatered sludge, buried waste and mine tailings. Electric power (4 MW and voltage 12,500–13,500 approx.) is supplied to the graphite electrodes introduced into the soil that heat them until 1,600–2,000 °C. These high temperatures decompose organic contaminants and volatize some elements such as Hg. The remaining molten soil cools to form a monolitic glass like product that incorporates the potentially toxic non-volatile elements such as metals and radionuclides. This chemically inert glass product has a similar aspect to volcanic obsidian. The vaporized gases are collected by a special ‘hood’ and passed through an off-gas treatment system (Fig. 7.2). To start the procedure, a conductive mixture of flaked graphite and glass frit is placed just below the polluted soil surface between the electrodes to act as a starter path, since dry soil is usually not electrically conductive.

Vitrification has been used to remediate As, Cr, Sb, Sn, Co, Cu, Ni, Zn, Pb, Be and radionuclide polluted soils. After the vitrification technique, the soil is molten

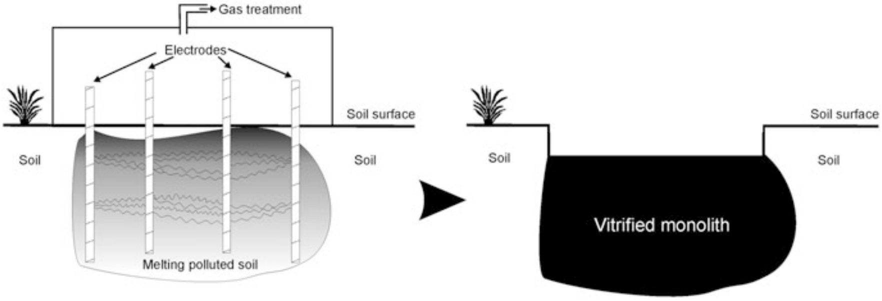


Fig. 7.2 Example of vitrification (drawing by N. Roca)

and very hot, sometimes taking more than 1 year to cool down. A disadvantage of this technique is the high energy intensity required. It is economically wise to keep the treatment zone as dry as possible prior to treatment. Wet soils are more expensive to treat because additional electric energy is needed to evaporate the water. Another disadvantage is the danger of subsidence due to volume reduction of 20–50 % of organic components and volatile metals (e.g. Hg). Moreover, the depth of the treatment of vitrification is currently limited to about 4–5 m. in a single melt. Deeper volumes of contaminated soil may be treated using a combination of staging and in situ treatment (USEPA 1995/540/R-94/520).

2.3 Stabilization or Fixation

Stabilization or Fixation is a remediation method that although does not destroy or remove the contaminants, reduces their mobility, toxicity and bioavailability through the use of soil amendments. These amendments can adsorb, complex or coprecipitate the potential toxic elements. This immobilization or fixation usually is in situ immobilization (Guo et al. 2006; Wang et al. 2009). The metals, metalloids and radionuclides of the contaminated soil after this remediation method remain in the soil, but in a form that is much less harmful, and the nature of the soil in contrast to solidification remains more or less intact. In reality, it is a chemical stabilization, a type of assisted natural remediation or attenuation. There are two main groups of amendments or fixing additives: inorganic and organic.

2.3.1 Inorganic Amendments

– Iron compounds: metallic Fe or zerovalent Iron, $Fe_{0,}$ is used as amendment in form of iron grit and steel shot for stabilize Cr, Cu and As contaminated soils (Bes and Mench 2008; Kumpiene et al. 2006) and removal soluble arsenate (Melitas et al. 2002). Moreover, the Fe_0 added to contaminated soil form iron oxides of high specific surface area that favorise the trace element sorption (Kumpiene 2010). Fe metal was also used as an amendment for immobilization of As in the reclamation of the closed mine of Salsigne (S. France). Iron Oxides can reduce the mobility of AS, Cd, Cu, Ni, Pb and Zn by sorption, co-precipitation or formation of secondary minerals which contain trace elements (Kumpiene 2010). $FeSO_4$ and $Fe_2(SO_4)_3$ reduce As mobility (Hartley et al. 2004). Red mud, an industrial by- product of the aluminium metallurgy that contains Fe and Al is efficient in the immobilisation of Cu, Cr and Zn (Kumpiene 2010).

- Mn oxides: these can bind and immobilize trace elements such As in form of precipitate of manganese arsenate. Moreover, Mn oxides can immobilize Pb, Cd and Zn (Kumpiene 2010). Likewise, synthetic oxide such birnessite have been used as sorbent of Pb and Cd, as well as of As (Mannig et al. 2002a).
- Al oxides: Al-natural oxides or components of waste by-products such as red mud, beringite and ettringite, derivated of aluminium manufacturing (from bauxite ore) have a high adsorption capacity and can immobilise Cd, Cr, Cu, Ni, Pb and Zn in processes in situ and ex situ.
- Liming compounds: liming materials such as lime ($CaCO_3$), quicklime (CaO) and $Ca(OH)_2$, dolomite Ca, $Mg(CO_3)_2$ and industrial by-products such as sugar foam (sugar beet lime) rich in $CaCO_3$, marble wastes and LSB (lime stabilized biosolid) are applied. These liming agents are effective in the reduction of the mobility of metal cations such as Cd, Cu, Ni, Pb and Zn, but the results are variable for oxyanions such as As and Cr. Moreover, liming increases the soil pH, which favours the oxidation of Cr^{3+} to the more mobile and toxic Cr^{6+}. The precipitation of As by carbonates needs more research.
- Gypsum ($CaSO_4 \cdot 2H_2O$) amendments were used in reducing Pb and Cd mobility in contaminated soils (Kumpiene 2010). Pb mobility is reduced because it precipitates as anglesite ($PbSO_4$). Gypsum was used for chemical mitigation of Pb pollution in urban soils (Tahaoun and Abdel-Bary 2000). The immobilization of oxyanions with gypsum is lower than with metal cations. This can be due to increased competitive sorption between $SO_4^{2-}$and, for example AsO_4^{3-}anions. The by-product phosphogypsum is also used to amend contaminated soils. However, the concentration of Cd, U, Th and some other harmful trace elements of the phosphogypsum must be controlled.
- Phosphates: the presence of trace elements in phosphate rock has been studied for some time. These elements are adsorbed and fixed in the lattice of the apatite by exchange and more or less partial replacement of Ca by other metals such as Pb in pyromorphite, $Pb_5(PO_4)_3Cl$. This affinity of metal cations to react with phosphates suggested the use of several phosphate amendments for soil remediation purposes. This reaction has been experimented with Cd, Cu, Ni, Pb and Zn. Bes and Mench (2008) assessed the stabilization of Cu-contaminated soils in this way. Chrysochoous et al. (2007) assessed Pb immobilization. Besides, phosphate minerals such as rock phosphate and phosphorites, phosphate-based salts and phosphoric acid have also been investigated. Industrial by-products like phosphatic slag and biogenic phosphate such as bone meal amendments for

remediation of Zn, Pb and Cd soil pollution (Sneddon et al. 2006) have also produced significant results. Phosphate amendments should be avoided when soil is contaminated with oxyanions such as As and Se, because phosphate competition with arsenate for sorption sites may increase As mobility and bioavailability. This technique of remediation must take in account that several phosphorite deposits have significant concentration of hazardous trace elements such Cd, Se, U, Th and others (Bech et al. 2010).

- Aluminosilicates: clays are fine-grained phyllosilicates built up of tetrahedrally (Si, Al, Fe^{3+}) and octahedrally (Al, Fe^{3+}, Fe^{2+}, Mg) sheets or chains. A special combination of sheets forms a layer. Clays are available for sorption of cationic elements and radionuclides due to the mainly negative surface area by ion exchange, chemysorption and surface precipitation. The cation exchange capacity (CEC) of clays ranges from 2 to 130 $\text{cmolc} \cdot \text{kg}^{-1}$ (e.g. kaolinite 2–15, illite 15–40, montmorillonite 80–130). Sepiolites are Mg-rich clays with fibrous texture and chain structure. Their CEC ranges between 4 and 50 cmolc/Kg. Recent studies referred to by Kumpiene (2010) treated the ability of clays for fixing As, Pb, Cd, Cu, Zn, Ni and Mn and radionuclides such as Cs, Sr, U, Th from contaminated soils. Bentonite (commercial name for montmorillonite) was used to fix Pb, Zn, Cu and sepiolites have been used to amend Cd, Cu, Pb, Zn contaminated soils. Kaolinites at low pH can develop a positive charge, and are therefore able to sorb anions, such as arseniate, in acidic soil conditions. The immobilization of As with bentonite to be pH dependent. At pH 4.6 there had been an apreciable fixation, but at pH 3.8 bentonite was shown to become incapable of sorbing As (Kumpiene 2010). A disadvantage of the use of bentonite are the possible problems of swelling by hydration and shrinking by drying. This dynamics can produce cracks which are negative in stabilization approaches.
- Zeolites: zeolites are tectosilicates of a $(Al,Si)O_4$ tetraedra framework with a robust open structure, pores and cavities, but without swelling and shrinking properties of the majority of clays. Because of the open structure Na^+, K^+, Ca^{2+} cations occupy these cavities and are exchangeable with ions of the contaminated soils. The immobilization of these potential toxic elements depends on the elements, pH and other properties of the soils and zeolite types (e.g. clinoptilolite). Zeolites have a high selectivity for Cd and Pb, but can also fix Cu, Zn, Tl, Mn, Co and As (reported by Kumpiene 2010). Muhabadi et al. (2007) referred soil Cd stabilization using an Iranian natural zeolite. Neutral pH is unfavourable for As immobilization. It seems that Fe-improved zeolites can be better for As sorption.
- Fly ashes and slags: coal fly ashes consist of ferroaluminosilicates rich in Ca, Mg, Na, K and with several concentrations of trace elements such As, B, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn (Kumpiene 2010; Kumpiene et al. 2008). The pH of fly ash ranges from acidic to alkaline depending on the coal, fuel or wood original composition. Alkaline ashes can improve the pH of acidic soils and mine spoils. Ashes can also improve the texture of sandy soils and actually immobilize potentially toxic elements of contaminated soils and decrease their

bioavailability and harmfullness. Fly ashes can immobilize cationic trace elements such as Cd, Cr, Cu, Ni, Pb and Zn, but not be adequate for the stabilization of oxyanions such as arsenates and chromates. It seems that the fixation of cationic elements is due to an increase in pH that causes their precipitation, and the increase of surface area of the soil promotes the sorption, complexation and cation exchange reactions. The composition of ash varies largely and must be analysed, especially its trace element contents, when used as an amendment for the stabilization of contaminated soils.

2.3.2 Organic Amendments

Tables I and III of the work of Guo et al. (2006) summarises the most important immobilizing organic agents used for soil remediation. These are mainly waste components, and their fixation of metals is due to the sorption to oxygen-containing functional groups such as –COOH, phenol and –OH. These groups can dissociate their H^+ ions, which favorise ion exchange, complex formation, and the adsorption and chelation with trace elements. The most spread waste is sewage sludge, by-product of wastewater treatment processes used as “biosolid”. They are also used for fixing potential harmful elements of contaminated soils, domestic refuse, manure compost, poultry and cattle manure, useful to fix Cd, Cu, Pb, Zn. The use of the cited biodegradable wastes however, can give reasons for concern in the release of their own trace elements. But the use of waste as amendments for contaminated soils is a possible option for reclamation because the concentrations of trace elements in domestic biosolids are lower than those found in industrial and mining areas. Other resources of organic amendments for metal immobilization are: straws of cotton, rice and maize and rice hulls used to fix Cd, Cr, Pb, bagasse of sugarcane for Pb, waste water of paper mills for Cd, Cu, Hg, Ni, Pb and Zn and bark and sawdust. The latter are effective because of their high tannin content. The phenolic hydroxyl groups of tannin easily form chelates with metals when ion exchange happens. Both mechanisms can favorise the fixation of Cd, Hg, Cu and Pb of contaminated soils. Peats have a great affinity for Cd, Cu, Pb and Zn (Kumpiene et al. 2008). A disadvantage of peat is its high affinity for water and a tendency to shrink and swell by drying and weeting, producing bad stability. Brown coal had been used as a detoxicant of soils polluted with Pb, Cu and Zn (Shestopalov and Bezuglova 2000).

3 Remediation with Decontamination: Remotion, Clean-Up and Destruction of Contaminants

3.1 Physical Separation Techniques

3.1.1 Excavation, Transport and Disposal to Landfills

Excavation and physical removal of the contaminated soil has been the conventional remediation method most used up to now. Excavation of contaminated soil involves digging it for ex-situ treatment using a mobile treatment facility brought to the site. If the soil is treated on site, the soil may be used to fill in the excavated area. Advantages of excavation are: (1) to be a cost-effective approach for small amounts of contaminated soil and (2) the complete removal of the contaminants relatively and a rapid clean up of a contaminate site. Disadvantages: (1) the contaminants are simply moved to a different place, with the exception of the complementary use of a mobile treatment facility, and (2) the excavated soil transport needs safety precautions (e.g. swelling processes, oxidative reactions, spreading prevention, etc.).

3.1.2 Mechanical Separation

Some processes based in the mining industry are used ex-situ to remove smaller more polluted particles, versus the larger ones. Size and density are two decisive factors in separation procedures. Dry conditioning procedures can be combined with particle size separation by using static and vibratory screeners. Air flow or centrifugal force can be used. Air cyclone separators are frequently used. By wet conditions procedures the material can be treated by sedimentation and flotation. Addition of froths and aeration causes the contaminated particles to float (Mulligan et al. 2001). Materials such as ferrous slag are removed by magnetic overhead belts (Meuser 2013).

3.2 Chemical Treatment

The chemical treatments are based on the redox reactions and used to change harmful contaminants into less toxic or less mobile ones.

In situ chemical oxidation or “ISCO” uses “oxidant agents” such as potassium permanganate, persulphate, hydrogen peroxide, hypochlorite, chlorine gas and chloride dioxide. These oxidants are injected into wells and spread into the surrounding contaminated soil and groundwater. One example of oxidation is As^{3+} toxic to As^{5+} less toxic. In situ chemical reduction or “ISCR” uses “reducing agents” such as sodium dithionite, sulphur dioxide, sulphite salts, ferrous sulphate

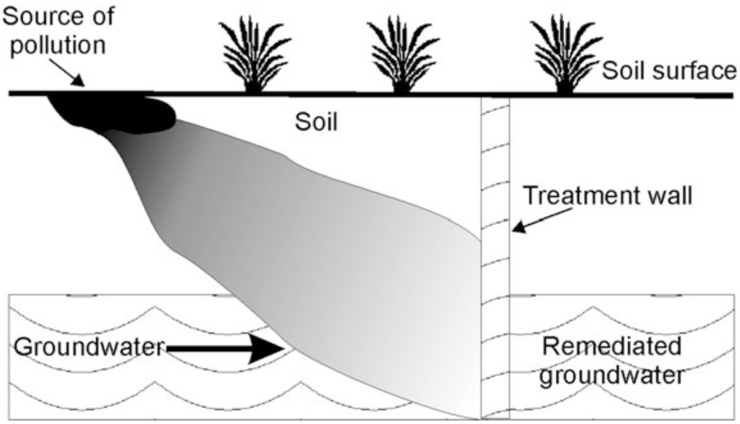


Fig. 7.3 Model of in situ treatment with a PRB (Drawing by N. Roca)

and zero valent metals (e.g. zero valent iron ZVI). These reducing agents change contaminants into their less toxic or less mobile species. ISCR can clean up elements such as Cr^{6+} that is reduced to Cr^{3+}, less toxic and less soluble in water. The most usual ways of ISCR (USEPA 2012) are two: (a) direct injection, and (b) the use of a permeable reactive barrier or PRB. Both techniques are in situ treatments, which are advantageous because they avoid excavation, always environmentally drastic and expensive in equipment.

(a) Direct injection involves mixing the reducing agent with water to create a slurry, which is pumped down holes drilled directly into the contaminated soil.
(b) A PRB or permeable reactive barrier, also named a permeable treatment wall, is built below ground by digging a trench and filling it with several of the cited reducing agents. Iron filings of ZVI are commonly used. The figure shows the soil and/or groundwater contaminated with Cr^{6+} flowing through the PRB allowing Cr^{6+} to react with the reducing Iron ZVI and flowing out the other side with Cr^{3+}.

ISCR using direct injection can clean up a contaminated soil in a few months, while PRBs may take several years. But the actual clean up time vary from site to site (Fig. 7.3).

3.3 Soil Washing

Soil washing is a minimisation treatment by concentration of heavy metals into a smaller volume of soil by physical separation, usually followed by a chemical extraction (Dermont et al. 2008). It is done mainly ex situ, and less in-situ, without excavation. This technology is widely used in Northern Europe, America and

Japan. A case cited by Meuser (2013), it was the soil remediation process used in the Olympic Park in Stratford, London.

Physical separation processes exploiting differences between particle grain size, density, hydrophobic surface behaviour, magnetic susceptibility and others, to separate harmful trace elements bound preferentially to clay and silt fractions, from the coarse fractions sand and gravel. The techniques used, based in mining and metallurgical industries are: mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, attrition scrubbing and others. The polluted sludge, mainly associated to the clay and silt fractions, separated and dried, must be passed through filter presses. Finally, the "filter cake" obtained must be decontaminated (e.g. by solidification, thermally, etc.). Chemical extraction or chemical leaching using various solubilising agents such as inorganic acids: H_2SO_4, HCl, HNO_3 (pH <2), salts: sodium citrate, sodium dithionite, organic acids: acetic, iminodiacetic, citric, malic, oxalic, tartaric (pH <4), bases: NaOH, Na_2CO_3, CaO (pH >9), chelating agents: citric acid, tartaric acid, EDTA, DTPA, NTA (Wuana et al. 2010). Some workers had been used HCl and H_2SO_4 to extract: Pb, Cu, Zn, Cr, Hg and As (Moutsatsou et al. 2006; Meuser 2013). Others use citric acid, tartaric acid and EDTA for Cd, Cu, Ni, Pb, Zn (Wuana and Okieimen, 2011), EDTA for Cd and Pb in Laurion (Karvounis and Kelepertsis 2000), EDTA, DTPA and citric acid (Bricka 1997), citric and fluorosilicic acid for Cr and citric, fluorosilicic, DTPA and NTA for Cd and Pb (Neale 1997). The washing treatment has also been used to separate and concentrate radionuclides such as Plutonium, Americium, ^{137}Cesium and Uranium (Bradbury and Scrivens 1995; Grace et al. 1995). Though less used, we must cite in situ soil washing.

In situ soil washing: is a soil washing approach without excavation. It is a high pressure technique. Steel tubes are arranged with a vibrator and situated until about 10 m deep. A high pressure jet is used to loosen the soil and to form a sludge that is pumped out of the ground (Meuser 2013). This soil-water suspension, with pollutants is treated with a suitable decontaminant. This technological approach is possible in sandy soils. Clayey and humic soils are not adequate to this technique. In general, ex-situ and in-situ soil washing provides a cost effective way of reducing soil contamination, especially at larger sites, but does not destroy the potential harmful elements of contaminated soils. The contaminants are simply moved to a different place, and is therefore not adequate to wash complex waste mixtures of metals and organics.

3.4 Soil Flushing

Soil flushing is an in-situ remediation technology that removes the contaminants from the soil with water or water with additives injected at high pressure to enhance contaminant solubility. The flushing solution passes through in place contaminated soils using an injection or infiltration process (Khan et al. 2004). The potentially toxic elements are moved to an area where the flushing wastewater charged with

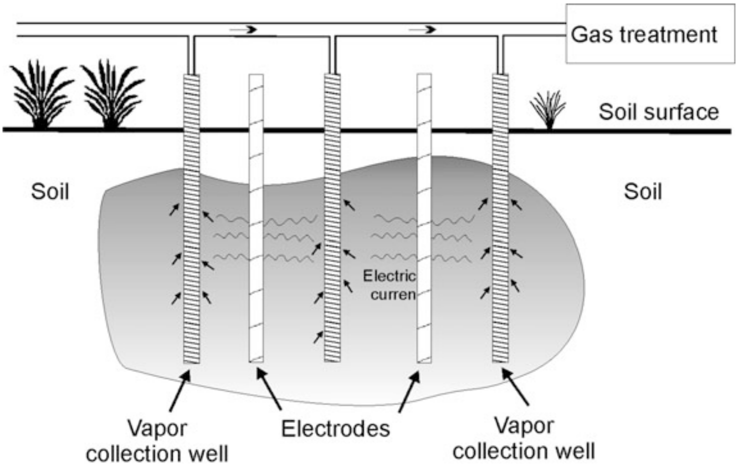


Fig. 7.4 An example of thermal treatment (Drawing by N. Roca)

them is captured and pumped to the surface using groundwater extraction wells. This wastewater must be treated to remove the metals which can be reutilized into the flushing process. The chemical enhanced flushing includes addition of solvents and complexing agents, previously cited in the Soil Washing section. The use of non toxic additives is recommended to minimize soil degradation. Soil flushing is currently used as an in situ soil washing process. Soil flushing can be applied in the remediation of contaminated soils by heavy metals and radionuclides. Some examples are: Cd (Urlings 1990), Cr (USEPA 1996), Cu (Di Palma and Medici 2002; Tsang et al. 2007) and Cu and Zn (Swab et al. 2008). Soil flushing is a cost reasonable technique if the contaminated soil has a good permeability ($>1.0 \times 10^{-3}$ $\text{cm} \cdot \text{s}^{-1}$). Some limitations are: low permeability of clayey soils, heterogeneity of soil. Deeper groundwater results in higher costs.

3.5 Thermal Treatment

This is a physical remediation technology that heats contaminated soil. In situ the heat is applied underground directly to the contaminated area and the potentially toxic chemicals move through the soil toward wells where they are pumped off (Fig. 7.4). Three techniques were mainly used:

1. Steam enhanced extraction (SEE), injects steam underground that heats the contaminated site and mobilises and evaporates contaminants.
2. Microwave heating, shows a high degree of effectiveness for removing organic pollutants from soils with low permeability like clayey soils (Meuser 2013).

3. Thermal conduction heating (TCH) uses heaters located in underground steel pipes.

Ex situ (on side and off site) thermal treatments involve several types such as: thermal desorption, pyrometallurgical processes and incineration.

3.5.1 Thermal Desorption

Removes but does not destroy contaminants from soil in a machine called a "thermal desorber", usually a rotary kiln and thermal screw to evaporate the contaminants, mainly organics. It is not generally used to treat metals, but can partially remove some such as Hg and the metalloid As. There are two groups of procedure based on the operating temperature of the desorber: (1) Low temperature Thermal Desorption (LTTD) in which contaminated soil is heated between 90 and 320 °C and High Temperature Desorption (HTTD) in which wastes are heated from 320 to 560 °C (FRTR) or 700 °C according to Chang and Yen (2006). HTTD can eliminate Hg and reduce the concentration of As an Cd of contaminated soils, but without their complete volatilization.

3.5.2 Pyrometalurgical Processes

Many installations during the high temperature phase in a second rotary kiln operate without oxigen- pyrolysis-. This is named pyrometallurgical separation, and is used to volatize metals (Mulligan et al. 2001). Separation of metals is not easy due to their high boiling points (e.g.: Hg, 357; As, 613; Cd, 767; Zn, 907; Pb, 1,740, Cu, 2.395; Cr, 2.599 °C). With the exception of Hg and As, metals cannot usually be treated with this process.

3.5.3 Incineration

Is the process of burning hazardous materials at temperatures high enough (970–1,200 °C) to destroy contaminants. The incineration usually operates in presence of oxygen. This technique can eliminate Hg, As, Cd and Zn, but not Cr and Pb. Mulligan et al. (2001) including Pb, Au and Pt between the metals that can be recovered by pyrometallurgical separation, but USEPA (2012) asserts that incineration does not destroy metals such Pb and Cr. For Meuser (2013), incineration causes vitrification of the metals, and at least immobilises them temporarily. An exception was Cr, which in alkaline conditions can generate toxic and mobile chromate (Cr^{6+}) (Fig. 7.5).

Fig. 7.5 Example of offside incinerator (Mataró, NE Spain)

3.6 Electrokinetic Remediation

Electrokinetic treatment is mainly an in situ remediation technology (but can also be used ex situ), designed to remove radionuclides and heavy metal contaminants from soil by passing a low intensity electric current between a cathode and an anode embedded in the contaminated soil (Acar et al. 1995). Positively charged metal or metalloid cations such as Cr^{3+} and As^{3+} migrate to the negatively-charged electrode (cathode), while metal or metalloid anion such chromate (CrO_4^{2-}) and arsenate ($H_2AsO_4^{-}$) move towards the positive charged electrode (anode). Upon their migration to the electrodes the contaminants may be removed by electroplating, precipitation, co-precipitation, pumping near the electrode or complexing with exchange resins. The electroremediation technique can be applied at great soil depths. In most cases, one central cathode is installed surrounded by a number of external anode electrodes. The maximum distance between electrodes should be restricted to 10 m, the usual maximum depth is 12 m and the tensions (voltage) applied vary from 20 to 100 Vm^{-1}, exceptionally 500 Vm^{-1} (Meuser 2013). Most soils contain water in the pores between the soil particles and have an inherent electrical conductivity that results from salts present in the soil. Electrokinetic remediation uses the current that mobilizes charged species, particles and ions in the soil. The main strategies used are: electromigration, electroosmosis and electrophoresis (Meuser 2013) (Fig. 7.6).

3.6.1 Electromigration

Electromigration is based on the transport of soluble cations, anions and no polar substances, mass flow or advection, dissolved in the pore fluid. It is feasible in different textural classes, but most effective in coarse grained soils. The ion velocities of electromigration are 5–40 times higher than those of the electroosmosis. The water content must correspond to 50–70 % of the field capacity. An

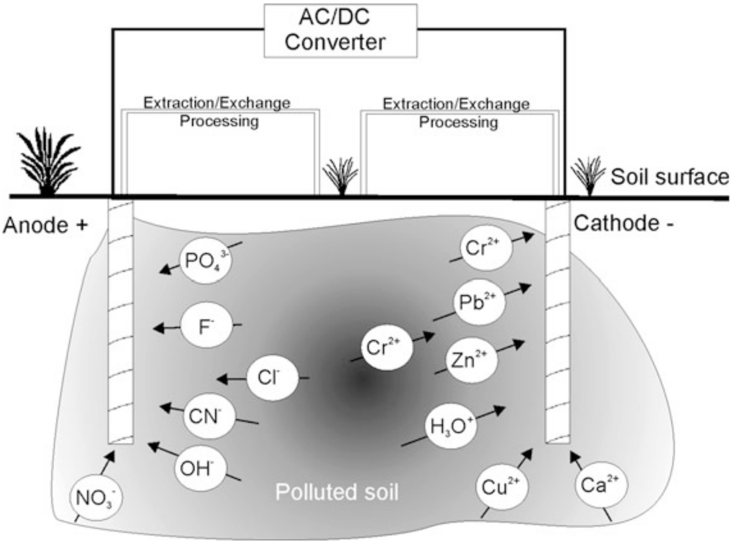


Fig. 7.6 An example of electrokinetic remediation (Drawing by N. Roca)

electrical gradient initiates movement of charged chemical species and follows with their transport to the electrode of opposite charge.

3.6.2 Electroosmosis

Electroosmosis is the movement or transport of pore fluid under an electrical gradient from the anode to the cathode that follows the principle of a cation and water film movement through the diffuse double layer of clay minerals. Clay minerals provide diffuse double layers with negatively charged surfaces. The electroosmosis treatment is preferentially applied to silty and clayey soils because the presence of clay minerals is required. This option is advantageous in soils with low permeability difficult to treat by traditional technologies. The suitable water content must be of 80 % of the field capacity.

3.6.3 Electrophoresis

Electrophoresis is the transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner (Van Cauwenberghe 1997). This charged particle movement under an electric gradient is mostly present in sandy and pebbly soils, coarse-grained soils with a lot of macropores (Meuser 2013). The best water content corresponds to 50–70 % of the field capacity.

3.6.4 Factors Affecting Electrokinetic Technology

The efficiency of the electrokinetic treatment is influenced by several factors:

- Contaminant properties: the applicability of electrokinetics to contaminated soil depends of the cation type and concentration, their solubility in the specific soil, their electrical charge and ionic mobility and their location and form in the soil.
- Salinity and cation exchange capacity (CEC): this technology is most efficient when these parameters are low. The electrical conductivity (EC) of the pore water is a decisive factor in determining the efficiency of the electrokinetic process.
- Soil moisture: electrokinetic treatment requires adequate soil moisture. It is possible in saturated and unsaturated soils, but is most applicable to saturated soils. There is a minimum moisture content at which electromigration can take place that corresponds to residual moisture called "immobile water". For optimum results, it should be less than saturation (Van Cauwenberghe 1997). Therefore, addition of a conducting pore fluid may be required.
- Soil type, grain size and structure: electrokinetic remediation technology is most applicable to homogeneous soils with high permeability, but may also be applicable to low permeable soils such as clayey soils, due to their large surface area which provides numerous sites for reactions necessary for electrokinetic processes.
- pH: the pH gradient influences the movement of the ions. The pH can affect the electrochemical process and cause precipitation of contaminants, reducing soil permeability and inhibiting recovery. The deposition of precipitated solids may be prevented by flushing the cathode with water or a dilute acid (Van Cauwenberghe 1997).

3.6.5 Technology Advantages

Electrokinetics can be used either in situ or ex situ and can be very cost-effective in both uses. This technology can be used in saturated or unsaturated soils because of the insertion of pore fluid. This process is an effective method of inducing movement of water through clay soils, of low permeability, which normally are very difficult to treat by traditional technologies such as soil flushing. Electrokinetic remediation may be able to be performed without the addition of chemical agents, such as strong acids that could destroy the soil structure. This technology applied in situ does not require excavation of contaminated soil and can work at great soil depths. Electrokinetics in situ not only avoids excavations that are dangerous adjacent to buildings and difficult areas, but can even be used under buildings.

3.6.6 Technology Limitations

The effectiveness of electrokinetic treatment may be limited by a variety of cation type and concentration, soil characteristics such as texture, organic matter, carbonates and pH. Heavy metals in their metallic state have not been successfully dissolved and separated from soil samples. The treatment depth is limited by the depth to which the electrodes can be placed. Heterogeneous soils with large rocks or gravel, or containing technogenic substrates such as building foundations, rubble, buried metallic or insulatic material can interfere with the electrical conductivity of the soil and therefore the voltage gradient, and even short circuit the system. Electroremediation can enhance the soil temperature, eventually reaching more than 60 °C, causing soil drying and a cessation of the fluid flow. Moreover the edaphon will be strongly disturbed.

In situ electroremediation has a detrimental impact on soil microorganisms because at the anode (pH 2) base- tolerant species are killed and at the cathode (pH 12) acid-tolerant species are also destroyed. Several polarization effects can decrease the electric potential and therefore the effectivity of the electrokinetics process. Most of the cations will precipitate at the cathode as oxides, hidroxides and carbonates because the pH 12 favours the precipitation, but a successful decontamination depends on permanent maintenance of the metal solubility. Thus, a high precipitation rate may reduce the effectiveness of the electroremediation, since clogging of the pores may occur resulting in a cessation of the flow.

3.6.7 Combining Electrokinetics with Other Techniques

In this section some methods developed by combining electrokinetics with other techniques are cited. There are mainly trademarked or patented commercial processes:

- Extraction and removal by electrodeposition, separation, condensation, precipitation or ion exchange either at the electrodes or in a treatment unit (Electrokinetics, Inc and EPA).
- Use of electrode well for both anodes and cathodes and the management of the pH and electrolyte levels in the electrolyte streams of the anode and the cathode (Patent of Geokinetics International, Inc., GII, 1995).
- Electrokinetic movement and capture of Uranium in contaminate soil (Isotron Corporation).
- Electroacustical soil decontamination is a technology that combines electrokinetics with sonic or ultrasonic energy to remove metals (Battelle Memorial Institute and EPA 1992).
- Lasagna is an in-situ remediation process, combining electroosmosis and in-situ sorption in treatment zones (Ho et al. 1995).
- Combination of organo-acid leaching of metals of the contaminated soil and electrolysis of the extract, avoiding the deposition of highly contaminated

residue. The leachate thus, can be reused for leaching. This process is applied for soil contaminated with Cu, Pb, Sb and Cd (Thöming and Calmano 1995).

3.6.8 Summary of More Cited Treatable Contaminants

The following potential toxic elements have been remediated by electrokinetic treatments in situ at full-scale, pilot scale and bench-scale applications and efficiency reduction range between >74–95 %.: Pb, 14 citations; Cr, 13 cit.; Zn, 11 cit., Cd, 9 cit.; Cu, 8 cit., Ni and Hg, 7 cit., As, 6 cit., Fe, 2 cit.

Between Radionuclides: U, 5 citations, Th, 3 cit., Ra, 2 cit., ^{90}Sr, 1 citation, ^{137}Cs, 1 cit. Cr and As have been remediated either such as cations Cr^{3+}, Cr^{6+}, As^{3+}, As^{5+} or anions arsenate $H_2AsO_4^-$and chromate CrO_4^{2-}.

This summary is mainly based on the data reported by: Acar et al. 1995; USEPA 1997; Van Cauwenberghe 1997; Puppala et al. 1997; Sobral and Thoming 1998; Reddy and Chinthamreddy 1999; Mulligan et al. 2001; Virkutyte et al. 2002; Page and Page 2002; Gent et al. 2004; Sharma 2004; Mascia et al. 2007; Beukes et al. 2012; Meuser 2013.

3.7 Bioremediation

Conventional physicochemical technologies to remediate heavy metals-contaminated soil and sediment have many problems such as low efficiency, high cost and occurrence of byproducts. Recently bioremediation technology is getting more and more attention. Bioremediation is defined as the use of biological methods to remediate and/or restore the contaminated land. The objectives of bioremediation are to degrade hazardous organic contaminants and to convert hazardous inorganic contaminants to less toxic compounds at safe levels (e.g., Lovley et al. 1989; Lovley and Phillips 1992). The use of bioremediation in the treatment of heavy metals in soils and sediments is a relatively new concept. Bioremediation using microbes has been developed to remove toxic heavy metals from contaminated soils in laboratory scale to the contaminated field sites. Recently, the application of cost-effective and environment-friendly bioremediation technology to the heavy metals-contaminated sites has been gradually carried out in Korea (Lee et al. 2005; Lee et al. 2006; Park et al. 2006; Chon et al. 2011; Kim et al.2011a).

The merits of bioremediation include low cost, natural process, minimal exposure to the contaminants, and minimum amount of equipment. The limitations of bioremediation are length of remediation, long monitoring time, and sometimes, toxicity of byproducts for especially organic contaminants. From now on, it is necessary to prove the applicability of these technologies to contaminated sites and to establish this highly effective, low-cost and easy bioremediation technology.

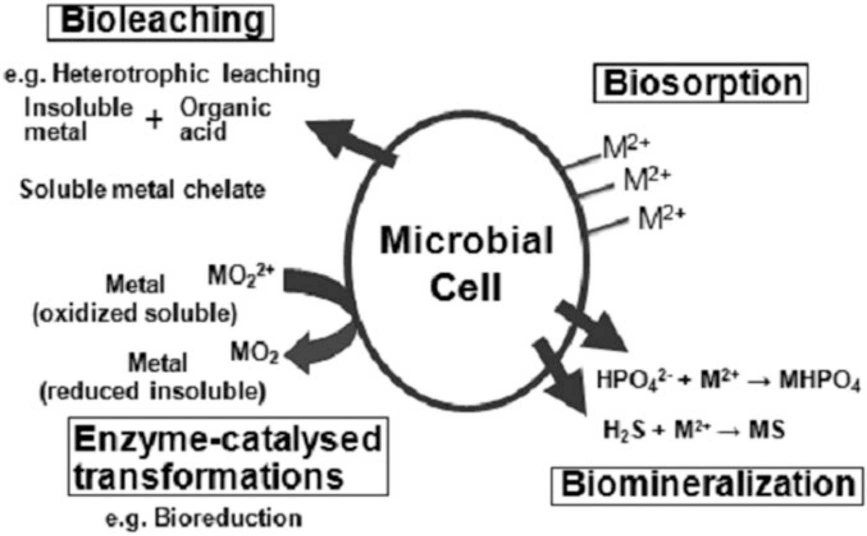


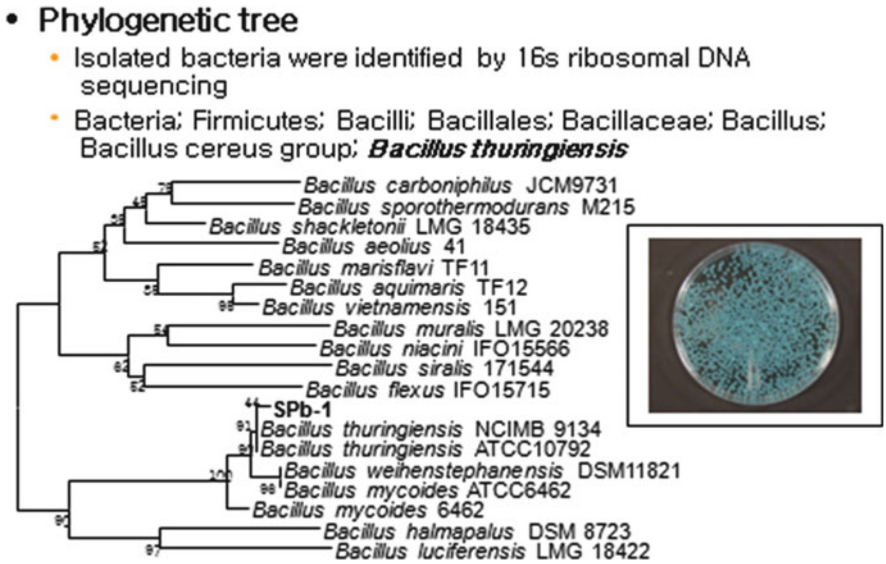
Fig. 7.7 Metal-microbe interactions; biosorption, bioreduction, biomineralization and bioleaching

Four categories of metal–microbe interactions are generally (1) biosorption, (2) bioreduction, (3) biomineralization and (4) bioleaching (Fig. 7.7). In this chapter, some case studies of the above metal-microbe interactions which were published recently in Korean domestic journals and international journals will be introduced and summarized (for example, Kim et al. 2009a, b; Lee et al. 2008a, b; Jang et al. 2009; Kim et al. 2011b; Lee et al. 2011).

3.7.1 Biosorption of Heavy Metals in Soils

Bacterial cell walls are negatively charged under circumneutral pH conditions and they can passively adsorb positively charged metal ions. This electrostatic complexation is followed by further deposition of dissolved metals and, then, development of biominerals at the cell surfaces (e.g., Beveridge and Murray, 1980). Some experiments have been designed to determine whether complexation and subsequent mineralization of metals onto microbial cell walls can be explained by surface complexation models as has been applied to inorganic particles (Fein et al. 1997; Warren and Ferris 1998).

Biofilms are microcosms consisting of microorganisms distributed throughout a matrix of fibrous and highly hydrated, extracellular polymeric substances (EPS), which are often exopolysaccharides. By forming biofilms in natural settings, a community of bacteria can better obtain nutrients in oligotrophic environments and protect themselves from a variety of unfavorable conditions such as dehydration, chemical toxicity and predation (Costerton et al. 1995). The local effects of



- Phylogenetic tree
  - Isolated bacteria were identified by 16s ribosomal DNA sequencing
  - Bacteria; Firmicutes; Bacilli; Bacillales; Bacillaceae; Bacillus; Bacillus cereus group; ***Bacillus thuringiensis***

Fig. 7.8 Identification of the isolated bacterium from contaminated soil (SPb-1) (Kim et al. 2009a)

biofilms on geochemical processes, such as redox and pH, could drastically alter the state of metals and metalloids thereby influencing the degree of metal accumulation or mineral dissolution (Lee and Beveridge 2001).

Kim et al. (2009a, b) studied the biosorption of Pb and Cd to apply for the remediation of contaminated sites through the reduction of heavy metal mobility by using indigenous bacteria from the soil, and to evaluate the characteristics of biosorption onto biofilm according to various environmental factors which can affect the sorption of toxic heavy metals. Indigenous bacterium having a tolerance to high Pb (353 mg kg^{-1}) and Cd (3.2 mg kg^{-1}) toxicity was isolated from Pb and Cd-contaminated soil which was concomitantly contaminated with TPH (total petroleum hydrocarbons). The bacterium was identified as *Bacillus thruingiensis* by 16 s rRNA sequence analysis and named SPb-1 (Fig. 7.8).

As a result of batch-type biosorption experiments using SPb-1, the highest removal rates of aqueous Pb and Cd were observed with the initial concentration of Pb and Cd less than 100 mg L^{-1} and 5 mg L^{-1}, respectively (Fig. 7.9). The optimal operating conditions of Pb and Cd biosorption were as follows; culture age of over 16 h to stationary growth phase, biomass amount of more than 2 g L^{-1}, pH 5–9, and temperature at 25 °C and 35 °C for Pb and Cd, respectively (Fig. 7.10).

Acrylic columns with dimension of 5 cm diameter and 31 cm height were filled with the contaminated soils and a variety of carbon sources – acetate, lactate and glucose – and deionized water as a control were made to pass through the columns to instigate formation of biofilm. Effluent volume ratio through the columns with acetate, lactate and glucose supply showed 98.5 %, 97.3 %, and 94.7 %,

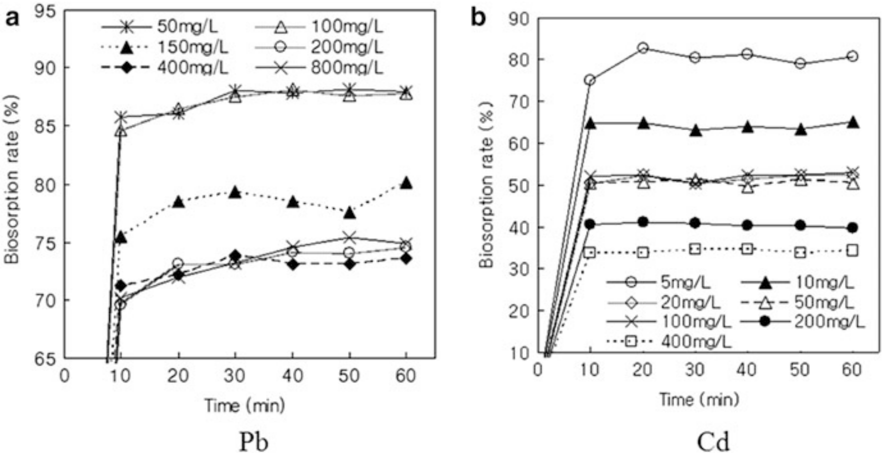


Fig. 7.9 Biosorption rates of Pb and Cd by Spb-1 according to the initial concentration of heavy metals (Kim et al. 2009a)

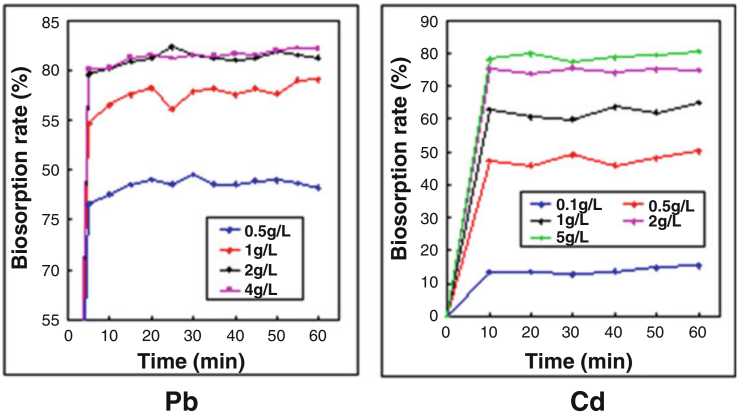


Fig. 7.10 Biosorption rate of Pb and Cd with bacteria concentration (Kim et al. 2009a)

respectively, when compared to deionized water. This was likely due to the biofilm formation in pore and the flow of injected carbon source solution might be limited.

Biofilm developed onto the soil particles through supply with carbon sources adsorbed higher concentrations of heavy metals than control. Maximum removal rate of metals by sorption onto biofilm depended on the type of carbon sources; for example, glucose for Cr and Cd adsorption and acetate for Cu and Zn adsorption (e.g., Fig. 7.11). The results suggest that in-situ stabilization of dissolved toxic

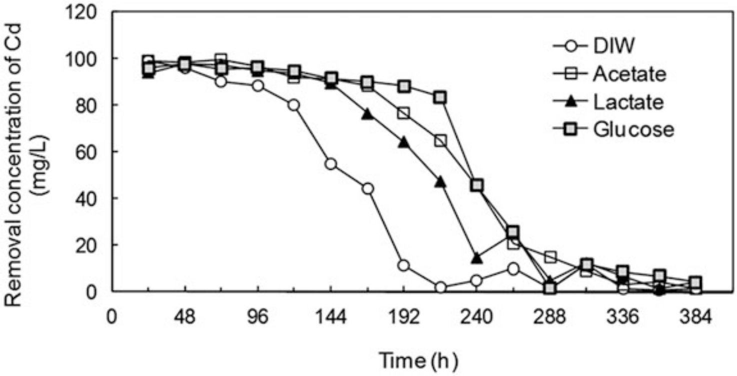


Fig. 7.11 Removal of dissolved Cd by biosorption to biofilm developed onto soil particles (Kim et al. 2009b)

metal ions can be possible and used effectively for the remediation of heavy metals-contaminated soils by biofilm formation.

3.7.2 Bioreduction of Cr (VI) to Cr (III) in Sediments

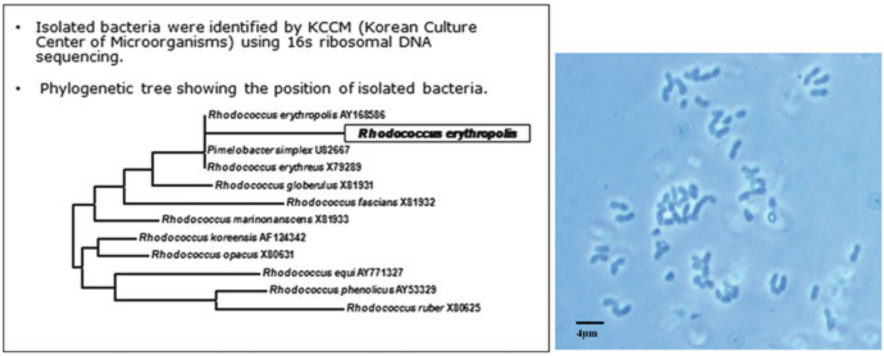
Treatment technologies for removing Cr (VI) is generally ion-exchange, electro-deposition and chemical reduction with iron- and sulphur-containing solutions by precipitation. The problem is that these techniques are quite costly, generate large amounts of secondary waste products due to various reagents used in a series of treatments and require high energy input or large quantities of chemical reagents (Lee 2006). Recently, bioreduction using microorganisms offers an attractive treatment option, because the technology is cost-effective and environmentally compatible. The oxidation-reduction reactions of Cr are controlled in the presence of a strong reducing and oxidizing materials. Reduction of Cr (VI) to Cr (III) can occur in natural systems in the presence of reductants, such as Fe(II) and sulphides.

$$\mathrm{Cr}\ (\mathrm{VI}, \mathrm{toxic}) + 3\mathrm{Fe}\ (\mathrm{II}) \rightarrow \mathrm{Cr}\ (\mathrm{III}, \mathrm{less\ toxic}) + 3\mathrm{Fe}\ (\mathrm{III})$$

Microbiological reduction of Cr (VI) by indigenous bacteria in Cr-contaminated sediment with industrial wastes was studied for the first time in Korea (Lee et al. 2006, 2008a, b). Sediment samples were collected in June of 2004 and 2005 from sediment bed in the area of the pigment manufacturing factories in Dongducheon city which is located in the northern part of Seoul, Korea (Fig. 7.12). The average concentration of Cr in sediments by aqua regia digestion was 708 mg kg^{-1}. It was found that isolated indigenous bacteria in Cr-contaminated sediment from the pigment manufacturing factories, which can reduce Cr (VI) to Cr (III), were identified as *Rhodococcus erythropolis* (Fig. 7.13).

- **Source of bacteria**
  : **Sediment samples from stream bed in the area of the pigment manufacturing factories, Dongducheon city, Korea**
- **Sampling period : June in 2004 and 2005**

Fig. 7.12 Source of bacteria in Cr-contaminated sediments collected from the area of the pigment manufacturing factories (Lee 2006)



- Isolated bacteria were identified by KCCM (Korean Culture Center of Microorganisms) using 16s ribosomal DNA sequencing.
- Phylogenetic tree showing the position of isolated bacteria.

Fig. 7.13 Identification of isolated bacteria, *Rhodococcus erythropolis* (Lee 2006)

The removal efficiency of Cr (VI) by *Rhodococcus erythropolis* increased with time and decreased with an increase of Cr (VI) concentration with mediums of living and heat-killed cells (Fig. 7.14). The reduction rate of Cr (VI) by *Rhodococcus erythropolis* increased with an increase in biomass concentration (Fig. 7.15), while the contact time required for the reduction of Cr (VI) decreased with an increasing biomass concentration. Also Mn-oxides could effect on the behavior of chromium (Fig. 7.16).

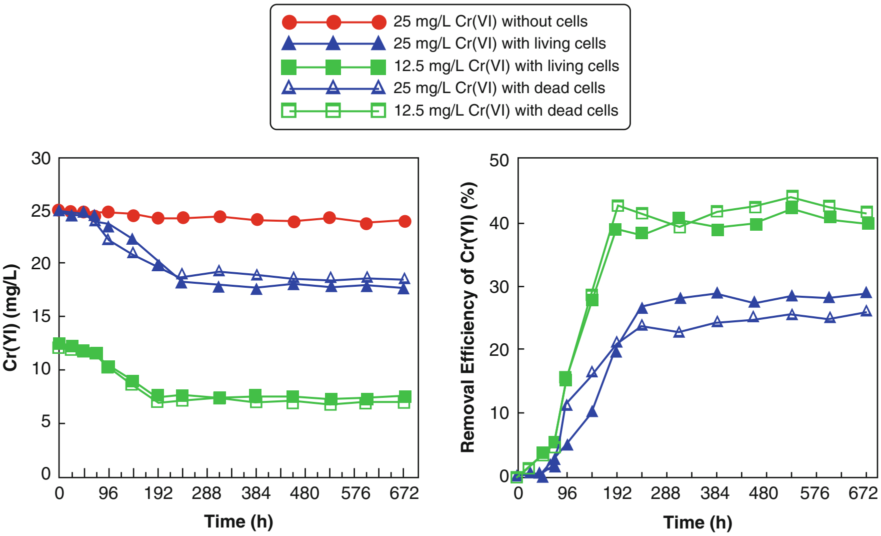


Fig. 7.14 Cr(VI) reduction by *R. erythropolis* in CRB medium

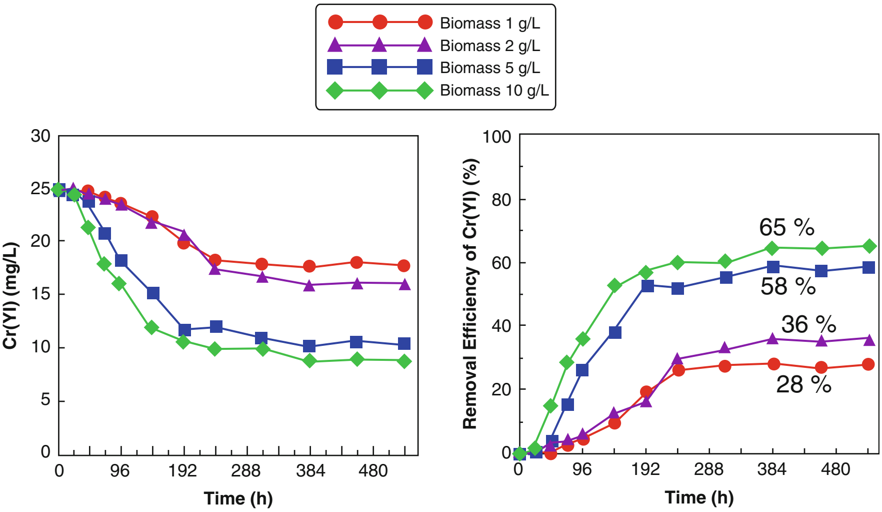


Fig. 7.15 Effect of biomasss concentration on Cr (VI) reduction by *R. erythropolis* in CRB medium

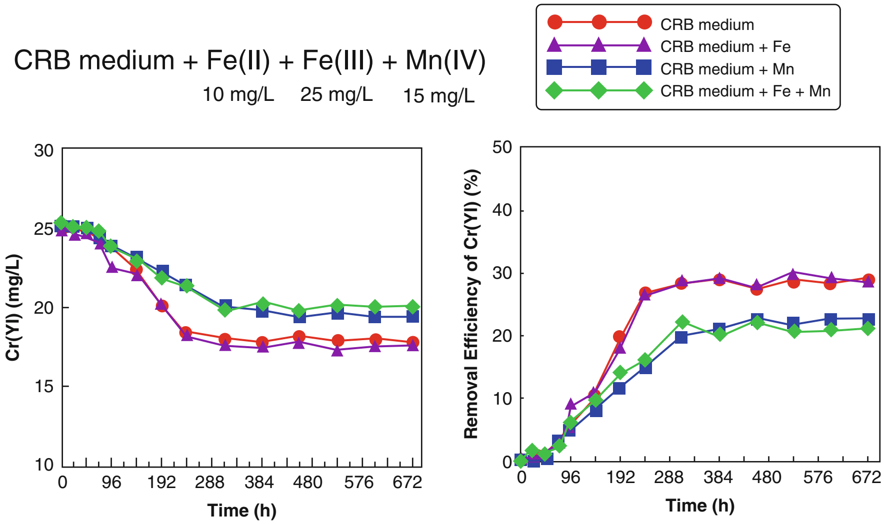


Fig. 7.16 Effects of Fe and Mn on Cr(VI) reduction by *R. erythropolis* in CRB medium

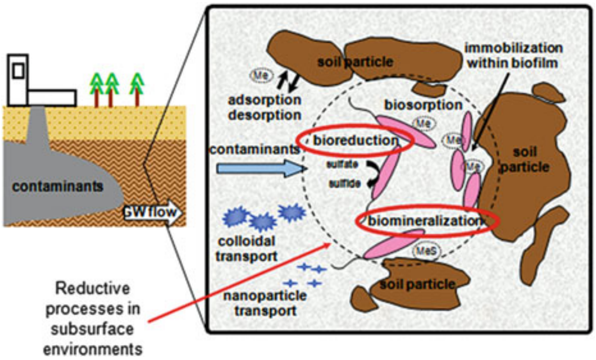


Fig. 7.17 The main reductive processes in subsurface environments are bioreduction and biomineralization

3.7.3 Biomineralization (Bioprecipitation): In-Situ Precipitation of As and Heavy Metals in Soils by Microbiological Sulphate Reduction

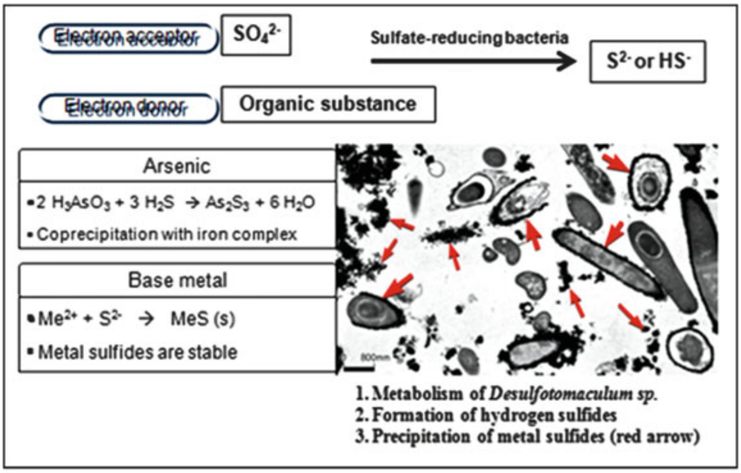
The main reductive processes in subsurface environments are bioreduction and biomineralization as shown in Fig. 7.17. Microbiological sulphate reduction is the transformation of sulphate to sulphide catalyzed by the activity of sulphate-reducing bacteria using sulphate as an electron acceptor. Low solubility of metal sulphides leads to the precipitation of sulphides (biomineralization) in solution. The applicability of in-situ metal precipitation based on biological sulphate reduction (BSR) was tested for the immobilization of As and Cu in a more realistic condition and the long-term stability of stabilized As and Cu was evaluated (Jang et al. 2009). Mean concentration of As and Cu in subsurface soil (by *aqua regia* digestion) around the abandoned Songcheon Au mine site in Korea was estimated as 1,311 mg/kg and 146 mg kg^{-1}, respectively. Inoculation of indigenous bacteria was extracted from the contaminated mine soils. From sequential extraction test, As exists mainly as Mn-oxide bounds (35 %) and Fe-oxide bound (52 %), and Cu as relatively high sulphide fractions. In batch-type experiments, indigenous sulphate-reducing bacteria rapidly decreased sulphate concentration and redox potential and lead to substantial removal of dissolved As and Cu from solution. More than 98 % of injected As and Cu were removed in the effluents from both microbial and chemical columns designed for metal sulphides to be precipitated. Black precipitates formed in the microbial column during the experiments were identified as iron sulphide and copper sulphide. Arsenic was observed to be adsorbed on the surface of iron sulphide precipitate (Jang et al. 2009) (Figs. 7.18 and 7.19).

3.7.4 Bioleaching of As in Contaminated Soils

Bioleaching technique is the increasing mobility of heavy metals and As by metabolism of bacteria. The principle of bioleaching for As is the increasing of As mobility in contaminated soil. Direct metabolism of the bacteria, direct As (V) – reducing bacteria, makes the reduction of As (V) to As (III) which has greater mobility than As(V). Iron (Fe)-reducing bacteria dissolve Fe minerals (e.g. Fe hydroxide) by altering Fe (III) to aqueous Fe (II), and subsequently As associated with Fe mineral(e.g. As adsorbed on Fe hydroxide) in contaminated soil is leached out into solution (Nickson et al. 2000).

A study on the bioleaching As in contaminated soil collected from an old smelting site in Korea was carried out using metal reducing bacteria (Lee et al. 2011). Two types of batch experiments, biostimulation and bioaugmentation, were conducted for 28 days under anaerobic conditions. The biostimulation experiments were performed through activation of indigenous bacteria by supply with glucose or lactate as a carbon source. The results indicated that the maximum concentration of the extracted As was 11.2 mg L^{-1} at 4 days from the onset of the experiment when 20 mM glucose supplied, and As removal efficiency was in the range of 60–63 % in the biostimulation experiment (Fig. 7.20).

In the case of bioaugmentation the highest dissolved As concentration was 24.4 mg L^{-1} at 2 days though it dramatically decreased over time through readsorption onto soil particles (Lee et al. 2011). This novel technique of bioleaching may be practically applied to remediation of As-contaminated soil after determination of optimum operational conditions such as operation time and proper carbon source and its concentration.



Electron acceptor SO_4^{2-}

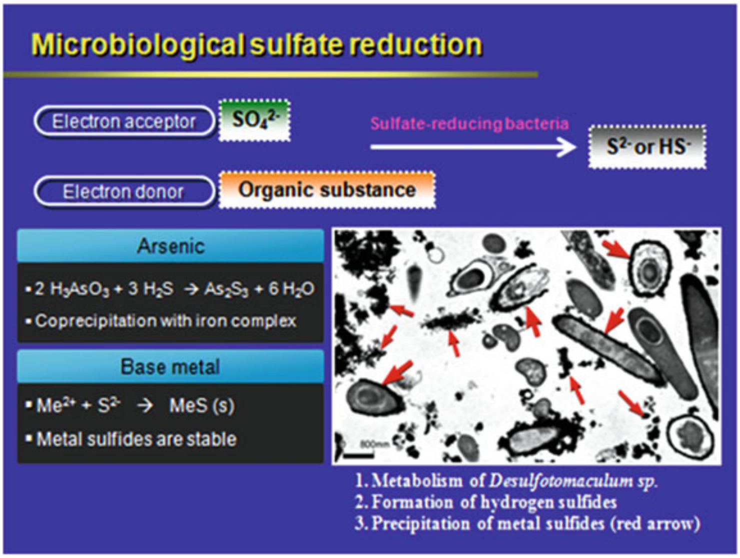
Electron donor Organic substance

Sulfate-reducing bacteria → S^{2-} or HS^-

Arsenic
- $2\ H_3AsO_3 + 3\ H_2S \rightarrow As_2S_3 + 6\ H_2O$
- Coprecipitation with iron complex

Base metal
- $Me^{2+} + S^{2-} \rightarrow MeS\ (s)$
- Metal sulfides are stable

1. Metabolism of *Desulfotomaculum sp.*
2. Formation of hydrogen sulfides
3. Precipitation of metal sulfides (red arrow)



Microbiological sulfate reduction

Electron acceptor SO_4^{2-}

Electron donor Organic substance

Sulfate-reducing bacteria → S^{2-} or HS^-

Arsenic
- $2\ H_3AsO_3 + 3\ H_2S \rightarrow As_2S_3 + 6\ H_2O$
- Coprecipitation with iron complex

Base metal
- $Me^{2+} + S^{2-} \rightarrow MeS\ (s)$
- Metal sulfides are stable

1. Metabolism of *Desulfotomaculum sp.*
2. Formation of hydrogen sulfides
3. Precipitation of metal sulfides (red arrow)

Fig. 7.18 Black precipitates formed in the microbial column and identified as Fe sulfide by SEM-EDS analysis (Jang et al. 2009)

3.8 Phytoremediation

The cleanup of contaminated sites with heavy metals is necessary, but environmental remediation strategies are often expensive, energy consuming, lead to CO_2 emissions and are intrusive (McGrath et al. 1995), so the soil itself can rarely be utilized after the treatment. Thus, it is important to develop low-cost and environmentally friendly strategies. In these conditions, phytoremediation could be the

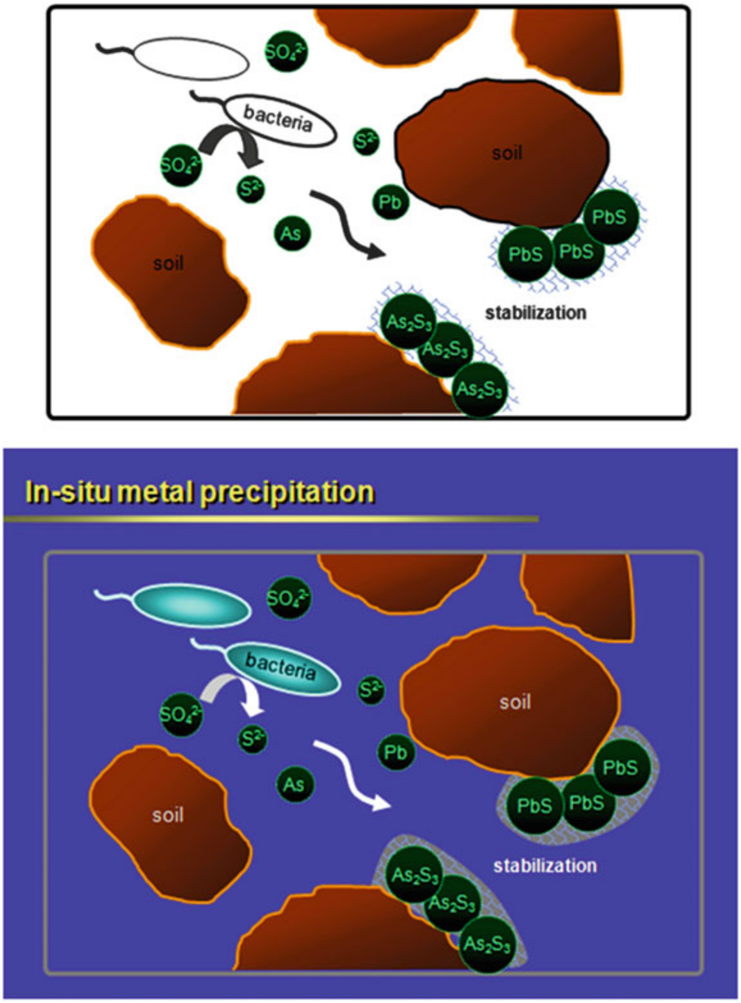


Fig. 7.19 Removal of arsenic with various concentrations of sulfate (Jang et al. 2009)

cheapest and simplest option among the available soil clean-up strategies. USEPA (2000) defines phytoremediation as “the use of plants for containment, degradation or extraction of xenobiotics from water or soil substrates”. Thus, phytoremediation takes advantage of the inherent ability of plants to take up water, soluble mineral nutrients and their associated co-contaminants through their roots, to transpire through leaves, and to act as a transformation system to metabolize organic compounds, or to adsorb and bioaccumulate toxic trace elements including heavy metals (Purakayastha and Chhonkar 2010).

Phytoremediation can be practiced in order to scavenge both organic and inorganic pollutants present in solid substrates (e.g. soil), liquid substrates

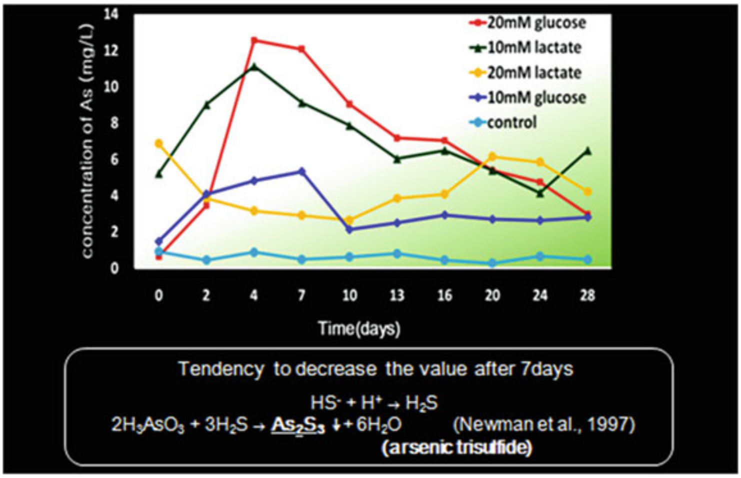


Fig. 7.20 Leaching of As with various concentration of carbon sources in biostimulation batch experiment (Lee et al. 2011)

(e.g. water) and the air. There are various phytoremediation approaches that can be employed:

- Phytoextraction, accumulator plants are planted on contaminated soil to absorb, translocate and concentrate hazardous compounds, particularly heavy metals, in aboveground biomass and later harvested in order to remove these hazardous compounds from the soil.
- Rhizofiltration, roots of accumulating plants absorb concentrate, and/or precipitate hazardous compounds, particularly heavy metals or radionuclides, from polluted effluents and are later harvested to diminish the metals in the effluent.
- Phytodegradation, plants and associated microorganisms degrade organic pollutants into less toxic forms or render them immobile in order to prevent their entry into the food chain or environment.
- Phytostabilization, metal-tolerant plants are used to reduce the mobility of hazardous compounds, particularly heavy metals. Thus, the pollutants are stabilized in the substrate.
- Phytovolatilization, plants are used to volatilize pollutants.

Phytodegradation can only be of use in the case of degradable wastes. Plants and associated microorganisms degrade organic pollutants into less toxic forms, and thus it has limited applicability to the remediation of heavy metal contaminated soils (Purakayastha and Chhonkar 2010). Rhizofiltration can only occur in water bodies and aqueous waste streams. The advantages associated with rhizofiltration are the ability to use both terrestrial and aquatic plants. Another advantage is that contaminants do not have to be translocated to the shoots. Although several publications have shown the ability of aquatic plants for heavy metal removal, the majority of them have been performed under laboratory conditions (Olguín and

Sánchez-Galván 2012). These metal uptake capacities may be entirely different when plants are under natural conditions with environmental factors less favourable (Lu et al. 2011). Therefore, specific remediation of soil trace elements (hereafter, heavy metals) by plant species includes (Ghosh and Singh 2005): phytoextraction, phytostabilization, and phytovolatilization.

3.8.1 Phytoextraction

Phytoextraction seems to be most attractive due to its versatility in usage; however it depends heavily on the efficiency of the metal accumulating plants used. Robinson et al. (2006) list the potential limitations in using phytoextraction to remediate contaminated sites: (i) long period required for cleanup; (ii) limited number of target metals which can be phytoextracted; (iii) limited depth that can be accessed by roots; (iv) difficulty in producing a high biomass crop of the desired species; (v) potential of plant metals to enter environmental food chains, and (vi) inevitable leaching of metals if chelators are added to induce phytoextraction. Thus, it is important to develop the research on various plant species in relation to the phytoextraction of metal from contaminated soils.

Up to now, more than 450 angiosperm species that can accumulate high concentration of metals (As, Cd, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, Zn,) into their aboveground have been reported (Rascio and Navari-Izzo 2011). These plants include trees, vegetable crops, grasses and weeds. Metal hyperaccumulation occurs in approximately 0.2 % of all known species and is particularly well represented in the Brassicaceae (Krämer 2010). About 25 % of discovered hyperaccumulators belong to the family of Brassicaceae (Bini et al. 2012; Marchiol et al. 2004) and in particular to genera *Thlaspi* and *Alyssum*. However, new reports of this kind of plants continue to accrue, so that it is conceivable that many yet unidentified hyperaccumulators may occur in nature. *Arabidopsis halleri* and *Sedum alfredii*, together with *Thlaspi caerulescens* and *Thalaspi praecox*, are the four recognized species that besides Zn, hyperaccumulate Cd (Rascio and Navari-Izzo 2011). Sun et al. (2008) noticed *Solanum nigrum* (Solanaceae) as the fifth Cd hyperaccumulator. The first As hyperaccumulator described was *Pteris vittata*, which accumulated up to 7,500 mg As kg in its fronds at an As-contaminated site containing 18–1,600 mg kg total As in the soil (Ma et al. 2001).

Plants that accumulate very high concentrations of metals in any aboveground tissue in their natural habitat are called hyperaccumulators (Baker 1981). A metal hyperaccumulator is defined as a plant that is able to accumulate about 100–1,000 times the metal concentrations as compared to normal plants growing in soils with background metal concentrations and about 10–100 times that of most other plants growing in metal-contaminated soils (McGrath and Zhao 2003). Therefore, the criteria to define hyperaccumulation of As, Co, Cu, Cr, Ni, Pb and Se is a concentration of 1,000 mg kg^{-1} or greater, on a dry leaf basis, whereas the threshold value for Zn and Mn hyperaccumulation is 10,000 mg kg^{-1} (Baker and Brooks 1989; Kabata-Pendias and Mukherjee 2007). Additionally, hyperaccumulation for Cd is defined as values larger or equal to 100 mg kg^{-1} (Baker and Brooks 1989).

Hyperaccumulators are also characterized by a shoot to root metal concentration ratio (i.e., the translocation factor (TF)) of more than 1, whereas non-hyperaccumulator plants usually have greater metal concentrations in the roots than in the shoots. Several authors (Baker 1981, Baker et al. Baker et al. 1994; Krämer et al. 1996; Sun et al. 2008) included the bioaccumulation factor (BF) as an element for classification as a hyperaccumulator species. The BF refers to the plant metal concentration and the soil metal concentration ratio. This ratio should be greater than one for inclusion into the hyperaccumulator category. Besides, plants with bioaccumulation factor greater than one and translocation factor less than one (BF >1 and TF <1) have the potential for phytostabilization (Yoon et al. 2006).

The hyperaccumulators should be vigorous herbaceous perennial plant with a high rate of biomass production and with broad ecological amplitude, especially in disturbed areas. For example, *Thlaspi caerulescens* was identified as a hyperaccumulator of Zn and Cd due to more 40,000 mg Zn kg^{-1} accumulated in shoots in some of its ecotypes; however, the slow growth rate and small size is a great limitation for phytoremediation. Recent evidence suggests that moderately accumulating high-biomass species such as Indian mustard (*Brassica juncea*) can accumulate four times more Zn than *T. caerulescens* (Purakayastha and Chlonkar 2010). For these reasons research on phytoextraction has focused on crops such as maize (*Zea mays*), tobacco (*Nicotiana tabacum*), Indian mustard (*Brassica juncea*), oat (*Avena sativa*), barley (*Hordeum vulgare*), pea (*Pisum sativa*), poplar (*Populus sp.*) and sunflower (*Helianthus annuus*).

The use of native plants for phytoremediation can be a useful option, because these plants are better adapted to the environmental conditions of the region than plants introduced from other environments (Antonsiewicz et al. 2008; Yoon et al. 2006). There has been a continuing interest in searching for native plants that are tolerant to heavy metals (e.g. Bech et al. 2012a, b; González and González-Chávez 2006; Lorestani et al. 2011; Shu et al. 2002). For example, the common dandelion (*Taraxacum officinale* Web) is a very common species, widely diffused in Central and Southern Europe, greatly adaptable to every substrate and capable of uptaking and storing heavy metals (Bini et al. 2012). Heavy metals can cause severe phytotoxicity, and may act as powerful force for the evolution of tolerant plant populations.

3.8.2 Chelate-Assisted Phytoextraction

The availability of metals for plant uptake is greatly restricted by their adsorption to solid soil fractions. The degree of availability for uptake is affected by numerous soil factors, such as cation exchange capacity (CEC), pH and organic matter content. In addition, the speciation of the metal, which is correlated to the factors mentioned above, and the metal species itself, play an important role. Regardless of the plants used, availability of heavy metals to plant roots is considered the key factor limiting the efficiency of phytoextraction (Evangelou et al. 2007). The addition of chelating agents and the consequent formation of metal-chelate complexes prevents precipitation and sorption of the metals in the soil, thereby maintaining their availability for plant uptake (Marques et al. 2009) and translocation to harvestable above-ground parts of high biomass crops (Meers et al. 2008).

In the last decade, the use of persistent aminopolycarboxylic acids (APCAs) such as ethylene diamine tetraacetic acid (EDTA) have been used in various phytoextraction experiments. Compared to EDTA far fewer studies investigating the enhanced mobilisation and uptake capability of others APCAs have been published. Different synthetic APCAs are hydroxylethylene diamine tetraacetic acid (HEDTA), diethylene triamino pentaacetic acid (DTPA), trans-1,2-cyclohexylene dinitrilo tetraacetic acid (CDTA), ethylene bis[oxyethylenetrinitrilo] tetraacetic acid (EGTA), ethylenediamine-N,N0bis(o-hydroxyphenyl)acetic acid (EDDHA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), and N,N0-di (2-hydroybenzyl) ethylene diamine N,N0-diacetic acid (HBED). Recently, the biodegradable APCAs, ethylene diamine disuccinate (EDDS), iminodisuccinic acid (IDSA), methylglycinediacetic acid (MGDA) and nitrilo triacetic acid (NTA) have been proposed as an alternative to EDTA and other persistent APCAs (Grĉman et al. 2003). Several experiments using low molecular weight organic acids (LMWOA) have also been performed as chelating agents (Evangelou et al. 2007). The population density and composition of symbiotic and non-infecting microorganisms in the rhizosphere can enhance root exudation and the concentration of organic acids, for example malic and citric acids, chelators and acid phosphatases released as ectoenzymes from roots, or form microorganisms including arbuscular mycorrhizal fungi as microbial metabolites (Khan et al. 2000), increasing the effectiveness of metal mobilization.

Despite the possible usefulness of this technology, some concerns have been expressed regarding the potential inherent risk of leaching of metals to groundwater. Increased metal solubility could also affect soil microbial communities due to metal toxicity (Grĉman et al. 2001). Environmentally- persistent chelates can also cause eutrophication due to their nitrogen-rich composition (Carsten and Heinz-Jurgen 2004). Some chelates, such as EDTA, are also toxic to photosynthetic organisms, inhibiting cell division, chlorophyll synthesis and production of biomass (Oviedo and Rodriguez 2003). Although EDTA has been shown in several publications to be effective in enhancing phytoextraction, heavy metals amounts mobilised in the soil are higher than the uptake. Chen et al. (2004) and Grĉman et al. (2001) observed that Cu, Pb and Zn were leached down the soil profiles during EDTA treatment. Kos and Leštan (2003) found that 2.5–10 mmol $\cdot$ kg^{-1} of EDTA caused the leaching of a large portion of the total Pb initially present in soil, and suggested that uncontrolled EDTA treatments may not be acceptable for environmentally safe phytoextraction. Svenson et al. (1989) reported that the half lifetimes of DTPA and EDTA iron complexes in aqueous solution were 8 and 11 minutes, respectively. Means et al. (1980) also demonstrated that DTPA is more rapidly degraded than EDTA.

To avoid these environmental risks, the use of biodegradable chelates (EDDS, ISDA, NTA and MGDA) has been suggested. These chelates have short half-life (days), in comparison with the conventional chelates whose persistence in the environment endures for years (Tandy et al. 2004). In case of EDDS no toxicity to microorganisms has been observed. Similar to EDTA, EDDS increased the uptake of heavy metals, but as in the case of EDTA only a fraction of the mobilised metals are effectively absorbed by the plant and subsequently translocated to the shoot (according to Komarek et al. (2010) up to a 65-fold increase). In studies by Meers et al. (2005) and Luo et al. (2005) the uptake of Cu and Zn was more enhanced by the addition of EDDS than by the addition of EDTA, whereas Cd and Pb were more explicitly mobilised by EDTA than by EDDS. In comparison to synthetic APCAs, NTA was more effective than HEIDA, HEDTA, EDTA, EGTA, CDTA and DTPA in the extraction of As and Zn from soil (Chiu et al. 2005). However, heavy metal leaching cannot be omitted during the process. González et al. (2011) evaluated the effects of MGDA on Cu increase phytoextraction by *Oenothera picensis* and the minimal leaching of Cu through the soil.

The solubilisation of metals through the application of natural chelating agents on the soil may be attractive due to the mitigation of adverse effects related to synthetic chelates. Citric acid has been one of the most studied natural chelates for phytoextraction. In comparison to EDTA, citric acid is more readily biodegradable but less effective in the removal of metals due to it complexation with other cations (Evangelou et al. 2007). In fact, Gheju and Stelescu (2013) reported that EDTA was found to be the most efficient chelating amendment among the three chelants tested EDTA, disodium oxalate (OX) and trisodium citrate (CI). The less effective uptake of Zn by plants for CI and OX was attributed to the neutral or slightly alkaline pH of these two chelates. On the other hand, the results obtained by Pérez-Esteban et al. (2013) showed that higher concentrations of organic acids increased metal desorption, and citric acid was more effective at facilitating metal desorption than tartaric acid. Freitas et al. (2013) noticed that the use of citric acid in phytoremediation of soils contaminated by battery recycling activities substantially increase the uptake and translocation of Pb to the shoots.

Luo et al. (2008) hypothesized that the root exudates from one crop such as barley (*Hordeum vulgare* L.) in one mixed culture system of peas and barley played an important role in the process of solubilizing metals in soil and facilitating the uptake of metals by peas. Although the improved efficiency from these experiments was relatively low, it may indicate a potential approach to the remediation of metal-contaminated soils in a naturally enhanced way. In Quartacci et al. (2009) the growth of the spontaneous metallicolous populations of *Pinus pinaster*, *Plantago lanceolata* and *Silene paradoxa* increased the extractable metal levels in the soil, which resulted in a higher accumulation of metals in the above-ground parts of *Brassica carinata* in comparison with the same plants grown in soil not previously planted. The fact that accumulation of metals is similar to that shown by *B. carinata* following amendments with biodegradable chelants such as NTA and EDDS, indicates a possible approach to naturally enhanced phytoremediation of multiple metal-contaminated soils.

3.8.3 Phytostabilization

Phytoestabilization is a site stabilization technique that reduces the mobility and bioavailability of pollutants in the environment either by immobilization or by prevention of migration (Vangronsveld et al. 1995). Converting the pollutant, especially heavy metals, into less soluble forms will likely diminish the leaching of the metal through the soil profile, and the chances of any biological interactions with humans, animals or plants. For example, the reduction of Cr^{6+}, which poses an environmental risk, to Cr^{3+}, which is highly insoluble and not demonstrated to pose an environmental risk, by deep rooted plants can be very effective. Chemical species of Pb in soil are usually bioavailable if the soil is ingested by children, livestock or wildlife, whereas a Pb phosphate mineral, chloropyromorphite, is both extremely insoluble and non-bioavailable. In the case of Pb phytoextraction, there are another two major limitations: the low Pb bioavailability in soil and the poor translocation of Pb from roots to shoots (Pulford and Watson 2003). Therefore, phytostabilization appears to have a high potential for these two toxic elements, Cr and Pb.

In this technique, the soil surface is covered with plants to prevent or reduce the dispersion of metal contaminated particles by water and wind erosion and reduce water percolation (Zanuzzi and Faz 2010). The choice of plants is a crucial aspect for the practical use of phytostabilization (Freitas et al. 2004). Plants should develop an extensive root system and a large amount of biomass in presence of high concentrations of heavy metals while keeping the translocation of metals from roots to stems and leaves as low as possible (Rizzi et al. 2004). Possible mechanisms of phytostabilization might include sequestering the contaminant in or on cell wall ligning (lignification), absorption of contaminants to soil humus, via plant or microbial enzymes (humification), or other mechanisms whereby the contaminant is sequestered in the soil, e.g. by binding to organic matter (Prasad 2004).

Phytostabilization of metals using trees is often promoted, although the influence of different tree species on the mobilization of metals is not yet clear. Trees can potentially be very well suited for phytostabilization purposes due to their extensive root systems and high transpiration capacity (Pulford and Watson 2003), especially when it is uneconomic to use other treatments or there is no time pressure on the reuse of the land (Riddell-Black 1993). On the other hand, tree growth might enhance metal leaching because of soil acidification and production of dissolved organic matter (Mayer 1998). Hence, with respect to risk control, it is very important to select tree species for phytostabilization purposes that cause low soil acidification and a minimal translocation of metals to their leaves (Mertens et al. 2007). Van Nevel et al. (2007) identified three main risks associated with the accumulation of metals in aboveground plant parts: (i) metals entering the food chain through herbivores, (ii) dispersion of contaminated plant material to adjacent environments and (iii) accumulation of metals in the topsoil. Furthermore, on highly contaminated soils, or on mining wastes, tree establishment may be inhibited by high concentrations of heavy metals. Under such conditions root immobilisation may not be able to prevent toxic amounts of metal being translocated to the aerial parts of the plant (Pulford and Watson 2003). In less-contaminated soils, other factors may limit plant growth; such as macronutrient deficiencies and physical conditions, especially those properties leading to poor water holding, aeration and root penetration (Mullins 1991).

The potentiality of Salicaceae, such as poplars and willows, for the remediation of soil and water from metal pollution has been highlighted (Kuzovkina and Quigley 2005; Meers et al. 2007). Poplars are characterised by high variability and adaptability to environmental constraints, in addition to having an extended root system and a low impact on trophic chains. Poplars also grow relatively fast, and they are widely used in agroforestry because of their high biomass production, which can be used to generate heat or electric power. The possibility of obtaining both ecological benefits (i.e. remediation and energy production) has recently been proposed for Salicaceae (Witters et al. 2009). Férnandez et al. (2012) expose the great capacity of Zn accumulation especially in roots and the milder alterations occurred in the development of plants biomass, structural parameters and photosynthetic activity of *Populus deltoides x maximowiczii* – clone Eridano.

However, Van Nevel et al. (2011) demonstrate an accumulation of total Cd and Zn concentrations in the topsoil under aspen trees, only after 10 years of tree growth. The topsoil is particularly vulnerable as it is the biologically most active part of the soil system and biological activity has been shown to be highly sensitive to metal pollution (Bergkvist et al. 1989). In general, aspen and *Populus* species should be avoided for afforesting Cd and Zn contaminated lands because they translocate high amounts of Cd and Zn into the foliage (Van Nevel et al. 2011). On the other hand, the higher pH and CEC values in the topsoils of this species reduce the bioavailable of Cd and Zn concentrations. This indicates that in more acid conditions the accumulated Cd and Zn in the topsoil will yet become more mobile and thus bioavailable. This could be a problem if the aspen trees would be harvested and replaced by more acidifying species (Van Nevel et al. 2011).

3.8.4 Phytoremediation in Mining Activities

There are a large number of sites worldwide polluted with trace elements as a result of human activities. Extraction of metals from sulphide minerals usually results in large amounts of tailings which often contain elevated concentrations of potentially harmful metals such as Cd, Cu, Pb and Zn. Tailings usually provide an unfavourable substrate for plant growth because of their extreme pH, low organic matter and nutrients, high concentrations of trace elements and physical disturbance, such as bad soil structure, and low water availability (Mullins 1991). Heavy metal contamination has also been one serious problem in the vicinity of mine sites due to the discharge and dispersion of mine-waste materials into the ecosystem (Jung and Thornton 1996; Navarro et al. 2008). The presence of vegetation reduces water and wind erosion, which may decrease the downward migration of contaminants into the groundwater and improve aesthetical aspects (Wong 2003).

Therefore, the use of plants to remediate hazardous soils is considered as a highly promising approach for improving the environmental quality of the tailings.

Plants growing on naturally metal-enriched soils are of particular interest in this perspective, since they are genetically tolerant to high metal concentrations, have an excellent adaptation to this multi-stress environment (Ernst 1989; Barceló and Poschenrieder, 2003). Bech et al. (2012d) observed that the native mine spoil ecotype of *Agrostis capillaris* plants can grow on these acid soils with high burdens of potentially toxic trace elements due to efficient restriction of uptake and translocation of Sb, As, Pb and Cu. In contrast, a commercially *A. capillaris* variety that has not evolved under these extreme soil conditions is unable to prospect because of the high accumulation of these trace elements in roots and shoots. Therefore, the conservation of the genetic diversity of these metallophytes is of enormous importance for the future development of efficient plant for phytoremediation purposes.

Several authors have developed important studies. In the case of Caveira and Sao Domingos (Portugal) mine areas, Abreu et al. (2012a) analysed the behaviour (trace elements uptake, accumulation and translocation from roots to shoots) of different populations of *Cistus salviifolius* plants growing spontaneously in these contaminated mines. *Cistus salviifolius*, plants included in Mediterranean communities, showed tolerance for moderate acid soils developed on different waste materials, presenting relatively small fertility and great total concentrations of trace elements. Although the populations of *Cistus salviifolius* L. plants were no considered hyperaccumulators, all the plants stored up phytotoxic elements (As, Sb and Pb) in roots, as a possible mechanism of exclusion. Similar behavior was observed for *Cistus populifolius* L. and hybrid, *Cistus* × *hybridus* Pourr. (Abreu et al. 2012b).

South American countries are rich in valuable ore deposits and mining activities that have quickly developed all over the continent. In general, the environmental impact of mines in Europe and North America has been evaluated in detail, for example Conesa and Schulin (2010) and Conesa et al. (2006). In contrast, data on impact assessment of the mining activities in South America countries are still very poor. Frequently, native farmers, living downstream of the copper mine, had observed unidentified toxic effects in natural vegetation and crop plants and some health problems of inhabitants and cattle in zone downstream of the mines (Bech et al. 1997). There are 172 hyperaccumulator species described in the literature for Latin America (Ginocchio and Baker 2004).

In 2002, Bech et al. reported the first results of the screening of plant species from three mining areas (Canchaque district of Piura department in the Western Andes, Mina San Bartolomé in Ecuador, Mina El Teniente in Chile) in South America (Figs. 7.21 and 7.22). The different plant species collected on the polluted soils exhibited large differences in shoot accumulation of heavy metals and As. Among the grass species (Poaceae), the highest shoot As concentration were found in *Paspalum sp*. (>1,000 μg/g) and *Eriochola ramose* (460 μg/g) from the Cu mine in Peru and in *Holcus lanatus* and *Pennisetum clandestinum* (>200 μg/g) from the silver mine in Ecuador. *Paspalum racemosum* also accumulated considerable concentration of Cu and Zn. The species from the genus *Bidens* (Asteraceae) were able not only to accumulate high shoot As concentrations (>1,000 μg/g in

Fig. 7.21 *Cortaderia nitida*, a Cu-Pb-Zn accumulator plant from San Bartolomé mine in Ecuador (Photo by J. Bech)

B. cynapiifolia from Peru) but also considerable amounts of Pb (*B. humilis* from Chile). The highest Cu shoot concentrations were found in *Mullinum spinosum* (870 μg/g) and in *B. cynapiifolia* (620 μg/g). The shoot accumulation of Zn was highest in *Baccharis amdatensis* ($>$1,900 μg/g) and in *Rumex crispus* (1,300 μg/g) from the Ag mine in Ecuador.

Bech et al. 2012a also proposed *Plantago orbignyana* Steinheil as Pb hyperaccumulator, due to its ability to accumulate more than 1,000 mg Pb kg^{-1} in the shoots, with TF and BF values greater than one. This species can also accumulate Zn in the shoots and had a TF greater than one, but the BF was smaller than one. These results are of great interest because Pb is considered a target metal when undertaking soil remediation, because it is usually quite immobile and not readily accumulated in upper plant parts (Fig. 7.23). Moreover, Bech et al. (2012b) also remark the potentiality of *Bidens triplinervia* L. for phytostabilization due to its capacity to restrict the accumulation of elevated amounts of Pb and Zn in the shoots. Flores-Tavizón et al. (2003) reported that *Eleocharis sp*. absorbed up to 301 mg kg^{-1} of As and It is apparently an accumulator species. Plant metal analysis in El Bote mine near to Zacatecas city (Mexico) revealed that most species did not translocate metals to their shoots. However, *Polygonum aviculare* accumulated Zn at

Fig. 7.22 *Chenopodium ambrosioides*, a Cu-accumulator plant from El Teniente mine in Chile (Photo by J. Bech)

Fig. 7.23 *Plantago orbignyana* Steinheil has been proposed as Pb hyperaccumulator (Photo by J. Bech)

Fig. 7.24 *Moricandia moricandioides* growing naturally around lead mining in Bellmunt (Spain) (photo by J. Bech)

concentrations near to the criteria for hyperaccumulator plants (9,236 mg kg^{-1}). *Jatropha dioica* also accumulated high Zn (6,249 mg kg^{-1}) concentrations (González and González-Chávez 2006).

Much less information is available on metal uptake by natural vegetation in neutral to alkaline abandoned mining sites with high metal burdens (Conesa et al. 2006; Martínez-Sánchez et al. 2012; Poschenrieder et al. 2001). Investigations on the natural vegetation simultaneously adapted to high soil carbonate and high metal availability can be important for both the fundamental knowledge on metal uptake and tolerance mechanisms and for the characterization of germplasm for phytoremediation of large areas of near neutral to alkaline mine spoils (McCabe and Otte 2000; Schroeder et al. 2005). Poschenreider et al. (2012) propose *S. aspera* for phytostabilization of metal contaminated soils in Mediterranean area due to its efficiency in metal exclusion of Cd, Pb and Zn from leaves. Bech et al. (2012c) highlighted that all analysed plants growing naturally around lead mining in Bellmunt (Spain) showed enhanced root and shoot concentrations of Cu, Pb, Zn, and Sb when growing on the more polluted soils. Except for one, they all restricted the translocation of metals from roots to shoots exhibiting shoot/root concentration ratios lower or close to unity. A notable exception was *Moricandia moricandioides* (Boiss.) Heyw [M. ramburii Webb] where shoot/root Zn concentration ratios up 5.5 were observed. This metal accumulation pattern was only observed for Zn (Fig. 7.24).

3.8.5 Phytovolatilisation

This method is a specialized form of phytoextraction that can be used only for a small number of contaminants that are highly volatile. Pollutant trace elements like mercury (Hg) or selenium (Se), once taken up by the plant roots, can be converted into nontoxic forms (Prasad 2004). However, instead of accumulating inside the plant, the trace element is enzymatically transformed and volatilized into the atmosphere from the roots, shoots or leaves. Phytovolatilization has been primarily used for the removal of mercury (Hg), the mercuric ion is transformed into less toxic elemental mercury. The disadvantage is that mercury released into the atmosphere is likely to be recycled by precipitation and then redeposited back into ecosystem, repeating the production of methyl-mercury by anaerobic bacteria (USEPA 2000).

Wang et al. (2012) carried out an extensive review of Hg phytovolatilisation. Much of the following text is based on that review. Very few studies have reported the use of plants for the phytovolatilization of Hg, because Hg emission from leaf tissues is strongly affected by environmental parameters such as light intensity and air temperature (Leonard et al. 1998a). Leonard et al. (1998a, b) presented the higher mercury emission rate (92.6 ng m^{-2} h^{-1}) in the daytime for *Caulanthus sp*. An interesting proposed approach is the use of transgenic plants that volatilize Hg (for example: Bizily et al. 2000; Meagher and Heaton 2005). However, genetically modified organisms are not allowed by European laws (Davison 2010). Genetic engineering can integrate genes from other organisms to enhance the phytovolatilization capabilities of plants. Of the known bacterial mercury resistance systems, the Mer (mercuric ion resistance) determinant is unique in terms of the orientation of the mercury transporter it encodes (Sasaki et al. 2006). Mercuric reductase, which is encoded by the merA gene, can reduce mercuric ions (Hg^{2+}) to the less toxic and volatile elemental mercury form (Fox and Walsh 1982). Unfortunately, the MerA gene fails to protect against organic-mercury, more toxic and environmentally relevant (Wang et al. 2012). Another important enzyme-organomercurial lyase (MerB) catalyzes the protonolysis of the carbon–mercury bond. The products of this reaction are a less toxic inorganic species and a reduced carbon compound (Bizily et al. 1999). Both the MerA and the MerB genes are needed to protect cells from organic-mercury (Ruiz and Daniell, 2009). Hussein et al. (2007) reported that transgenic tobacco plants engineered with MerA and MerB genes via the chloroplast can accelerate the plant uptake of mercury from the substrate.

Alternatively, studies have been conducted to increase Hg availability for plant uptake by the application of soil additives. Among them, interesting results have been obtained using thioligands (Moreno et al. 2005; Pedron et al. 2013) and halogen salts (Wang et al. 2003), which are nontoxic chemicals commonly used in agriculture for their fertilizing properties. In this case, caution must be taken with the metal leaching into deeper soil horizons. Moreover, Hg volatilization does not appear to occur in assisted Hg phytoextraction using *Brassica juncea* plants and ammonium thiosulfate (TS) as soil amendment (Moreno et al. 2005). Cassina et al. (2012) provides evidence that the combination of cytokinins and ammonium thiosulfate contributes favourably to enhancing Hg phytoextraction in the tested crops. This study shows that Hg-volatilization related issues are of no concern, since they did not observe any evidence of Hg loss by phytovolatilization.

In the natural environment Se occurs primarily in two forms – selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}) (Adriano 2001). Organic Se may also be present in soil solutions (Abrams et al. 1990). The concentration and bioavailability of different forms of Se depend on soil properties such as pH, organic matter content, texture, microbiological activity and the presence of competing ions and organic compounds (Dhillon et al. 2010). Selenate is generally the toxic form in soils (Bisbjerg and Gissel-Nielsen 1969), whereas selenite can be toxic to plants grown in solution culture (Spencer and Siegel 1978). Volatilisation rates for selenite are generally two- to three-fold higher than those for selenate. Thus, selenate reduction seems to be a rate-limiting step for selenium volatilization by plants. In soil, the redox reactions of Se are mediated by soil microorganisms. Soil microbes have the capacity to remove Se from a contaminated medium with or without plants, by metabolizing it into a non-toxic volatile gas form like dimethyl selenide or dimethyl diselenide (Zhang and Moore 1997). Plants volatilise relatively low amounts of selenate or selenite in the absence of bacteria; though the mechanisms are not clear (Terry et al. 2000). Volatile Se can be recovered in recyclable forms free from other metals, salts, and organic matters using a gas trapping process. However, such a hypothetical process has not been practically established because microbial Se volatilization is generally too slow for industrial processing (Kagami et al. 2013).

Selenium can be taken up by plants of the Brassica genus and other wetland plants. For example, Bañuelos (2000) and other earlier research demonstrated that planting certain *Brassica* species, led to reductions of total soil Se up to 40 % under greenhouse conditions and up to 20 % under field conditions after one growing season. Brassica species have high affinity for sulphur (S) and its apparent inability to discriminate between absorbing Se and S species from the soil (Anderson and Scarf 1983). Most of the Se was removed by plants, although there may have been biological volatilization of Se. Understanding and then promoting the natural pathway of Se methylation with plants will increase the efficacy of phytoremediation of Se (Bañuelos 2006). Pilon-Smits et al. (1998) working with the poplar hybrid *Populus tremula x alba* reported that almost 70 % of the SeMet that was taken up by poplar was volatilised compared with 3 and 4.5 % for selenite and selenate. These authors stated that poplar volatilisation rates and biomass productivity were comparable with those of cattail, making it an attractive species for phytoremediation. Dhillon et al. (2010) reported that application of organic manures and fresh plant material helped in increasing the rate of Se volatilization from the seleniferous soil. Organic Se forms constitute an important pool which regulates the availability of Se to plants as well as Se volatilization.

The complexities of Se behavior in soil-plant systems arise because of the several different valence states of the element that can occur and because of the potential significance of volatilization from both soils and plants. Pérez-Sánchez et al. (2012) proposed a simplified model has been developed that represents the annual cycle of soil hydrology and estimates the effects of that annual cycle on the transport of Se-79 in soil and its uptake by plants. Furthermore, the model incorporates the effects of plant growth, cropping and the transfer of Se-79 from plant residues to organic matter in soils from whence it can be released by mineralisation reactions.

3.8.6 Phytomining

Phytomining involves the use of the plant biomass as an alternative ore with monetary value (Chaney et al. 2010). The process involves growing repeated crops of a hyperaccumulator on a polluted area. The plant material would be burnt to produce a ‘bio-ore’. This metal-rich ash, typically only 7 % of the weight of the dried plant material, could be stored in a safe area or conceivably even be sold as feedstock to a smelter to recoup some of the cost of the operation (Robinson et al. 1997). The economics of phytomining basically depends on the metal content in the soil, metal uptake by the plant, plant biomass and most importantly the price of the metal. The principal advantage of phytomining is its low cost relative to conventional mining methods, allowing economic exploitation of mineralised soil, mill tailings, overburdens or low-grade ores that is too metal-poor for direct mining operations (Nedelkoska and Doran 2000). The best candidates for phytomining are Au, Th, Co and Ni due to their high cost and high metal concentration in hyperaccumulator biomass. Although metal prices of U are comparatively high, its reported metal concentration (100 $\mathrm{mg \cdot kg^{-1}}$) in biomass (10,000 $\mathrm{kg \cdot ha^{-1}}$) is low, which makes it uneconomical for phytomining (Sheoran et al. 2009). Since the initial proposal by Chaney (1983), intensive trials were designed specifically to study phytomining. However, the majority of the research has been conducted on laboratory scale and in relatively controlled conditions for a short period of time; the true potential of phytomining is yet to be established (Sheoran et al. 2009).

Gold has been suggested as a candidate for phytomining. However, plants do not normally accumulate gold; the metal must be made soluble before uptake can occur. Background levels of gold in plants are usually very low, rarely exceeding 10 $\mathrm{ng \cdot g^{-1}}$ dry weight. Some plants exude natural lixiviants that can mobilize gold in a soil. Therefore, hyperaccumulation can be induced by adding a chemical amendment. Anderson et al. (1998a) have proposed that hyperaccumulation of gold in plants be represented by 1,000 $\mathrm{ng \cdot g^{-1}}$ (1 $\mathrm{\mu g \cdot g^{-1}}$) in dry mass.

In an induced hyperaccumulation operation of gold, the geochemistry of the substrate will dictate the choice of the solubilizing agent necessary to affect the uptake of the gold. For low-pH sulphide tailings, gold is made soluble by thiocyanate, and for high-pH unoxidised sulphide tailings gold is soluble with thiosulphate (Anderson et al. 1999). Thiocyanates have low toxicity over cyanides. The toxicity of thiosulphate is even lower and is about equal to that of common salt (Anderson et al. 1998b). Use of thiocyanate would have to be strictly controlled to prevent leaching into ground and surface waters if these chemicals and its associated metals are not taken up by plants. It might also be possible to use transgenic plants expressing a bacterial thiocyanate degrading system in order to extract Au from auriferous substrates. Such an approach would solve the problem of thiocyanate toxicity to plants and perhaps allow them to extract more Au, but not non target metals (Anderson et al. 1998b).

Induced hyperaccumulation of Au appears to be relatively independent of plant species, so it should be possible to use plants such as chicory (Lamb et al. 2001), that might be easy to grow on mine tailings (Anderson et al. 1998a). However, according with Anderson et al. (2005) *Brassica juncea* (Indian mustard) showed the best ability to concentrate gold induced with sodium cyanide and thiocyanate grown on oxidized ore pile containing 0.6 mg · kg^{-1} gold. Gold phytomining has also been reported by Msuya et al. (2000) with five root crops (carrot, red beet, onion and two cultivars of radish) grown in artificial substrate consisting of 3.8 mg · kg^{-1} of Au. The carrot roots yield 1.45 Au kg · ha^{-1} of final worth $US 7,550. Phytomining not only produces gold ingots but more important are gold nanoparticles with in plant cells (crystallite or primary particles measuring less than 100 nm in size), which has great importance for rapidly expanding nanoparticle market (Reeves and Baker 2000; Harris and Bali 2008).

Moreover, the plants growing on soils affected by mining activities can also be used to generate useful products or ecosystem services. Ruíz-Olivares et al. (2013) results consistently, contrary to published information, showed that *Ricinus communis* L. had low metal shoot concentrations, high root metal concentrations, low metal translocation factors and in consequence this plant is participating in metal stabilization (phytostabilization). Moreover, this plant could be an energetic crop due to plants naturally growing in mine tailings with high concentrations of Cd, Pb and Zn had high oil yields (41–64 %). Currently, about 1 Mt of castor bean is harvested annually for oil production, with India, China and Brazil being the mayor producers (Mutlu and Meier 2010). Rajkumar and Freitas (2008) also mentioned that this plant is a crop with multiple non-food uses (industrial, medical and cosmetic products derived thereof) and is an excellent rotation and companion crop. Ruíz-Olivares et al. (2013) was the first report regarding combined oil production and a phytostabilization role for *Ricinus* plants in metal mine tailings and may give a new value to suitable metal-polluted areas.

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Chapter 8
Potential Hazardous Elements Fluxes from Soil to Plants and the Food Chain

Maria Manuela Abreu, Jaume Bech, Luisa Cristina Carvalho, and Erika Santos

Abstract Chemical elements exist naturally in the environment with different concentrations. However, human activities can increase these concentrations, what represent a serious threat to ecosystems and to the human health. In soil, the chemical elements are distributed in different physicochemical forms; inorganic species, organic complexes, adsorbed on solid phases or as constituents of solid phases with different solubility degrees. Plants can absorb only the elements present in the so-called available fraction, which is associated to the exchange complexes and soluble fractions in the soil solution. Absorption, translocation and accumulation of the elements in the plants depend on the species and ecotype as well as on the plant organ, climatic conditions and season of the year. Usually, essential elements (macro and micro-nutrients) are absorbed and translocated to the aerial part of the plant, while toxic elements are retained in the roots, however some hazardous elements are also transported to shoots. High concentrations of toxic elements in the plants can affect their biological processes and/or trigger different physiological

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responses to combat the oxidative stress (e.g. antioxidative enzymes, glutathione, phytochelatins). The elements accumulated in edible organs of crops or in spontaneous plants represent the major entry point in the food chain. Even at concentrations below phytotoxic levels, hazardous elements can pose health risks for humans due to the augmentation effect along the food chain. The objective of this chapter was to elucidate/clarify the pathways of the chemical elements in the soil-plant-human system as well as the physiological mechanisms that plants develop to respond to the absorption and accumulation of hazardous chemical elements.

Keywords Soil-plant system • Micronutrients • Hazardous chemical elements • Phytotoxicity • Food chain

1 Distribution of Chemical Elements in the Soil-Plant Systems

There are a number of chemical elements and compounds that are important contaminants of soils and waters. They include nitrates and phosphates, trace elements, and organic compounds as pesticides, petroleum hydrocarbons and volatile organic compounds. In the geochemical context, a chemical element that occurs in the lithosphere in small concentrations (<1,000 mg/kg) is termed trace element (Adriano 2001). However, according to the same author and for biochemical issues, trace elements usually reach concentrations lower than 100 mg/kg in plant or animal tissues. Some elements that occur as "trace" in biological materials are not "trace" in the Earth crust as is the case of iron.

Despite their occurrence at such small concentrations in living organisms, they may affect biological processes both positively as well as deleteriously (Robinson et al. 2006). Some of them, such as B, Cu, Fe, Mn, Mo, Ni and Zn, are essential for plant development as micronutrients, albeit in lower concentrations (Adriano 2001; Arnon and Stout 1939) but become toxic when absorbed above certain limits (Peralta-Videa et al. 2009). Other transition elements like Ag, Au and Co, and non-transition elements like Al can have a stimulatory effect on plant growth, but are not classified as essential (Ghanati et al. 2005). Plants also absorb elements with no known biological function and considered toxic, even at very low concentrations in soils, such as As, Cd, Cr, Hg, and Pb (Pinho and Ladeiro 2012). Since the brink of the industrial revolution, pollution of the biosphere with hazardous chemical elements has increased dramatically (Swaminathan 2003) provoking the alteration of the physiological response of the plants. Furthermore, chemical elements can be accumulated in edible plant parts entering in the food chain.

Soil–plant transfer of chemical elements is part of biogeochemical cycling, which is a complex process that depends on several factors like geochemical (soil physico-chemical and mineralogical characteristics, soil-water system, etc.), biological (plant species, microorganisms, etc.) and climatic (Kabata-Pendias 2011).

The presence of hazardous elements and their concentrations in soils, from natural and/or anthropic sources, can vary substantially at the spatial and temporal scales.

High total concentrations of hazardous chemical elements in the soil can reduce plant productivity and represent an ecological risk and human health hazard, if these elements enter the food chain or contaminate the aquifers. The actual effects for living organisms and for the environment due to the presence of trace elements in soil cannot be predicted, usually, by the quantification of their total concentration in soil because only a small fraction of this is available and able to be used by the organisms, and to be leached in the drainage waters (Abreu et al. 2007, 2008, 2010, 2012a, b; Adriano et al. 2004; Kabata-Pendias 2004; Neves and Abreu 2009; Santos et al. 2009, 2012, 2013a). The relation of chemical elements concentrations between the available and total fractions of the soil is not clear, and soils from contaminated areas do not always have concentrations of chemical elements in the available fraction higher than those from non-contaminated areas (Abreu et al. 2012a; Santos et al. 2012).

The available fraction (also called extractable, bioavailable, phytoavailable or bioaccessible) corresponds to the chemical elements in the soil solution and associated to the exchange complex of inorganic and organic soil colloids (Adriano 2001; Kabata-Pendias 2004). This fraction can change along time and space. The variation on the concentrations of chemical elements in leachates from sulfide mine wastes over the time was reported by Santos et al. (2010). Bioavailability is considered a dynamic process composed of two phases: "environmental bioavailability" related to the physico-chemical determined fraction and "toxicological bioavailability" measured by physiological induced effects (Peijnenburg et al. 1997).

Plant species, climatic (e.g. water regime) conditions, and physical, chemical, mineralogical and biological characteristics of the soils (e.g. texture, pH, redox potential, soil mineralogy, soil microorganisms activity, concentration and type of organic matter) can influence the availability of the chemical elements (Adriano 2001; Kabata-Pendias 2004; Wang et al. 2004). The formation of secondary soluble salts of metals and metalloids in wastes from mining areas and their deposition in soils represents an increase of the available fraction for the plants due to the metals/metalloids released by the percolation of water (Gonzalez-Fernandez et al. 2011; Pérez-López et al. 2008). Also, the continuous wastewater application to soil irrigation can change some chemical characteristics of the soil (like pH and organic carbon) and lead to the addition and/or the concentration increase of Cd, Cr, Cu, Ni, Pb and Zn in the soils and, consequently, in vegetation (Khan et al. 2008) depending on the species and its physiological response mechanisms, but with particular concern on edible plants. Some traditional agriculture practices allowing to the manipulation of the soil pH, as liming application, are effective to change the chemical elements availability as is the case of the Cd availability in soils (Fernandes et al. 1999).

The association of the chemical elements with soil components, mainly, with low soluble solid phases (e.g. included in the crystal lattice) in the so-called residual fraction (after sequential or differential chemical extractions) and iron and manganese oxides (adsorbed or coprecipitated) explain the low concentration of some metals (Cu, Mn, Pb, U and Zn) and metalloids (As and Sb) in the available fraction of some contaminated and non-contaminated soils (Abreu et al. 2009a, 2010, 2012a; Neves et al. 2009; Santos et al. 2012). Table 8.1 shows the percentage of the concentration of the elements ascribed to the available fraction, extracted with different aqueous solutions, when compared to their total concentration in some soils collected in contaminated and non-contaminated areas. The association of the hazardous chemical elements to the above referred soil compounds represents the smallest environmental risk when compared to the available fraction or even the fraction of the elements chelated by organic matter. The unavailability of As, Fe and Pb can be controlled by the presence of solid phases with low solubility, like arsenates, included in the residual fraction as it occurs in soils from São Domingos mine (Santos et al. 2012). The low availability of Pb for plant uptake can also be related to the existence of precipitates containing this metal, as phosphates and sulfates, adsorption on iron and manganese oxides, and complexes with organic matter (Peralta-Videa et al. 2009; Santos et al. 2012). In Miguel Vacas copper mine, the abundant presence of Cu phosphates with low solubility (libethenite and pseudomalachite) in the waste-rock piles can explain the absence of Cu contamination in the surrounding environment (water and soils) (Abreu et al. 2008). The chemical form (speciation) of some chemical elements as well as their partitioning among the soil components are then crucial to determine and explain their availability as well as to predict their mobility to adjacent areas (Kabata-Pendias 2004; Wuana and Okieimen 2011).

Although the determination of the available faction of a chemical element in the soil is an important parameter to understand plant uptake, its real prediction is difficult. The soil available fraction can be extracted with different aqueous solutions varying with soils and chemical elements (Anjos et al. 2012; Feng et al. 2005; Santos et al. 2012; Wang et al. 2004). Furthermore, the bioavailability of a particular chemical element is also specific to each plant species (Anjos et al. 2012). Each extractant aqueous solution usually simulates one single soil process (complexation, ion exchange, etc.) or extract chemical elements associated to certain soil solid phases, however several biological reactions can also occur together in the rizosphere area (Feng et al. 2005). For these reasons, Feng et al. (2005) suggested a rhizosphere-based method for the determination of chemical elements concentration in the available soil fraction. This methodology uses fresh rhizosphere soil, rather than bulk soil, and the extraction aqueous solution contains some low-molecular-weight organic acids identified in the exudates of plant roots and products of fungi and bacteria activity.

As was already referred, plant species is an important factor that should also be taken into account (Anjos et al. 2012; Wang et al. 2004). Thus, the interpretation of the concentrations of the elements extracted from soil with a specific reagent can give reliable information only for a particular soil–plant system (Kabata-Pendias 2011).

Table 8.1 Concentrations (mg/kg dry weight) of As, Cu, Pb and Zn in the total and the available fractions (extracted with different aqueous solutions) of the soils (min – max (mean percentage of the total concentration)) from mine areas (Braçal, Caveira, São Domingos) and non-contaminated sites (Caldeirão, Grândola and Pomarão)

Chemical elements concentrations (mg/kg)						
	Braçal mine	Caldeirão	Caveira mine	Grândola	Pomarão	São Domingos mine
Total						
As	–	18–20	666–1,280	24–26	16–17	1,940–3,030
Cu	37–712	43–99	339–500	43–45	99–171	210–237
Pb	1,480–13,400	37–67	5,550–8,900	31–50	36–55	5,280–9,210
Zn	62–905	43–93	193–514	82–108	63–93	36–57
Available fraction						
As		[a]<DL [b]0.02–0.3 (1 %) [c]<DL [d]<DL [e]<DL	[c]0.4–1.0 (0.1 %) [e]0.02 (<0.1 %) [f]2.1–8.5 (0.5 %)	[c]0.1–0.3 (1 %) [e]0.02 (0.1 %)	[a]<DL [b]<DL–0.01 (0.1 %) [c]<DL [d]<DL [e]<DL	[a]<DL–0.2 (< 0.1 %) [b]0.01–0.4 (0.1 %) [c]<DL [d]<DL [e]<DL
Cu	[a]0.05–2.8 (0.3 %) [b]0.5–42.4 (5 %) [c]0.2–14.9 (1 %) [d]<DL–2.5 (0.4 %) [e]<DL–12.3 (1 %)	[a]0.02–0.05 (0.1 %) [b]0.09–0.3 (3 %) [c]<DL [d]<DL [e]0.2–0.3 (1 %)	[c]0.5–1.9 (0.2 %) [e]0.02–0.09 (<0.1 %) [f]1.7–2.0 (0.5 %)	[c]0.2–1.9 (3 %) [e]0.02 (0.1 %)	[a]0.03–0.1 (0.1 %) [b]5.2–6.5 (2 %) [c]0.05–1.1 (0.3 %) [d]0.2–0.3 (1 %) [e]0.6–0.7 (1 %)	[a]0.2–0.7 (0.2 %) [b]10.1–13.5 (5 %) [c]0.3–1.5 (0.4 %) [d]3.0–9.1 (3 %) [e]2.5–7.2 (2 %)
Pb	[a]6.5–464 (1 %) [b]232–4,050 (37 %) [c]163–3,000 (24 %) [d]18.9–1,550 (8 %) [e]206–4,310 (27 %)	[a]2.3–3.5 (1 %) [b]0.8–3.6 (1 %) [c]<DL–8.4 (4 %) [d]27.2–33.1 (15 %) [e]0.3–1.1 (0.4 %)	[c]3.1–268.1 (3 %) [e]2.7–10.4 (0.1 %) [f]13.1–28.4 (0.3 %)	[c]0.4–2.6 (4 %) 0.1–0.2 (3 %)	[a]1.6–2.7 (4 %) [b]0.8–1.0 (2 %) [c]<DL [d]25.6–27.3 (45 %) [e]0.2–0.3 (1 %)	[a]8.0–30.3 (0.2 %) [b]64.2–152.1 (2 %) [c]4.3–20.0 (0.2 %) [d]55.6–91.4 (1 %) [e]8.3–67.3 (1 %)
Zn	[a]0.2–14.5 (1 %) [b]0.8–90.1 (3 %) [c]0.1–75.1 (3 %) [d]<DL–112 (5 %)	[a]1.1–1.3 (2 %) [b]<DL [c]1.3–2.6 (4 %) [d]6.5–7.9 (17 %)	[c]3.8–11.0 (3 %) [e]0.02–0.3 (< 0.1 %) [f]4.3–7.7 (2 %)	[c]0.9–3.5 (3 %) [e]0.02 (<0.1 %)	[a]1.2–1.3 (2 %) [b]<DL [c]0.3–2.1 (3 %) [d]5.3–8.5 (11 %)	[a]1.2–1.3 (3 %) [b]<DL [c]2.4–2.7 (6 %) [d]9.5–9.9 (27 %)

(continued)

Table 8.1 (continued)

Chemical elements concentrations (mg/kg)						
	Braçal mine	Caldeirão	Caveira mine	Grândola	Pomarão	São Domingos mine
	[e]3.0–17.9 (3 %)	[e]1.0–1.8 (8 %)			[e]2.3–3.2 (4 %)	[e]4.4–5.7 (12 %)

Adapted from Anjos et al. (2012), Abreu et al. (2012a, b), and Santos et al. (2009, 2011, 2012)

DL detection limit of the apparatus

[a] Water

[b] DTPA (0.005 mol/L diethylenetriaminepentaacetic acid + 0.1 mol/L triethanolamine + 0.01 mol/L calcium chloride; Lindsay and Norvell 1978)

[c] Ammonium acetate (1 mol/L and pH 7; Kabata-Pendias 2004; Schollenberger and Simon 1945)

[d] Calcium chloride (0.1 mol/L)

[e] Calcium nitrate (0.5 mol/L; Berti et al. 1997)

[f] Mixture of organic acid (10 mmol/L; Feng et al. 2005)

2 Uptake Mechanisms of the Chemical Elements by Plants and Soil-Rhizosphere System

The soil rhizosphere environment of a plant is significantly different from that of the bulk soil (Adriano 2001). Biological functions of plant roots as uptake, respiration and exudation contribute to changes in the chemical parameters in the rizosphere soil (concentration of nutrients and toxic elements availability, concentration of chelating and complexing agents, pH, etc.) and, consequently, type, number and activity of the soil microorganisms (Adriano 2001; Kabata-Pendias 2011; Hinsinger et al. 2006). The increase of microbial respiration as well as the activity of protease, phosphatase and cellulase due to the presence of plants (*Dactylis glomerata* L., *Briza maxima* L., *Erica australis* L., *Spergularia purpurea* (Persoon) G. Don fil. and *Chaetopogon fasciculatus* (Link) Hayek) was reported by Varennes et al. (2010a, b) in soil rehabilitation experiments.

The plant-related factors affected by the rhizosphere environment characteristics are the chemical elements transport in the rhizosphere, their level of absorption by soil organisms, their passage through the plants' plasmalemma at the root-soil interface (Robinson et al. 2006) as well as the level of elements accumulation in the roots (Nouri et al. 2009). These processes can be either amplified or delayed depending on the plant species and growth stage.

Plant roots are the foremost entry point for soil chemical elements, playing a key role in metals/metalloids filtration, adsorption and cation exchange, and can even induce chemical changes in the rhizosphere (Nouri et al. 2009). Plant roots can change the pH values of the rhizosphere and exudate compounds, which can have an important role in the availability of the elements. The acidification of the rhizosphere soil can promote the increase of the mobility and availability of elements, such as Al, Pb and Zn, leading to the increase of their uptake and, consequently, of their concentrations in plants (Hinsinger et al. 2006; Pinho and Ladeiro 2012).

The uptake of water and solutes from the soil by the plant roots can be considered an important factor in the changes of the elements concentrations in the soil available fraction (Hinsinger et al. 2006). The roots exudation and micro-organism activity in the rhizosphere affect biogeochemical cycles due to the effective release of the chemical elements from soil constituents (Hinsinger et al. 2006; Kabata-Pendias 2011). Roots can also contribute to the release of non-exchangeable elements as is the case of the root-induced weathering of micas and consequent release of interlayer K, as a direct result of the roots sink-effect, together with K depletion (Hinsinger 2002). On the other hand, plant exudate compounds can bind elements in the rhizosphere, thus limiting their uptake by the plant. At the roots surface, Pb binds to carboxyl groups of mucilage uronic acids restricting Pb uptake and functioning as important protective barrier of the roots systems (Sharma and Dubey 2005). The same authors also reported the retention of Pb in roots due to the extracellular precipitation of Pb as phosphates and carbonates, deposited in cell walls, and its binding to ion exchangeable sites on the cell walls.

Chemical elements can also be accumulated in or on the roots surface being the plants plasmalemma the first barrier for the selection and control of the uptake (Adriano 2001). The uptake rate can depend on the availability of the elements in the rhizosphere, roots system and element type (micronutrient, macronutrient or non-essential element) and plant demand, plant species and even population. However, variations on the chemical elements concentrations in soils, both in the available and total fractions, cannot explain the differences intra- and inter-population in the concentrations of the elements in the roots of some plant species (Abreu et al. 2012a, b; Fernandes et al. 2002, 2011; Santos et al. 2012).

The transfer coefficient of a chemical element determined by the ratio (roots element concentration)/(soil available fraction element concentration) or the relation between these two parameters can reflect plant capacity to uptake an element from the soil available fraction. The uptake of some elements can reach large quantities while other elements are more or less avoided, however these behaviours depend on several conditions, as previously mentioned.

In the roots of some *Cistus* species (*C. ladanifer* L., *C. monspeliensis* L., *C. populifolius* L., *C. salviifolius* L. and *Cistus* × *hybridus* Pourr.), growing in mine areas (Caveira, Chança and São Domingos) and in non-contaminated areas, were observed higher concentrations of macro- and micro-nutrients than in the soil available fraction, suggesting high uptake of these elements (Abreu et al. 2012a, b; Fernandes et al. 2011; Santos et al. 2012). However, the potential uptake restriction and low extent uptake of non-essential elements, like As, Pb and Sb, in those *Cistus* populations was only observed in some cases (roots concentrations $<$ soil available concentration). Nevertheless, *C. ladanifer* from Neves Corvo mining area seems to have an opposite behaviour for As (Batista et al. 2004). Rumex K-1 (*Rumex patientia* × *Rumex tianschanicus*) sown in a contaminated field near to Lechang Pb/Zn mine, showed concentrations of Pb and Zn in roots lower than those determined in the soil available fraction (extracted with DTPA) while concentration of Cd also in the roots was two-fold higher, and the Cu concentration was similar (Zhuang et al. 2009).

Mechanisms of uptake differ with the chemical element (Kabata-Pendias 2011). P-type heavy metal ATPases have been identified in plants functioning in the transport of several essential and toxic elements (e.g. Cd, Cu, Pb, Zn) across the membranes (Yruela 2005). Zinc is absorbed from the soil solution through membrane transporters. The main transporters are members of the ZIP family, namely ZIP1, a high-affinity Zn transporter (Ramesh et al. 2003), and ZIP3 that exist solely in the roots and ZIP4, in roots and shoots possibly moving Zn between tissues, into leaf cells, and into vacuoles (Grotz et al. 1998). Also, HMT4 protein was shown to control Zn transfer into the xylem of *Arabidopsis halleri* L., a Zn hyperaccumulator species (Hanikenne et al. 2008). When roots of *A. halleri* and *Thlaspi caerulescens* J. Presl. & C. Presl. were supplied with high Zn concentrations, Cd uptake decreased dramatically, showing that Cd influx is largely due to Zn transporters (Zhao et al. 2002). So far, specific transporters for Ni uptake have not yet been identified, but it is possible that Ni entrance into the roots occurs in the same way as Cd, using Zn transporters (Assunção et al. 2008).

Arsenic is an analog of P and in plants it competes for the same uptake carriers in the roots (Meharg and Hartley-Whitaker 2002). In root cells of the As hyperaccumulator *Pteris vittata* L. plasma membranes have a higher density of phosphate/arsenate (P/As) transporters than those of non-hyperaccumulators possibly due to constitutive gene over expression (Caille et al. 2005). Also, the increased of As uptake by *P. vittata* depends on the higher affinity for arsenate by the P/As transport systems themselves (Poynton et al. 2004) as well as on the plant's ability to increase As bioavailability in the rhizosphere by reducing pH through root exudation of dissolved organic carbon, increasing the amount of water soluble As that can be taken up by the roots (Gonzaga et al. 2009). Some grass species are As tolerant due to the suppression of the high-affinity P/As uptake system (Sharples et al. 2000). This mechanism helps lower As influx to levels that the plant can tolerate and detoxify (Meharg 1994). However, as tolerant grasses still absorb As, at low rates, the As accumulation throughout the life span of a plant growing on a contaminated soil can reach very high concentrations.

The uptake and distribution of Co into plants is species-dependent and controlled by different mechanisms (Kukier et al. 2004; Li et al. 2004). Copper uptake mechanisms are not still clear, however the rate of uptake of this metal differs with the species (Kabata-Pendias 2011). P-type heavy metal ATPase, COPT Cu transporters and Cu chaperones are some transporters identified for copper (Yruela 2005).

3 Chemical Elements Accumulation in Roots and Translocation Roots-Shoots-Fruit-Seeds

The distribution patterns and accumulation of the chemical elements into plants vary with the element and its concentration, plant species, population, plant organ and season. In potato tubers, the radionuclides accumulation depends on plant compartment, reaching in the peel, compared to the pulp tuber, 90–97 % of the total U concentration, 95 % of the Th concentration, more than 65 % of Po concentration, and 50–60 % of Ra concentration (Carvalho et al. 2009; Neves and Abreu 2009; Neves et al. 2012a, b). However, Mn presented an opposite trend being this element mainly concentrated within the tubers pulp than in the peel (67–78 % of the Mn total concentration), while the behaviour of Al was similar to the radionuclides (76–85 % of the total Al was concentrated in the potato peel) (Neves et al. 2012b).

Plant accumulation of chemical elements is the result of the uptake activity and translocation efficiency (Clemens 2006) being controlled (e.g. Co) by different mechanisms (Kukier et al. 2004; Li et al. 2004). The irregular variation in translocation and/or accumulation of chemical elements in plants growing under natural conditions can have no apparent relation with their soil concentrations, both in the total and available fractions, and with soil pH (Abreu et al. 2007, 2008, 2011, 2012a, b; Khan et al. 2008; Márquez-García et al. 2012; Santos et al. 2009, 2012). The same behaviour was observed in microcosm experiments under controlled conditions, and concerning Cr(III) and Cr(VI) application to soils at increasing doses (Fernandes et al. 2002). Therefore, the analysis of the plants behaviour by soil–plant coefficient transfer ([shoots element]/[total soil element]) and bioconcentration coefficient ([shoots element]/[element bioavailable soil fraction]) should be done carefully.

Water irrigation quality seems to have a great influence in plant behaviour. In field experimental assays, a significant increase of the concentrations of Utotal, Al and Mn in potato tubers and lettuce leaves irrigated with uranium-contaminated water was observed (Neves and Abreu 2009; Neves et al. 2012a, b). The increase of radionuclides concentrations in irrigation waters contributed to an accumulation of Utotal, U isotopes (^{234}U, ^{235}U and ^{238}U) and ^{226}Ra in potatoes tubers, but not of ^{230}Th and ^{210}Po, being the increase proportional to their concentration in the irrigation water (except for Ra; Carvalho et al. 2009).

In greenhouse pot experiment under controlled conditions, the increase of the soil available fraction (extracted with $CaCl_2$, HNO_3 or $NH_4C_2H_3O_2$) by the soil application of increasing doses of Cd provoked high Cd accumulation in *Sorghum sudanense* cv. Tama (Fernandes et al. 1999). The same was observed in the assay using *Raphanus sativus* L. at different application rates of Cr(III) and Cr (VI) (10, 50, and 100 mg/kg) to two quite different soils (Ferric Lixisol and Stagnic Luvisol) (Fernandes et al. 2002).

In general, elements chelation in the cytoplasm, oxidation-reduction processes, storage into vacuoles, and inclusion into functional or sequestering metabolites are

Table 8.2 Chemical elements concentrations (mg/kg dry weight) in different plant organs of spontaneous and cultivated plant species. Pegões is a non-contaminated soil

Plant species	Location	Chemical elements	Roots	Leaves/ shoots	Fruit/ tuber	Seeds
Cistus salviifolius	São Domingos mine area	As	6.2–18.9	0.9–10.0		
		Cu	5.6–39.2	5.3–19.5		
		Pb	18.4–41.5	1.3–23.2		
		Zn	30.0–101.4	109.2–206.8		
Cistus ladanifer		As	8.4–15.8	0.8–2.3		1.7–2.8
		Cu	5.2–16.6	6.6–9.6		8.0–9.7
		Pb	42.7–75.7	34.6–72.4		2.8–10.9
		Zn	30.9–54.8	113.7–184.5		58.8–62.7
		As		0.5–2.0		1.4–2.8
		Cu		5.3–10.5		6.4–7.7
		Pb		44.5–71.5		3.0–7.1
		Zn		72.0–117.8		50.0–53.7
		As		0.2–0.6		1.3–1.6
		Cu		5.4–10.4		5.5–6.6
		Pb		41.2–72.1		4.1–5.0
		Zn		67.8–102.1		45.4–51.4
Licopersicum esculentum	Penedono mine area	As	1,129 ± 85	21 ± 6	1.9–7.5[a]	
		Zn	524 ± 24	384 ± 24		
	Pegões	As	3.1 ± 0.4	0.7 ± 0.2	<0.1	
Petroselinum crispum	Penedono mine area	As	933 ± 11	53 ± 29		
		Zn	1121 ± 89	638 ± 304		
Solanum tuberosum	Cunha Baixa mine area	Al		950–1,811	19.8–64.3	
		Mn		163–1,027	8.3–14.8	
		U		0.9–4.5	0.007–0.6	
Lactuca sativa		U	0.1–6.0	0.03–2.6		

Adapted from Abreu et al. (2012b), Madeira et al. (2012), Neves et al. (2008, 2012b), and Santos et al. (2011, 2012)

[a] Fruits from plants growing on soils amended with organic matter or calcium phosphate

some retention (and tolerance) mechanism developed by plants (Adriano 2001; Kabata-Pendias 2011; Rascio and Navari-Izzo 2011). Adriano (2001) also states that the plant capacity to control the effect of non-essential elements, especially polyvalent cation species, after their uptake is also related to other process; the element remains in soluble form during the transport within plant by interaction with low-molecular-weight ligands.

Usually, the plants translocate essential elements to the aerial part while retaining most of the toxic elements within root cells (Table 8.2). However, there are some exceptions, and several toxic elements are actually transported to shoots, usually through the xylem. *Phragmites australis* (Cav.) Trin. ex Steud., growing in nutrient solution with and without additional Zn, retains Zn in roots, reducing the concentration of this element in leaves (Jiang and Wang 2008). In opposition, *Pteris vittata* translocates considerable amounts of As from the roots to the fronds (Cao et al. 2004).

Cistus species (*C. populifolius*, *C. salviifolius*, *Cistus* × *hybridus* and *C. ladanifer*), growing in different mining areas from Iberian Pyrite Belt or in non-contaminated areas, translocate macronutrients (Ca, K and Mg) and micronutrients (B, Cu, Fe, Mn, Mo, Ni and Zn) to the shoots and retain toxic elements (As, Pb and Sb) in their roots. However, variations inter- and intra-population in the behaviour of translocation and accumulation of those chemical elements were also observed (Abreu et al. 2011; 2012a, b; Santos et al. 2012). In Chança mine area, where the soils have low level of polymetallic contamination, *C. monspeliensis* and *C. ladanifer* plants translocated nutrients (Mn, Ni and Zn) and Cr to the leaves, but for As and V both translocation behaviours were observed (Fernandes et al. 2011). In *C. ladanifer* populations from Neves Corvo mine, total As and As(III) were always translocated from roots to the leaves, but As accumulated in leaves is mainly in the organic form (Batista et al. 2004). This is probably due to the fact that the inorganic compounds of As are, usually, more toxic than the organic forms (Chutia et al. 2009; Vaclavikova et al. 2007). In phytoplankton and macroalgae, methylated forms of As (e.g. DMA – dimethylarsinic acid and MMA – monomethylarsinic acid) are metabolized to phospholipids and arseno-sugars (Phillips 1990). Previously, some authors (Broeck et al. 1998; Meharg 1994) have only identified arsenate and arsenite in terrestrial plants. However, more recently Koch et al. (2000) and Meharg and Zhao (2012, and other references herein) found, in general, low concentrations of methylated As species such as MMA and DMA in several plant species. The uptake and accumulation of As was also reported in two species of the genus *Erica* collected in São Domingos mine area, however the aerial part of *E. australis* L. accumulates only As(III) while *E. andevalensis* Cabezudo & Rivera has both inorganic forms as well as DMA (Márquez-García et al. 2012). According to Oliva et al. (2009), the latter plant species shows no restriction on Cu, Ni, and S translocation to shoots.

A cultivated plant, *Rumex* K-1, grown on contaminated soils, accumulated low amounts of heavy metals (Cu, Cd, Pb and Zn) in shoots being most of the hazardous elements, especially Pb and Zn, located in the roots (Zhuang et al. 2009). Similar behaviour was reported in experimental assay with As-contaminated soil using parsley (*Petroselinum crispum* var. *latifolium* (Mill.) Nymen) and tomato (*Lycopersicon esculentum* L. var. *Elegy*, APT 403) where Al, As, and Zn were mainly accumulated in roots while the nutrients, Mg and Mn, were translocated to the leaves (Madeira et al. 2012). Even in non-contaminated soil both species retained As in roots (Madeira et al. 2012). In opposition, potato plants showed a low content of Al, Mn and U in tubers, being these elements translocated to the aerial tissues, independently of the level of U contamination in soils and irrigation waters (Neves et al. 2012b). Another species, *Raphanus sativus*, also cultivated in microcosm assay under controlled conditions, showed higher concentrations of Cr (III) and Cr(VI) in shoots than in roots and the accumulation of this chemical element in roots was only observed with the highest application rate of Cr to the soil – 100 mg/kg (Fernandes et al. 2002).

Cultivated plant species and cultivars present a wide variation in their capacity for Cd absorption and translocation to edible crop parts, differing enough in their ability to accumulate this element in different parts of the same plant (Cieslinski et al. 1994, 1996). Leafy vegetables like cabbage, lettuce and spinach accumulate Cd in the aerial parts but Cd tends to be also accumulated in the roots of some vegetables as in carrots, turnips and potatoes. The highest concentrations of Cd in plants cultivated in contaminated areas were always listed for roots and leaves, whereas this element seems to be excluded from the seeds (Kabata-Pendias 2011). In tobacco plants (*Nicotiana tabacum* L.) and strawberry tree (*Arbutus unedo* L.), Cd tends to accumulate in other tissues (leaves and stems) than in roots (Clemens 2006) but not in *A. unedo* fruits (Abreu et al. 2014; Godinho 2008). However, Cd accumulation in the shoots can be limited by several factors, including the transpiration rate and, possibly, root uptake, radial transport, and xylem loading (Salt et al. 1995). It has been reported that glandular trichomes can accumulate and excrete large amounts of metals, such as Mn and Pb, and might be the major compartment of Cd accumulation in leaves (Harada and Choi 2008).

Concerning Pb translocation within the plant, once in the root cortex it moves into the apoplastic space, using the transpiration conductive system (Wierzbicka 1999), by passing the endodermis and accessing the symplast in young and in lateral roots (Eun et al. 2000). Lead is able to enter and move within the cytoplasm and the proteins that mediate its movement across the membrane are the calmodulin-binding transporters CBP4 (Arazi et al. 1999). Variations on Pb translocation and accumulation rates can be related to the chemical species of the element being roots endodermis a barrier for the Pb translocation from the roots to other plant parts (Sharma and Dubey 2005). Also the root epidermis retains Pb, and partially Fe, as was observed in *E. andevalensis* (Oliva et al. 2009). Translocation of Zn in *Phragmites australis* seems to be also regulated by similar mechanisms as most of Zn is compartmentalized in roots cortex cells (intercellular space > cell wall > vacuole > cytoplasm) reducing its translocation to the leaves (Jiang and Wang 2008).

In the aerial part of a specific plant, element concentrations can vary with the plant organ (leaves, fruits and seeds), the organ age (young, mature and senescent leaves) and the season (Kabata-Pendias 2011; Santos et al. 2009, 2011). Even in the leaves, the chemical element compartmentalization through the different tissues depends upon the element, suggesting different tolerance mechanisms to protect photosynthetic processes as was observed for *Erica andevalensis* Cabezudo & Rivera, an endemic species of the Andévalo region (Spain), growing in Rio Tinto mining area, where Ni accumulation in leaves occurs preferentially in the adaxial epidermis, while Mn is accumulated in both photosynthetic (mesophyll) and non-photosynthetic tissues (epidermis) (Oliva et al. 2009).

Sharma and Dubey (2005) also reported that Pb accumulation capacity in the leaves depends on age. Studies carried out by Cao et al. (2004) on *Pteris vittata*, showed that for this species the capacity of As accumulation varied not only with leaves maturity but also with the As concentration in soil; young fronds of *P. vitatta* presented greater As concentration than mature fronds until a maximum of 20 mg As/kg in the soil, but for highest As concentration in soil the contrary was observed. Santos et al. (2009, 2011, 2013b) also reported the same behaviour for As and Zn in *C. ladanifer* where the concentrations are influenced by the season. In spring, concentrations of As, Pb and Zn increased with leaves development in *C. ladanifer* plants from São Domingos mine, however in non-contaminated areas this behaviour was only observed in Pomarão (region with the same climatic condition than São Domingos) for As. In summer, São Domingos plant population showed the same accumulation behaviour of Zn when compared with spring season (Santos et al. 2009, 2011). The high accumulation of chemical elements in senescent leaves can suggest a tolerance mechanism characterized by the exclusion of potentially toxic elements during the fall of the leaves (Ernst et al. 1992). Seasonal variation in *C. ladanifer* concentrations of As, Pb and Zn was observed (summer > spring) but was not standard for all the populations and elements (Santos et al. 2009, 2011, 2013b). This behaviour can suggest a tolerance mechanism that protects the plant in the period with great photosynthetic activity and growth. In opposition, *C. inflatus* shoots from Braçal mine area presented higher Pb concentrations in spring than in autumn (Abreu et al. 2009b).

Copper tends to be distributed uniformly through the plant (Kabata-Pendias 2011; Santos et al. 2009, 2011, 2012, 2013b). In Mediterranean plants, like *C. ladanifer*, N concentration decreases with leaf development and season (summer < spring) due to it translocation for young and photosynthetically active tissues (Correia 2002; Santos et al. 2013b).

Although distribution of Pb into the plant can differ with species, this element tends to decrease in the following order: roots > leaves > stem > flowers > seeds (Sharma and Dubey 2005) (Table 8.2). In *C. ladanifer* growing on soils with different contamination levels, no differences were obtained between As concentrations in leaves and seeds but higher concentrations of Pb and Zn were observed in leaves than in seeds (Santos et al. 2012). However, the Cu distribution pattern differed with the population collected in contaminated and non-contaminated areas (leaves ≈ seeds and leaves > seeds, respectively) (Table 8.2). The low concentrations of hazardous elements in seeds guarantee their viability. Studying tomato plants behaviour in pot experiments, Madeira et al. (2012) found that the As translocation within plant decreased from roots, shoots and fruit, independently of plant growing on uncontaminated or As-contaminated soil amended with organic matter or calcium phosphate (Table 8.2).

4 Food Chain

Soil contamination by chemical elements represents a serious threat to ecosystems and the human health. Humans and animals can become contaminated with hazardous chemical elements by contact with the contaminated soil, through the food chain by ingestion (soil-plant-human; soil-plant-animal or soil-plant-animal-human) or by drinking contaminated water. Indirectly, soil contamination reduces the food production and quality (safety and marketability) through phytotoxicity, and quantity through the reduction of available land for agricultural production (Ling et al. 2007).

Chemical elements accumulation in edible parts of crop plants or spontaneous plants represents the principal entry in the food chain. Chemical concentrations of As, Cu, Fe, Pb, U and Zn in some aromatic plants and vegetables are shown in Tables 8.3 and 8.4. The knowledge of the concentration of hazardous chemical elements (e.g. Al, As, Pb, mainly classified as toxic elements, and Cu, Fe and Zn, which are also micronutrients) in edible parts of plants is essential because their toxicity can affect both humans and other animals when plants are intaken. Although some elements present low toxicity (like macro- and micronutrients) the intake of some plants, with high concentrations, in the overall diet can lead to the excess of elements intake. This can be the case of *Thymus vulgaris* L. and *Mentha sylvestris* L. cultivated in kitchen gardens from São Domingos mine area, which have concentrations of Fe and K higher than the normal values for plants (Gonzalez-Fernandez et al. 2011). These aromatic plants can contribute, when included in a regular diet, to an excessive intake of these elements, which can pose health threat, especially K for some risk groups.

Concentrations of chemical elements in plants even below phytotoxic levels can contribute to potential risks for humans due to the augmentation effect in food chain. Concentrations of Pb and Cd declined along the food chain after *Rumex* K1 uptake from soils (soil-plant-insect- chicken muscle), but Cu and Zn accumulation in insects were higher than those in plants and chicken muscle (Zhuang et al. 2009). According to these authors, significantly higher Pb concentrations were measured in the muscle and liver of chicken that had been fed with contaminated insects when compared with control chicken. These values were above the Pb limit concentrations proposed by the EC Commission Regulation (Kabata-Pendias and Mukherjee 2007), and may pose potential health risks associated with Pb, if these animal organs are consumed.

Contamination of agricultural soils due to the vicinity of mine areas, soil irrigation with contaminated water or soil irrigation with wastewaters, and the possible accumulation of chemical elements in food crops have been studied (e.g. Gonzalez-Fernandez et al. 2011; Khan et al. 2008; Neves et al. 2008, 2012a, b). The health risk assessment can be evaluated by chemical elements exposure by vegetables intake. For this reason, the element's chemical exposure dose should be estimated considering the maximum content of elements in food, intake rate, adult

Table 8.3 Chemical elements concentrations (mg/kg dry weight) in edible plants growing on kitchen gardens from the vicinity of São Domingos mine (Portugal)

Chemical elements concentration (mg/kg)					
	As	Cu	Fe	Pb	Zn
Brassica oleracea	1.8–7	3.5–5.0	40–42	8–10	15–25
Coriandrum sativum	1.4–12	6.8–8.1	80–285	10–35	25–60
Grass	6.0–6.1	6.6–8.5	35–60	4.6–15	20–30
Mentha sylvestris	3.8–20	9.8–17	400–950	25–60	35–45
Petroselinum crispum	3.0–25	6.9–8.7	170–450	20–60	45–120
Thymus vulgaris	2.2	15	700	30	50

Adapted from Gonzalez-Fernandez et al. (2011)

Table 8.4 Uranium concentrations (μg/kg dry weight) in vegetable foodstuff growing on agricultural soils surrounding the former uranium mine (Cunha Baixa, Portugal)

Vegetable foodstuffs	U concentration (μg/kg)
Latuca sativa	189–5,373
Solanum tuberosum (tuber)	589
Phaseolus vulgaris (pods)	94–239
Daucus carota (peeled roots)	6–184
Brassica oleracea	14–255
Malus domestica (fruit)	11
Zea mays (grain)	22

Adapted from Neves et al. (2012a)

lifetime, exposure duration average body weight and average exposure time for non-cancer risk (USEPA 1997).

Food crops as radish (*Raphanus sativus* L.), maize (*Zea mays* L.), green cabbage (*Brassica juncea* L.), spinach (*Spinacia oleracea* L.), cauliflower (*Brassica oleracea* L.), turnip (*Brassica napus* L.), and lettuce (*Lactuca sativa* L.), growing on soils irrigated with wastewaters, were contaminated with Cd, Cr, and Ni, exceeding (partially and/or totally depending on species or element) the permissible limits defined by SEPA (2005), however no health risks are associated to their ingestion due to the low daily elements intake for both adults, and children (Khan et al. 2008).

The U concentrations in some edible parts of vegetables (lettuce, green beans and potato tubers), cultivated in agriculture soils included in a former U mine area, were very different reaching the highest values in lettuce leaves, specially those irrigated with U-contaminated water (Neves and Abreu 2009) (Table 8.4). Potato tubers accumulated Al, U, and ^{226}Ra, being their accumulation levels proportional to the increase of these elements in irrigation waters, however peeling removes most of these elements from potatoes and minimizes human exposure through ingestion (Carvalho et al. 2009; Neves et al. 2012a, b). According to the same authors, although concentrations of Al and U in soil, irrigation water and vegetables (lettuce, potato tubers and green bean) were high, the assessment of the health risk based on hazard quotient indicated no potential adverse health risks for adult and children during a lifetime.

In São Domingos mine area, several aromatic plants species (*Petroselinum crispum* (Mill.) Nyman ex A. W. Hill, *Thymus vulgaris* L., *Mentha sylvestris* L. and *Coriandrum sativum* L.) and a vegetable (*Brassica oleracea* L.) cultivated in kitchen gardens exceed the maximum allowed values for Pb and As indicating a possible health risk (Gonzalez-Fernandez et al. 2011) (Table 8.3).

The intake of tomato fruits and parsley growing on an As-contaminated soil poses an acceptable health risk for adults and adolescents (average weekly intake of 500 g of tomato and 20 g of parsley), although the As concentrations were relative greater than in plants growing on uncontaminated control soil (Madeira et al. 2012). Thus, these authors suggested that both vegetables if consumed separately did not represent serious health risk, but a cumulative effect can be achieved if other vegetables cultivated in the same contaminated soils are consumed by inhabitants of the region.

5 Phytotoxicity Effects

At high concentrations, all chemical elements have strong toxic effects and are regarded as environmental pollutants (Nouri et al. 2009). Their presence in the soil can even impair the biodegradation of organic contaminants (Maslin and Maier 2000).

Metabolic disorders of the plants occur in both deficiency and excess of chemical elements and, usually, are the result of several complex factors that depend on environmental conditions. In natural conditions, plant responses can be the result of the co-existence of different stress factors, as is the case of areas with polymetallic contamination or contaminated areas under xeric conditions.

Several plant reactions are related to the toxic effects of chemical elements and some of them correspond to visual toxicity symptoms, like chlorosis and necrosis (Adriano 2001; Kabata-Pendias 2011). Nevertheless, phytotoxicity studies in several species (*Brassica napus* L., *Crotalaria juncea* L., *Hordeum vulgare* L., *Lycopersicon esculentum* L., *Oryza sativa* L., *Pteris vittata* L., *Petroselinum crispum* (Mill.) Nyman ex A. W. Hill) have demonstrated the existence of adverse effects by elements accumulation (As, Cd, Co, Cr, Pb) in the plant, on plant growth and biomass yield, both shoots and roots (Cao et al. 2004; Li et al. 2009; Fernandes et al. 1999, 2002; Madeira et al. 2012; Pereira et al. 2002; Verma and Dubey 2003), however these effects depend on species. The plants growth inhibition/reduction can also be due to synergistic effects being an indirect response of the toxicity (Madeira et al. 2012).

In general, the excess of Co, Cr, Cu and Pb lead to a decrease of chlorophyll synthesis (Chatterjee and Chatterjee 2000; Peralta-Videa et al. 2009; Vajpayee et al. 2000) while Cd decreases the photosynthesis activity (Wojcik and Tukiendorf 2004; Mohanpuria et al. 2007). In *Cistus ladanifer* plants from São Domingos mine, the decrease of chlorophyll concentration was related to Pb concentrations in leaves but reduction of leaf area was due to both Pb and Zn concentrations (Santos et al. 2013b). On the other hand, high Pb concentrations in the plant inhibit the activity of S-containing enzymes because Pb reacts with sulfhydril groups affecting aquaporines, altering membrane proteins and disturbing channels of nutrients uptake (Yadav 2010).

High chemical elements concentrations (e.g. Cr, Cu, Hg, Pb) induce oxidative stress by increasing the production of reactive oxygen species (ROS) which can disturb metabolic pathways, disrupt the membrane lipids and damage macromolecules (Shanker et al. 2005; Hegedüs et al. 2001; Israr and Sahi 2006; Reddy et al. 2005; Sas-Nowosielska et al. 2008).

High levels of Hg are toxic to plant cells inducing visible injuries and impairing physiological functions (Zhou et al. 2007), such as the closing of stomata by binding to aquaporins, thus obstructing water flow (Sas-Nowosielska et al. 2008). Other harmful effects are the interference with electron transport in mitochondria and chloroplasts (Israr and Sahi 2006; Sas-Nowosielska et al. 2008).

High Ni concentration disrupts nutrient balance, causes disorder of cell membrane functions, affecting the lipid composition and H-ATPase activity of the plasma membrane (Ros et al. 1992). Increases in malondialdehyde (MDA) concentration in Ni sensitive plants has also been reported (Gonnelli et al. 2001), impairing membrane functionality and ion balance in the cytoplasm, particularly of K^+, the most mobile ion across the plant cell membrane. High Ni uptake also disrupts plant water balance, inducing a decline in water content, which can actually act as an indicator of the progression of Ni toxicity (Gajewska et al. 2006).

Several antagonistic and/or synergistic effects and responses among chemical elements observed on plants are summarised and reported by authors like Kabata-Pendias (2011), Mengel and Kirkby (2001) and Srivastava and Gupta (1996). The chlorosis may arise partly from an induced Fe deficiency as hydrated Zn^{2+} and Fe^{2+} ions have similar radius (Yadav 2010). Phosphorus deficiency, visible through a purplish-red colour in the leaves, can also be a consequence of Zn toxicity (Lee et al. 1996). Excess of Zn can give rise to deficiencies in other essential elements, such as Mn and Cu by stalling their transfer from root to shoot. Cobalt in excess restricts the Fe concentration and affects the translocation of Cu, Mn, P, S and Zn from roots to shoots (Chatterjee and Chatterjee 2000). In some species of *Cistus*, the low Mo concentration in aerial part is possibly due to the antagonistic effect of Fe which reduces Mo translocation (Abreu et al. 2012b).

The toxicity symptoms of the majority of the hazardous chemical elements (As, Cd, Cu, Cr, Ni, Pb, Zn, etc.) are various being the most frequent chlorosis, necrosis and/or growth inhibition. Cadmium can also lead to browning of root tips while Cr induces wilting of shoots and root wounds, and As also induces leaf wilting, and violet coloration (increased anthocyanin), root discoloration, and cell plasmolysis (Kabata-Pendias 2011; Mengel and Kirkby 2001; Srivastava and Gupta 1996; Wojcik and Tukiendorf 2004; Yadav 2010).

6 Physiological Responses of Oxidative Stress in Plants

Resistance to contamination or to high concentrations of chemical elements is species-dependent. Species such as *Allium cepa* L., *Hordeum vulgare* L. and *Zea mays* L. are able to tolerate Pb through complexation and inactivation, but species such as *Brassica napus* L. and *Phaseolus vulgaris* L., experience toxicity because Pb impairs several metabolic pathways (Wierzbicka 1999). Depending on oxidation states, trace elements can be highly reactive causing toxicity in plant cells in a variety of ways. Abreu et al. (2002) reported different response patterns of nutrient uptake to increasing levels of Cr applied to soil, according to the type of soil and oxidation state.

At the cellular level when the cytosolic metal concentration turns out of control, several physiological processes are inhibited, such as respiration, transpiration and photosynthesis, and the activities of several key enzymes are affected (Hossain et al. 2012). At the molecular level the effects of hazardous chemical elements are reflected in the inactivation and/or denaturation of enzymes, blocking of functional groups of metabolically important molecules, replacement of essential metal ions in biomolecules and functional cellular units, structural modifications and disruption of membrane integrity (Villiers et al. 2011), which is ultimately attributed to altered plant metabolism. Furthermore, redox homeostasis is disrupted by the generation of free radicals and reactive oxygen species (ROS) such as singlet oxygen ($^1O_2$), superoxide radicals (O_2•$^-$), hydrogen peroxide (H_2O_2), and hydroxyl radicals (•OH) (Sharma and Dietz 2009), either directly through Haber-Weiss reactions or through overproduction (Yadav 2010).

In plants, about one third of the proteins that have been structurally characterized are metalloproteins, with an essential metal in their active centre. In fact, the chemical properties that render metal ions vital for biological systems are the reason why they can become toxic when in excess (Jozefczak et al. 2012). In order to control fluctuations in metal availability and ensure their proper distribution, organisms have evolved a tightly controlled metal homeostasis network. In the last decade, it was also found an increase of methylglyoxal, a cytotoxic compound, in plants in response to metals (Singla-Pareek et al. 2006; Yadav et al. 2005). The increase in methylglyoxal in plant cells enhances the production of ROS due to its interference with crucial physiological and metabolic processes such as the inactivation of the antioxidant defence system (Hoque et al. 2010) and photosynthesis (Saito et al. 2011). The levels of ROS and methylglyoxal produced lead to lipid peroxidation, which can directly cause membrane deterioration. The presence of malondialdehyde (MDA), one of the decomposition products of polyunsaturated fatty acids of the membrane is in fact regarded as an accurate marker of oxidative stress (Demiral and Turkan 2005). The ROS produced will interfere with the electron transport chain (Qadir et al. 2004) causing a chain reaction and leading to higher ROS production. The metabolism of essential elements will be affected (Dong et al. 2006), followed by macromolecule deterioration, membrane dismantling, ion leakage, DNA-strand cleavage and finally death (Braconi et al. 2011;

Rascio and Navari-Izzo 2011). Secondary stresses such as nutrition stress and oxidative stress are triggered, which collectively affect plant development and growth (Krämer and Clemens 2005).

Some species or ecotypes did not show visual symptoms with chemical elements concentrations in leaves considered phytotoxic, but at the physiological level, several phytotoxic effects and responses may have occurred. Plants have developed a complex network of highly effective homeostatic mechanisms requiring the coordination of complex physiological and biochemical processes that include global changes in gene expression (DalCorso et al. 2010) in order to fight the adverse consequences of metal uptake, accumulation, trafficking, and toxicity. The components of this network can be classified in two major categories, "avoidance" when plants are able to contain metal uptake or "tolerance" when plants survive despite the high trace elements concentrations in the tissues (Hossain et al. 2012). However, both categories and/or strategies can co-exist in tolerant species and ecotypes in natural conditions.

Avoidance involves blocking the entrance of metals in the cells through extracellular precipitation, biosorption to cell walls, hindered uptake, or increased efflux at the plasma membrane. Tolerance to chemical elements occurs when they are chelated by amino acids, organic acids, glutathione (GSH), or metal-binding ligands such as metallothioneins (MTs) and phytochelatins (PCs); when metals are sequestered in vacuoles, and scavenged with the aid of the antioxidant defence system and the glyoxalase pathway (Cobbett 2001; Hall 2002; Seth et al. 2012; Singla-Pareek et al. 2006; Yadav 2010).

Plants have several antioxidative defence systems to scavenge ROS. Antioxidative defence includes two classes (Cao et al. 2004): low molecular weight antioxidants, which contain the lipid soluble membrane-associated antioxidants (e.g. β-carotene) and the water soluble reductants (e.g. glutathione (GSH) and ascorbate); and enzymatic antioxidants (e.g. catalase – CAT, guaiacol peroxidase – POD, and superoxide dismutase – SOD).

The most relevant low molecular weight thiols for toxic metal scavenging are GSH and cysteine. Glutathione (GSH) is a sulfur containing tri-peptide made of γ-glutamate (Glu), cysteine (Cys) and glycine (Gly). Glutathione synthesis is catalyzed by the ATP dependent enzymes γ-glutamylcysteine synthetase (GSH1) and glutathione synthetase (GSH2) and is dependent on sulfur availability. Glutathione is a substrate for phytochelatin (PC) synthesis and is paramount for detoxification of heavy metals such as cadmium and nickel (Freeman et al. 2005).

Glutathione is present in practically all cell compartments (cytosol, chloroplast, endoplasmic reticulum, vacuole, and mitochondria) and is one of the foremost sources of non-protein thiols in plant cells (Foyer and Noctor 2005). Its reactivity, stability and high water solubility make it an ideal molecule to protect against oxidative stress, metals/metalloids and organic chemicals. In fact, GSH plays an active role in scavenging H_2O_2 through the ascorbate-glutathione cycle (Pastori and Foyer 2002) and the ratio of its reduced (GSH) to oxidized (GSSG) forms is paramount in several redox signalling pathways and in ROS perception (Mullineaux et al. 2006). But, the effectiveness of GSH in xenobiotic or metals/

metalloids detoxification creates a transient decrease of cytosolic GSH content through direct metal-GSH binding, GSH oxidation and PC synthesis, shifting the GSH/GSSG redox potential towards the oxidative form, generating a new redox signal (Nocito et al. 2006). In fact, GSH reduces directly most ROS while glutathione reductase (GR) uses NADPH to reduce GSSG to GSH (Noctor and Foyer 1998).

Studies on the Cd effect on leaves of *Arabidopsis thaliana* (L.) Heynh. showed that GSSG/GSH ratios have decreased by 65 % in comparison with the control, whereas the activities of GR and nicotinamide nucleotide phosphate-reducing enzymes were significantly enhanced (Cuypers et al. 2011; Semane et al. 2007). However, in Pb treated rice seedlings GR increased suggesting the contribution of this enzyme in regenerating of GSH from GSSG under Pb toxicity conditions to increase GSH/GSSG ratio (Verma and Dubey 2003). Similar results were obtained for *Crotalaria juncea* L. exposed to Cd (Pereira et al. 2002). Recently, it has been suggested that GSH and GSH-related enzymes are the key players in metals/metalloids tolerance, controlling various physiological processes, such as ROS scavenging, metal uptake, translocation, chelation, and detoxification (Hossain et al. 2012; Pereira et al. 2002; Verma and Dubey 2003).

Glutathione is also indirectly involved in hazardous elements scavenging, as it is a precursor for the synthesis of PCs. Phytochelatins are small, cysteine rich polypeptides with the ability to bind heavy metals and were first identified in higher plants, in cell suspension cultures, after exposure to Cd (Grill et al. 1985). Their basic structure is $(\gamma\text{-Glu-Cys})_n\text{-Gly}$, in which “n” varies from 2 to 11 and their synthesis is catalyzed by the enzyme phytochelatin synthase (PCS) (Vatamaniuk et al. 1999). Since then, PCs have been found in other eukaryotes and their role in heavy metal detoxification and in the maintenance of ion homeostasis has been unravelled (Hirata et al. 2005; Zenk 1996). Phytochelatins form complexes with toxic metal ions in the cytosol and subsequently they are transported into the vacuole (Salt and Rauser 1995) protecting plants from damaging effects.

Upon plant exposure to heavy metals, such as Hg, Cu, Ni, Pb and Zn, the synthesis of PCs from GSH through PCS is induced. Synthesis of PCs in response to Pb and the formation of a PC-Pb complex is well documented (Piechalak et al. 2002) but that is not the case for the storage of this complex in the vacuole, which has not yet been established. Phytochelatins undergo long-distance transport between roots and shoots through the phloem and high ratios of [PCs]/[Cd] and [GSH]/[Cd] in the phloem indicate that both PCs and GSH function as long-distance carriers for Cd, in the form of PC–Cd and GSH–Cd complexes, respectively, in *B. Napus* (Mendoza-Cózatl et al. 2008). Increase in GSH biosynthesis enhanced tolerance to both Cd and Ni and increased Cd accumulation in the shoots of several species (Freeman et al. 2004). An *Arabidopsis* mutant (*cad2*) with reduced capacity to produce GSH is hypersensitive to both Cd and Cu (Cobbett et al. 1998; Howden et al. 1995).

Limited information is available regarding the membrane transport of GSH-metal complexes. ATM3, a mitochondrial ATP binding cassette transporter, is implicated in the cross-mitochondrial membrane transport of the complex GSH–

Cd and in the regulation of cellular GSH levels, as the induction of the expression of *AtATM3* in *Arabidopsis* roots following Cd and Pb treatment suggests (Kim et al. 2006).

The glyoxalase pathway also plays a role in heavy metal stress tolerance because it helps maintain glutathione redox ratio. *Nicotiana tabaccum* over expressing *glyocalase I* and *glyoxalase II* showed high levels of reduced glutathione (GSH) and tolerance to heavy metal stress (Singla-Pareek et al. 2006). As GSH levels are kept high during heavy metal stress PCS is activated and catalyzes the formation of the PC–metal complex, comprising two GSH molecules forming a thiolate with a heavy metal (Cd.GS2 or Zn.GS2). The PC–metal complex is transported into the vacuole to form high molecular weight complexes that are the more stable and permanent storage form of heavy metals (Mendoza-Cózatl et al. 2005).

Under oxidative stress, plants can produce or stimulate antioxidative enzymes that remove and neutralize ROS (Shah et al. 2001). Superoxide dismutase (SOD) function is to catalyse the transformation of superoxide generating H_2O_2 while catalase (CAT) and guaiacol peroxidase (POD) are involved in the removal of H_2O_2 generated by SOD (Cao et al. 2004). The increase of the activities of these enzymes has been reported in plants exposed to different chemical elements (As, Pb, and co-existence of various elements) growing in natural environment or experimental conditions (Cao et al. 2004; Miteva and Peycheva 1999; Pang et al. 2003; Pereira et al. 2002; Santos et al. 2009, 2011; Słomka et al. 2008; Verma and Dubey 2003). In all cases, the activities of antioxidative enzymes increased until a maximum of the chemical element concentration tolerated by the plants and after that the activities are reduced. The tolerance process corresponds to the balance between the generation of ROS and their detoxification by the enzymatic activity depending on the plant species, plant organ (leaves or roots) and chemical element. For instance, the reduction of CAT under stressful conditions can be related to the inactivation or decrease of enzyme protein due to ROS, decrease of enzyme synthesis, and change in the assembly of enzyme units or combination of some of these factors (Pereira et al. 2002).

Enzymes can be present in different main active forms within the plant cell in what concerns their cellular localization: soluble in the cell's aqueous media (soluble forms), linked to cell wall components through electrostatic interactions (ionically bound forms) or strong interactions (covalently bound forms) (Jarvis 1984; Penel and Greppin 1994). This differentiation is based on the extraction treatment (McDougall and Morrison 1995) and can imply different physiological responses. In *C. ladanifer* growing in field conditions (on soils with polymetallic contamination and non-contaminated areas with different climatic conditions) the levels of the activity of each form (soluble and ionically bound) of CAT, POD and SOD enzymes varied with plant population, enzyme and season, and can also be related with the co-existence of different stress factors (concentrations of As and Zn considered toxic in leaves, temperature, UV radiation and drought) (Santos et al. 2009, 2011).

A relationship among leaves development, their sensitivity to chemical elements and the enzymes activities was reported by several authors (Cao et al. 2004; Miteva and Peycheva 1999; Santos et al. 2009, 2011). Usually young plant tissues are more sensitive than the mature ones. Nevertheless, Pang et al. (2003) observed great differences in the changes of the CAT, POD and SOD activities in shoots and roots suggesting distinct mechanisms of ROS scavenging. Similar results were observed by the same authors for other protective substances, namely concentrations of proline and abscisic acid (ABA). Słomka et al. (2008) reported higher SOD activity in *Viola tricolor* L. roots due to the presence of two additional isoforms, manganese superoxide dismutase (MnSOD)-like form (MnSODI) and Cu/ZnSOD-like form (Cu/ZnSODIV), which were not detected in leaves.

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Chapter 9
Trace Elements and Food Safety

Teodoro Miano, Valeria D'Orazio, and Claudio Zaccone

Abstract Food is our energy source and limited access to food impacts health in multiple ways. Typically, food is thought to have a positive impact on health by providing energy and essential nutrients to living beings. Despite this, often it is so detrimental to health and several foodborne diseases clearly indicate that food safety not only involves availability and access to food, but that the food must be wholesome as well. The threat to food security is depending on urbanization, income disparity, overpopulation, ecosystem degradation, animal health, etc.

Trace elements are essential components of biological structures, but at the same time they can be toxic at concentrations beyond those necessary for their biological functions. Variation in uptake in the gastrointestinal tract varies depending on chemical form, salt or ionic form, dietary matrices, and interactions with other nutrients.

Adverse effects can occur from too low or too high intake of an essential element. Therefore, it may not be possible to arrive at recommendations that working for all individuals, since some persons with genetically determined metabolic disorders may require intakes that are higher or lower than those indicated by the acceptable range of daily oral intake.

Important advances has been made in the last decades in our understanding of the environmental biochemistry, biological effects and risks associated with trace elements.

This chapter provides a general picture on the essentiality of trace elements as a function of their role as catalytic or structural components of larger molecules, trying to focus the attention on the fine line between Essentiality and Toxicity.

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A general survey, because of the impossibility to draw a common guideline for all elements considered, is reported for each elements, that is on their geochemistry and biological functions in humans. In details, for each element an account is given of the mean total quantity accumulated by the human body, the distribution in the main organs, the most important pathways for their uptake and the recommended daily intake.

Keywords Food safety • Trace elements • Bioavailability • Speciation • Toxicity • Recommended daily intake

1 Introduction

1.1 Essential Trace Elements

Trace elements play a crucial role in the proper functioning of our organism, being essential triggers for many biological mechanisms in the digestive, muscular, circulatory and cerebral systems. Our organism is made up of billions of cells, each of which acts like a microscopic laboratory, constantly carrying out chemical reactions to ensure that the organism functions properly. All these reactions depend for their success on tiny workers known as enzymes which trigger biochemical reactions. For these reactions to take place, the enzyme needs a “spark”: the trace elements.

Equally important is the role of trace elements as structural components of larger molecules with specific functions, mainly proteins. In particular, a growing list of trace element-dependent proteins and trace element utilization pathways highlights the importance of these elements for life. More recently, interesting studies have been carried out in comparative genomics of trace elements, and the dependence of user proteins on these elements has been explored (Zhang and Gladyshev 2011).

Comparative genomics of trace elements provides a foundation for investigating the fundamental properties, functions, and evolutionary dynamics of trace element dependence in biology. For example, many zinc protein families evolved in some representatives forms that lack this metal, whereas selenocysteine in proteins is dynamically exchanged with cysteine.

Although present in only minute quantities in the body (concentration < 100 mg kg^{-1} of body weight, i.e. <7 g in an adult weighing 65 kg), trace elements are essential if the body is to function properly and maintain a healthy balance. The “essential trace elements” daily requirements range from 50 μg to 18 mg day^{-1}, depending on the element (Merian et al 2004).

On the whole, we can distinguish as follows:

- Non-essential trace elements: e.g., Aluminium (Al), Silver (Ag), Bismuth (Bi), Lithium (Li) and Gold (Au).

They are not usually found in the human organism, have no natural physiological effect but they do have pharmacological properties.

- Essential trace elements:

Over 80 elements have been identified in man, but a mere 15 of them appear to be indispensable to proper functioning of the human organism. They are classified as "essential" because they act as catalysts.

These trace elements are mineral ions which our body cannot produce for itself and which are thus only to be found in our diet, and a lack of any one can lead to problems.

All cells draw their nourishment from the extracellular fluid, thus water and the dissolved minerals it contains should therefore be thought of as the driving force behind all cellular mechanisms, and as such, it is vital for our organism. The action of all these mineral ions naturally restores optimum performance to each cell.

Generally speaking, an element is recognized as essential when it has a well defined function (as stabilizer, structural, hormonal or as enzymatic cofactor) and when it is always present in tissues and organs in well defined concentration ranges, when it induces reproducible physiological effects, and when it is possible to prevent and treat consequences due to its deficiency by its supplementation.

Recently, the Expert Consultation of World Health Organization (WHO)/Food and Agricultural Organization (FAO)/International Atomic Energy Agency (IAEA) defined essentiality of a trace element as follows: "An element is considered essential to an organism when reduction of its exposure below a certain limit results consistently in a reduction in a physiologically important function, or when the element is an integral part of an organic structure performing a vital function in the organism" (Mertz 1998). This definition omits a previous postulate that the mechanism of action of an essential trace element should be well defined; it also supersedes another criterion, once suggested for essentiality, a normal, rather than log-normal distribution of an element's tissue concentrations. The Expert Consultation offers no generally applicable criteria for the physiological importance of functions, and that determination is left to expert groups charged with setting national and other nutritional recommendations. The use of the term "physiological" rather than "biochemical" strongly implies that neither changes of an element's concentration nor of a specific enzyme function alone are proof of essentiality. Among physiologically important functions are growth, reproduction, longevity, and all metabolic and hormonal functions that bear a clear, inverse relation to disease risk. Finally, the term "consistent" states the need for independent confirmation of the original data, before an element can be recognized as essential.

The keystone of European Union (EU) risk assessment regarding food and feed safety is the European Food Safety Authority (EFSA), that, in close collaboration with national authorities and in open consultation with its stakeholders, provides independent scientific advice and clear communication on existing and emerging risks.

The European Food Safety Authority (EFSA) was set up in January 2002, following a series of food crises in the late 1990s, as an independent source of scientific advice and communication on risks associated with the food chain. EFSA was created as part of a comprehensive programme to improve EU food safety, ensure a high level of consumer protection and restore and maintain confidence in the EU food supply.

In the European food safety system, risk assessment is done independently from risk management. As the risk assessor, EFSA produces scientific opinions and advice to provide a sound foundation for European policies and legislation and to support the European Commission, European Parliament and EU Member States in taking effective and timely risk management decisions.

EFSA's remit covers food and feed safety, nutrition, animal health and welfare, plant protection and plant health. EFSA also considers the possible impact of the food chain on the biodiversity of plant and animal habitats. The Authority performs environmental risk assessments of genetically modified crops, pesticides, feed additives, and plant pests. In all these fields, EFSA's most critical commitment is to provide objective and independent science-based advice and clear communication grounded in the most up-to-date scientific information and knowledge.

1.2 Classification of Trace Elements

The classification of chemical elements into major and minor or trace element categories is somewhat arbitrary.

Some definition for "Trace elements":

- Elements that are not stoichiometric constituents in phases in the system of interest (for example, soil systems would have different "trace elements" than aqueous systems)
- Elements that do not affect chemical or physical properties of the system as a whole to any significant extent
- Elements whose activity obeys Henry's Law (*i.e.* has ideal solution behaviour at very high dilution)

Anyway, despite all attempts, the term "trace element" is still a bit hard to define.

In fact, the first definition "*trace elements are those elements that are not stoichiometric constituents of phases in the system of interest*" represents a good operational definition for igneous and metamorphic systems (and sedimentary rocks for that matter), but this definition is a bit ambiguous, suggesting that a trace element in one system is not one in another. For example, in mid-ocean ridge basalts (MORB), K concentration never rarely exceeds 1,500 $\mu g\ g^{-1}$; but K is certainly not a trace element in granites. For most silicate rocks, O, Si, Al, Na, Mg, Ca, and Fe are 'major elements'. On the contrary, H, C, S, K, P, Ti, Cr, and Mn, often referred to as 'minor elements', are sometimes "major elements" in the sense that they can be stoichiometric constituents of phases.

Thermodynamically, a minor element may be defined as one that is partitioned between coexisting phases in compliance with laws of dilute solutions, such as Henry's law.

Henry's law ascertains that at constant temperature, the amount of a given gas dissolved in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid. This law can be expressed mathematically by the following equation:

$$C = k\ P_{gas} \tag{9.1}$$

where

- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas. (often in units of Atm)

In geochemical parlance, however, trace elements are usually categorized on the basis of abundance data. In this context, the mineral, rock or environment containing the chemical elements must be defined as well as the concentration boundary separating a major and trace element. If we consider the abundance of the elements in the silicate portion of the Earth (the "Bulk Silicate Earth"; BSE), just six elements, O, Mg, Si, Fe, Al, and Ca represent about the 99.1 % of the silicate Earth. If we include the core and consider the composition of the entire Earth, then only Ni, and perhaps S, need be added to this list. The remaining elements, though sometimes locally concentrated (e.g., in the crust, in the hydrosphere, in ores), can be considered trace elements.

A well known classification has been introduced by Goldschmidt, and represents a geochemical classification which groups the chemical elements according to their preferred host phases. On the basis of the geochemical characteristics of the elements, Goldschmidt recognized four broad categories: atmophile, lithophile, chalcophile, and siderophile (Kabata-Pendias and Mukherjee 2007), as shown below (Adapted from W.M. White 2013):

Siderophile	Chalcophile	Lithophile	Atmophile
Fe[a], Co[a], Ni[a]	(Cu), Ag	Li, Na, K, Rb, Cs	(H), N, (O)
Ru, Rh, Pd, Zn, Cd, Hg	Be, Mg, Ca, Sr, Ba	He, Ne, Ar, Kr, Xe	
Os, Ir, Pt	Ga, In, Tl	B, Al, Sc, Y, REE	
Au, Re[b], Mo[b]	(Ge), (Sn), Pb	Si, Ti, Zr, Hf, Th	
Ge[a], As[a], W[c]	(As), (Sb), Bi	P, V, Nb, Ta	
C[c], Cu[a], Ga[a]	S, Se, Te	O, Cr, U	
Ge[a], As[b], Sb[b]	(Fe), Mo, (Os)	H, F, Cl, Br, I	
	(Ru), (Rh), (Pd)	(Fe), Mn, (Zn), (Ga)	

[a] Chalcophile and lithphile in the earth's crust
[b] Chalcophile in the earth's crust
[c] Lithophile in the earth's crust

Atmophile elements are generally extremely volatile (i.e., they form gases or liquids at the surface of the Earth) and are concentrated in the atmosphere and hydrosphere, whereas lithophile, siderophile and chalcophile refer to the tendency of the element to partition into a silicate, metal, or sulfide liquid, respectively. In detail, Lithophile elements are those showing an affinity for silicate phases and are concentrated in the silicate portion (crust and mantle) of the earth. Siderophile elements have an affinity for a metallic liquid phase. They are depleted in the silicate portion of the earth and presumably concentrated in the core. Chalcophile elements have an affinity for a sulfide liquid phase.

There is some basis for Goldschmidt's classification in the chemistry of the elements. In particular, the lithophile elements occur mainly at either end of the periodic table, siderophile elements are mainly group 8, 9 and 10 elements (and their neighbors), chalcophile elements are mainly group 11, 12 and the heavier group 13–16 elements, while the atmophile elements are mainly the noble gases. Goldschmidt's classification is relevant mainly to distribution of elements between the Earth's major geochemical reservoirs: the core, the mantle and crust, and the hydrosphere and atmosphere.

1.3 Functions of Trace Elements

Essential trace elements are required by man in amounts ranging from 50 μg to 18 mg day^{-1}. Acting as catalytic or structural components of larger molecules, they have specific functions and are indispensable for life. Marginal or severe trace element imbalances can be considered risk factors for several diseases of public health importance, but proof of cause and effect relationships will depend on a more complete understanding of basic mechanisms of action and on better analytical procedures and functional tests to determine marginal trace element status in man.

The synthesis of pharmacological techniques and concepts into ecology holds considerable promise for gaining new insights into old questions, uncovering new priorities for research and, ultimately, for consolidating a new sub-discipline within the ecological sciences-PharmEcology. From a functional viewpoint the dividing lines between chemicals traditionally considered as "toxins", "medicines" and "nutrients" are often thin, vague, heavily contingent and non-stationary. Nutrients and toxins are not so different, medicines and nutrients are not so different, and even in cases in which nutrients, medicines and toxins can be categorically distinguished, the biological actions of these compounds are heavily interdependent.

We cite two well-established phenomena to illustrate the point: hormesis and Bertrand's rule. Hormesis and Bertrand's rule are both modern restatements of the ancient wisdom that "only the dose makes the poison" (attributed to Paracelsus 1538) (Stumpf 2006).

Hormesis is a concept developed in toxicology, in which the effects on biological systems (cells, tissues, organs, organisms, and populations) of a substance are reversed with increasing exposure (Calabrese and Baldwin 2003). Hormetic dose-response relationships can take two forms. The most common of these is the inverted U-shape, describing the situation where low doses of a substance are stimulatory and high-doses inhibitory of beneficial biological responses.

A second form is the "J-shaped" curve, where low doses reduce and high doses enhance a deleterious response.

Over recent decades, however, it has become apparent that hormetic responses are ubiquitous-they have been observed across a wide range of chemicals, taxa, and biological responses (Calabrese et al. 1999; Calabrese 2005). In addition, some workers in the general area of hormesis have noted the commonality between dose-response curves for toxins and nutrients (Luckey and Stone 1960; Hayes 2007).

Bertrand's rule, developed in 1912 by Gabriel Bertrand, established the mathematical foundations of a rule concerning the dose-response curve for mineral nutrients. According to this rule: "a function for which a nutrient is essential is very low or absent in a theoretical, absolute deficiency, and increases with increasing exposure to the essential nutrient. This increase is followed by a plateau representing the maintenance of optimal function through homeostatic regulation, and a decline of the function toward zero as the regulatory mechanisms are overcome by increasing concentrations that become toxic (Mertz 1981)". In other words, at low doses of a nutrient increased intake is associated with increasing benefits, but beyond an optimal intake any further increase results in health costs.

Based on this considerations, it appears well evident that in the time the need arised to identify some critical thresholds in order to have some references in terms daily intakes of trace elements, obviously as a functions of different parameters.

1.4 Doses, Nutrients, Toxins

In the USA the Institute of Medicine has defined four kinds of dietary reference intakes (DRI) (Fraga 2005). Estimated average requirement (EAR), a nutrient intake value that is estimated to meet the requirement of half of the healthy individuals in a life stage and gender group; recommended dietary allowance (RDA), the dietary intake level that is sufficient to meet the nutrient requirements of nearly all healthy individuals in a life stage and gender group; adequate intake (AI): a recommended intake value based on observed or experimentally determined approximations or estimates of nutrient intake by a group (or groups) of healthy people that are assumed to be adequate (used when an RDA cannot be determined); tolerable upper intake level (UL), the highest level of nutrient intake that is likely to pose no risk of adverse health effects for almost all individuals in the general population. As intakes increase above the UL, the risk of adverse effects increases (Food and Nutrition Board 2001).

2 Speciation Analysis

2.1 Importance of Speciation Analysis

Although the total element concentration is still an extremely useful information, the concentration of the analyte element in its different forms, or *species*, has become increasingly important. In the last decades, the elemental determinations at pg level can be determined, by means of the increasing advances in instrumental techniques. In particular, *speciation* of each elements can be performed, that is the distribution of an element among defined chemical species. In relation to this aspect, it must consider two structural aspects:

1. *Isotopic composition*. Often it is important to carry out a speciation analysis in order to assess the distribution of an element among its measurable isotopic forms, because of natural abundance distribution of isotopes for an element may change by effects of nuclear activities, experiments and accidents (anthropic origin).
2. *Electronic and oxidation states*. Oxidation state of an element is often important in many cases of speciation analysis. For example, it is well known that As^{3+}, $AsO_3{}^{3-}$, and Cr^{6+}, $CrO_4{}^{2-}$, are significantly more toxic than As^{5+}, $AsO_4{}^{3-}$, and Cr^{3+}, respectively.

Furthermore, the chemical characteristics of a given molecule depend not only on the elements of interest contained, but also on the rest of the molecule. As a consequence, all the chemical and physical characteristics, such as size, polarity, solubility, adsorption and bonding ability of the molecule, affects its interactions in biological systems with consequences related to essentiality, bioavailability and toxicity. In general, the relatively small molecules are more important in toxicity, the larger molecules have higher bioavailabilities.

Aras and Ataman (2006) highlighted four groups related to molecular speciation, as following:

1. *Inorganic compounds and complexes*: elements occurring in a compound or in a complex form with inorganic ligands such as chloride, sulphide, oxide or hydroxide. Hydroxo forms are the most commonly occurring species.
2. *Organic complexes*: some elements are present in organic chelates very stable, such as ferrioxamine, others can change their chemical forms during analysis. In this case, it is fundamental to consider kinetic and thermodynamic effects.
3. *Organometallic compounds:* elements are bound covalently to a carbon atom, and are generally originated from methylation, alkylation and phenylation reactions. On the whole, organometallic forms are more toxic than the inorganic ones, such as methylation of Hg, but for some elements, such as As and Se, methylation produces non-toxic species.

4. *Macromolecular compounds and complexes*: elements are bound to large molecules such as proteins, such as Fe(III) carrier transferrin, or polyanions such as humic acid.

Speciation analysis represents the unique approach in toxicological studies, thus it is extremely useful for human life. In fact, all processes as well as the fertilizers, insecticides, pesticides and herbicides used in food production caused and increasing environmental pollution that have made the toxicological analysis an absolute necessity. On the other hand, often a detailed speciation analysis may prove that the presumed toxicity is actually lower than the value apparently suggested by the total element concentration. The well-known example is the As content in foodstuffs, in particular sea products, since now it is known that a large majority of this element is present as the non-toxic arsenobetaine. Similarly, arsenocholine and arseno-sugars are non-toxic.

Furthermore, the speciation analysis is also important for food preservation; for example free copper ions (Cu^{2+}) have been found to be responsible for deterioration of milk, oils and fats.

2.2 Environmental Mobility and Bioavailability

The soil overlying the surficial lithosphere is the main source of most of the chemical elements indispensables for life. In general plants are able to control the several mechanisms of biological selection of chemical elements, but their capability can be somewhat limited in respect to trace elements. As a consequence, often concentrations of trace elements in plants can result positively correlated with their abundance in growth media, and this creates several problems for plants, animals and humans, associated either with deficiency or with excess. An appropriate balance between trace and major elements ensures the adequate performing of the various biochemical processes, even if the quantitative differences between essential amounts and biological excesses of trace elements are very small.

A schematic trophic chain showing the chemical elements translocation from soil to humans is reported on Fig. 9.1.

A brief overview on the importance of the anthroposhere, the sphere affected by man's activity, is right and proper, also in consideration that if geological, geochemical and biological alterations of the lithosphere have been very slow, the most changes caused by humans have been accumulated extremely quickly in the last decades. The anthroposphere does not represent a separate sphere, but represents any part of the biosphere that has been changed under an influence of technical civilization. All anthropogenic changes, if associated with chemical pollution, can lead to a degradation of the natural human environment, and among all chemical pollutants, trace elements are of a special ecological, biological and health significance. The more important source of trace elements as contaminants, in addition to some agricultural activities such as application of sludges, mineral fertilizers and

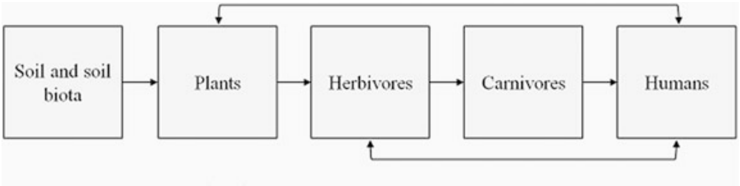

Fig. 9.1 The transfer of chemical elements in schematic terrestrial trophic chain

pesticides, is related to the production of energy and to the depletion of natural resources (Kabata-Pendias and Mukherjee 2007). In this case, when the rate of mining of a given element exceeds the natural rate of its cycling by a factor of ten or more, the element should be considered a potential pollutant (Bowen 1979).

Soil represents the main source of trace elements for plants, both as micronutrients and as pollutants, and the soil-plant transfer of trace elements is an essential part of chemical element cycling. Trace elements uptake by plants from a given growth medium depends on numerous abiotic and biotic factors, natural and/or affected by humans, that control elements' behaviour in soil.

The forms and adsorption of trace elements in soil are greatly affected by weathering processes, which are, in turns, controlled by numerous reaction such as oxidation, reduction, hydrolysis, hydration, solution, and chelation, all depending by chemical equilibria of the particular environment (Kabata-Pendias and Mukherjee 2007), as expressed (see below) by their anthropogenic mobilization factors (AMF_S).

Furthermore, often weathering processes cannot be easily distinguished from pedogenic processes, because of they take place simultaneously and at the same sites, and a large part of these processes appear strictly correlated. The principal types of these processes include: podzolization, alkalization, aluminization, laterization, sialization, and hydromorphic processes. All these processes control the distribution and behaviour of trace elements in distinct layers of soil profiles that are related to sorption and desorption and to the formation of various species of elements.

Mean content (measured in milligrams per kilogram) of metal and metalloid elements and their anthropogenic mobilization factors (AMF_S)

Element	Crust[a]	Soil[b]	AMF[c]	Element	Crust[a]	Soil[b]	AMF[c]
Li	18	20	3	Cu	25	17	632
Be	2.4	0.6	2	Zn	65	48	115
Na	23,600	5,900	2	As	1.7	5.2	27
Mg	22,000	4,400	<1	Sr	333	120	3
Al	79,600	47,000	<1	Zr	203	180	4
Si	288,000	310,000	<1	Mo	1.1	0.6	80
K	21,400	15,000	<1	Ag	0.07	0.05	185
Ca	38,500	9,200	2	Cd	0.1	0.2	112
Ti	4,010	2,400	1	Sn	23	0.9	65
V	98	58	14	Sb	0.3	0.5	236

(continued)

Element	Crust[a]	Soil[b]	AMF[c]	Element	Crust[a]	Soil[b]	AMF[c]
Cr	126	37	273	Cs	3.4	4.0	12
Mn	716	330	10	Ba	584	440	4
Fe	43,200	18,000	16	Hg	0.04	0.06	342
Co	24	7	4	Pb	14.8	16	127
Ni	56	13	56	U	1.7	2.3	12

Adapted from Sposito (2008)[a]Wedepohl (1995)

[b]Schacklette and Boerngen (1984)

[c]AMF = mass extracted annually by mining and fossil fuel production ÷ mass released annually by crustal weathering and volcanic activity. Data from Klee and Graedel (2004)

Most of trace elements that are essential to humans are also essential to plants, with the difference that the amounts of most elements that may be harmful to humans and animals are not toxic to plants. This gap has created an increased transfer of some elements in the food chain, with diverse effects, such as deficiency, overdose, or imbalances that have a negative effect on health (Mertz 1981; Nielsen 1988a; Prasad 1988).

A good mineral balance is of importance to animals and man. However, it is not the dose of a mineral that is important to maintain balance, but rather the amount that is bioavailable. The bioavailability of these elements is variable and is controlled by specific properties of abiotic and biotic media as well as by physical and chemical properties of a given element.

For example, in the small intestine several components of our food form soluble or insoluble complexes with minerals and trace elements. These food components may influence the bioavailability of these minerals and trace elements by influencing their availability for absorption. Components that may have a positive effect on the bioavailability of minerals and trace elements are citric acid, ascorbic acid, lactose and some amino acids (Wolters et al 1993).

Bioavailability is a term used in pharmacology, nutritional and environmental sciences. Generally speaking, this term indicates the degree and rate at which a substance (as a drug) is absorbed into a living system or is made available at the site of physiological activity.

Referring to the occurrence of trace elements in the environment and to their relevance in a variety of human diseases, the term “bioavailability” indicates the proportion of trace elements in the diet that are utilised for normal metabolic functions.

This information is extremely important for the derivation of dietary recommendations for trace elements when physiological needs are transformed into dietary intakes. Further, for the elements having a narrow range between the values of essentiality and toxicity, such as Fe and Se, a critical balance exists in the body.

It is well known that often various foods are fortified with trace elements, but it is extremely important to understand that high intakes of one or more trace elements may generate adverse effects on the absorption and/or metabolism of other trace elements, and, in turns, on the whole health (Fairweather-Tait 2002). Thus, a correct use of supplementary trace elements needs an exhaustive knowledge of all factors that control trace elements absorption.

2.3 Essentiality and Toxicity of Some Trace Elements

In terms of nutrition, databases for food content of trace elements are rather well established (www.fao.org/infoods/directory_en.stm; www.nal.usda.gov/fnic/foodcomp). However, the trace elements content in most foods will vary significantly depending on the trace elements availability in the soil in which the fruit, vegetable or animal is grown.

There are other factors to consider that can define the requirements for essential elements beyond their presence in foods, such as: (i) interaction among nutrients, e.g. interactions between iron and other metals; (ii) the presence in the diet of certain compounds, that can impair metal absorption, e.g. phytates bind Zn, preventing absorption; (iii) genetic defects, e.g. Zn absorption is decreased in acrodermatitis enteropathica; (iv) drug–nutrient interactions, e.g. penicillamine used in the treatment of Wilson's disease causes Zn deficiency (Aschner 2000; Lestienne et al. 2005; Wang et al. 2004; Schilsky 2001).

In the past little or no attention was directed on the effects of nutrients on the development of diseases different than those caused by the nutrient deficiency, and the passive acceptation of the concept that "more is better……" has led to unjustified high supplementation with many trace elements.

Actually, it is possible to establish clear separations among essentially, health benefits and toxicity. The DRI should guide any intention of supplementation beyond normal food consumption to prevent toxicity.

Other important variables that should be considered when the levels of TE are increased in the body are the effects genetic and individual differences in the population, life-style, nutra-genetic interactions, and other individual factors that can determine the effects of the nutrient on the disease.

2.4 Trace Elements and Food Safety

Food safety is a global problem requiring globally linked but locally based solutions. It is extremely important to combine food safety training and technical support so developing countries can improve their food safety systems and benefit from better compliance with food safety standards. There can never be an absolute guarantee that our food is safe. It is simply impossible to test every single item for every imaginable toxin, contaminant, adulterant, or foodborne pathogen. Recently, an emerging threat to food safety possibly comes from the increasing use of nanomaterials, which are already used in packaging materials, even though their toxicity remains largely unexplored.

Increasingly it is becoming important to study and manage aspects of food production in relation to the total food chain implications and not one stage in isolation. Every country has an agency that oversees food safety, defined as a "reasonable certainty of no harm," and regulates what additives are allowed in food and what levels of unavoidable contaminants are acceptable. Actually, the International Food Safety Authorities Network (INFOSAN) links together national authorities in Member States responsible for managing food safety emergencies. INFOSAN is a joint programme of Food and Agriculture Organization (FAO) and World Health Organization (WHO), with the Secretariat in WHO.

Most of the trace elements serve a variety of functions, depending upon their chemical form or combination and their location in the body tissues and fluids.

On the whole, trace elements serve in two general roles, that is as structural material and in regulating numerous biological activities.

On Table 9.1 is reported the main trace elements known to be essential in human nutrition and their functions. For the trace elements B, Cr, Co, Cu, I, Fe, Mn, Mo, Ni, Se, Si, Sn, V, Zn a short summary of their geochemistry and biological functions in humans is presented. In particular, for each element an account is given of the mean total quantity accumulated by the human body, the distribution in the main organs, the most important pathways for their uptake and the recommended daily intake. These last values obviously do not take into consideration the synergic or antagonist action due to the intake of other substances that very often can modify the absorption and the metabolism of the element considered.

Finally, it is extremely important, when considering the results obtained by the analyses of the trace elements in foods, that they may not show the exact elemental values taken by human daily, that may be lost due to contamination during washing, cooking and eating procedures.

2.5 Boron (B)

The B content in soils is associated with the clay fraction and with the organic matter, while pH is the guiding factor for its mobility and phytoavailability. In agricultural soils, B ranges from 1 to over 400 mg kg^{-1}, at a common range between 10 and 100 mg kg^{-1}.

Boron is an essential element needed for the growth and development of vascular and some aquatic plants while bacteria, fungi, and green algae do not require this element (Loomis and Durst 1992). The lowest B contents have been always found in seeds and grains, while the highest B level, >100 mg kg^{-1}, has been often cited for sugar beet leaves.

Little is known of the biochemical function of B in human and animal tissues. Boron is distributed throughout the tissues and organs of animals and humans at concentrations mostly between 0.05 and 0.06 μg $g-^{1}$ FW, and several times these concentrations in bones.

Consumption of foods of plant origin, and thus of B, is often higher in countries with a lower incidence of osteoporosis. However, no comprehensive epidemiological studies establishing relationships between B status and osteoporosis have been conducted. Because the signs of chronic B toxicity have not been clearly defined,

Table 9.1 Functions of some trace elements and potentially toxic elements

Trace elements	Functions in the body
Boron	Control of membrane function and nucleic acid biosynthesis
Chromium	Associated with insulin and required for the release of energy from glucose
Cobalt	Part of vitamin B_{12}, which involves in nerve function and blood formation
Copper	Absorption of iron, part of several enzymes
Iodine	Part of thyroxin, which regulates metabolism
Iron	Haemoglobin formation, part of myoglobin, energy utilization
Manganese	Facilities enzyme functions and many cell processes
Molybdenum	Facilities enzyme functions and many cell processes
Nickel	Constituent of urease, reduced haemopoiesis
Selenium	Helps protect body compounds from oxidation
Silicon	Structural role in connective tissue and osteogenic cells
Tin	Interactions with riboflavin
Vanadium	Control of sodium pump: inhibition of ATPase, *p*-transferases
Zinc	Part of many enzymes, present in insulin, involved in making genetic material and proteins, immunity, vitamin A transport, taste, wound healing, making sperm, normal fetal development
Potentially toxic element	
Arsenic	Increased arginine urea + ornithine, metabolism of methyl compounds
Beryllium	Unknown function
Cadmium	Stimulates elongation Betois in ribosomes
Lead	Many enzyme effects
Mercury	No metabolic functions

it remains uncertain whether there are areas in the world where the population may be affected by it.

The daily intake of B by humans can vary widely depending on the proportions of various food groups in the diet (Nielsen 1988b). Foods of plant origin, especially fruits, leafy vegetables, nuts and legumes are rich sources. Wine, cider and beer are also high in B, whereas meat, fish and dairy products are poor sources. The B content in some foods and food plants is reported in Table 9.2.

Because the chronic toxicity of B has rarely been studied or recognized, setting a threshold toxicity level is difficult. The richest food sources of B, such as nuts and dried fruits, generally supply 15–30 μg g^{-1} (Nielsen 1986). An acceptable safe range of population mean intakes for B for adults could well be 1.0–13 mg day^{-1}.

2.6 *Chromium (Cr)*

The world median content of Cr in soils has been established as 54 mg kg^{-1}, although soils developed from serpentines can reach Cr concentrations higher than 100 g kg^{-1} (Kabata-Pendias and Mukherjee 2007). The speciation of Cr is Eh-pH

Table 9.2 Boron content (mg kg^{-1}) in some foods and food plants

Rye, grains	4.3	Been, pods	13
Onion, bulbs	10	White floor	0.45
Carrot, root	9.9	Cows milk (FW)	0.2
Potato, tubers	6	Egg white (FW)	0.14
Tomato, fruits	6	Egg yoke (FW)	0.008
Orange and apple, fruits	8.3–8.4	Barley (FW)	2.3

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

dependent under most environmental conditions, but other soil factors, including organic substances, have a crucial impact on Cr forms and behaviour.

Contents of Cr in food plants have recently received much attention due to the knowledge of its importance as an essential micronutrient in human metabolic processes, but also because of its carcinogenic effects. Thus, both forms and transformation of Cr in soils have great environmental and health implications. As a consequence, an adequate rate of nutritional Cr has become an important issue. Chromium is an essential nutrient that potentiates insulin action and thus influences carbohydrate, lipid and protein metabolism. It probably works closely with the hormone insulin to help the cells take up glucose and break it down for energy (Boyle and Zayla 1992). Chromium is widely distributed in human tissues in extremely low and variable concentration. Chromium concentrations in vegetable tissues range from 0.01 to 1 mg kg^{-1}, with the levels in most plants lying between 0.1 and 0.5 mg kg^{-1}.

The content of Cr in some food plants is reported in Table 9.3.

Countries in which refined food predominates in the diet are likely to have Cr deficiency since appreciable losses of Cr occur in the refining, especially in the process of sugar refining, so that white sugar contains very little Cr compared with the amounts in brown or raw sugar (Anderson 1988).

2.7 Cobalt (Co)

The range of world mean values of Co in surface soils is between 4.5 and 12 mg kg^{-1}. Several soil factors govern the Co distribution in soils; however, hydrous oxides of Fe and Mn are of the greatest importance. The speciation of Co in soils depends on several factors, among which the pE and pH play a significant role: in particular, both the reduction of soil pE and a decrease in soil pH may result in the solubilization of precipitated or adsorbed Co.

The relatively large variations in Co levels in cereals and food plants apparently reflect the impact of various factors, among which plant genotypes and environmental conditions play significant roles. Cobalt concentrations in some foods and food plants are reported in Table 9.4.

Cobalt is widely distributed throughout the body, without excessive accumulation in any particular organ or tissue. The highest concentrations generally occur in the liver, kidneys and bones. In general, the total content of Co in the body of a

Table 9.3 Mean Cr content (μg kg^{-1}) in some food plants

Rye, grains	60	Legumes	90
Barley, grains	20	Onion, bulbs	160
Wheat, grains	10	Carrot, root	130
Potato, tubers	40	Spinach	80
Tomato, fruits	90	Almonds	110
Apple, fruits	80	Hazelnuts	160

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

Table 9.4 Range of variation of Co concentration (μg kg^{-1}) in some foods and food plants

Oats, grains	10–300	Carrot, roots	37–120
Barley, grains	4.4–44	Apple, fruits	8–16
Wheat, grains (Sweden)	1.1–18	Orange, fruits	19–45
Wheat, grains (Australia)	13–231	Beef liver (FW)	43–74
Wheat, grains (Egypt)	160–380	Pork (FW)	1–12
Onion, bulbs	28–80	Pork liver (FW)	10–23
Potato, tubers	37–160	Milk and milk products (FW)	14.3–29

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

70-kg man has been reported to average around 1.1 mg (Underwood 1971). The primary function of Co is as a constituent of vitamin B_{12}. Cobalt is likely to be bound by some proteins and to replace other divalent cations (e.g., Zn, Mn) in various enzymes, and also contributes to the formation of red blood cells. Cobalt is distributed widely among foods; most human diets provide Co in the range 15–60 μg day^{-1}.

2.8 Copper (Cu)

The average total Cu contents in soils of different types all over the world are reported to range between 20 and 30 mg kg^{-1} by Alloway (1995), and between 2 and 250 mg kg^{-1} by Aaseth and Norseth (1986) and ATSDR (1997). The behaviour, phytobioavailability and toxicity of Cu are influenced by its species, and are not a function of its total concentration (Allen 1993). Several soil variables control the Cu solubility and thus bioavailability; these include: pH, oxidation and reduction potential, organic matter, soil texture, mineral composition, temperature, and water regime.

Copper is widely distributed in biological tissues, where it occurs largely in the form of organic complexes, many of which are metalloproteins and function as enzymes. Copper enzymes are involved in a variety of metabolic reactions, such as the utilization of oxygen during cell respiration and energy utilization. In humans, acute Cu poisoning is rare and usually results from contamination of foodstuffs or beverages by Cu containers or from the accidental ingestion of Cu salts. Symptoms of acute Cu poisoning include salivation, nausea, vomiting and diarrhoea, all of which are probably due to the irritant effect of Cu on the gastrointestinal mucosa

Table 9.5 Range in Cu content (mg kg^{-1}) in some food plants and animal tissues (i.e., liver, kidney and muscle)

Wheat, grains	1.3–10	Cow	1.4–8.2
Barley, grains	4–15	Lamb	1.5–89.8
Onion, bulbs	4–6	Chicken	0.7–4.6
Carrot, roots	4–8.4	Turkey	0.8–7.1
Potato, tubers	3–6.6	White-tailed deer	29–122
Tomato, fruits	6–9	Rabbit	11.9–21.5

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

(Williams 1982). Copper is widely distributed in plants and animals. Substantial species differences exist in the Cu content of animal tissues used as food. Thus, ruminant liver and kidney can be high in Cu. Good dietary sources of Cu (2 μg g^{-1}) include seafood, organ meats, legumes and nuts, while refined cereals, sugar, milk and many other dairy products are low sources of this metal (Sanstead 1982). Ranges in Cu concentration in some food plants and tissues of livestock and poultry are reported in Table 9.5.

Recent studies based on the analysis of duplicate diets suggest that the actual intake of adults may be in the range 1–1.5 mg day^{-1}. Of potential significance is the contribution that Cu pipes can make to Cu intake from drinking water; this can vary from 0.1 mg day^{-1} in hard water areas to 10 times that level with some extremely acid soft waters (Underwood 1971).

Several constituents occurring naturally in food have been found to affect the absorption of Cu from the intestine and to increase or decrease its bioavailability. Apart from a low intake of dietary Cu, which appears to increase the efficiency of Cu absorption, the other main dietary factor, which enhances the bioavailability of Cu, appears to be a high level of protein intake (100–150 g day^{-1}) (WHO 1996).

2.9 Iodine (I)

The grand mean of I in surface soils has been estimated as 2.8 mg kg^{-1}; its concentrations range from <0.1 to 10 mg kg^{-1}, although higher concentrations have been reported in coastal areas (150 mg kg^{-1}) and volcanic soils (340 mg kg^{-1}). Recently, great attention has been focused on the distribution and fate of I radioisotopes (^{129}I and ^{131}I), released to the environment by nuclear bomb testing and nuclear accidents, in surface soils and corresponding groundwaters.

Iodine has not been shown to be essential to plants, that take up this element relatively easily from the soil solution. There is a great variation observed in the I contents of plants, and it seems to be a function of both plant species and growth conditions, and distance from the seacoast.

The main role of I in nutrition arises from the important role played by the thyroid hormones in the growth and development of humans and animals. The effects of I deficiency on growth and development are seen at all stages of development. The I contents of foods and of total diets differ appreciably. Marine fishes and shellfishes have the highest I content, 830 and 800 mg kg^{-1} FW, respectively. Eggs, meat, milk and cereal grains have I in the range of 50–90 mg kg^{-1}. Cooking reduces the I content of food, and in particular frying reduces the I content by 20 %, grilling by 23 % and boiling by as much as 58 % (Artur and Beckett 1989). The usual recommended level for the population mean intake of I is 100–150 mg day^{-1}. This level is adequate to maintain the normal thyroid function that is essential for normal growth and development.

2.10 Iron (Fe)

Iron is the most important metal and one of the major constituents of the lithosphere (its average content of the Earth's crust is about 5 %). Iron in soils ranges between 0.1 and 10 %, and occurs mainly in forms of oxides and hydroxides and chelates with humic and non-humic organic substances, especially in topsoil layers.

The redox behaviour and solubility of Fe in soils has been broadly studied and described in several textbooks (Sparks 1995), as well as mechanisms of Fe uptake and transport by/within plants and metabolic functions (Kabata-Pendias and Pendias 2001).

There are almost 4 g of Fe in the body, of which about 60–70 % is found in haemoglobin and the related myoglobin. Iron is also required for the activity of certain enzymes involved in energy production and the remaining 20–30 % of Fe is stored in the liver as a complex salt called ferritin.

Vitamin B_{12}, ascorbic acid and Cu also play an important role in the effective utilization of Fe, and consequently have an influence on the daily requirement. Good dietary sources of Fe are meat, which on average provides 25 % of the intake (especially liver and kidney), egg yolk, bread, flour and other cereal products, potatoes and vegetables. Iron is found in cereals, but due to refining, 50 % may be lost. Iron content in some food plants is reported in Table 9.6.

The recommended daily allowance is 10–12 mg of Fe for male and 15 mg of Fe for female. Deficiency of Fe is seen in many countries, mostly due to low meat and meat product consumption.

2.11 Manganese (Mn)

Contents of Mn in soils are highly diverse and range approximately from 10 to 9,000 mg kg^{-1}, showing a world grand mean of 437 mg kg^{-1}. All Mn compounds are very important constituents of soil (where Mn is likely to occur as oxides and hydroxides) because this metal is essential in plants nutrition and controls the microbial activity of soils. The mobility of Mn in soils is highly dependent on the pH and redox potential.

Manganese has been shown to be an essential element in every animal species studied. Manganese is found in the liver, skin, bones, kidney and muscles of

Table 9.6 Range of Fe content (mg kg^{-1}) in some food plants

Rye, grains	34–43	Beet, roots	71–82
Barley	33–218	Onion, bulbs	33–50
Wheat, grains	17–50	Carrot, roots	16–67
Oats, grains	54–140	Been, pods (FW)	17–89
Potato, tubers	21–58	Almonds and nuts	9–67

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

Table 9.7 Range of Mn content (mg kg^{-1}) in some food plants

Rye, grains	10–87	Beet, roots	36–113
Barley, grains	12–34	Onion, bulbs	16–24
Wheat, grains	8–103	Carrot, roots	9–28
Oats, grains	17–121	Been, pods	4–25
Potato, tubers	4–15	Almonds and nuts	10–42

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

animals. The human body has about 12–20 mg Mn in a 70-kg man. This quantity is only 20 % of the estimated total of Cu and 1 % of that of Zn (Underwood 1971). Whole grains and cereal products are the richest dietary sources of Mn, and fruits and vegetables are somewhat less (Table 9.7).

Dairy products, meat, fish and poultry are poor sources. Tea is a rich source of Mn, while typical drinking water consumed at the rate of 2 L d^{-1} contributes only about 40–64 μg or about 2–3 % of the amount furnished by diet. A provisional daily dietary Mn intake of 2–5 mg is recommended for adults.

2.12 Molybdenum (Mo)

Molybdenum occurrence in soils ranges from 0.1 to above 7 mg kg^{-1}, with a global mean of 1.8 mg kg^{-1}. Molybdenum behaves both like a chalcophile and a lithophile element and its chemistry in soils is related mainly to anionic species ($MoO_4^{2-}$and $HMoO_4^{-}$).

Molybdenum is an essential nutrient to all plants, but the requirement for this element by most plants is relatively low (average Mo content of cereal grains is 0.5 mg kg^{-1}).

Molybdenum is important in nutrition primarily because of the danger of toxicity to grazing animals; plants grown on soils high in this mineral can accumulate such high levels that they poison the animals feeding upon them (Rajakopalan 1987).

Estimates of the daily intake of Mo differ widely. For example, vegetables, especially those grown on neutral or alkaline soils, are rich in this element, whereas vegetables grown on leached acid soils may be Mo-deficient. The foods that contribute the most to the Mo intake are milk, beans, breads and cereals. Legumes, cereal grains, some dark green vegetables, liver and kidney are good sources of this mineral ion (Table 9.8), while animal products, with the exception of liver, are generally poor sources of Mo.

Table 9.8 Range of Mo content (mg kg^{-1}) in some food plants

Rye, grains	0.12–1.3	Oats, grains	0.28–1.9
Barley, grains	0.2–1.2	Potato, tubers	0.1–0.25
Wheat, grains	0.2–2.4	Onion, bulbs	0.16–0.24

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

The provisional recommended range for the dietary intake of Mo based on average reported intakes is set at 75–250 μg d^{-1} for adults and older children (NRC 1987).

2.13 Nickel (Ni)

Nickel concentration in soils throughout the world ranges from 0.2 to 450 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007), although the common background range of mean Ni contents seems to vary between 20 and 40 mg kg^{-1} (Adriano 2001). Nickel in soils is slightly mobile, and its mobility is inversely related to the soil pH.

As the content of Ni in food plants seems to be highly controlled by soil properties and origin, average contents of Ni in cereal grains is quite different among countries.

The Ni is essential for the functions of four typical Ni-containing enzymes occurring in plants and microorganisms (urease, hydrogenase, methylcoenzyme-M reductase and carbon monoxide dehydrogenase). If the nickel deficiency is severe, growth and haematopoiesis are depressed, especially in animals with a marginal Fe status or in methyl-depleted animals. On the contrary, serum concentrations above 1.0 μg of Ni L^{-1} likely indicate a chronically excessive intake of Ni. Total dietary Ni intakes of humans vary greatly with the amounts and proportions of food of animal (low-Ni) or plant (high-Ni) origin consumed, and with the amount of refined or processed foods in the diet. Approximately 50 % of the total daily intake of Ni is usually derived from the consumption of bread, cereals and beverages. The range of Ni concentrations in some food plants is reported in Table 9.9.

Recent reports indicates that most monogastric animals have a Ni requirement of less than 200 μg kg^{-1} of diet (Nielsen 1988b). Thus, it is reasonable to suggest a basal Ni requirement of less than 100 μg d^{-1} for adults.

2.14 Selenium (Se)

Selenium contents of worldwide soils have been calculated at an average value of 0.33 mg kg^{-1}, but the range of its concentrations is very broad, i.e., from 0.005 to 3.5 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007; Roman et al. 2013).

Table 9.9 Range of Ni content (mg kg^{-1}) in some food plants

Wheat, grains	0.17–0.67	Peas and beans, seeds	0.2–0.25
Barley, grains	0.1–0.67	Cucumber, fruits	1.3–2
Oats, grains	0.2–8	Carrot, roots	0.26–0.98
Tomato, fruits	0.43–0.48	Cocoa, powder	5–10
Potato, tubers	0.29–1	Hazelnuts and walnuts	1.6–1.7

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

Selenium is one of the elements playing a most important role in human and animal health. Consequently, Se contents of soils and its mobility, that can be expected to be higher in soils with high pH and Eh, have received much attention, especially in countries where its deficiency in human and animal has been recognized.

The Se content of crops recently received much attention because of its importance in the food chain. Cereal grains, as the most common source of Se in diets, have received special attention.

Selenium occurs in all the cells and tissues of the body in concentrations that vary with the tissue and with the level of Se in the diet, and it functions as part of an antioxidant enzyme and can substitute for vitamin E in some of that vitamin's antioxidant activities.

Seafood, kidney, liver and to a lesser extent other meats are consistently good Se sources, whereas grains and other seeds are more variable, depending on the Se content of the soils in which they are grown. Recommended dietary allowance for adult man is set at 70 μg d^{-1}, for adult women is set at 55 μg d^{-1}, for children is 20–30 μg d^{-1}. If Se is lacking in the environemnt, children and women can develop the "Keshan disease", a Se-responsive endemic cardiomyopathy particulalry widespread in certain areas of China.

Typical values of the Se content of various foods are the following (μg kg^{-1}, FW): liver, kidney and seafood, 0.4–1.5; muscle meats, 0.1–0.4; cereals and cereal products, 0.1–0.8; dairy products, 0.1–0.3; fruits and vegetables, 0.1. Apart from these natural differences in the Se content of foods, the amount of Se ingested in the diet is a function of the food habits of the individual (*i.e.* consumption patterns) and particularly of the geographical origin of the food (*i.e.* whether it comes from regions with Se-rich or Se-poor soils). Futher, if most of the dietary Se is derived from cereals, its bioavailability will be higher than if it is derived from certain fish, such as tuna.

In general, Se in the range of 50–200 μg d^{-1} was suggested as safe and adequate for adults, with correspondingly lower levels for infants and children.

2.15 Silicon (Si)

Silicon, the second most abundant element in the Earth's crust, occurs mostly as oxide and silicates.

Although it is not defined to be essential, Si is a common mineral constituent of plants. Silica, in the form of dissolved silicates (e.g., H_4SiO_4), is readily absorbed by plants and is deposited as a solid amorphous SiO_2.

The essential function of Si has been independently demonstrated by two groups of researchers in two species of experimental animals. Regardless of dietary composition, all experiments in which Si deficiency has been induced have demonstrated the importance of the element for the normal development of connective tissue and bone in chickens and rats (Schwarz and Milne 1972).

The general manifestations of Si toxicity are collectively described as silicosis. As with other essential elements, certain chemical forms of Si are toxic if inhaled or ingested in large amounts. It is well known the carcinogenic effects of asbestos fibres used extensively in the past.

Foods of plant origin contain more Si than those of animal origin. Silicon content in plants vary greatly, mainly upon species; for example, mean Si contents in grasses range between 0.3 and 1.2 %, whereas its concentrations in leguminous vary from 0.05 to 0.2 %. Rice plants are known as accumulators of Si and can contain it up to 10 % in hulls and up to 4 % in grains (Alyoshin et al. 1988).

The factors governing the biological availability of Si have not been adequately defined and human requirements for Si can yet be estimated.

2.16 Tin (Sn)

In uncontaminated soils, Sn is largely derived from its content in the bedrocks, and occurs at the background level.

There is no evidence that Sn is either essential or beneficial to plants. It is considered as toxic to both higher plants and fungi. Common range of Sn in food plants is reported to be between <0.04 and <0.1 mg kg^{-1}, and in grass from 0.2 to 1.9 mg kg^{-1} (Kabata-Pendias and Pendias 2001).

Tin in the inorganic form is considered as being non-toxic, whereas some organotins are mainly toxic, especially triethyltin (Et_3SnOAc) (Huang and Matzner 2004).

Most fresh and frozen foods probably contain a Sn concentration <1 μg g^{-1}. The major source of Sn is canned foods; some canned fruits and juice may contain Sn at the range from 141 to 2,000 mg kg^{-1} (FSA 2002). Usually, the dietary intake of Sn in different countries is 1.0–2.3 mg kg^{-1} of diet (Greger 1988).

2.17 Vanadium (V)

Vanadium world median content in soils has been established at 90 mg kg^{-1} (Reimann and de Caritat 1998); its average contents vary from 10 mg kg^{-1} in sandy soils to 500 mg kg^{-1} in calcareous soils.

Contents of V in food plants vary broadly, from about 10–700 μg kg^{-1} and do not show any clear regularity in the distribution among plant species and plants organs.

The discovery of V-activated enzymes in lower forms of life lends credence to the view that V has similar roles in higher animals. Vanadium-dependent enzymes in lower organisms include nitrogenase in bacteria.

Anke et al. (1986) reported some reasonably well-substantiated deficiency signs in goats which, when fed only 10 ng of V per g of diet, as opposed to 2 μg of V per g of diet, exhibited a higher abortion rate and produced less milk during the first 56 days of lactation. Toxic effects resulting from the intake of large amounts of V in the diet are unlikely. Toxicity usually occurs only as the result of industrial exposure to high levels of airborne V. Signs of excessive V intake in humans include gastrointestinal disturbances and green tongue. The body of a normal adult man has been estimated to contain 10–25 mg of V, most of which is present in the bones, teeth and fat. A diet high in unsaturated fatty acids from vegetable sources results in higher V intake than one containing saturated fats from animal sources. Large concentrations of V up to 43 mg kg^{-1} were found in soyabean oil and in corn, olive, linseed and peanut oils; also spinach, parsley, mushrooms and oysters, contain relatively large amounts of V (see Table 9.10). Beef, pork, deer and chicken fats were relatively rich in this element.

The daily dietary intake of V is of the order of a few tens of μg and may vary widely as a function of countries (Pennington and Jones 1987).

2.18 Zinc (Zn)

Zinc concentration ranges between 10 and 300 mg kg^{-1}, with a mean of about 50 mg kg^{-1} (Malle 1992). It is very mobile during weathering processes and its easily soluble compounds are readily precipitated or sorbed.

Zinc has very important role in several enzymatic reactions; it participates in the synthesis and degradation of carbohydrates, lipids, proteins and nucleic acids, and has shown to play an essential role in the processes of genetic expression.

Zinc is generally found in the body in the liver, muscle, bones, skin and blood. The whole body of a 70-kg man is estimated to contain 1.4–2.3 g of Zn. Good sources of Zn include red meat, liver, kidneys, whole grain cereals, eggs, shellfish, nuts and cheese, whereas Zinc content of fruits, vegetables and refined foods is low. Ranges of Zn concentration is some food plants are reported in Table 9.11.

The recommended allowance for men is set at 15 mg d^{-1}, while for a women is set at 12 mg d^{-1} (NRC 1987).

The principal clinical features of severe Zn deficiency in humans are growth retardation, a delay in sexual and skeletal maturation, the development of dermatitis, diarrhoea, alopecia, a failure of appetite and the appearance of behavioural changes. The best source of Zn is the lean red meat, whereas fats, oils, sugar and alcohol have very low Zn content. Green leafy vegetables and fruits are only modest

Table 9.10 Range of V content (μg kg^{-1}) in some food plants

Wheat, grains	7–10	Lettuce, leaves	280–710
Barley, grains	0.9–7.6	Spinach	533–840
Onion, bulbs	22–58	Asparagus	52–128
Potato, peeled	458–606	Wild mushrooms	50–2,000

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

Table 9.11 Range of Zn content (mg kg^{-1}) in some food plants

Wheat	23–37	Lettuce, leaves	43–73
Barley	20–30	Carrot, roots	21–27
Rice	1–41	Tomato, fruits	17–26
Onion, bulbs	22–32	Potato, tubers	10–26

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

sources of Zn (as of energy) because of their high water content. The daily intake of Zn in industrialized countries from diets characteristically high in fat, refined sugar and animal protein has been reported to be approximately 10–12 mg or 1.0–1.2 mg Zn per MJ.

2.19 Potentially Toxic Elements (As, Be, Cd, Pb, Hg)

The main threats to human health from the so called "heavy metals" are associated with exposure to As, Be, Cd, Hg and Pb. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO. Although several adverse health effects have been known for a long time, exposure to heavy metals continues, and is even increasing in some parts of the world, in particular in less developed countries.

2.20 Arsenic (As)

The recent estimation of As in global soils was at 5.0 mg kg^{-1} (Koljonen 1992). Agricultural practices may be a significant source of As, as its content may be elevated in agricultural chemicals, such as pesticides, herbicides, cotton desiccant, and wood preservatives, and in additives to animal foods, all of which have a direct impact on the environment. All soil properties, and especially Eh-pH regime, influence the sorption capacity to As (Bissen and Frimmel 2003).

Arsenic is one of those elements that is both essential and toxic. Inorganic species are more toxic; for most common species an order of toxicity may be given as As(III) > As(V) > monomethylarsonate (MMA) > dimethylarsinate (DMA) > arsenobetaine (AsB). Most of species present in fish and other sea products are rather non-toxic species such as AsB, arsenocholine and As-containing sugars. Although As compounds are best known historically for their toxicity, their pharmacological action is also well documented. Less well documented is the increasing evidence of the essential function fulfilled by very low dietary As intake in four species of experimental animals. The biological effects of As depend markedly on the chemical form in which the element is presented, inorganic compounds being more toxic than most organic ones. Most living organisms convert the former by methylation into a large variety of less toxic organoarsenic compounds, which are then excreted. These compounds contribute substantial amounts of As to human diets containing fish and other seafood.

The major cause of concern in connection with As is the potential toxicity of its compounds to humans. Consumption of water containing 0.8 mg of As per L over extended periods of time and a dietary intake of approximately 3 mg d^{-1} of As for 2–3 weeks have been identified as causes of intoxication. However, the toxicity of As compounds depends so greatly on their chemical nature that general estimates of safe intakes cannot be made with confidence. The beneficial effects of substantially lower intakes of As have been demonstrated in three independent studies involving four animal species offered basal diets providing less than 1 μg g^{-1} of As. Most foods and feeds of terrestrial origin contain less than 7 μg of As g^{-1} dry weight (Parr and Cawley 1990); the levels present in those of marine origin are substantially higher, ranging up to 80 μg g^{-1}. Dietary intake is therefore greatly influenced by the amount of seafood in the diet. Based on recent surveys in several countries, the daily As intake of adults is estimated to be $<$ 200 μg, and often below 100 μg d^{-1} (Parr and Cawley 1990). It is unlikely that the As intake from uncontaminated diets poses a risk of toxicity. Extrapolation from animal experiments suggests that human adult intake in the range 12–25 μg d^{-1} is probably adequate to meet any possible requirement (Nielsen 1986).

Because inorganic As is known to be carcinogenic in humans, there is understandable concern to limit human exposure to excessive environmental concentrations of this element. However, the metabolism and effects of As can differ markedly, depending on the chemical nature of the As source. These differences partly account for the provisional nature of the recommended safe exposure limit for adults of 15 μg kg^{-1} of body weight per week (WHO 1989). Since experimental As deficiency has been produced in four species, the element may have an essential function. If a human requirement for As does exist, it is probably close to 20 μg d^{-1} for adults and is easily met by most diets.

2.21 Beryllium (Be)

The mean background Be contents for worldwide soils range from 0.48 to 3.52 mg kg^{-1} (Kabata-Pendias and Pendias 2001), although higher values have been reported (Armiento et al. 2013). Beryllium occurs most often as divalent cation, and its complex ions also are mainly divalent: $(BeO_2)^{2-}$, $(Be_2O_3)^{2-}$, and $(Be_2O)^{2+}$. Common anionic complexes in alkaline environments are $Be(OH)CO_3^-$ and $Be(CO_3)_2^{2-}$. Although Be appears to be rather immobile in soils, its salts (e.g., $BeCl_2$ and $BeSO_4$) are easily soluble and available, and therefore potentially toxic to plants. Beryllium is also highly mobile under acidic condition (Krám et al. 1998).

Mechanisms of the Be absorption by plants seem to be similar to those involved in the uptake of Mg^{2+} and Ca^{2+}; mean contents of Be in plants vary broadly from <1 to >100 μg kg^{-1}.

Beryllium is one of the most toxic elements in the periodic table. It is responsible for the often-fatal lung disease, Chronic Beryllium Disease (CBD) or berylliosis, and is listed as a Class A EPA carcinogen. Beryllium is an important industrial metal because of its unusual material properties: it is lighter than aluminum and six times stronger than steel. Often alloyed with other metals such as copper, beryllium is a key component of materials used in the aerospace and electronics industries.

Data concerning beryllium content of foods are meagre. In limited studies of Be in Australian and German foods, the levels in the former were generally low and ranged from 0.01 to 0.10 ppm (99), while those in German foods were slightly higher (100). The most likely means of be entry into the food chain would appear to be via root, tuber, and forage crops grown on acid soils, and, in particular, plant toxicity and availability of Be in potatoes (Solanum tuberosum) and oats (Avena sativa) has been greatest in acid soils (Bohn and Seekamp 1979). There is no evidence of beryllium being transformed or biomagnified within food chains.

Beryllium abundance in a reference man is calculated to be 0.5 μg kg^{-1} (Li 2000), with values ranging from 20 μg kg^{-1} in bones to 210 μg kg^{-1} in lungs (ATSDR 2002). Beryllium is highly toxic to all organisms, especially when inhaled as aerosol dust of its compounds (e.g., BeF_2 and BeO). Also skin exposures to Be may result in local immune or inflammation reactions. Oral ingestion of Be has not been associated with any clinical diseases, possible due to low rate of absorption estimated at 0.006 % of ingested Be (Rossman 2004). The EPA guidelines applicable to Be is 20 μg kg^{-1} d^{-1} for food of adults (ATSDR 2002).

2.22 Cadmium (Cd)

The global average soil Cd concentration is estimated to range between 0.06 and 1.1 mg kg^{-1}, and to average 0.5 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007).

Cadmium is considered as being one of the most ecotoxic metals that exhibits adverse effects on all biological processes of humans, animals, and plants. This metal reveals its great adverse potential to affects the environment and the quality of food. Really, exposure to cadmium through food is typical for most people but is not a major health concern. This is because the cadmium present in the body from our diet is about 0.0004 mg/kg/day, and this value is about ten times lower than the level of cadmium that causes kidney damage from eating contaminated food.

Cereals and other vegetables normally account for about 50 % of Cd intake which, in children, is typically in the range 2–25 μg d^{-1}, and in adults 10–50 μg d^{-1}. The highest values within these ranges were all reported from countries noted for

Table 9.12 Range of Cd content (μg kg^{-1}) in some food plants

Wheat, grains	20–70	Lettuce	29–400
Barley, grains	13–22	Carrot	30–240
Legumes	1–30	Spinach	43–150
Cabbage	5–10	Potato	16–300

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

extensive industrial activities involving the processing of Cd-rich ores or other raw materials.

Concentrations of Cd in most foods are typically less than 0.15 mg kg^{-1}. Notable exceptions are shellfish and kidneys, the former containing typically 1–2 mg of Cd per kg and the latter 0.5 mg kg^{-1}. Plants have no metabolic requirement for Cd, however its relatively easy availability to plants reveals serious health risk. Contents of Cd in food plants varies in the range of 5–400 μg kg^{-1} (Table 9.12) and is a little bit higher in leafy vegetables and in roots than in other parts of plants.

The Cd content of vegetable and cereal crops is influenced by the soils in which they are grown if these are polluted by Cd-rich industrial or urban sludges/wastes or are derived from geological parent materials containing the Zn–Cd ore, sphalerite. The World Health Organisation (WHO) has established a provisional tolerable weekly intake (PTWI) for cadmium at 7 μg/kg of body weight This PTWI weekly value corresponds to a daily tolerable intake level of 70 μg of cadmium for the average 70-kg man and 60 μg of cadmium per day for the average 60-kg woman. Clearly, the daily cadmium intake for the general population from food, which is by far the dominant source of cadmium, is well below the guidelines established by the World Health Organisation. The average daily cadmium intake for the general population in the Western World has shown a distinct downward trend from 1970 to 1992 (Van Assche and Ciarletta 1992), a reduction presumed to be due to the marked decreases in direct atmospheric deposition of cadmium onto crops and soils.

There is considerable information in the literature regarding the cadmium contents of foods grown in contaminated areas (Elinder 1985; WHO 1992; OECD 1994). Detailed studies have indicated that only a small percentage of these contaminated areas were actually utilised for growing foods which were subsequently consumed with the exception of rice fields in Japan where considerable cadmium did find its way into the average person's diet through rice grown on contaminated rice fields (Elinder 1985). In specific cases, management measures to reduce the transfer of cadmium from historically contaminated soils into the local food chain have proven successful (Staessen et al. 1991).

2.23 Lead (Pb)

Lead is a persistent pollutant which causes harmful effects to humans, animals and ecosystems. Lead is widely distributed in rocks and soils; its overall mean value of

Table 9.13 Range of Pb content (mg kg^{-1}) in some food plants

Wheat, grains	0.2–0.6	Lettuce, leaves	0.7–3.6
Barley, grains	0.1–0.4	Carrot, roots	0.5–3
Tomato, fruits	1–3	Apple, fruits	0.05–0.2
Cabbage, leaves	1.7–2.3	Potato, tubers	0.5–3

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

Pb for different soils has been calculated to be, in the average, at 25 mg kg^{-1} (Kabata-Pendias and Pendias 2001). The highest Pb concentrations have been found in localities in which it has accumulated by geochemical mineralization and particularly where Pb-rich ores have been mined and the waste has been dispersed on land used for cultivation or grazing. Other methods of industrial or urban waste disposal and the presence of road traffic can also increase oil Pb and, since its phytoxicity is low, such high Pb concentration, as often, remain unsuspected.

The variation of Pb contents of food plants is highly influenced by environmental factors. When plants are grown in uncontaminated sites, its level is relatively stable. Its lower contents (<1 mg kg^{-1}) are in cereal grains and fruits and higher (>1 mg kg^{-1}) in roots and tubers. Also leafy vegetables and fodder plants contain elevated amounts (>2 mg kg^{-1}) (see also Table 9.13).

Bread, cereals and beverages account typically for about 35 % of the daily intake of Pb, the remainder being derived from a variety of food types. Mean dietary intakes of children have been reported to be in the range 9–278 μg d^{-1} of Pb and 20–282 μg d^{-1} for adults.

2.24 Mercury (Hg)

Background levels of Hg in soils are not easy to estimate due to the widespread Hg pollution; natural Hg contents in soils are fairly low and seldom exceed 1 mg kg^{-1}.

The concentration of Hg in plants, especially food and fodder plants, has recently received much attention, because of its pathway into the food chain. Especially Hg in potatoes and cereal grains, as its main dietary sources, has been intensively studied. The background value of Hg in vegetation has been reported to be 100 μg kg^{-1} (Lindqvist 1991). However, its contents vary highly, depending on plants species and growth conditions and is lower in cereals than in leafy vegetables (Table 9.14).

The European Food Safety Authority (EFSA) has established Tolerable Weekly Intakes (TWIs), or ‘safe levels’, intended to protect consumers from adverse health effects posed by the possible presence of the main forms of mercury found in food: methylmercury and inorganic mercury. Methylmercury is the predominant form of mercury in fish and other seafood, and is particularly toxic to the developing nervous system including the brain. Whereas average exposure to methylmercury in food is unlikely to exceed the TWI, the likelihood of reaching such a level

Table 9.14 Range or mean of Hg content (μg kg^{-1}) in some food plants

Wheat	<0.1–34	Lettuce, greenhouse	38.5
Barley	1.1–34	Carrot	16.9
Tomato, greenhouse	22	Tea, leaves	34–46
Spinach	68.5	Potato	13.5

Data from Kabata-Pendias and Mukherjee 2007, and ref. therein

increases for high and frequent fish consumers. This group may include pregnant women, resulting in exposure of the fetus at a critical period in brain development. Inorganic mercury is less toxic and can also be found in fish and other seafood as well as ready-made meals. Exposure to inorganic mercury through food is unlikely to exceed the TWI for most people, unless combined with other sources of exposure.

More precise data on food consumption and on mercury levels in food have allowed the Panel to more accurately assess human exposure to methylmercury through the diet. Fish meat, particularly tuna, swordfish, cod, whiting and pike were identified as the most important contributors of methylmercury exposure in Europe for all age groups, with the addition of hake for children. Exposure in women of child-bearing age was especially considered and found not to be different from adults in general. Exposure through food in high and frequent fish consumers was in general some twofold higher than for the total population (EFSA 2012).

The Joint FAO/WHO Expert Committee on Food Additives (WHO 1978) provisionally recommends that total Hg intake should not exceed 5 μg kg^{-1} of body weight per week with not more than 3.3 μg kg^{-1} per week as methylmercury. With the exception of the accidental consumption of cereal grains dressed with organomercurials, the potential threat posed by terrestrial pollution with Hg compounds is appreciably less than that arising from the alkylation of Hg by aquatic components of the food chain.

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Chapter 10
Risk Assessment of PHEs

Claudio Bini

Abstract Nowadays risk assessment is assuming more and more importance in the solution of problems connected with land sustainability and human health. Indeed, the risk assessment criteria are applied to identify and classify the various sites on the basis of the actual land characteristics, and the potential hazard to exposed population.

There are various exposure pathways of toxic substances to general population: direct pathways are soil ingestion, dust inhalation, dermal contact; indirect ingestion through the food chain is one of the most important pathways for the entry of PHEs into the human body.

In order to avoid possible consequences to humans and the environment, it is necessary to investigate the source, origin, pathways, distribution in all the environmental compartments, and to ascertain if metal bioaccumulation is likely to occur, affecting human health.

Risk assessment procedures include two components, the Environmental Risk Assessment and the Human Health Risk Assessment. The former has been used mainly for comparative and priority setting purposes with reference to contaminated sites. The latter refers to the possible consequences of human exposure to contaminant sources. The ecological risk is generally considered a second priority in comparison to human health risk.

Estimate of exposure levels is a central step in Ecological Risk Assessment to evaluate ecotoxicity risks posed by PHEs. For example, agricultural soils contaminated with metals result in elevated uptake and transfer of metals to vegetables; consequently, severe health hazard can be caused by the consumption of metal-contaminated vegetables. Bioaccumulation of heavy metals in edible parts of vegetables is thus responsible for major health concern.

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Human health risk assessment has been used to determine if exposure to a chemical, at any dose, could cause an increase in the incidence, or adverse effects, on human health.

Biological monitoring is a promising method of assessing environmental and human health risk by analysing PHEs concentration in environmental matrixes (e.g. plants, animals), or in human tissues (hairs, nails), or in a biological matrix (blood, urine). Concerning human health, biological monitoring is usually described as the measurement of a particular chemical substance, or a metabolite of that substance, in a suitable biological matrix (e.g. blood, urine, serum, and tissues such as hairs, nails, sweats), that act as an effective biomarker, allowing identification of potential hazards.

Examples of how the risk assessment process may be carried out are given with reference to exposure levels and exposure-response relationships for the contaminants of concern.

Keywords Risk assessment • PHEs • Bioavailability • Bioaccessibility • Bioaccumulation factor

1 Introduction

Environmental contamination is a concern whose importance has been recently perceived by public opinion, and constitutes one of the great emergencies of twenty-first century (Bini 2009). Modern society is paying increasing attention to its effects on the human health, and is acquiring more and more consciousness of the health risk connected to exposure to chemicals and toxic products (e.g. heavy metals, radionuclides, asbestos, hydrocarbons, dioxins). Yet, a serious concern exists about the presence of chemicals in the environment and their bioaccumulation in foodstuff (Martorel et al. 2010).

Many organic substances (pesticides, fertilisers, PCB, PAH, etc.) contribute to contaminate ecosystems and are very poisonous to living organisms and to human health. Correspondingly, inorganic compounds (e.g. heavy metals, volatiles, anions) from different non-point and point sources have a potential to contaminate soil and water. Moreover, potentially harmful elements (PHEs), when present at high concentration in the environment, are critical or toxic to living organisms (Salomons 1995). Environmental contamination rises from double driving forces: natural or anthropogenic. Indeed, supergenic alteration processes may lead to the release of potentially toxic elements, particularly heavy metals, in the environment. Possible “natural” accumulation of elements into the ecosystems may be related to heavy metal-bearing rocks (e.g. Ni and Cr in serpentine: Angelone et al. 1993) or to mineralized areas (e.g. Pb and Zn from mixed sulfide mines), while anthropogenic accumulation is almost related to industrial activities (e.g. Cd in metallurgy, Cr in varnish and leather factories: Bini et al. 2008), agriculture and urban sewage sludge (e.g. Zn and Cu from fertilizers: De Luisa et al. 1996; Cd, Pb, Cr from sludge:

Petruzzelli 1989). Metals can be dispersed in the environment and/or accumulated in plants and animals, and taken in by human beings through the food chain (Lim et al. 2008). The local physico-chemical, climatic, biologic, geologic conditions control the ultimate fate of a toxic element, that is, if it will precipitate as an insoluble phase or will be adsorbed on the surface of some other phase, or will be released, transported and eventually taken up by plants (Brummer 1986; Langmuir 1997).

Actually, the identification of the sources responsible for soil contamination is an important issue, since high loads of heavy metals applied to soils with sludge, or discharged and stored in soils, may cause soil quality degradation, surface and groundwater pollution, accumulation in plants, phytotoxicity and possible adverse effects on human health. Just one – or more – heavy metal(s) could determine irreversible damage to the environment and/or to resident population (Chon et al. 2011).

Indeed, all trace elements, including those essential to living organisms (e.g. Cu, Mo, Ni, Se, Zn) are toxic if taken up in concentrations markedly larger than the nutrient requirements. In particular Ag, As, Be, Cd, Ce, Ge, Hg, Pb, Tl are suitable examples of potentially harmful elements (PHEs) that have no proven essential functions, and are known to have adverse physiological effects at relatively low concentrations (Abrahams 2002).

Examples of toxicity by heavy metals are known since the Antiquity (Nriagu 1983). For instance, one of the supposed causes for the Roman Empire collapse is the increasing lead toxicity from Pb-bearing potteries and wine containers, as it was found in Roman findings and bones. Lead (plumbism) and Hg (mercurialism) poisoning cases were frequently recorded in workers employed in mining industry and even in hat factories in Tuscany (Dall'Aglio et al. 1966). At present, diseases and toxicity related to microelement contamination (Cd, Cr, Cu, Ni, Pb, Tl, Zn,) of air, water and soil from industrial activities are well established (Thornton 1993; Abrahams 2002). For example, the most notable cause of Tl poisoning occurred adjacent to a cement plant in Germany (Abrahams 2002).

Environmental and human health risk assessment, therefore, is assuming more and more importance in the solution of problems connected with land restoration. Indeed, the risk assessment criteria are applied to identify and classify the various sites on the basis of intervention priority, to establish objectives and standard of decontamination, to select the more appropriate and site-specific technology (Pizzol et al. 2009).

The risk arising from metals depends on their bioavailability, which in turn depends on the form in which they occur (Adriano et al. 1995). This is the reason why the risk to human health cannot be assessed on the basis of the total concentration of the toxic metal. Background values correspond to the total content of metals in soils not affected by human activities, i.e. they are the *reference values* for most countries. Soil guide values have been introduced in the late1950s in Japan, in 1980 in The Netherlands, in 1986 in Switzerland, in 1987 in Great Britain, in 1994 in Germany. Since that time, many countries, notably the U.S.A., Canada, Great Britain and the Netherlands, have progressed further in setting standards for hazardous constituents in soil, health-risk based soil screening levels and soil remediation. However, legislation on maximum admissible levels of heavy metals in the environment in the EU is rather confusing. Indeed, a general regulatory guideline on the maximum trace element concentration in soils has not yet been established, the current references being related to the total metal content in waste and sewage sludge to be spread on soil (Adriano et al. 1995).

2 Bioavailability and Bioaccessibility

Although total metal concentrations do not give an actual indication of the potentially plant-available or 'bio-accessible' fractions of a metal in a soil, they provide a useful indication of whether a soil has anomalously high or low concentrations. This will show whether this soil is contaminated and/or geochemically enriched and thus poses a possible risk of toxicity to some species of plants, soil fauna or microorganisms (Alloway 2013). For example, serpentine soils present Ni concentration up to 800 mgkg^{-1}, but only a small part of it is available/accessible to plants growing on this kind of substrate, with the exception of hyperaccumulator plants (e.g. *Alyssum bertoloni*, a well known endemic species growing on serpentine soils) that are able to absorb high quantities of metals (Brooks 1998).

Knowledge of the total metal concentration in soils, in most cases, is not sufficient to assess element mobility and bioavailability (Abollino et al. 2009; Rao et al. 2008; Menzies et al. 2007). Availability is driven by several factors and processes that enhance metal mobilization, namely: pH, redox status, complexing ligants, soil solution activity, plant roots exudates, available water, etc. (Alloway 1995).

As a matter of facts, the potential toxicity of contaminants is strongly determined by the speciation of the elements involved. Total element concentration includes all forms of that element in soil: readily soluble in the soil solution, bound to organic matter, adsorbed on surfaces of clay minerals, oxides, carbonates, bound in the crystal lattice. In many cases, much of the total content of an element is not available for immediate uptake by plants. Conversely, the available metal fraction refers to the portion of the total content which is potentially available to living organisms (Alloway 2013). Sequential extractions, therefore, are currently performed to determine element fractionation. Several reports on fractionation methods have been published in recent years (see f.i. Abollino et al. 2009; Rao et al. 2008; Menzies et al. 2007; Peijnenburg et al. 2007). The suggested procedures allow evaluating element mobility and bioavailability (Obrador et al. 2007; Kabata-Pendias and Mukherjee 2007; Quevauviller 1998). Water-soluble and EDTA-exchangeable elements are considered *bioavailable* to plants, while those linked to Fe-Mn oxides, to carbonate and to organic matter are considered *potentially bioavailable* (He et al. 2005). In recent years, single extractants are widely utilized (Rao et al. 2008) to evaluate the plant uptake and possible transfer to the aerial parts and to the food chain. Single extractants most utilized are chelating agents as EDTA or DTPA, and neutral salts (e.g. $CaCl_2$), which proved the best agents to estimate available metal pool, plant uptake and transfer to humans through the food chain (Menzies et al. 2007).

There are various exposure pathways of toxic substances to humans: direct pathways are soil ingestion, dust inhalation, dermal contact; but indirect ingestion through the food chain is one of the most important pathways for the entry of these toxic pollutants into the human body (Khan and Cao 2012). Food chain contamination is of increasing concern because of the adverse impact on the quality of food and health. Bioaccumulation in the edible parts of vegetables depends on numerous factors including soil characteristics (e.g. pH, SOC), metal concentration in soil, physiological characteristics of vegetables and transfer routes. SOC acts as a huge sink of heavy metals and organic pollutants, and modulate metal bioavailability.

Vegetables grown on wastewater contaminated soils accumulate metals at a concentration enough to cause human health risk. Several mechanisms including sorption (from soil particles), uptake rate through transpiration, volatilization, and re-deposition on plant leaf surfaces are responsible for the metal transfer from soil ecosystem to plant tissues and to the food chain. Yet, food is considered the major source of PHEs and POPs to humans, accounting for 70 % of the total exposure. Therefore, it is necessary to investigate the source, origin, pathways, distribution in agricultural soils, and bioaccumulation of metals to assess the possible human health risk caused by consumption of metal-contaminated vegetables (see Chap. 3, this volume). Agricultural soils contaminated with metals result in elevated uptake and transfer of metals to vegetables; consequently, severe human health risk can be caused by the consumption of metal-contaminated vegetables. Bioaccumulation of heavy metals in edible parts of vegetables is responsible for major health concern. The benchmark contamination levels for HM vary from country to country, but so far many countries have not established the tolerable limits for HM in both soil and vegetables (Kabata-Pendias and Mukherjee 2007).

3 Bioaccessibility and Human Health

Many chemicals are recalcitrant, mutagenic and carcinogenic pollutants, present in the environment as a result of different anthropogenic activities, and are implicated in different types of diseases, including breast, lung and colon cancer in humans (Khan and Cao 2012).

In human health risk assessment, oral exposure is typically stated in terms of the external dose or intake, instead of in terms of absorbed dose or uptake (Lim et al. 2008). Intake is typically defined as the process by which an agent crosses the outer exposure surface of a human without passing an absorption barrier, while uptake is the process by which an agent crosses an absorption barrier into living organisms (plants, animals or humans). For example, it has been demonstrated by several studies (Zupan et al. 1995; Basta et al. 2005; Bini et al. 2008, 2013; Maleci et al. 2013) that Cr is unable to cross the root barrier opposed by several vascular plants, including food crops (e.g. plantain, marigold, dandelion, wheat and maize) to metal fluxes.

Bioavailability of a compound to humans can be defined as the fraction of an administered dose that reaches the central blood compartment (i.e. the vascular system), whether through the gastrointestinal track, skin or lung. Bioaccessibility is the fraction of a chemical in an environmental medium that is available for absorption based on "in vitro" extraction, but not necessarily absorbed (Lim et al. 2008). The term "bioaccessible" is used to indicate the "in vitro" fraction of the chemical intake that is directly available for absorption. Therefore, bioaccessible metal concentrations are more important for risk assessment than total metal contents in the environment.

4 Bioaccumulation Factors

Element distribution in soil is determined by various processes occurring in soil (Kabata-Pendias 2011): weathering, decomposition, precipitation-dissolution, absorption-desorption, oxidation-reduction, chelation (He et al. 2005; Adriano 2001). Such processes in soil are regulated by soil parameters: pH, redox potential, cation exchange capacity, clay content, organic matter. The aqueous phase (soil solution) is the medium where most chemical equilibria, including metal absorption by roots, occur. The root sorption process, that is the prominent mechanism of element flux from soil to plants, is influenced by soil properties, element speciation, plant physiology, environmental conditions (Adriano 2001).

The metal transfer from soil to plants, and from plants to animals (including humans), is achieved through the food chain. The bioaccumulation factor is one of the key pathways of human exposure to PHEs through consumption of vegetable and/or the food chain, and is commonly assessed with specific coefficients. The value of the bioaccumulation factor depends on the nature of PHEs, physiology of plant, and content of elements in growing media. Metal concentrations in soils, roots, shoots and fruits of edible vegetables are currently utilized to calculate the PHEs bioaccumulation factors, since soil-to plant transfer is one of the major pathways for pollutants to enter the food chain (Bini et al. 2013).

In order to investigate the health risk associated with PHEs, it is essential to assess the bioaccumulation factors.

Several bioaccumulation factors have been proposed so far. The Biological Adsorption Coefficient (BAC) (or Transfer Coefficient – TC – according to Hao et al. 2009), is defined as the ratio between metal concentration in plant roots and metal concentration in soil (Chojnacka et al. 2005):

$$\mathrm{BAC} = \mathrm{Cplant}/\mathrm{Csoil}$$

The Translocation Factor, i.e. the metal flux from plant roots to the aerial parts, is calculated by the ratio of metal concentration in shoots and roots (Singh et al. 2010; Mendez and Maier 2008; Yoon et al. 2006):

$$\mathrm{TF} = \mathrm{C\ shoot}/\mathrm{Croot}$$

Evaluation of human exposure as a consequence of pollutants translocation from contaminated soils to edible vegetables has been proposed quite recently by Khan and Cao (2012), who suggest to consider separately all the vegetable components. Root concentration factor (RCF), shoot concentration factor (SCF) and fruit concentration factor (FCF) are calculated as follows:

$$\begin{aligned}\mathrm{RCF} &= \mathrm{C\ root}/\mathrm{Csoil}\\ \mathrm{SCF} &= \mathrm{C\ shoot}/\mathrm{Csoil}\\ \mathrm{FCF} &= \mathrm{Cfruit}/\mathrm{Csoil}\end{aligned}$$

where Croot, Cshoot, Cfruit and Csoil represent the contaminant concentration in root, shoot, fruit and soil on dry basis, respectively.

The PHEs daily intake due to consumption of contaminated vegetables results from the following equation:

$$\mathrm{DI}_{\mathrm{PHEs}} = \mathrm{C}_{\mathrm{PHEs}} \times \mathrm{C}_{\mathrm{factor}} \times \mathrm{V}_{\mathrm{intake}}/\mathrm{BW},$$

where DI is the total PHEs daily intake, $\mathrm{C}_{\mathrm{PHEs}}$ is the total PHEs concentration in vegetables (mgkg^{-1}), $\mathrm{C}_{\mathrm{factor}}$ is a conversion factor from fresh weight of vegetables to dry weight (0.085 following Rattan et al. 2005), $\mathrm{V}_{\mathrm{intake}}$ is the daily intake of vegetables ($0.350\ \mathrm{kg\ person}^{-1}\mathrm{day}^{-1}$), and BW is the average body weight (64 kg).

5 Risk Assessment

While risk may be defined as the combination of the probability, or frequency, an hazardous event to occur, and the magnitude of consequences of its occurrence, hazard is commonly defined as “a property or situation that in particular circumstances could lead to harm” (Critto and Suter 2009). Consistently, risk assessment is the systematic procedure with which the risks associated with hazardous substances, processes, activities or events are identified, described, analyzed and estimated either qualitatively and quantitatively (Korre et al. 2002).

Risk assessment procedures include two components, the Environmental Risk Assessment and the Human Health Risk Assessment. The former has been used mainly for comparative and priority setting purposes with reference to contaminated sites. The latter refers to the possible consequences of human exposure to contaminant sources on human health. In the contest of comparative risk analysis, risk is used as an indicator, not as an absolute quantitative measurement of the adverse effects of contamination on the environment and/or on human health (Korre et al. 2002).

5.1 Quantitative Risk Assessment

Many countries utilize a multi-level risk-based methodology in regulating and managing contaminated sites (ASTM 2000; Critto and Suter 2009; UK-EA 2009). The risk-based methodology provides quantitative methods for the estimation of human and ecological risks using analytical models of contaminant fate and transport, and assessment of human and ecological exposure (Geng et al. 2014). Common to this approach is the adaptation of a multi-tiered framework, along with the requirement for developing risk-based screening levels in an earlier tier, and site-specific target levels in a later tier, thus allowing risk assessment to be undertaken in a progressive and cost-effective manner.

Conversely, development of a robust conceptual model of a contaminated site is an integral part of a successful risk assessment. It provides a qualitative evaluation of potentially contaminant sources, pathways and receptors at the site, based on plausible contaminant – pathway – receptor linkages under current and future land use of the site. For example, Geng et al. (2014) investigated a Mo-contaminated industrial site in China, whose future land use would be residential. After examination of the historic records of the site and field-scale site investigation, they developed a conceptual model on the site risk assessment. The principal linkages in the assessment procedure (source – pathways – receptors) are identified as follows: groundwater – drinking water and dermal contact – residents and workers. These pollution linkages have been subjected to a quantitative risk assessment and have been used as the basis for calculating the site specific target level. The results of model application proved Mo contamination in the local streams due to inflow of polluted groundwater will not pose unacceptable risks to aquatic biota (Geng et al. 2014). Conversely, Mo was highly concentrated in the groundwater, and the risk associated with this should not be neglected. Based on the toxicity data from the database of the International Agency for Research on Cancer (WHO 2013) and the Integrated Risk Information System (USEPA 2013), Mo has no carcinogenic effect on living organisms. Therefore, only non-carcinogenic risk was assessed: Mo will pose unacceptable non-cancer risks for on-site children when they directly drink the groundwater.

5.2 Environmental Risk Assessment

The environmental risk assessment is the procedure of evaluating risks resulting from hazards in the environment that threaten soil, ecosystems, plants, animals and ultimately human population.

Within the environmental risk assessment procedure, in the 1990s the US Environmental Protection Agency (US-EPA 1992, 1998) set up a framework and the related guidelines for the Ecological Risk Assessment as the process of organizing and analyzing data, assumptions and uncertainties to evaluate the adverse ecological effects on ecosystems (Critto and Suter 2009). Ecological Risk Assessment (ERA) is the appropriate process for identifying environmental quality objectives and the ecological aspects of major concern (Semenzin et al. 2009). The principles and procedures that have been established at international level (US-EPA 1998, UK-EA 2003 and several applications) point to a ERA framework based on a hierarchical approach, including: (1) a screening phase allowing the definition of land use-based soil screening values, and (2) a site-specific phase in order to achieve a more comprehensive risk characterization. Within risk characterization, US-EPA (1998) suggests to apply Weight of Evidence methods to determine possible ecological impacts determined by chemical contamination, following three lines of evidence: chemicals characterization, laboratory-based toxicity tests, and characterization of living organisms communities, as indicated by Long and Chapman (1985). The first level includes preliminary investigations that can be stopped when the estimated risk is considered *acceptable* by experts. In the case it is unacceptable, the second level is run to reduce uncertainty in the risk estimate. Site-specific aspects of particular interest (e.g. specific plant communities or typical endemics) can be analyzed in the third level, thus reducing costs and duration of analysis. A specific software, called ERAMANIA, has been developed with the aim at comparing the different tests included in the three levels of analysis (see Semenzin et al. 2009 for details). To overcome the uncertainties included in the assessment procedure, increased attention has been paid to developing a probabilistic risk assessment methodology, as opposed to the deterministic risk assessment approach (US-EPA 1999).

The ecological risk is generally considered a second priority in comparison to human health risk; however, it is very difficult to propose remediation techniques for restoration of contaminated sites if the potential risks to biological communities are not considered (Moreno-Jimenez et al. 2011). For example, the risk posed by mining sites, which comes mainly from tailings with high concentration of potentially harmful elements (PHEs) (e.g. As, Cd, Cu, Pb, Zn), represents a serious environmental concern. Since abandoned mine sites are widely diffused, particularly in developed countries (Bini 2012; see also Chap. 5, this volume), there is the need to develop new (or to implement existing) methods of risk assessment to be applied to these sensible areas, in order to better quantify the potential environmental risk, also in the perspective of secondary poisoning to animals and even humans.

A new screening methodology for quantitative impact assessment based on Environmental Risk Assessment (ERA) has been proposed recently (Moreno-Jimenez et al. 2011); it applies general principles for chemical risk assessment, as described in EU Technical Guidance Document (EC 2003), and develops in two steps. The first establishes eight risk levels according to the values of hazard quotients (HQs). HQs are calculated as the ratio between environmental

Table 10.1 Ranking of risk indexes based on hazard quotients and level of disturbance (Adapted from Moreno-Jimenez et al. 2011)

Hazard quotients	Risk index	Level of disturbance
<1 (predicted non-effect)	0	Negligible effects
1–10 (predicted non-effect)	1	Sensitive species
1–10 (non-observed chronic effects)	2	Standard species
10–100 (non-observed chronic effects)	3	Community
>100 (non-observed chronic effects)	4	Ecological structure
1–10 (50 % lethal acute effects)	5	Standard species
10–100 (50 % lethal acute effects)	6	Community
>100 (50 % lethal acute effects)	7	Ecological structure

concentrations (i.e. exposure or daily intake) and toxicity values (i.e. reference dose or acute toxic dose). Consistently, a scoring system of 8 risk indexes (RIs) is defined according to the level of disturbance. RIs from 0 to 4 are based on chronic exposure and RIs from 5 to 7 are based on acute exposure (Table 10.1) (see Moreno-Jimenez et al. 2011, for details).

The second step evaluates the overall potential impacts of a contaminated site based on the Impact Index (ImI). This is obtained as the sum of the chronic and acute RIs. Finally, the ImI obtained is assigned to five different categories, from negligible to very high impact according to the following criteria:

$$\mathrm{RI(HQchronic)} + \mathrm{RI(HQacute)} = \begin{array}{ll} \mathrm{ImI} \le 1 & \text{(negligible impact)} \\ \mathrm{ImI} \le 2 & \text{(low impact)} \\ \mathrm{ImI} \le 7 & \text{(moderate impact)} \\ \mathrm{ImI} \le 9 & \text{(high impact)} \\ \mathrm{ImI} > 9 & \text{(very high impact).} \end{array}$$

In order to select the ecological receptors and exposure routes, three protection goals are considered: soil organisms (plants, earthworms and microorganisms), aquatic organisms (algae, invertebrates and fish) and terrestrial vertebrates (birds and mammals).

The exposure concentration of soil organisms (Csoil) is represented by the metal concentrations measured in soil. The same Csoil values are also taken into account when assessing the exposure of terrestrial vertebrates.

For the aquatic compartment, the exposure for aquatic organisms and terrestrial vertebrates (through drinking water) is represented by the metal concentration in the water samples (Cwater).

Three main exposure routes are considered for terrestrial vertebrates: oral food ingestion, soil accidental ingestion and drinking water. Unlike to soil and aquatic organisms, exposure levels for terrestrial vertebrates are estimated using exposure models, admitted by different regulations (EC 2002a, b, 2003). The daily dose of metals through oral food ingestion (DDfood) is calculated by the following equation:

$$\mathrm{DDfood} = \mathrm{FIR}/\mathrm{W} \times \mathrm{Cfood} \times (100 - \mathrm{MC})/100\ \mathrm{mg/kg\ b.w./day},$$

where FIR is the food intake rate of indicator species (kg food fresh material per day), W is the body weight (b.w.) of indicator species (kg), Cfood is the concentration of metal in food related to fresh material (mg/kg food), and MC is the moisture content of food source (%).

The total DDfood for terrestrial vertebrates is the sum of values obtained from each exposure pathway (food, soil and drinking water). The risk quantification indicates potential risk to sensitive species (HQ >1) in all the investigated compartments. Soil organisms are expected to suffer acute effects both to species and community, while chronic effects to standard species are likely to occur, and this may lead to possible overestimation of risk. A more realistic risk estimate is quantification of the bioavailable metal fraction in soils, although it is not generally admitted (Berthelot et al. 2008). In any case, the whole ecosystem seems to be highly impacted by (heavy) metals, and the site recovery seriously compromised.

Taking into consideration time and costs of risk assessment procedures, an alternative way to reduce uncertainty, time and costs is applying regression models, based on soil properties, for estimating metal concentration in vegetables (Karo Bester et al. 2013). Yet, regression models identify statistically significant soil properties which have an influence on the accumulation of metals by plants. Identifying effective soil properties enables to drive metal transfer to the food chain, reducing the risk to human health. As application of the method, Karo Bester et al. (2013) developed a regression model to predict Cd concentration in selected vegetables grown on garden soils as a function of significant soil parameters (pH, SOC, clay content). Based on regression analysis, the most predictive soil properties for metal uptake by most of the vegetables examined were soil Cd concentration, pH and SOC, as expected. The Cd level exceeded the EU legislative maximum level (EC 2006) in carrots, followed by red beet, onion, chicory and endive.

The main advantage of regression models is that they are time and cost effective, reducing the size of data sets needed to identify the statistically significant soil properties. However, the results of regression models are reliable when the sampled soils and vegetables are a statistically representative sample. Moreover, there may be also interactions between soils and other environmental properties, as geology and meteorological conditions. Therefore, the model results must be interpreted correctly.

5.3 Exposure Assessment

The exposure assessment identifies the pathways by which living organisms are potentially exposed to toxicants and estimates the magnitude, frequency and duration of these actual and/or potential exposures (Lee et al. 2008).

Estimate of exposure levels is a central step in Ecological Risk Assessment to evaluate ecotoxicity risks posed by chemicals (Bertazzon et al. 2006). Although in general regulatory guidelines emphasize that exposure conditions are a function of spatial factors, exposure estimate methods ignore frequently site-specific conditions that can be accounted for in risk assessment. Therefore, estimates derived from non-spatial models are unreliable and potentially misleading.

A method for the characterization of contaminant exposure, based on data spatial dependence which produces a spatial interpolation of the sampling points in a GIS framework, has been proposed by Bertazzon et al. (2006). According to the scale of the problem to be assessed, the method provides two different approaches, the site-specific spatial risk assessment, and the regional one (Critto and Suter 2009). The former is performed at local scale using site-specific data to define the spatial distribution of risk, and provides reliable risk maps; its use has increasing interest, combining quantitative information with spatial data. The latter is of more general interest, dealing with problems that affect large geographical areas with multiple habitats; it is used especially by policy makers facing problems caused by multiple sources of hazards (e.g. subsidence, sediment contamination, benthic communities population, fishing, etc.). For example, Micheletti (2006) produced maps showing the spatial distribution of single and cumulative ecological risk for As, Cd, Ni, Zn and PCBs in the lagoon of Venice, while Ungaro et al. (2008) expanded a previous soil survey mapping the As probability of exceeding regularity thresholds in the Venice lagoon watershed.

Interest in site-specific spatial risk assessment is more and more increasing. This novel approach combines quantitative risk assessment procedures and spatial distribution of stressors (e.g. contaminated sites or groundwater) and receptors (e.g. plant community, human population) to facilitate understanding and communication (Gay and Korre 2006).

Bertazzon et al. (2006) applied the spatial analysis to a complex case study, the lagoon of Venice (Italy), characterized by noteworthy spatial variability both in morphology and in contaminated sediment distribution and properties. The proposed model allowed estimating chemicals exposure levels of receptor organism (clam: *Tapes philipinarum*) at any location in the lagoon, as well as hot spots, thus preventing any concern with respect to human health by consuming contaminated clams. Different site-specific risk assessment applications are available, concerning in particular contaminated sites. Carlon et al. (2008) developed a technical software (DESYRE), aimed at performing a spatial risk assessment, accessed directly in the popular GIS platform ArcGIS 9.2. Pizzol et al. (2009) illustrated in detail the structure of DESYRE. It is a Decision Support System (DSS) structured into six modules (*Socio-economy, Characterization, Risk Assessment, Technological Assessment, Residual Risk Assessment, Decision*) which represent the main phases of contaminated sites management. The DSS objective is the creation of different scenarios and their comparison in terms of residual risk following site remediation. It integrates large volumes of georeferenced heterogeneous information (e.g. land uses, industrial activities, population density, traffic, geology, hydrology, contaminant concentration), performing a spatially resolved environmental risk assessment (see Pizzol et al. 2009, for details). The risk assessment module, in particular, provides tools for human health risk analysis of soil contaminants, and allows a risk-based zoning of the site. Considered exposure pathways in the module are the ingestion and dermal contact with soil and groundwater, and inhalation of vapours and particulate emissions.

Currently, risk assessment approaches are becoming widely used in Europe to support the EU recent policies and EC Directives on environmental concerns (e.g. Commission's White Paper 2001, European Thematic Strategy for Soil Protection 2006, REACH regulatory 2013), also with specific networks for contaminated sites, such as CARACAS, CLARINET and NICOLE (Critto and Suter 2009). Although there exist several differences among the Member States in terms of approach, there is a general consensus for developing a common data base and a set of models devoted to risk assessment of natural hazards, including contaminated sites. With this perspective, the EU Council has developed a set of guidelines for national risk assessment and mapping (EC 2010), in order to implement the methodology and to provide risk management instruments for policy-makers. Three basic steps are defined:

1. Risk identification, which is the process of recognizing and describing risks;
2. Risk analysis, which is the process of understanding the nature of risk and quantifying the risk level in function of probability, exposure and vulnerability;
3. Risk evaluation, which is the process of comparing risk analysis with risk criteria to determine the acceptance level.

To support the risk assessment process, risk maps should be developed to inform about the hazards and the vulnerability of land and residents, and to show the spatial distribution of major hazards, in order to develop a risk attenuation strategy. Risk assessment and management techniques, therefore, are a useful tool for: (i) the development of environmental regulations, (ii) providing a basis for site-specific decisions, (iii) ranking environmental risks, and (iv) comparing risks (Critto and Suter 2009).

5.4 Human Health Risk Assessment

The second aspect of risk assessment procedure refers to the probability of occurrence of an event, and the probable magnitude of adverse health effects on human exposure to environmental hazards (NRC 1983; Paustenbach 2002).

Human health risk assessment has been used to determine if exposure to a chemical, at any dose, could cause an increase in the incidence or adverse effects on human health (Lim et al. 2008).

According to the procedure for human health risk assessment proposed by the US National Academy of Sciences (1993), as reported by Chon et al. (2011), four interactive and iterative steps compose the basic framework for risk assessment:

1. hazard identification;
2. exposure assessment;
3. toxicity (dose–response) assessment;
4. risk characterization.

1. *Hazard identification*. The purpose of hazard identification is to identify chemical substances which can affect a harmful effect in human body. A hazard is a source of risk but not a risk itself. The concern of chemicals (COCs) is selected by a risk assessor in this stage (Lim et al. 2008). The hazard identification process is accomplished through the sampling of different environmental media (soils, waters and plants), and the subsequent determination of the contaminant level of PHEs in these samples.

2. *Exposure assessment*.- Exposure assessment, as in the ecological risk described above, is an important analytical tool for evaluating the extent of actual or potential exposure of receptors to the source of a chemical hazard, and is an important component of any health risk assessment and epidemiological study (Nieuwenhuijsen et al. 2006). The aims of exposure assessment are identification of potential receptor(s), evaluation of exposure routes and pathways, and quantification of exposure. The exposure assessment identifies the pathways by which humans are potentially exposed to toxic substances and estimates the magnitude, frequency and duration of these actual and/or potential exposures (Chon et al. 2011). As direct associations need to be established between actual human exposure and health effects, exposure assessment is a crucial element of epidemiological research (Nieuwenhuijsen et al. 2006). Some environmental epidemiological studies use simple proxies such as distance from a point source (e.g. a factory), while others are categorised as industrial sources, agriculture land use, mining or urban zones. Many of the former studies have reported positive associations with health outcomes; however, it is difficult to attribute the incidence or prevalence of a disease to a particular industry or chemical.

Conducting an exposure assessment involves analyzing contaminant releases, identifying exposed populations, identifying all potential pathways of exposure, estimating exposure point concentrations for specific pathways, and estimating contaminants intakes for specific pathways (Lee et al. 2008; Chon et al. 2011). As already stated, the most common pathways for toxicant intake are via direct (oral) soil ingestion, food and drinking water assumption, dust inhalation, skin absorption. The (receptor) exposure estimate is achieved through calculation of the average daily dose intake of a given contaminant, or of the sum of several contaminants, whose effect could be biomagnified.

The average daily dose (ADD) of the contaminant via the identified pathways (i.e. soil ingestion, dust inhalation, food ingestion and drinking water pathways) indicates the quantity of chemicals ingested per kilogram of body weight per day (Kolluru et al. 1996; Paustenbach 2002):

$$\mathrm{ADD} = \mathrm{C} \times \mathrm{IR} \times \mathrm{ED} \times \mathrm{EF}/\mathrm{BW} \times \mathrm{AT} \times 365,$$

where:

C = concentration of the contaminant in the environmental media (mgkg^{-1}),
IR = ingestion rate (mg/day)
ED = exposure duration (years)
EF = exposure frequency (days/year)
BW = body weight of the receptor (kg)
AT = averaging time (life expectancy)
365 = conversion factor from year to days.

Based on US-EPA database IRIS (US-EPA 1997), Chon et al. (2011) applied this model to As-contaminated agricultural soils in Korea, and found that exposure factors to chemicals of an adult farmer (IRsoil = 50×10^{-6} kg/day; ED = 30 years; EF = 350 days; AT = 76 years, BW = 60 kg), accounted for an As average daily dose of 7.8×10^{-5} mg/kg-day by soil ingestion, 2.56×10^{-4} mg/kg-day for drinking water consumption, and 2.3×10^{-3} mg/kg-day for rice consumption (i.e. two orders of magnitude with rice in comparison to direct soil ingestion), by far highest than rice consumed at non-contaminated sites, as reported by Lee et al. (2008) for similar conditions.

3. *Toxicity assessment* – The purpose of toxicity assessment (i.e. dose–response assessment) is to estimate the potential for selected chemical substances to cause harmful effects in exposed people and to provide an estimate of the relationship between the extent of exposure and the increased likehood of harmful effects (Lim et al. 2008). The two principal toxicity indexes, as proposed by US-EPA (1992) are known as slope factor (SF) and reference dose (RfD). The SF is a conservative estimate of the increasing probability of an individual developing cancer as a result of exposure over a lifetime, and RfD is the estimated amount of the daily exposure level for the population that is likely to be without an appreciable risk of deleterious effects during a lifetime. The toxicity indexes of selected elements are presented in Table 10.2

Concerning PHEs, accurate prediction and quantification of the toxicological risk for population resident in a contaminated region should be performed. Hazard indexes for non-cancer risk (HInc) induced by selected elements from mine sites have been calculated by Chon et al. (2011). Arsenic and Cd presented HInc > 1 in most samples, thereby indicating possible individual threats for human health, while Zn HInc was <1, suggesting threats to be unlikely. Conversely, cancer risk for As via soil ingestion pathway was acceptable in all the examined sites (range 2.0×10^{-5}–6.8×10^{-7}), and was unacceptable with water consumption and especially with food (up to 8.5×10^{-4}).

Currently, the risk assessment models incorporate PHEs data for a range of important exposure pathways (drinkable water, beverages, food, dust inhalation, soil ingestion) from which a total human intake is derived (Kolluru et al. 1996; Heikens 2006; Yi et al. 2011; Chon et al. 2011; Alvarenga et al. 2013).

Table 10.2 Toxicity indexes of selected elements (Adapted from Zhou et al. 2010)

Element	Slope factor dose	Reference
As	1.5	0.003
Cd	6.1	0.001
Cr	–	0.005
Cu	–	0.038
Hg	–	0.0001
Pb	–	0.004
Zn	–	0.30

4. *Risk characterization* – Toxic risks refer to the non-carcinogenic harm occurring due to the exposure level (Chon et al. 2011), and the extent of the harm is indicated by US-EPA (1992, 1998) in terms of hazard quotient (HQnc):

$$\mathrm{HQnc} = \mathrm{E}/\mathrm{RfD}.$$

The exposure level (E), is the average daily dose (ADD), and the reference dose (RfD) is the daily dosage that enables the exposed individual to sustain this level of exposure over a prolonged time period without experiencing any harmful effect.

The hazard index (HI) is the overall toxic risk resulting from the sum of individual toxic risk due to a single PHE. If HI <1.0, the non-carcinogenic adverse effect is considered negligible.

The cancer risks refer to the probability one may develop cancer at a given lifetime exposure level. High carcinogenic risk levels are expressed by the following equation (US-EPA 1998):

$$\mathrm{Risk} = 1 - \exp(-\mathrm{CDI} \times \mathrm{SF}),$$

where CDI is the chronic daily intake over 70 years and SF is the slope factor (see above).

Chon et al. (2011) proposed a similar calculation of cancer risk, which is determined as the product of the lifetime exposure level (ADDlife) by the slope factor (SF):

$$\text{Cancer risk} = \mathrm{ADDlife} \times \mathrm{SF}.$$

The above model has been widely accepted and used, but has been also improved and adapted to specific purposes, combining human health with ecological risk assessment (Korre et al. 2002).

For example, an integrated procedure has been proposed so far by Covello and Merkhofer (1993), which consists of seven steps, and include:

(a) problem formulation;
(b) hazard identification;
(c) release assessment;
(d) exposure assessment;

(e) consequence assessment;
(f) risk estimation;
(g) risk evaluation.

The *problem formulation* is the planning process for performing the risk assessment. Its main goals are: (i) the selection of assessment endpoints (i.e. one or more ecosystem components or attributes); (ii) identification of the pathways by which human activities induce effects on the assessment endpoints, and (iii) identification of data needs and methods of data generation to continue the risk assessment (Critto and Suter 2009).

The *hazard identification* is aimed at identifying the potential threat for the environment (e.g. a landslide or flooding, or waste disposal on soil and groundwater) or which can determine a harmful effect in human body (e.g. PHEs). As previously stated, the hazard identification process is accomplished through the collection of environmental data (e.g. sampling of soils, waters and plants, and the subsequent determination of the contaminant level of PHEs in these samples).

The *release assessment* step involves the identification and monitoring of the source, and the use of statistical analysis, spatial analysis (Bertazzon et al. 2006) and modelling techniques to quantify the source of risk.

The *exposure assessment* process entails the characterization of exposure, identification of the exposure routes, and description of the exposed population, and the analysis of all the critical variables of the exposure scenario (Korre et al. 2002). The analytical phase points to the *consequence assessment*, and allows quantification of the land constraints (e.g. rock detachment, soil liquefaction, release and fate of contaminants), and characterization of ecological effects, and defines the exposure-response relationships.

The last two steps, *risk estimation* and *risk evaluation* provide risk estimates through the integration of results of exposure and effects.

Concerning human health, in general, the PHEs exposure routes related to soil are direct soil ingestion and dermal absorption. It is known from literature (Veerkamp 1994; Korre et al. 2002) that dermal absorption is significant in the case of organic substances (dioxins, PAHs) and organometallic compounds (e.g. Hg-methyl, Pb-tetraethyl, Sn-trialchylchloride), but is negligible in the case of heavy metals. Therefore, only the ingestion pathway is generally investigated. For example, with lead exposure the Chronic Daily Intake (CDI) of Pb deriving from the pathway of direct ingestion of contaminated soil is calculated as follows (Korre et al. 2002):

$$\mathrm{CDI} = (\mathrm{Cs} \times \mathrm{IR} \times \mathrm{CF} \times \mathrm{FI} \times \mathrm{EF} \times \mathrm{ED})/(\mathrm{BW} \times \mathrm{AT})$$

where Cs is the Pb concentration in soil (mgkg^{-1}), IR is the ingestion rate of soil from all sources (mgday^{-1}), CF is a conversion factor (10^{-6} mgkg^{-1}), FI is the fraction ingested from the site as a fraction of the total from all sources (in range 0.0–1.0), EF in the exposure frequency (days year^{-1}), ED is the exposure duration (years), BW is the body weight (kg) and AT is averaging time (days). For non-cancer risk AT = ED × 365.

Advanced geostatistics coupled with exposure assessment of residents at a Pb-contaminated site (Korre et al. 2002) allowed to estimate the fraction of Pb absorbed into the vascular system after ingestion; it was considered maximum and was set to one. This represent the worst-case scenario, which enlarges the influence of the ingestion pathway.

The US-EPA generic reference dose (RfD) is a commonly used estimate of exposure for the human population (US-EPA 1992, 1998). Several RfD values for Pb exist in the literature; among the most commonly reported, US-EPA proposes 0.1 $\text{mgkg}^{-1}\text{day}^{-1}$ (Petts et al. 1997), and AERIS (Aid for Evaluating the redevelopment of Industrial Sites) proposes 0.0035 $\text{mgkg}^{-1}\text{day}^{-1}$ (AERIS 1991). The former is a generic reference level (maximum value in the literature), the latter one is the smallest oral exposure RfD.

After the completion of the risk assessment steps, Korre et al. (2002) calculated a sensitivity index (SI) based on the model parameters, applying the following equation:

$$\text{SI} = 1 - \text{CDImin}/\text{CDImax}$$

where CDI is the chronic daily intake. The closer to zero is SI, the smaller is the correlation between the input parameter and the resultant chronic daily intake. If SI is close to one, the investigated parameter was labelled as sensitive, and has a significant effect on the resultant CDI.

The CDI of Pb at contaminated sites, deriving from the pathway of direct ingestion of contaminated soil was estimated for two population groups (see the CDI equation above): male adults with maximum exposure to soil (gardeners, farmers) and children 1–6 years old. The spatial representation of the results by a GIS model yielded a comprehensive picture of the risk to human health from direct ingestion of soil.

The results showed that the highest risk probability is consistent with high heavy metal concentrations. Yet, the effect of the selection of the reference dose was significant: when a low RfD was chosen, the probability of high exposure was significant for the target populations. On the contrary, when a high RfD was chosen, the probability of high exposure was smaller.

6 Urban Soils Contamination and Risk Assessment

Most frequently, high contamination levels affect urban soils, as a consequence of various anthropic activities (industry, traffic, waste disposal etc.), which determine PHEs concentration levels that can pose significant human health risks due to direct soil ingestion, inhalation of volatiles and dermal contact (Siciliano et al. 2009), especially in public parks and playground areas (see Angelone and Udovic 2014, Chap. 6, this volume). Particularly children and senior citizens are most vulnerable, because of their less immunological defence and the possible exposure to PHEs (Luo et al. 2012). For instance, lead contamination is ubiquitous in urban soils, and can be re-suspended in the air posing ongoing threats particularly to children because of its effects as a neurotoxin that inhibits development (Schmidt 2010).

In comparison with agricultural soils which mainly influence human health indirectly via food chain (see Chap. 3, this volume), soils in residential areas and urban parks have special recreational functions. Due to open space activities such as jogging, sporting, playground etc., re-suspended dust and hand-to-mouth oral ingestion can be a critical pathway of exposure for both adults and children, and it is important to quantify the various PHEs exposure risk levels for citizens.

Urban soil contamination has been generally evaluated by analysing total metal concentrations compared with corresponding soil guidelines values, that may overestimate the actual health risks, as is the case of Ni in serpentine soils (Angelone et al. 1993).

The risk posed by PHEs with ingested soil depends on the element fraction that is soluble in the gastrointestinal tract available for subsequent absorption (i.e. only a fraction of the total soil metal content is bioaccessible). Luo et al. (2012) have developed an *in vitro* digestion model to assess the human bioaccessibility, simulating the successive solubility of metal under stomach (gastric acid) and intestinal tract conditions. The proposed *in vitro* bioaccessibility extraction test is a static gastric model by which bioaccessible metals are extracted under acid conditions simulating those in human stomach. The percentage of ingested bioaccessible fraction (BAF%) of each metal is calculated as the percentage of the fraction soluble in simulated stomach acid (Cbioacc mgkg^{-1}) relative to the pseudo-total concentration (Ctotal, mgkg^{-1}) of the sample using the following equation:

$$\mathrm{BAF\%} = \mathrm{Cbioacc}/\mathrm{Ctotal} \times 100.$$

Exposure of humans to PHEs in urban soils can occur via three main pathways: direct oral ingestion of substrate particles (also called Chronic Daily Intake by ingestion: CDI ingestion), inhalation of dust re-suspended from soil through mouth and nose (Chronic Daily Intake by inhalation: CDI inhalation), and absorption of heavy metals-bearing soil particles by exposed skin (Chronic Daily Intake by dermal contact: CDI dermal). Both non-carcinogenic and carcinogenic risks of these exposure routes are considered in literature, taking particularly care of the non-carcinogenic hazard exposure for children (Luo et al. 2012). The dose received (chronic daily intake, CDI, i.e. average daily dose ADD) through the main exposure routes is calculated by the adapted US-EPA (1989, 1997) and US-DOE (2011) models (acronyms are the same as above).

Non-carcinogenic hazard for children is determined as the summation of:

$$\begin{array}{l}\text{CDI ingestion} = (\text{C} \times \text{IR} \times \text{EF} \times \text{ED/BW} \times \text{AT}) \times 10^{-6} \\ \text{CDI inhalation} = \text{C} \times \text{EF} \times \text{ET} \times \text{ED/PEF} \times 24 \times \text{AT} \\ \text{CDI dermal} = (\text{C} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED/BW} \times \text{AT}) \times 10^{-6} \\ \qquad\qquad\qquad (\text{see Luo et al.2012, for details})\end{array}$$

The carcinogenic risk for adults is calculated for the lifetime exposure, estimated as the incremental probability of an individual developing cancer over a lifetime as a result of total exposure to the potential carcinogen. The dose received (chronic daily intake, CDI, i.e. average daily dose ADD) through the main exposure routes is calculated by the adapted US-EPA (1989, 1997) and US-DOE (2011) models (acronyms are the same as above).

Carcinogenic risk for adults (see Luo et al. 2012, for details):

$$\begin{array}{l}\text{CDIingestion} \;= (\text{C} \times \text{IR} \times \text{EF/AT}) \times 10^{-6} \\ \text{CDI inhalation} = (\text{C} \times \text{EF} \times \text{ET} \times \text{ED/PEF} \times 24 \times \text{AT}) \times 10^{3} \\ \text{CDI dermal} = (\text{C} \times \text{ABS} \times \text{EF} \times \text{DFS/AT}) \times 10^{-6} \\ \text{DFS} \;= \text{soil dermal contact factor-age-adjusted.}\end{array}$$

Though interactions between some metals might result in a synergistic response (Xu et al. 2011), it is assumed that all the metal risks are additive, hence it is possible to calculate the cumulative non-carcinogenic hazard expressed as the Hazard Index as the sum of the three Hazard Quotients ($\text{HI} = \sum \text{HQ ing} +$ HQ inhal + HQ der), and carcinogenic risk expressed as the total cancer RISK:

$$\left(\text{total RISK} = \sum \text{Risk ing} + \text{Risk inhal} + \text{Risk der}\right).$$

Considering the site-specific oral bioaccessibility, the human exposure estimate to the main exposure pathway (soil ingestion) is adjusted when calculating the HQ ingestion and Risk ingestion:

$$\text{CDI ingestion} - \text{adjusted} = \text{CDI ingestion} \times \text{BAF\%}.$$

Concerning hazard quotient, as a general rule, the greater is the (positive) value of HQ, the greater is the likehood to have adverse health effects. Hence, $\text{HQ} \leq 1$ suggests unlikely adverse health effects, whereas $\text{HQ} > 1$ suggests adverse health effects to be likely. Concerning (total) cancer risk, the value 10^{-6} is considered the carcinogenic target risk by USEPA (2011): the cancer risk lower than 10^{-6} (a probability of an individual in one million to develop cancer) is considered to be negligible, while cancer risks above 10^{-4} are considered unacceptable by most international regulatory agencies (Luo et al. 2012). Though the human health risk levels of PHEs at urban sites are not negligible, the metal levels are often lower than various current guideline values. Hence, soil quality criteria still based on total metal concentrations might not accurately estimate the real risks (Baize and Van Oort 2014) and are just appropriate for worst-case scenarios. Overall, the actually occurring adverse effects of heavy metals in urban soils are site-specific. Moreover, the importance of exposure pathways, metal bioaccessibility and soil properties in assessing the realistic risks of soil metals should be highlighted.

7 Land Uses and Risk Assessment

Besides urban soils, different land use types significantly control the soil metal exposure and corresponding human health risks. Six types of land use are generally considered: residential, agricultural, forest, water, mine and bare land. Residential soils, as urban soils, may be affected by PHEs released by human activities (e.g. traffic, road dust Angelone and Udovic 2014, Chap. 6, this volume); agricultural soils suffer for large use of fertilizers and herbicides (Simon 2014); mine soils are naturally enriched in PHEs that might pose serious problems to human health (Wahsha 2014, Chap. 5, this volume), and also forest soils may be enriched in heavy metals released by the geological composition of parent rocks (Chap. 4, this volume), especially with acidic conditions that enhance mineral weathering. Therefore, in some developed countries such as Canada (CCME 2007), UK (UKEA 2009) and USA (USEPA 2011), the soil guideline values of contaminants have been proposed for different land use (Table 10.3).

A methodology to calculate the human health risk from heavy metals has been proposed recently by Zhao et al. (2012), based on a dose–response model, including different land uses. Three factors are considered in a dose–response health risk assessment: the sources, pathways and receptors. The first two are different for each land use (residential, agricultural, forest, water, mine and bare land). Sources can be dust, water, crops/food; exposure pathway is generally ingestion (soil and food) or inhalation (dust). Receptors are living organisms and especially local population that lives near the source.

The models used to predict the heavy metal contents of food (rice and vegetables) are developed using a multiple regression analysis based on metal concentration in food and in soil, in relation to soil pH:

$$\mathrm{logMetal(crop)} = \mathrm{a} + \mathrm{b} \times \mathrm{logMetal(soil)} + \mathrm{c} \times \mathrm{pH\ soil},$$

where a, b, c are coefficients that vary depending on the soil, heavy metal, climate and crop type.

By applying this model to rice and large leaf vegetables, Zhao et al. (2012) found a significant positive correlation for metal concentration (Cd, Cu and Zn) in vegetables and in soil. This is typical of metal tolerant (i.e. indicator) plants, as stated by Baker (1981). The relationship of metal intake to its relative reference dose (HQ = CDI/RfD) was used to assess the human health risk. Food daily intake was estimated to be 370 g/day for adults (65 BW); the reference dose was in the range 0.001–0.3 mg/kg/day (the lowest for Cd and the highest for Zn), consistent with US-EPA (2006, 2009). The maximum HQs for Cd and Cu exceeded 1.0, indicating a potential human health risk associated especially with Cd concentration in soil and its transfer to food chain and local population. Yet, Cd level in blood

Table 10.3 PHEs concentrations at various sites and guidelines values for different land uses

Location	Land use	Cd	Cr	Cu	Ni	Pb	Zn
China (21 cities)	Residential	0.39	69	40	25	55	109
Europe	Agricultural	0.79	53	195	27	39	68
Europe (34 cities)	Residential	0.95	59	46	22	102	130
Canadian guidelines	Agricultural	14	64	63	50	70	200
Canadian guidelines	Residential	10	64	63	50	140	200
Canadian guidelines	Industrial	22	87	91	50	600	360
UK guidelines	Residential	10	100	36	130	85	140
UK guidelines	Industrial	230	–	–	1,800	–	–
US-EPA soil screening level	Residential	70	120	3,100	1,500	400	23,000
US-EPA soil screening level	Industrial	800	1,500	41,000	20,000	800	31,000
Italy	Mine soils	33	95	412	54	306	657

of local residents in the investigated area was in the range 24.10 (highest exposure) −1.87 (lowest exposure) μg/L, as reported by Wang et al. (2011).

The modelling proposed (Zhao et al. 2012) provides a reasonable assessment of human health risk by integrating a spatial analysis of contaminant concentrations and land use.

Other approaches have become common in the last decade in the Environmental Risk Assessment. One of these is based on the Weight of Evidence (WoE), a system which allows determination of environmental risks by weighting multiple Lines of Evidence (LoEs) that report the quality, extent, and congruence of data (e.g. chemical analyses) that pertain to important aspects of the environment (Smith et al. 2002). Another approach is the Sediment Quality Triad (SQT), which is based on a standard combination of three LoEs, namely Sediment chemistry, Sediment toxicity and Benthic community structure. Each LoE provides distinct and complementary information about the investigated environment. Moreover, the latter is the assessment endpoint that changes in response to exposure to a certain stressor: the model is widely used, and is continuously improved (Chapman et al. 2002).

8 Biomonitoring

As previously stated, it is difficult to attribute the incidence of a disturbance at any environmental compartment, or some adverse effects to humans, to a particular industrial activity or a chemical substance (Nieuwenhuijsen et al. 2006), as is the case of arbitrary waste disposal on the land (e.g. chromium-rich effluents from leather industry, see f.i. Bini et al. 2008), or emissions in the atmosphere (see Chap. 1, this volume). This is further complicated by other factors such as the fate of chemicals (Alloway 1995), their pattern of dispersion, or the influence of local geological, hydrological and meteorological conditions (Dall'Aglio et al. 1966). Biological monitoring, also called biomonitoring, is a promising method of assessing environmental and human health risk by analysing PHEs concentration in environmental matrixes (e.g. plants, animals), or in human tissues (hairs, nails), or in a biological matrix (blood, urine).

Concerning human health, biological monitoring is usually described as the measurement of a particular chemical substance, or a metabolite of that substance, in a suitable biological matrix (e.g. blood, urine, serum, and tissues such as hairs, nails, sweats), that act as an effective biomarker. For example, Cd levels in toenail were analysed in relation to prostate cancer (Vinceti et al. 2007); Chuang et al. (2007) found significant relationships between blood PHEs and hearing function; Se in human blood was related by Schalin (1980) to the aetiology of multiple sclerosis; depleted U was determined in urine of military personnel involved in the Bosnia war (Roth et al. 2001), and Cd in urine of exposed workers was found as a result of various health problems due to prolonged exposure (Han et al. 2009); quite recently, Giaccio et al. (2012) considered heavy metals in serum as the main responsible for male infertility.

The application of biomonitoring as a direct method of measuring possible contaminant exposure is frequently limited by the availability of adequate samples (Nieuwenhuijsen et al. 2006). For example, in the environmental compartments, mosses proved so far useful traps for airborne PHEs supply (Steinnes 1980), and unusually low Se concentration in pastures was considered responsible for disorders in grazing animals in several parts of the world (Schalin 1980).

In human population, blood and urine are often the preferred media, since many toxic substances are easily measured in these media. For example, urine Cd proved consistently associated with various renal and bone diseases (Bernard 2008), and effective biomonitoring with urine and nails showed that human As exposure decreased with distance from a power station (Wilhem et al. 2005). Biomonitoring techniques can also be used to assess early biological or physiological changes that are correlated with the uptake of toxic substances. These may induce molecular and/or cellular alterations that occur along the temporal pathway connecting ambient exposure to a chemical toxicant, as reported by Maleci et al. (2013) in *Taraxacum officinale*. Similarly, Sarkar et al. (2013) found that the outcome of Cd exposure could be apoptosis, growth inhibition, proliferation or carcinogenicity in animal cells.

Indirect methods of estimating exposure such as simulation studies, GIS mapping, mathematical models as well as other statistical techniques are also currently explored since the last years of last century (Goovaerts and Journel 1995; Bailer et al. 1997; Ungaro et al. 2008). One of the most known environmental and human concern is exposure to asbestos, a sneaky carcinogenic substance which may have adverse effect on human health (lung cancer) with long incubation. A number of studies were conducted during the period 1950–1990 to determine exposure of car mechanics to asbestos released from brakes, but unfortunately certain characteristics of exposure were not studied at that time when the risk posed by asbestos was not considered (Nieuwenhuijsen et al. 2006).

Simulation studies have been conducted recently to fill possible data gaps (see f.i. Paustenbach et al. 2003), particularly with the finest aerosol particulate (PM_1,

$PM_{2.5}$; see Rampazzo et al. 2014, Chap. 1, this volume). Also useful to this aim are retrospective simulation studies with historical records on metal distribution in water, soils and sediments carried out since the 1960s (e.g. Dall'Aglio et al. 1966), and in human bones (Martinez-Garcia et al. 2005). More recently, Khan and Cao (2012) paid particular attention to organic environmental contaminants such as dioxin, PCBs and PAHs. This information, coupled with the recently updated mortality data, could be used to estimate accurately the daily intake and the carcinogenic potency of such toxicants.

In recent years, mathematical modelling has become an important tool in environmental research (Goovaerts 1997), and has been greatly enforced by the use of geographical information systems (GIS) and geostatistical techniques. A model may help to explain a complex system and to study the effects of different components, and to predict the behavior of components (e.g. PHEs in environmental media). Models are typically applied to study impacts of individual sources (hot-spots), multiple-source industrial facilities, metropolitan areas, or larger regional areas (Rampazzo et al. 2014, Chap. 1, this volume). For example, regional models allow solving important pollution phenomena and concentration gradients in areas where point sources are present (e.g. mine areas). The spatial scales range from up to few kilometers (for large industrial point sources), to 100 kilometers (for individual urban areas), to few 1,000 kilometers (for larger regional areas). The development of GISs (Geographical Information Systems) has further enhanced the facility of analysis, combining all the territorial data sets (e.g. population statistics, social and environmental data, land use, etc.) in information layers, which allow understanding relationships not always evident from single data sets. In the last decades, modelling techniques have greatly improved the assessment of local pollution patterns on the basis of monitored data, and are likely to be important in further studies.

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Chapter 11
Potentially Harmful Elements and Human Health

Claudio Bini and Mohammad Wahsha

Abstract Potentially harmful elements, or more generally trace elements, are now considered to be among the most effective environmental contaminants, and their release into the environment is increasing since the last decades. Metals released by different sources, both natural and anthropic, can be dispersed in the environment and accumulated in plants and, ultimately, in human body, causing serious health problems as intoxication, neurological disturbances and also cancer. Widespread interest in trace elements has risen as major scientific topic only over the last 50 years, when it was realized that some elements were essential to human health (e.g. Fe, Cu, Zn), whereas some others were toxic (e.g. As, Hg, Pb), and likely responsible for serious human diseases, with frequent lethal consequences.

Since that time, great progresses in knowledge of links between environmental geochemistry and human health have been achieved, in combination with epidemiology.

The effects of most trace metals on human health are not yet fully understood, partly because of the interactions between them, and partly because of the complex metabolic reactions in the human body. Despite the copious research addressed to this topic, there is still a paucity of quantitative information on the relations between elements in soils and human health. Much is known about the functions of most elements in human body, but there is increasing evidence that the interactions among them are more complex than originally thought. Uncertainty is still prevailing, particularly with non essential elements that are "suspected" to be harmful to humans.

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The nonessential elements As, Cd, Hg, Pb have attracted most attention worldwide, due to their toxicity towards living organisms. Other elements (Al, B, Be, Bi, Co, Cr, Mn, Mo, Ni, Sb, Sn, Tl, V, W, Zn) are likely harmful, but may play some beneficial functions not yet well known, and should be more investigated.

Keywords PHEs • Geomedicine • Human health • Toxicology • Carcinogenic elements

1 Introduction

Chemical elements of both geogenic and anthropogenic origin are usually present in large amounts in soils, sediments and waste materials which often contain elevated concentrations of potentially harmful elements (PHEs) such as As, Cd, Cr, Cu, Ni, Pb, Zn and others (Helios-Rybicka 1996; Lee et al. 2001; Navarro et al. 2008). Heavy metals, in particular, are considered to be among the most effective environmental contaminants, and their release into the environment is increasing since the last decades. Metals released in the environment may result from many different activities and sources and may enter into the environment by a wide range of processes and pathways (Hassanien and El Shahawy 2011). They can be transported, dispersed in the environment and accumulated in plants (Davies 1987; Alloway 1995, 2013), and then may pass, through the food chain, to human people as the final consumer, causing serious health problems as intoxication, neurological disturbances and also cancer (Bernard 1995, 2008; Steinnes 2009).

The metal-enriched areas, therefore, represent an ideal natural laboratory where to study the processes in order to provide descriptive models of the interactions between PHEs, the pedosphere, the biosphere and the hydrosphere. Environmental threats arise when a certain amount of potentially harmful elements (PHEs) is released in the surrounding areas and to waterways. Indeed, it is well known that PHEs may have toxic effects on living organisms (microbes, plants and animals, including humans). Depending on the nature of rocks and soils, a wide dispersion of these PHEs both in solution and in particulate form is possible (Sivri et al. 2010).

Atmospheric emissions are probably the most harmful to the environment, and consequently, to human health due to either the great quantity involved, or their widespread dispersion which may originate many different exposure pathways. In particular, three heavy metals (Hg, Pb and Cd) are of great concern to human health and to the environment, mostly due to their ability to travel long distances in the atmosphere before deposition (Hassanien and El Shahawy 2011).

It is generally recognized that environmental contamination with PHEs has increased dramatically since the dawn of the Industrial Revolution (Nriagu 1979), and the main receptor of contamination is soil. Soil is a complex system with several functions, not only ecological, but also social and economic, and fundamental to living organisms, including human population (Moreno-Jimenez et al. 2011). Yet, it is the primary source of several elements and substances that humans intake with daily diet, and 98 % of food derives directly or indirectly from the soil (Coccioni 2011). Soil health, therefore, is of fundamental importance for human health, that is largely determined by mineral nutrition supplied by plants growing on soil: if a soil is contaminated, it is likely that also food crops are contaminated, posing potential concern to consumers.

The main soil and land contamination sources are both natural (rock weathering and soil genesis) and anthropic (industrial) processes, mining activities, agricultural practices, vehicular traffic, atmospheric fallout; all these are responsible for the disposal on land of potentially toxic substances such as sewage sludge, fertilisers and pesticides, persistent organic pollutants (POPs), polycyclic aromatic hydrocarbons (PAHs), polychlorobiphenils (PCBs) as well as heavy metals and other harmful chemicals.

Besides local pollution episodes, the most significant world soil pollution events in the recent history date back to the last century. A relevant amount of methyl mercury was released by a chemical factory in Japan over a long period (1932–1968), and entered the food chain determining acute poisoning by mercury to the local population, provoking severe neurological disturbance (Minamata disease). In the same years (1950), Cd-enriched wastewater from a mining plant was discharged on rice fields in Japan, determining chronic poisoning (itai-itai disease) with severe consequences in kidney functioning and bone deformation. A significant long-term contamination, lasting 15 years (1952–1966), occurred in the town of Hinkley (California, USA), where groundwater contaminated with Cr (VI)-rich wastewater from a chemical plant determined several cases of cancer to resident population. More recently (1976), an accident to the ICMESA chemical plant in Italy determined the release of dioxin in the atmosphere, and successive fallout to soils of a large area in Lombardy, with ca 250 persons affected by chlorine dermatitis. Moreover, dioxin is a known highly teratogenic substance responsible for severe foetal malformation, with still relevant effects after more than 30 years (Coccioni 2011). At Bhopal (India), in 1984, 40 tons of methyl isocyanate were discharged from a chemical plant producing pesticides, provoking 10,000 victims, and the mortality is still higher in that area than in other parts of India.

Besides possible lethal consequences to residential population, severe environmental accidents have occurred all over the world due to the discharge of chemicals on the land, in surface water or in the sea. Chromium-sludge discharged by leather tannery plants in the industrial district of Vicenza (Italy) has been shown to have contaminated hundred ha of agricultural land up to 10,000 mg kg^{-1} Cr (Bini et al. 2008). Petrol-chemical plants active at Porto Marghera (Venice, Italy) since the 1950s have been considered to be responsible for the contamination of the lagoon of Venice with several PHEs and organic chemicals (Bini 2008). The whole area has been classified as contaminated site of national interest, and a restoration project is ongoing. Heavy metals (As, Cd, Cr, Cu, Hg, Mn, Pb, Sb, Se, Zn) and organic compounds (PAH, PCB, Dioxin) have been identified as the main contaminants, owing to agrochemicals and industrial wastes discharged on soils and convoyed to the lagoon, provoking water and sediment contamination, decreasing biodiversity and shellfish disappearance (Bini 2008 and references therein).

In 1986, in the village of Schweizerhalle (Switzerland), 20 tons of herbicides and pesticides were discharged in the Rhine river, contaminating dramatically the whole area. In Italian territorial waters (Ionian sea), in 1974, the Yugoslavian cargo Cavtat carrying 900 drums containing more than 250 tonnes of Pb-tetramethyl and Pb-tetraethyl collided, and more than 20 tonnes were lost at a depth of 100 m below the sea surface (Tiravanti et al. 1980). Minor environmental effects were recorded 1 year afterwards.

Mining areas too are potential sources of severe environmental contamination (Bini 2012; this volume, Chap. 5), and resident population in the vicinity of mine sites is at high risk of suffering from serious diseases, with an elevated rate of enteric tumours (Zhao et al. 2012). Mine spoils are often disposed (or have been in the past), during active working periods, in the proximity of mine sites and conterminous land, provoking frequent accidents. In 1998, in Spain, 5 M cubic meters of highly contaminated sludge from a mining basin were convoyed to the Guadalquivir river to save the local natural reserve. In 2000, in Rumania, a fracture in a gold-mine dam determined outcome of more than 100,000 tons of mud containing cyanide. Fortunately, in both cases no victims were recorded. More recently, in 2010, the flotation basin of an aluminium plant ceased suddenly, provoking the outcome of 1 M cubic meters of highly alkaline red mud containing iron oxide and heavy metals in the Danube basin: it is estimated that this accident has been one of the biggest environmental disaster in the world, that will have important repercussions on human health for next decades (Coccioni 2011).

Perhaps the most known and impressive environmental disasters are those provoked by nuclear accidents like Chernobyl and Fukushima. In 1986, April, a reactor at the Chernobyl Nuclear power Plant in the former URSS (now Ukraine) exploded. The Chernobyl accident determined the emission in the atmosphere of about 85 PBq of radioactive materials, and the consequent fall-out of radioactive particles to vegetation and soils of several European countries. Radionuclides, in particular ^{137}Cs, were released at low altitude (<1,500 m), and their spatial distribution was strongly influenced by rainfall intensity and local topography. In NE Italy (nearly 2,000 km from Ukraine), because of radioactive particulate, forage for cattle was inhibited for some years, as well as fungi collection and cheese production in the contaminated areas (Giovani et al. 1991). The consequences of the accident on human health, particularly in Ukraine and Russia, were (and still are) very impressive: although the official report indicates only 65 persons dead, and possibly 4,000 affected by cancer and leukaemia, an estimate of presumable deaths related to the accident indicates tens thousands to millions of victims (Coccioni 2011).

At Fukushima, Japan, in 2011, March, a strong earthquake followed by a very anomalous ocean wave (tsunami) determined the breakdown of the Nuclear Power Plant, and the release of radiation in the atmosphere at a rate of 900PBq, with radiation levels exceeding the annual limits over a distance of 60 km. As of June, 2013, the exact chain of events was not known. The total amount of radiation released is also not known, and the likely number of deaths cannot be determined with the information available. Authorities spoke of two persons of the plant personnel who died; however, one might expect around 1,000 extra cancer deaths related to the disaster.

Other nuclear fatalities occurred elsewhere in the world, and it was reported by newspapers that globally more than 300 patients receiving treatment for different cancer forms suffered radiation injuries, and at least eight died for over-exposition by ^{60}Co.

1.1 Soils and Human Health

The connection between soils and human health is still little recognized by general population. Also the medical profession, as pointed out so far by Voisin (1959), has largely ignored soils in their efforts to improve human health, but soil science should be the foundation of preventive medicine, as stated by Brevik (2013).

The idea that soils influence human health is not new, it has existed for thousands of years (Bible, Numbers, 13: 18–20), and received considerable attention in the twentieth Century (Brevik 2013). The scientific community started to pay attention to this concern since the 1960s (Webb 1964), and flourished in subsequent years, in combination with increasing epidemiological studies. Geochemical applications to epidemiology brought to develop the *landscape geochemistry*, i.e. the study of complex interactions within the system lithosphere-pedosphere-hydrosphere-biosphere, that is concerned with the mobility and distribution of elements in the environment. The relationships between environmental geochemistry and human health, including the incidence of disease patterns, have been investigated since the 1970s, particularly by Russian scientists (Kovalsky 1970). Afterwards, relevant contributions were given by several authors from different countries (Fortescue 1980; Lag 1980, 1984, 1987; Thornton 1993; Alloway 1995; Oliver 1997; Kabata-Pendias and Pendias 2001; Adriano 2001; Abrahams 2002; Deckers and Steinnes 2004; Van Oostdam et al. 2005; Kabata-Pendias and Mukherjee 2007), and ultimately by Alloway (2013), Brevik (2013), Hannigan and Darrah (2013) and Censi et al. (2013).

The early Russian approach (Vernadsky 1942; Perel'man 1966; Kovalsky 1970) included regional geochemical maps showing biogeochemical zones which reported the incidence of diseases as a result of geoepidemiological surveys at regional scale, and the first attempts to relate trace elements with diseases. Approximately in the same period, Thornton and Webb (1979) described the relationships between the level of Co in stream sediments and the incidence of pains in cattle and sheep. Parallel studies by Lag (1980, 1984) introduced the new concept of geomedicine as a multidisciplinary approach including geology, soil science, botany, zoology, microbiology, agriculture, animal husbandry, epidemiology and public health (Thornton 1993).

Born from the above (and others) contributions, the new scientific branch of the *medical geology* (termed *Geomedicine* by Prof. Lag), is based on the utilizing innovative approaches related to the most recent epidemiological, sanitary and geochemical knowledge. Medical geology is an emerging discipline, but since the

Antiquity people discovered links between geology (in particular soil as the natural substrate for food crops; Brevik 2013) and health, as reported by the early physician Paracelsus (1493–1541), who stated that *all substances are potential poisons, and the correct dose makes the difference between poison and medicine*.

A further evolution at worldwide level, initially referred to as medical geology, is now termed *health geography*, that is *"the application of geographical information, perspectives, and methods to the study of health, diseases, and health care of human population groups"*. It is grounded on the study of the relationships between environmental risk factors and adverse health effects, taking into consideration the worldwide distribution of illnesses, and the regional characteristics of pathological processes that generate geographically significant phenomena, thus allowing identification of areas where health hazard is higher.

Medical geology is now recognized as one of the exciting new areas of geological and pedological research, although at present this is not a formally established subfield of soil science. Nevertheless, as stated by Brevik (2013), increasing research in soils and human health is essential to protect the environment and to enhance general population health.

1.2 PHEs and Human Health

There is not a general agreement on the number and functions of chemical elements in the human body. According to Brevik (2013), there are 14 elements that are essential for plant growth, that come from the soil, and many of them are essential also for human health. Additional elements are needed by organisms. Eleven elements comprise 99.9 % of the atoms found in the human body: H, O, C, N, Na, K, Ca, Mg, P, S, Cl. Eighteen additional elements are considered essential in small amounts in the human diet: Li, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, W, Mo, Si, Se, F, I, As, Br, Sn, and most of them are supplied by plants.

Conversely, 22 chemical elements are considered by Coccioni (2011) essential to human health, owing to their physiological functions (Table 11.1). Only a part of them, however, are readily ingested with diet, absorbed and metabolized by the human body.

Some heavy metals, as copper (Cu), zinc (Zn) and iron (Fe), serve as micronutrients at low concentrations but they are toxic when in excess, while other heavy metals and metalloids, as lead (Pb), cadmium (Cd), mercury (Hg), inorganic arsenic (As), aluminum (Al) and nickel (Ni), are toxic even at very low concentrations, hence they are of particular health concern (Hassanien and El Shahawy 2011). Heavy metals have the ability to bioaccumulate in food chain, and children can be chronically exposed to them from different sources as air, water and food, leading to their accumulation in body tissues of children and causing various diseases, since they act as systemic toxins with specific neurotoxic, nephrotoxic, foetotoxic and teratogenic effects and can directly influence behaviour and impair mental and

Table 11.1 Biological functions of selected essential elements

Essential macroelements (×70 kg body weight)	Biological function
Ca 1,000 g	Bone structure, neurotransduction
Mg 30 g	Bone structure, electrochemical regulation, enzymatic catalysis
Na 1.5 g	Electrochemical regulation, acid-base equilibrium, osmosis control
K 150 g	Electrochemical regulation, acid-base equilibrium, osmosis control
Cl	Electrochemical regulation, acid-base equilibrium, osmosis control
P 700 g	Bone structure, membrane structure, metabolic regulator
Essential microelements	Biological role
Fe	Oxygen and electron transport
Cu	Enzyme catalysis
Zn	Enzyme catalysis, protein structure
I	Metabolism regulator
Se	Enzyme catalysis, redox regulator, antioxidant,
Ni	Enzyme catalysis, redox regulator, antioxidant,

Adapted from Coccioni (2011)

neurological functions via influencing neurotransmitter production and utilization (Obiria et al. 2010).

The primary sources of PHEs in the environment are geogenic and anthropogenic, the latter being the major cause of concern. Human health concern related to geological materials and processes, therefore, is more common than it was thought years ago: over three billions people have health problems connected to geological materials. Currently, there are few areas in the world not affected by metal pollution, as suggested by long-distance transported Pb in snow profiles in Greenland, which is approximately tenfolds that of Antarctic ice (Barbante et al. 2013).

Human health is vulnerable not only to individual sources, but also to the combined effects of various contamination sources. As stated by Nriagu and Pacyna (1988), nearly every industry discharges at least one metal into water or soil, with annual inputs of 82 t As, 22 t Cd, 954 t Cu, 25 t Ni, 796 t Pb and 1,372 t Zn, which are released to the environment from industry and other sources. However, it is important to remind that all the potentially toxic elements of concern to humans are present as natural background in small amounts in soil, water, food and air, as a consequence of rock weathering. Yet, it is well known the case of Cr and Ni in serpentine soils, and that of Cd and Mo in marine black shales. Thornton (1993) reports that excess Mo in soils from black shales causes Cu deficiency diseases such as ataxia in sheep and hypocuprosis in cattle. Conversely, a pedogeochemical survey in the Lake Nakuru national Park (Kenia), revealed low concentrations of Cu, Co, Se and P in volcanic soils, indicating Cu deficiency and the need of supplement for wildlife species in the Park (Thornton and Webb 1979).

Besides these natural geochemical anomalies, geochemical survey may also focus attention on anthropogenic anomalies (hot spots) related to chemicals discharged on land by mining activities (Bini 2012; see this volume, Chap. 5), industry and urban sources (Bini et al. 2008; see this volume, Chap. 6). A famous example of a large environmental health investigation is that of an hotspot area with up to 500 ppm Cd around the village of Shipham (U.K.), one of the biggest Zn mine in EU (Thornton 1993).

A noteworthy concern is the finding of elevated Pb concentrations in the home environment, that may have significant implications on the health and mental development of children that habit the site, and are exposed to Pb-contaminated dust (Thornton 1993). The same apply to multi-element contaminated home gardens where vegetable is grown for kitchen: both gardeners and children playing in the garden are exposed to contaminated soils, and all the family may be affected by metal-contaminated vegetable consumption.

As a matter of fact, few causal relations have been shown until now between potentially harmful elements and human diseases. An exception to this statement includes the well known relationship between F content in water, human fluorosis and dental caries. Other exceptions are I concentration in food and endemic goitre, low Se intake, Keshan disease and Kaschin-Beck disease in China (Thornton 1993). All these aspects will be discussed in the next Sect. 2.

1.3 PHEs and Toxicology

The main effects of land contamination on human health are due to the contact with contaminated soils. Direct effects are brought about by ingestion, inhalation, and dermal absorption of soil components. Indirect links are through the atmosphere, hydrosphere and biosphere (see Abrahams 2002 for details).

From the toxicological point of view, ingestion of contaminated water, intake of toxicants by the food and inhalation of gaseous compounds are particularly relevant.

Toxic effects of PHEs to humans (Table 11.2) may occur with acute, subacute, subchronic and chronic symptoms. Chronic exposure to Cd may have effects such as lung cancer, prostatic proliferative lesions, bone fractures, kidney dysfunction and hypertension (Zhao et al. 2012). Chronic oral and inhalation exposure to As can lead to skin lesions and lung cancer, respectively. Exposure to Pb may cause plumbism, anaemia, gastrointestinal colic and central nervous system disturbance (Zukowska and Biziuk 2008). Hexavalent Cr is considered a human carcinogenic by both USEPA and IARC. Nickel can cause lung cancer, chronic bronchitis, emphysema and asthma.

One of the major concern to deepen is the essential element deficiency/excess; the imbalance may cause problems to crop production for human consumption, animal nutrition and ultimately to human health, as reported by Thornton (1993). Indeed, in some cases, toxic effects may occur in consequence of deficiency instead of excess of

Table 11.2 Effect of PHEs on human health

Element	Toxic effect
Arsenic	Liver cirrhosis, skin, liver and lungs cancer, Embryo theratogenesis
Beryllium	Lung cancer
Cadmium	Chronic kidney failure, bones deformation, loss of breathing capacity, high blood pressure, lung and prostate cancer, embryo theratogenic
Mercury	Neurological damage (*mercurialism*) asthenic-vegetative syndrome or Minamata disease. kidney damage, toxicity to the foetus and embryo theratogenic
Lead	Gastrointestinal damage, damage to both the neuro-muscular system and nervous system (*plumbism*), decreased fertility and sperm damage
Antimony	Respiratory system damage
Silver	Gastrointestinal, respiratory and liver damage,
Barium	Gastroentheritis, muscle paralysis, ventricular fibrillation and extrasystoles
Thallium	Neuronal damage, kidney and liver disease, foetus toxicity
Titanium	Irritation
Uranium	General biosystems and renal damage
Vanadium	Damage to the respiratory tract, skin and eyes, tremors, depression, kidney damage

Adapted from Coccioni (2011)

a given metal (Table 11.3). Several adverse health effects can arise from nutrient deficiencies; for example, the World Health Organisation (WHO 2007) estimates about two billion people to be anaemic due to iron deficiency. Another soil-related form of malnutrition is iodine deficiency which leads to goitre, severe cognitive and neuromotor deficiencies and other neuropsycological disorders.

Selenium is now considered an essential microelement to animals, including humans. A low level of Se in diet can cause Keshan disease, a heart disease that likely has a viral component, and Kashin-Beck disease which results in chronic degenerative osteoarthrosis. Insufficient Se levels may also be associated with cancer, stunting of growth, immune system and reproductive problems, and multiple sclerosis (Schalin 1980; Roman et al 2014). Zinc-deficient soils are widespread and include about half the world's soils. Zinc deficiency may cause stunted growth, anorexia, skin lesions, diarrhoea, and impaired immune and cognitive functions.

Several elements normally required for human health may become toxic when present in high amounts (e.g. Co, Cr, Cu, Fe, Se, Zn, and others) (Abrahams 2002). Their effects on human health will be discussed in the next section.

Elements tend to have synergistic or antagonistic effects in the human body, so it is inadequate to discuss only single-element studies (e.g. Cd-Zn-Fe). Soil pH also influences nutrient and toxic element availability, with I and Se less available at acidic pH (Oliver 1997), and Fe, Al, Mn, Pb, Cd, Ni more available. Examples of antagonism include As against P and Sr against Ca, Zn against Ca, Fe, Cu, Ni (Oliver 1997).

Soils can also provide elements such as Pb, Cd, As, as well as radioactive elements (U, Cs, Ra, Rn), at levels that are detrimental to human health. Airborne dust can carry additional materials such as pathogens, harmful gases, organic chemicals, heavy metals, and radioactive materials that can cause other health

Table 11.3 Toxic effects on human health due to PHEs deficiency and excess

Element	Deficiency effects	Excess effects
Cobalt	Anaemia; weight loss; retarded growth rate	Possible inhibition of vitamin B12; goiter aggravation; cardiomyopathy; respiratory system irritation
Chromium	Alteration of glucose metabolism, with possible effects on the growth and metabolism of lipids and proteins	Kidney damage; respiratory system damage; chronic ulcers, perforation of the nasal septum
Iron	Anaemia	Vomiting; liver cirrhosis; defects in blood clotting; diabetes; arthritis; sexual malfunction; lung cancer
Magnesium	Kidney disorders; alcoholism; myocardial ischemia; conjunctivitis;	Decrease in blood pressure; respiratory paralysis; heavy fume fever
Manganese	Bone diseases, goiter aggravation	Epithelial cell necrosis and proliferation of mononuclear cells; neuropsychiatric disorders; liver cirrhosis; decrease in fertility
Molybdenum	Tachycardia, shortness of breath, headache, blindness, nausea, vomiting	Gout disease, toxicosis
Nickel		Cancer of the respiratory tract; dermatitis; headache; nausea, vomiting, cyanosis; gastrointestinal disturbances; weakness; edema; death
Copper	Anaemia, bone deformities	Abnormality of the nervous system, liver and kidneys; death
Selenium	Heart failure and various degrees of cardiomegaly osteoarthropathy	Weakness on hair and nails, skin lesions on sole, hands and neck; foetal toxicity
Zinc	Delay in growth and sexual maturation; dermatitis; susceptibility to infection and neuropsychological abnormalities in infants	Reductions in immune function and HDL cholesterol, fever

Adapted from Fortescue (1980) and Coccioni (2011)

problems. Airborne dust containing such toxins may carry these materials into the lungs, where they can enter the bloodstream.

Heavy metals originate naturally from the weathering of rocks, but have also been introduced to soils through human activities. They may occur as a by-product of mining ores and are therefore present in mine spoils and in the immediate surroundings of metal-processing plants. Electronic appliances such as computers and mobile phones are also becoming a increasing source of heavy metals such as Pb, Sb, Hg, Cd, Ni. Urban soils are particularly susceptible to significant accumulations of potentially harmful elements. Fertilizers and agrochemicals are another source of PHEs additions to soils and chicken feed (As) and swine feed (Cu, Zn). The same PHEs, however, are likely found in sewage sludge, thus contributing significantly to environmental pollution.

There are several elements, both essential and non-essential, that cause concern from a human health perspective; these include, among others, Cu, Fe, Zn, Cr, Cd, Hg, Pb. Human exposure to these metals can occur through different routes, such as inhalation of dust. Metal transport occurs mainly through the atmosphere (see this volume, Chap. 1), and influxes of African dust have been considered responsible for elevated levels of elements such as Hg, Se, Pb in European soils.

Other common pathways of exposure are consumption of contaminated crops and incidental or purposeful consumption of contaminated soil (geophagy) (Abrahams 2002).

Geophagy is the deliberate ingestion of soil, and offers several potential benefits to those who practice it, but there is the potential for serious health problems as well. The most frequently cited benefit is using the soil as a source of mineral nutrients. Medical uses of ingested soil material include the treatment of some types of poisoning and of gastrointestinal disorders (stomach aches, acid indigestion, nausea, diarrhoea (Abrahams 2002). Nevertheless, despite the potential advantages of geophagy, there are a number of negative effects due to soil ingestion: heavy metal toxicity, iodine deficiency disorders, soil parasitic infection.

Heavy metals are known to be bound to enzymes; metal bonding with enzymes may affect human health since enzymes cannot function normally. Damage to the central nervous system is common, leading to problems such as coordination, eyesight, the sense of touch, lowering intelligence quotient (IQ), bone deterioration, hypertension, increased cancer rates. Lead is the most problematic heavy metal due to the extensive variety of its sources.

Important radioactive elements sources are both natural (Rn from decay of uranium found in rocks) and anthropogenic (nuclear weapons manufactory and testing, accidental release from nuclear facilities such as Chernobyl (1986) and Fukushima (2011), burning of coal, smelting of non-ferrous metals, mining activities and medical waste). The most common health risks include various forms of cancer and genetic mutations. The level of risk and health problems are highly dependent on both the dose received and the amount of exposure time (see this volume, Chap. 10).

1.4 PHEs and Cancer

Some elements, such as mercury (Hg), cadmium (Cd), arsenic (As) and chromium (Cr), are toxic or carcinogenic even at low concentrations. Poisoning by exposure to PHEs is well known to affect central nervous system functions, damage blood composition, lungs, kidneys, liver and other vital organs. Long-term exposure can cause slower progressing physical, muscular, and neurological degenerative processes. Allergies may also occur and repeated long-term contact with some metals, or their compounds, may become carcinogenic.

Carcinogenic elements present common exposure pathways; the main way is inhalation, and the main target organs are those of the respiratory system (bronchus and lung), although other organs such as skin, stomach, prostate, kidney, urinary bladder, are reported as possible target organs (Apostoli and Catalani 2008).

Among the mechanisms which make plausible the carcinogenic action of metals, is reported their ability to generate reactive oxygen species (ROS) and other intermedia able to induce direct damage to DNA by interacting with several enzymes and with cellular proliferation regulators. ROS act on cells with a direct effect on proteins, altering the activity and the conformation, or acting on redox-sensible proteins. The formation of metal-protein complexes, moreover, may interfere on cellular homeostasis, and determine conditions for an increase of cellular clones with mutagenic phenotypes.

Metals generally interact little and weakly with DNA; when it happens, interaction occurs mainly through two binding strategies: phosphate group of skeleton, and a variety of base electron-donors. Binding of metal with bases enhances spatial modifications which influence the interaction of specific enzymes with DNA (Franco et al. 2009).

Carcinogenic metals, therefore, are only a little mutagenic. As, Cd, and Ni inhibit DNA repair mechanisms, contributing to augment tumour inizialization induced by other agents, playing an important role in cellular proliferation, and favouring neoplasm development. Some metals, moreover, may induce codifying genes for cell-protective proteins such as metallothionein, and stress proteins (Apostoli and Catalani 2008).

The interaction of development factors on receptors through mutations or augmented expressions is among the mechanisms responsible for invasivity and metastatic characteristics of tumours. Other mechanisms responsible may be the communication block cell-to-cell, lipid peroxidation stimulation, flaming processes induction, endogenous DNA damage with possible chronic mutagenesis augmentation, increased intracellular radicals, interaction with detoxification mechanisms, redox reaction catalysis, DNA alchylation, cellular homeostasis alteration (Leonard and Bernard 1993).

It is generally accepted that the metal species (or the metal complex) influences in a determinant way the biological and toxicological activity of that metal. The effect induced by that element depends on its ability to enter the cell and to interact with target sites such as DNA. Crucial, therefore, are the chemical species, the oxidative state, charge, solubility, binding properties, stereochemistry, possibility to interact with other xenobiotics (Apostoli et al. 2006).

Since many elements present a more prominent oxidation state for carcinogenic activity (e.g. 2+ for Co and Ni; 3+ for Sb and As), it has been hypothesized that such metals utilize specific mechanisms that mediate their bioavailability as protein-carrier, transmembrane channels and formation of specific ligands. For example, bivalent metals may substitute for (or simulate) essential elements in many biological systems, enzymes and co-enzymes.

Oxyanions with V, Cr, As are chemical forms with high oxidation state, stable and able to cross cell membrane utilizing normal transport systems (phosphate or sulphate) and, once inside the cell, may act on specific enzymes. Besides common characteristics, however, every element is characterized by its own mechanisms, and by species and compounds more involved in carcinogenesis with respect to others.

Table 11.4 International classification of selected carcinogenic elements

Elements	IARC[a]	ACGIH[b]	DFG[c]	EU[d]
Antimony	2B	A2	2	–
Arsenic	1	A1	1	R45
Beryllium	1	A1	1	R49
Cadmium	1	A2	1	R49, R45
Cobalt	2B	A3	2	R49
Chromium (VI)	1	A1, A2	2, 3B	R49
Nickel	2B	A1	1	R40, R49
Lead	2A	A3	2	R40
Vanadium	2B	A3	2	R68

Adapted from Apostoli and Catalani (2008)

[a] International Agency for Research on Cancer

[b] American Conference of Governmental Industrial Hygienists

[c] Deutsche Forschungsgemeinschaft

[d] European Union

The identification and classification of metal carcinogenicity by several associations and scientific societies results in different positions, particularly concerning the chemical species and compounds, as reported by Apostoli and Catalani (2008) (Table 11.4).

The International Agency for Research on Cancer (IARC 2006) attributed *certain carcinogenicity* with sufficient evidence for carcinogenicity for humans to compounds of Ni, As, Cr (VI), Cd, Be. *Suspected carcinogenicity* was attributed to metal Ni and alloys; instead, no carcinogenic effects were attributed to Cr (III), although a Cr (III) chronic phytotoxic effect was reported by Maleci et al. (2001). Inorganic Pb compounds are classified by IARC as *probable carcinogenic* for humans (class 2A), and soluble Co (II) salts, V and Sb compounds are suspected to have carcinogenic effects (class 2B).

Producing activities where exposure to PHEs is likely to occur are smelters (iron and steel founding with potential exposure to Ni, Cr, and several organic compounds such as PAH, phenols, amines), glass factories (exposure to As, Cd, Cr, Cu, Pb, Sb, Se, Zn,) (class 2A), steel welding and Ni-Cr alloys (class 2B); moreover, possible co-exposure to silica, asbestos, etc. are likely.

The Industrial Hygienists Association of the USA (ACGIH 2007) attribute to group A1 (substances known as carcinogenic to humans) inorganic insoluble compounds of Ni, As, Cr(VI), Be; furthermore, Pb-chromate, Ca-chromate, Sr-chromate, Cd compounds and Sb trioxide are included in group A2 (suspected carcinogenicity); Pb, Co, their inorganic compounds, and V oxide are included in group A3 (known carcinogenic for animals but with unknown relevance for humans). Inorganic soluble compounds of Ni and Cr(III) are included in group A4 (not carcinogenic for humans), elemental Ni in group A5 (unsuspected carcinogenic).

The German Association (DFG 2006) has included Ni and As, as well as their inorganic compounds, Pb-chromate and metals such as Cd and Be in group 1 (substances which cause cancer to humans, demonstrated by epidemiological studies and by evidence that the substance induces cancer through action mechanisms relevant to humans). Group 2 includes Cr(VI) inhalable compounds, Pb, V, Co, as carcinogenic as results from long-time studies on animals (Apostoli and Catalani 2008). The same organization (DFG 2006) suggests exposure equivalents for carcinogenic substances for insoluble Ni compounds, and for Co, As and V compounds.

The European Union includes metals and related species in the list of carcinogenic and/or mutagenic substances according to the EC Directive 67/548/2006, and attributes cancer risk classes R49 (substances which can induce cancer by inhalation), R45 (substances which can induce cancer) and R40 (possibility to induce carcinogenic effects – insufficient proofs). In particular, Ni, Cr (VI), Cd, Be, Co and their compounds are assigned the R49, while As oxides, arsenates, Zn-chromate, Sr-chromate, Cd-chloride, Cd-fluoride are assigned the R45.

It is noteworthy to point out, however, that consistently with current legislation, carcinogenic substances are exclusively those chemical species and compounds that are assigned the cancer risk classes R45 and R49 proposed by EU (EC Directive 67/548/2006), and specifically substances, preparations, processes and works that expose workers to dust, fumes produced during metal refining at high temperature, or when the concentration of one (or more) substance (s) overcome the admitted limits for the classification of a chemical in carcinogenic categories 1 or 2 (IARC 2006).

The above recorded differences in the regulations are reflected also in environmental and biological indicators to be selected, and on the meaning of reference values, or biological limits, assigned to chemicals, as indicated in Table 11.5. For example, the environmental limit for a specific chemical species is frequently reported in comparison to the concentration value of the element such as it is, as well as a biological indicator of soluble compounds is utilized for monitoring exposure to the element such as it is.

The American Conference of Industrial Hygienists (ACGIH 2007) has set up biological limits for six elements (As, Co, Cr, Cd, Pb, V), and moreover established environmental threshold values for all the elements and related compounds. The German organization (DFG 2006) too has set up threshold values for the carcinogenic metals, with the exception of Be and Sb.

The Italian Society for Reference Values (SIVR 2005) has set up reference values for all the elements considered, specifying the different matrices by indication of the element as such, with the exception of As.

The Scientific Committee for Occupational Exposure Limits of the European Commission (SCOEL-EC 2008) has suggested occupational exposure levels (OELs) for the time weighted average (TWA), for short-term exposure limits (STELs), and biological limit values (BLVs). In particular, for those carcinogenic elements at exposure levels below which no carcinogenic effect is recorded, the OEL is not defined, but it is suggested that the lower is exposure, the less will be cancer development. Time weighted average(s) (TWAs) are expressed for Pb, Cr and their inorganic compounds.

Table 11.5 Reference concentration values for selected elements

Elements	ACGIH μg/l urine	DFG μg/l urine	EU – SIVR[a] μg/l urine
Antimony	–	–	0.01–0.15
Arsenic	35	50–130	0.1–15
Beryllium	–	–	0.001–0.006
Cadmium	5.0	15	0.1–1.5
Cobalt	15	6–300	–
Chromium (VI)	10–25	12–40	0.05-0.30
Nickel	–	15–70	0.1–2.0
Lead	300	400	<0.5–3.5
Vanadium	50	35–140	0.1–1.0

The range is related to different metal compounds (Adapted from Apostoli and Catalani (2008))
[a]European Union and Società Italiana Valori di Riferimento

The major problem, both theoretical and applicative, is posed by the speciation of the element of concern, which may influence environmental and biological measurements of exposure, risk assessment and sanitary/epidemiological surveillance (Apostoli et al. 2006). Yet, fractionation of chemicals by selective extractions may enhance identification of the various compartments in which the element of concern is present, but chemical transformations and/or potential contamination may occur during analysis. Moreover, possible interferences among metals and other substances should be considered.

1.5 Concluding Remarks of Sect. 1

Differences in metal absorption, distribution, imbalance between toxicant effects and metal excretion can be explained, besides time exposure and prevention measures, from the physico-chemical characteristics of metals, as species, solubility, chemical reactivity. These could be utilized to interpret the different response of human organs towards carcinogenic metals, in terms of morbidity and/or mortality, as well as the high variability of epidemiological investigations on occupationally exposed workers, including clear evidence in some cases (e.g. roasting of Ni-bearing rocks), and little or no evidence in other cases, where the element of concern is determined at concentration levels even higher than background population values (e.g. Ni in serpentine soils and plants).

The need of information concerning chemical species and compounds actually classified as carcinogenic (or suspected) is recorded also in official documentation related to:

- registration of the total amounts of carcinogenic or mutagenic substances produced and utilized, or present as impurities or by-products in other substances;
- workers exposure (intensity and duration) measures;
- sanitary surveillance of workers showing somewhat health risk.

More accurate epidemiological investigations, combined with environmental and biological data which actually may qualify population exposure, and in collaboration with other disciplines as metallurgy, industrial hygiene, analytical chemistry etc. could enhance comprehension of the effective risk posed by PHEs to human health.

2 Widely Recognized and Emerging Harmful Elements and Human Health

Potentially harmful elements (PHEs) in the environment may result from many different activities and sources and may enter into the environment by a wide range of processes and pathways. Generic sources of harmful elements include mining and industrial production such as foundries, smelters, oil refineries, petrochemical plants and chemical industry, untreated sewage sludge, dispersed sources such as metal piping, traffic and combustion by-production from coal burning power plants (Hassanien and El Shahawy 2011). Atmospheric emissions are probably the most harmful to the environment, and consequently, to human health due to either the great quantity involved, or their widespread dispersion which may originate many different exposure pathways.

Recent studies have focused on identifying the amount and distribution of some of the most common PHEs in the environment, and investigating the factors that cause contaminant exposure of human population. Some of these contaminants (e.g. Cd, Pb, Hg, As) are widely recognized as poisonous to human health (Filippelli et al. 2012); cadmium is known for kidney damage and bone pains which may lead to cancer; mercury for neurological disturbances; lead is known for its severe cognitive and behavioural disturbances; atmospheric dust may cause a variety of pulmonary diseases (Iskandar et al. 2012). Arsenic is a lethal poison, as represented also by the register Frank Capra in the famous fiction “Arsenic and old lace” (1944), and may provoke skin lesions and tumours, although at clinically achievable concentrations is used to induce apoptosis in malignant cells (Franco et al. 2009, and references therein). Conversely, elements known to be essential for health are the first row transition elements: Fe, Mn, Ni, Zn, Cu, V, Co and Cr, together with Mo, Sn, Se, I and F (Oliver 1997). Each has its specific role in the metabolism, and it cannot be wholly or partly replaced by any other element. Most of them act primarily as catalysts in enzyme systems (Oliver 1997 and references therein). Their roles range from weak ionic effects to highly specific associations with metalloenzymes; for example Cr acts as cofactor for insulin, and I makes the hormone thyroxine active. Chromium and selenium are essential to humans; their deficiency may induce illness, while excessive intake may induce cancer; Cr has been recognized as highly carcinogenic since the late nineteenth century (Adriano 2001), and Se proved lethal at intake up to 20 mg kg^{-1}.

There is no general agreement on the potential harm of certain elements, while some others are historically recognized as PHEs. In the next Sect. (2.1) most of the widely recognized PHEs (Cd, Pb, Hg, As, Cr, Se) will be discussed. Other contaminants such as Al, B, Be, Bi, Co, Cu, F, I, Mn, Mo, Ni, Sb, Sn, Tl, V, W etc. are likely to affect negatively human health, but they are poorly studied at typical environmental concentrations, and little is known about their health effect at chronic exposure levels (Filippelli et al. 2012). Some of these "new" PHEs are referred to in Sect. 2.2 as Emerging Harmful Elements.

2.1 Widely Recognized Harmful Elements

2.1.1 Cadmium

Cadmium is typically a metal of twentieth century, even though large amounts of Cd have been emitted by non ferrous smelters during the nineteenth century (Bernard 2008). The trend in its end uses in the last two decades showed a steep increase (from 55 to 73 % of the total western world consumption) for batteries and a decrease in other applications. In the immediate future, it has been previewed by the World Health Organization (WHO 2003) that Ni-Cd battery market will grow continuously (e.g. power tools and telecommunication devices).

Cadmium does not have any physiological function within the human body (Godt et al. 2006), and is considered one of the most dangerous PTEs to human health, causing acute and chronic intoxications, even at very low exposure levels, on health and environment. It is not degradable in nature and once released to the environment, remains in circulation, being relatively water soluble, and tends to bioaccumulate (WHO 2003). It can persist in soils for decades; from soil, it is translocated to plants and the food chain, and ultimately accumulates in the body of people eating contaminated food. Cadmium is also present in tobacco smoke, further contributing to human exposure. By far, the most salient toxicological property of Cd is its exceptionally long half-life (estimate is 20 year) in the human body, particularly in kidneys and other vital organs such as liver and lungs (Bernard 2008).

The International Agency for Research on Cancer (IARC 2006) classifies Cd in Class 1 "*the agent is carcinogenic to humans*", and it has been identified as a priority hazardous substance under the EC Water Framework Directive (2006). Cadmium has been ranked at the sixth in the Top 20 list of toxic substances for significant human health hazard by US Poison and Disease Registry (Akynloye et al. 2006), and has been a focus of study on environmental pollution in the UN Environmental Programs (UNEP) and the International Commission on Occupational Health Organization (Han et al. 2009).

The acute toxicity, as first described by Friedrich Stromeyer (1817, cited in Godt et al. 2006), can lead to kidney, bone, and pulmonary damages, while chronic effects have been recognized much later (1930–1940). Chronic exposure to Cd can have severe effects such as lung cancer, prostatic proliferative lesions, bone fractures, kidney dysfunction and hypertension (Zhao et al. 2012). Other effects are disturbance of Ca metabolism, *hypercalciuria* and formation of stones in the kidney.

Cadmium is a source of concern for industrial workers since the first investigations (1930–1940) on pulmonary, renal and bone lesions, and for population living in polluted areas (Bernard 2008). A survey on Polish workers of a lead-acid batteries plant, and exposed to Cd, showed significantly higher Cd levels in blood in comparison to general population (Wasowicz et al. 2001). Cadmium is absorbed by the body by inhalation (through the lungs) and by ingestion (through the digestive tract). This route of absorption plays an important role in case of bad hygienic habits such as not cleaned hands, ingestion of contaminated food, and smoking during occupational exposure.

An epidemic occurrence of bone pains, with patients showing a wide range of symptoms such as low grade of bone mineralization, high rate of fractures, increased rate of osteoporosis, developed in Japan since 1940s. The disease with the above symptoms (called *itai-itai*), was associated with Cd poisoning, and was related to consumption of rice grown on fields irrigated with highly Cd-polluted water (Godt et al. 2006). Further evidence was found by Honda et al. (2003). Similar findings were recorded in a study on 1,000 people from southern Sweden, with significant negative correlation between urinary Cd and low bone mineral density, particularly on persons aged more than 60s. Individuals included in this study were either battery plant workers, or inhabitants close to the battery plant. The exact mechanism of interference between Cd and bone mineralization remains to be discovered; it may be an indirect influence of renal dysfunction (Berglund et al. 2000).

After that early reports, a number of epidemiological studies were carried out worldwide in order to characterize Cd toxicity and assess exposure levels which could threaten human health. As a result, from the 1990s it has been suggested that Cd can generate adverse effects even from much lower exposure levels than was believed before. Kidney results the critical organ for which dose-response relationships are best documented (Bernard 2008).

The major pathway of exposure to Cd is both by ingestion and inhalation. Food ingestion is the primary exposure source for general population; the amount of Cd ingested daily with food in most countries ranges between 10 and 40 μg per day (WHO 2003; Bernard 2008). Cereals account for about 50 % of Cd intake. The WHO has established a provisional tolerable intake of 7 μg/kg body weight, i.e. 70 μg Cd for averaging 70 kg man, and 60 μg Cd for 60 kg woman, while the recommended intake for children is 2–25 pg day^{-1} (WHO 1996). However, even small concentrations in foods can have a significant effect in the long term because Cd accumulates in the body (Oliver 1997). The maximum permissible Cd value in blood for workers in Germany is 15, compared with the average blood Cd concentration in non smokers that is 0.5 μm/l (Godt et al. (2006).

Tobacco smoking is an important additional source of exposure for smokers. Since one cigarette contains approximately 1–2 μg Cd, smoking one pack per day results in a daily uptake of Cd that approximates that derived from food. As reported by Bernard (2008), absorption by the oral route varies around 5 % but can be raised to 15 % in subjects with low iron store. When exposure is by inhalation, between 10 and 50 % of Cd is absorbed, depending on the particle size. With tobacco, an average of 10 % of Cd is absorbed. The absorption via lung is higher than gastrointestinal absorption (via the stomach): up to 50 % of the inhaled Cd may be absorbed. A major part of Cd in the human diet comes from agricultural products, the most important source being atmospheric deposition, followed by application of sewage sludge and waste products. Absorption through the skin, instead, is negligible.

The highest concentrations of Cd (10–100 mg kg^{-1}) are found in internal organs of mammals, mainly in the kidneys and liver, as well as in some species of fish, mussels and oysters. Accumulation in kidneys and liver is due to the ability of these tissues to synthesize metallothionein, a Cd-inducible protein that protects the cell by tightly binding the toxic Cd^{2+}ion (Bernard 2008). The protective effect of Zinc, an essential metal in human metabolism, towards Cd toxicity, determines the selective accumulation of Cd in the proximal tubular cells and thus in the renal cortex, where it increases during the person's life span. A possible perturbance of phosphorus and calcium metabolism may occur, with formation of kidney Ca-stones (Godt et al. 2006).

The major health hazard of Cd occurs when its concentration exceeds 200 pg Cd kg^{-1} BW, and the effects on health are greater in ageing people. *Proteinuria* (loss of low molecular weight proteins from the kidneys), *glucosuria* (loss of sugar) and *aminoaciduria* (loss of amino acids), and the excretion of Cd are early signs of Cd intoxication of the kidney (Oliver 1997). Diseases of the bone, (osteomalacia and osteoporosis) have been observed only in Japan where the effects of Cd toxicity were exacerbated by dietary deficiencies of Ca, vitamin D and protein. It seems that Cd affects Ca and vitamin D metabolism resulting in the decalcification of bones (WHO 1996).

Cadmium chronic poisoning causes two different kinds of health effects: damage of target organs, and non-specific changes for population as weakness, ease to suffering from illness, rise of morbidity and mortality (Han et al. 2009). Target organs are kidney, bones, prostate (urogenital system). Kidney damage is the main problem for patients chronically exposed to Cd; it is the first organ to display signs of toxicity, which probably represents the critical health effect both in general population and in occupational exposed workers. Cd nephropathy has been described in industrial workers exposed mainly by inhalation and in general population exposed via contaminated foods, with a total Cd concentration at 150–200 mg kg^{-1} in renal cortex (Bernard 2008).

Early indices of kidney damage are Cd concentrations in blood and urine; the earliest manifestation of Cd-induced renal damage consists in an increased urinary excretion. Indeed, Cd is mainly eliminated via the urine, but daily excretion is very low (0.005–0.01 % of the total body burden, which corresponds to a biological half-life of more than 20 year). As a severe secondary effect, the development of Cd-induced proteinuria is predictive of an increased mortality by heart failure, cerebral infarction, nephritis and nephrosis (Bernard 2008).

The disturbances of Ca and phosphate metabolism accompanying Cd nephropathy can cause bone demineralization through direct bone damage or indirectly as a result of renal dysfunction (Uchida et al. 2007; Agneta et al. 2006), formation of kidney stones and bone fractures. Usually, bone damage has been considered a delayed sign of severe chronic Cd poisoning. Based on reports concerning the epidemic occurrence of Itai-Itai disease in China and Japan (1940–1950s, see above), a population-based study showed an association between skeletal damage and low-level environmental Cd exposure (Han et al. 2009). Conversely, higher Cd exposure by food (rice) ingestion determined consequent health effects such as renal injury, higher mortality, shorter survival time, and more unfavourable prognosis. Mortality of people by Itai-Itai caused by higher environmental Cd exposure has been reported to achieve 76 %, against 50 % of the control group (Han 2009).

Early indices for bone injury are bone mineral density, urine calcium, urine phosphorus; instead, association between urinary Cd and bone mass density has not yet proven. Skeletal damage (osteoporosis) too, accompanied with pain in the back, difficulties in walking, multiple bone fractures and renal dysfunction may be a critical effect of Cd exposure, but it is still unclear.

Other effects of Cd exposure are reported in literature, that concern various biological systems. Godt et al. (2006) report that the main pathway of Cd absorption is by inhalation, and Cd absorption through the human gastrointestinal tract is only 5 % of the ingested Cd amount (e.g. by food). Several factors can increase this amount, such as low intake of vitamin D, and Cd-counteracting nutrients such as calcium and trace elements as Zn and Cu. The respiratory system is affected severely by inhalation of Cd-contaminated air; Bernard (2008) points to the impairment of the pulmonary function suggestive of mild obstructive syndrome in workers exposed to relatively high concentrations of Cd by inhalation. Respiratory insufficiency and increased mortality rate from obstructive lung disease has been seen in workers with high exposure in the past (WHO 1992). One of the pathways of Cd absorption by a relevant portion of general population is inhalation of cigarette smoke. The human lung resorbes 40–60 % of Cd in tobacco smoke, in the form of Cd-cysteine complexes (Godt et al. 2006). Non-smokers show an average Cd blood concentration of 0.5 μg/l, while smokers generally have Cd blood levels 4–5 times those of non-smokers.

Adverse effects on the reproductive system biology due to Cd exposure are reported by several authors. Low dosage of Cd proved to stimulate ovarian progesterone biosynthesis, while high dosage inhibit it (Godt et al. 2006). Pregnant women exposed to environmental Cd might have an adverse effect in prenatal period (e.g. foetal growth retardation, premature birth, low birth weight, birth deformities, and an increase of spontaneous abortion) and a possible cause of male infertility (Falcon et al. 2002; Han et al. 2009). However, Cd does not cross easily the placental or the hemato-encephalic barriers, thus explaining its very low toxicity to the foetus and the central nervous system as compared with other heavy metals (e.g. Pb, Hg).

Further adverse effects are reported to be caused by Cd intoxication: intake of Cd-contaminated food causes acute gastrointestinal effects, such as vomiting and diarrhoea (Nordberg 2004). Mortality for heart failure, cerebral infarction and pancreatic dysfunctions too are reported as effects of Cd exposure among inhabitants living in a Cd-polluted area in Japan (Nishijo et al. 2006; Lei et al. 2007), while Cd levels in blood, but not in urine, were associated in USA with a modest elevation in blood pressure levels (Bernard 2008).

Sarkar et al. (2013) report that Cd is toxic, nonessential and classified as a human carcinogen. Generally, it forces the expression of the stress proteins and depending on factors such as amount of exposure, time of exposure, the cell line and presence of other chemical species, the outcome could be apoptosis, growth inhibition, proliferation or carcinogenicity in animal cells. The mechanisms leading to cadmium carcinogenesis are primarily those involving oxidative attack by ROS, inhibition of DNA repair mechanisms and augmenting or diminishing the tendency to apoptosis (Sarkar et al. 2013).

There is proved evidence that Cd can cause several tumours. A prolonged exposure has proven to be carcinogenic to liver, kidney, lung, prostate, hematopoietic and other systems. Occupational exposure is linked to lung cancer and prostate cancer and severe testicular necrosis followed by high incidence of testicular tumours (Godt et al. 2006), while links between Cd and cancer in liver, kidney and stomach are considered equivocal (Waalkes 2000). Cadmium plays a recognized role in the aetiology of prostate cancer in battery plant workers. Vinceti et al. (2007) observed a dose-response relationship between Cd exposure and prostate cancer risk. The association between Cd exposure and risk was also confirmed by a multivariate analysis including body mass index, smoking, family history of prostate cancer, protein and lipid consumption. The biological plausibility of a Cd-prostate cancer relation in humans is also supported by the results of several experimental studies, which suggested the possible existence of a threshold above which Cd exposure becomes of concern (Vinceti et al. 2007).

Early investigations (Kolonel 1976) suggested an association of Cd and renal cancer in humans, recently confirmed (Il'yasova 2005). Consequently, the IARC decided to classify Cd as a human carcinogen group I, *mainly due to Cd assumption by respiratory system pathway*. Depending on factors such as amount of exposure, time of exposure, the cell line and presence of other chemical species, the outcome of Cd exposure could be growth inhibition, proliferation or carcinogenicity in animal cells, and apoptosis (Franco et al. 2009; Sarkar et al. 2013).

The mechanisms leading to cadmium carcinogenesis are primarily those involving oxidative stress, inhibition of DNA repair mechanisms and augmenting or diminishing the tendency to apoptosis. The majority of Cd is transported in the circulatory system bound to proteins such as albumin and metallothionein. The first organ reached after uptake into the gastro-intestinal-blood is the liver. Here Cd induces the production of metallothionein. After consecutive hepatocyte necrosis and apoptosis, Cd-metallothionein complexes are washed into sinusoidal blood; part of absorbed Cd enters the entero-hepatical cycle via secretion into the biliary tract (Godt et al. 2006). However, the mechanism of Cd carcinogenesis remains largely unknown (Bernard 2008).

Diagnosis of chronic Cd poisoning basically relies on the screening of proximal tubular renal dysfunction and the assessment of the cumulative exposure to Cd using environmental or biological indicators. Biomarkers offer the possibility not only of evaluating the human exposure to environmental pollutants, but also to study the potentially harmful effects for the health associated with such exposure. For example, Begona Zubero et al. (2010) found increased levels of urine Cd in population living close to an incinerator plant, with levels similar to those carried out in Europe and USA. Studies on industrial workers in the 1980s have derived a threshold of urinary Cd of 10 μg/g creatinine for the development of tubular proteinuria. This threshold serves now the basis for occupational exposure limit of 5 μg/g creatinine currently in application in most industrialized countries (Bernard 2008). However, studies in Belgium and Sweden have concluded that tubular dysfunction is likely to occur in the general population from thresholds of urinary Cd in the range of 1–2 μg/g creatinine.

There are no efficient treatments for chronic Cd poisoning. Even after cessation of exposure, renal dysfunction and pulmonary impairment may progress. The only possible intervention is removal from exposure, and primary prevention is needed in order to maintain low levels of Cd in the environment or in the food chain.

2.1.2 Lead

Lead has been probably one of the first pollutants to receive widespread attention as a causative agent for health-related effects (Apostoli et al. 2002; Bierkens et al. 2011). It has been used for centuries since the Roman age, and has been known as toxic since the second century BC in ancient Greece (Oliver 1997).

Over decades, lead has been used in many different applications: building materials, pigments for glazing ceramics, batteries and pipes for transporting water (Hassanien and El Shahawy 2011); in the last century, in particular, it was largely used as additive in fuel for engine, posing important health concerns. Yet, lead poisoning is currently one of the most prevalent public health problems in many parts of the world (Nriagu 1988), especially considering the intake of concentrations regarded as nontoxic over long periods (Davies and Wixson 1987).

Numerous cases of lead poisoning have been reported since the 1980s. On February, 21, 1988, local newspapers in U.S.A. reported that it was a miracle that Mr and Mrs Wallace survived to lead intoxication induced by kitchen artistic pottery. This case poses the problem of the release of toxic elements, often necessary for manufacturing of fine articles (pottery, food containers, etc.). Refined Pb-glasses (“crystal glasses”) are effective metal-retaining objects, and information on metal release is not current. Conversely, ceramic pots with high Pb content are well known for releasing fluorine if not oven-dried at the correct temperature.

As a consequence of large utilization, lead is a widespread contaminant of the soil, generally arising from pollution from mineral exploitation and industrial wastes, and from atmospheric deposition (Oliver 1997). The high occupational exposure-related hazard occurs in the processes of lead ore smelting, welding and cutting of metal constructions, lead-containing paints, casting of non-ferrous metals, production of batteries etc. The main pathways for Pb exposure, that may affect both general population and exposed workers, are via inhalation of atmospheric particles, and ingestion of contaminated food. Actual levels of lead found in air, food, water and soil/dust vary widely throughout the world and depend upon the degree of industrial development, urbanization and lifestyle factors (WHO 1985). In general, lead-contaminated house dust and soil is the major source for blood lead levels in children (Lanphear et al. 2002). Lead levels in dust depend on factors such as the age and condition of housing, the use of lead-based paints, lead in petrol and urban density (Bierkens et al. 2011).

Lead is currently classified as number 2 in ATSDR's (Agency for Toxic Substances and Disease Registry) Top 20 list (ATSDR 2007).

The WHO (1996) reported that dietary intakes of Pb range on average between 20 and 282 pg day^{-1} for adults, and between 9 and 278 pg day^{-1} for children, who can take up more if there is too little Fe in their diet (WHO 1996; Oliver 1997). A large intake is regarded as 2,500 pg day^{-1}. A concentration of 250–550 pg Pb L^{-1} in the blood of children indicates poisoning (WHO 1996).

Because of the established link between exposure to lead and cognitive development, children are considered an important and vulnerable target population (Bierkens et al. 2011). Indeed, the nervous system of small children is especially sensitive to Pb, because of the incomplete development of the barrier between blood and brain, and the children can become retarded (Pharoah 1985; Oliver 1997).

Pocock et al. (1994) related Pb blood concentrations of 100–200 pgL^{-1} with intelligence (IQ) in children over 5 years of age. The results of the study showed an inverse association between IQ and Pb concentration. Lead also causes metabolic disorders and neurophysical deficits in children, and affects the haematopoietic and renal systems (Hutton 1987). Lead interferes with the incorporation of iron into the protoporphyrin leading to anaemia, and causes renal damage (WHO 1996). Lead has been also the first metal to be linked with failures in reproduction (Peereboom-Stegeman 1987): it can cross the placenta easily. Moreover, Pb is transferred from the mother to the foetus, and young children show a higher exposure pattern per unit body weight due to their higher contact with soil and dust, and higher intake rates. It also affects the brain, causing hyperactivity and deficiency in the fine motor functions (Oliver 1997).

Occupational Pb exposure may result in chronic poisoning. It mostly affects the hematopoietic and nervous systems, and may cause plumbism, anaemia, nephropathy, gastrointestinal colic, and above all damage of the central nervous system (Zukowska and Biziuk 2008; Zhao et al. 2012; Hassanien and El Shahawy 2011).

The neurotoxicity of Pb is more critical for the developing foetus and the growing children. Pruvot et al. (2006) report that infantile lead poisoning in the vicinity of the main European smelter showed 10–15 % of children from 2 to 3 years having a Pb-blood level higher than 100 μm PbL^{-1} of blood, owing to strong lead contamination by indoor and outdoor dust of the schools and houses of these children. The ingestion of vegetables produced in kitchen gardens in the contaminated area, and the ingestion or inhalation of contaminated soil particles, proved the main key routes of exposure to lead, in particular via hand-to-mouth transfer. In addition, many studies (e.g. Dudka et al. 1996; Douay et al. 2005) have described the metal transfer to crops grown on soils contaminated by atmospheric deposits, and values recorded in the produce often exceed the European reference values (EU Directive March, 8, 2001) thought to cause a medical risk (Hough et al. 2004). The highest metal concentrations were measured in wheat and barley grains (range 0.02–14.42 mgPbkg^{-1}) and to a lesser extent in maize (Pruvot et al. 2006). Previous epidemiological studies carried out in the investigated area (Leroyer et al. 2000) showed that metals present in the various compartments of the environment contributed in a substantial way to the exposure of local population. In particular, lead accumulates mainly in bones (95 %) and teeth in the form of chelates, as reported by Martinez-Garcia et al. (2005), who examined bones of inhabitants in territories where mining activity took place so far, and are in contact with processed metals.

Another human health effect due to lead exposure is reported by Giaccio et al. (2012). A comparison of data on heavy metal pollution with data related to the semen quality in the town of Neaples (Italy), the core of the Vesuvian volcanic district, showed a consistent evidence for an association between Pb (and also Sb) concentration in soils and reduced semen quality. The density distribution of subjects with male infertility problems is higher in areas where the concentration of Pb and Sb (traffic related elements) is greater. People living in unpolluted areas are exposed at lower infertility risk while those who live in polluted metropolitan areas are exposed to higher infertility risk.

Lead (Pb) is probably the most intensively biomonitored chemical with continued concern about its potential health impact (Smolders and Schoeters 2007). Pb is an ubiquitous environmental pollutant with a long history in human biomonitoring (HBM) programs (Bierkens et al. 2011).

Although lead has been monitored extensively in the European population, a consistent biomonitoring dataset is not yet available. Data diverge with regard to regional scale, gender, age groups and sample size. Especially for women of childbearing age and young children more data are required as they are the most susceptible to the impact of Pb on the developing brain.

There are only few reports concerning human antioxidant barriers under occupational exposure to lead. Wasowicz et al. (2001) report that occupational Pb exposure may result in chronic Pb poisoning (up to 500 μg Pb L^{-1}), with cell damage. An increase in lipid peroxidation (measured as thiobarbituric acid reactive substances-TBARS) has been recorded in blood of exposed workers, together with a decrease in essential Zn concentration, compared with the reference group.

It is also important to recall that knowledge acquired from experienced cases of workers affected by diseases related to inappropriate protection to metal exposition needs decades to perform adequate legislation acts aimed at improving the quality of life. Yet, it is unlike that old professional diseases as plumbism, but also asbestosis, silicosis, fluorosis, mercurialism nowadays could be ascribed to new agents. The demonstration of effects of lead, (e.g. reduced learning capacity particularly on children, damage to reproductive apparatus), besides the brain damage (Chem. Eng. News, 1982, August, 9), was largely far from determining a reduction/disappearance of the Pb-tetraethyl from fuel for engine, as it was achieved years after. Indeed, during the last century, the lead content in fuels was a main source of pollution to the environment and, particularly, the lead released to the atmosphere was especially hazardous to children. Today most of the 25 millions of tons of lead produced every year is used in batteries. Exposure assessment to emissions of lead implies to identify and quantify the sources, how it can be dispersed in the environment and which adverse effects it might cause on human health and on the ecosystem.

2.1.3 Mercury

Mercury, as well as lead, is considered non-carcinogenic; instead, it is a known neurotoxic. Industrial utilization of mercury (chemicals, electronics, pharmaceuticals, agro-zootechnicals) is of particular environmental concern. Although it is present in the industrial emissions in the elemental form Hg, it forms easily organic and inorganic compounds. Dimethyl-Hg is highly volatile, and may disseminate contamination in areas not immediately proximal to the pollution source. Methil-Hg, instead, is stable in aquatic environment, and passes easily to the food chain following the sequence phytoplankton – zooplankton – predator fish – humans, having the ability to concentrate up to 10,000 times.

Mercury in the metallic state is less toxic than organic and inorganic compounds, being scarcely reactive with living substances. Hg-vapours, instead, are highly harmful, being promptly absorbed by the respiratory apparatus, generating systemic toxicity. Their maximum tolerable concentration is 0.050 $\mathrm{mgm^{-3}}$air. The ordinary pathways of Hg-compounds exposure are oral and inhalation; organic compounds are more toxic than inorganic ones (e.g. the toxic dose of methyl-Hg for cattle is 13 $\mathrm{mg\ kg^{-1}}$, while that of HgCl is 10 g), and are known to have provoked severe poisoning episodes in Iraq in 1972. The historically most known poisoning episode by methylmercury was that occurred at Minamata, Japan, in 1953. A local chemical plant, that utilized inorganic mercury as a catalyst, discharged waste material in the marine bay in front of this small village. Aquatic microorganisms transformed inorganic Hg into methylmercury, that was absorbed promptly by algae and phytoplankton, and afterwards concentrated in fish that feed plankton. Local inhabitants, who fundamentally eat local contaminated fish, were the first to present poisoning symptoms. The final balance was actually dramatic: 121 toxicant people (46 with lethal consequences), and a series of severe effects on infants of pregnant women at the moment of the accident.

Mercury compounds are protoplasma general poisons that bock the enzymatic activity, provoking protein precipitation and acting as direct corrosives. Endocellular metabolic ways are interrupted by enzyme inactivation operated by mercury. Mercury entered in the circulatory system is promptly oxidized to Hg^{2+}; this may bind the plasma and tissue proteins. A portion of Hg crosses the blood-brain barrier, enters the brain and there undergoes oxidation and reacts with functional groups-SH of proteins, accumulating in the brain tissue. The highest Hg concentration is generally found in kidney; the metal is excreted by the urinary system or by the faecal material.

Prolonged inhalation of Hg vapours may provoke respiratory system irritation and pulmonary inflammation, and acute edema, with insufficient respiratory activity and lethal evolution within 24 h. Acute poisoning by inorganic-Hg is characterized by stomatitis, oral cave and stomach pains, vomit, diarrhoea, anuria, shock conditions and finally death. Chronic intoxication evolves generally in a more sneaky way, with symptoms such as tremors, frequent diarrhoea, reduction of visual capacity. Gastro-enteric disturbances, acute nephrites, bronchitis, pulmonary edema, haemorrhagic episodes, liver necrosis, tubular renal necrosis also are likely to occur.

Toxicological effects of mercury compounds on both plant and animal life have long been recognised, but it was not until the above quoted disaster at Minimata Bay that the subject received worldwide attention (Rahman et al. 2000).

Exposure of mercury to the general population is mainly through the diet and dental amalgam. In foodstuffs, mercury is usually in the inorganic forms and of very low concentration. The exceptions are fish and fish products, which are the main sources of methylmercury in the diet.

The mercury content in hair is a useful indicator of exposure to methylmercury via fish intake in non-occupationally exposed people. When evaluating exposure to low concentrations of inorganic mercury, interference from methylmercury exposure can dominate blood analysis; therefore, an alternative biological matrix such as hair or urine is preferred.

2.1.4 Arsenic

Arsenic is present in nature as sulphides (As_2S_2 and As_2S_3, $FeAs_2S$), and as impurity in carbon, and is recovered as As_2O_3 from the fusion of mixed sulphide (Cu, Pb, Zn) minerals. Agrochemicals containing As have been widely used in the past, leaving diffused environmental contamination.

Arsenic is a toxic metal, especially in the state of AsIII. High contents of As naturally occurring in groundwater have caused severe problems in some regions. The most well known case is in the Bengal delta (Bangladesh and part of India), where over 40 M people were estimated to be at risk from As in drinking water (Steinnes 2009). Besides its toxicity, arsenic is well known also as a carcinogenic element that is widespread in the environment. Arsenic pollution has been reported worldwide, and some areas in South-East Asia and South America are particularly polluted (Liu et al. 2011).

Toxic effects of As compounds (e.g. oxide, arsenite, arsenate) are known since long time. Their toxicity is inversely proportional to the elimination velocity from the body, and increases in the following order: organic compounds $<$ arsenate $<$ arsenite $<$ arsine. Given the variable species-specific sensitivity and the multiple factors that influence its toxicity, it is difficult to assess the As toxic dose in animals; in many species, the lethal dose is in the range 1–25 mg kg^{-1} arsenite, while As_2O_3 is tenfold tolerated (Beretta 1984).

The As penetration pathways in the organism are oral, pulmonary and skin absorption. Ingestion is the main pathway of exposure to As, and arsenite is the best absorbed, while arsenate is slowly absorbed in the gastro-intestinal tract and is mostly eliminated by faeces. A prolonged ingestion proved a significant incidence of skin tumours as well as other cancer forms to lung and liver. Foetal malformations, moreover, have been recorded in pregnant subjects having assumed As (Shu 1973).

Acute poisoning by inorganic-As is responsible for elevated, and rapid, mortality. Death is preceded by colic pains, tremors, vomit, diarrhoea, prostration, collapse within 1–2 days.

Chronic poisoning is less frequent, and symptoms are skin lesions, damage to renal and gastro-intestinal apparatus, diarrhoea, intestinal mucous inflammation.

Human exposure to inorganic arsenic occurs via inhalation of industrial dust and ingestion of contaminated drinking water and food. Estimates of dietary intake range from 7 to 330 mg day^{-1}. Approximately 80–100 % of the inhaled and ingested arsenic is absorbed through the gastrointestinal tract and lungs but up to 50–70 % of the absorbed arsenic is eliminated mainly through urine and to a lesser extent through hair, nails and faeces.

In high doses arsenic is toxic, with the toxicity depending on the oxidation state. Toxicity decreases in the following order: arsine, inorganic As(III), organic As(III), inorganic As(V), organic As(V), arsonium compounds and elemental arsenic (Rahman et al. 2000).

Arsenic toxicity occurs if 3 mg day^{-1} are consumed for 2–3 weeks (Oliver 1997). Phillip et al. (1983) found evidence of a clustering of malignant melanomas where As concentration exceeds 30 g As kg^{-1}soil. They also reported that children, of 3 months to 36 months of age, are vulnerable to the effects of As. Thornton (1996) suggested that As in South-west England might account for the high incidence of malignant melanoma there.

There are elevated concentrations of As in drinking water in several countries in South-East Asia, and these are thought to cause skin disorders, *hyperkeratosis* (increased thickness of the upper layer of skin) of the palms of the hands and the soles of the feet together with *hyperpigmentation* (increased melanin), vascular disorders (e.g. Blackfoot disease, a form of gangrene), rashes (Tseng 1977; Thornton 1996), and cancer of the internal organs (Chen et al. 1992). When As is inhaled it increases the incidence of lung cancer, but when ingested it causes skin, lung, bladder, kidney and liver cancers. Steinnes (2009) reports that children exposed had a significantly lower body mass index, more underweight, more stunted.

Normal hair contains small quantities of As, ranging from 50 to 400 mg g^{-1}, but the level is greatly increased during excessive intake of arsenic. According to Rahman et al. (2000), the profound accumulation of arsenic in hair during exposure is of value in the diagnosis of arsenic poisoning.

Some authors have claimed that arsenic levels in human hair from healthy individuals should be <1 μg/g (Liu et al. 2011). However, others have suggested that the background concentration for human hair arsenic is <3 μg/g. Consistently, the mean arsenic concentration reported by Liu et al. (2011) in hair samples from children living in Pian de' Gangani (Montalto di Castro, Latium, Italy) was 0.159 μg/g and the median was 0.152 μg/g. Man et al. (2002, in LIU et al 2011) reported an arsenic concentration of 0.17 ± 0.14 μg/g in hair samples from children aged 6–15 years. The arsenic concentration in hair from blackfoot disease patients (0.56 ± 0.41 μg/g) in Taiwan, China was significantly higher than that in hair from healthy people (0.56 ± 0.41 μg/g) (Liu et al. 2011). The arsenic content in human hair samples from individuals in arsenic-affected areas of West Bengal, India ranged 0.17–14.39 μg/g, with a mean of 3.43 μg/g and median of 2.29 μg/g. The mean hair arsenic concentration for a patient group drinking contaminated water in Bangladesh was 14.1 μg/g, while in a group drinking uncontaminated water it was below 3.0 μg/g.

Human hair arsenic concentrations in children are typically higher than in other age groups. This may be caused by different rates of arsenic metabolism resulting in differing accumulation of arsenic. However, the levels of arsenic in human hair are likely variable because individuals live in areas with different background arsenic concentrations. For example, in Italy, in the Venice region, As concentration in soils exceeds the regulatory guidelines up to 50 mg As kg^{-1} soil, as reported by Ungaro et al. (2008), in comparison to conterminous regions that exhibit As levels below the guidelines.

Arsenic accumulation in the human body is related to the strength of the metabolism. Younger adults accumulate less arsenic than other age groups due to their robust metabolism. Children and the elderly have relatively weak metabolisms, and they may accumulate more arsenic than other age groups when exposed to the same levels.

Other illness and disturbances due to As exposure are reported in current literature. Arsenic poisoning is known to produce polyneuritis in children who burned coal with a high As content. Arsenic (and Mn) have also been suggested as ototoxins affecting hearing (Chuang et al. 2007).

2.1.5 Selenium

Few chemical elements have risen research interest in the last decades as Se, that is known since long time for its toxicity to mammals (Gennaro Soffietti and Nebbia 1984); only since some decades, instead, its role as microelement in physiological and pharmacological processes has been focused, and recent research allowed to identify numerous pathologic forms derived from its deficiency (Roman et al. 2014). Indeed, selenium is now recognized as an essential nutrient for animals: Se-containing enzymes and proteins are essential for normal growth, development and metabolism in animals. Se concentrations in soils, pastures and animal blood correlate closely with each other, and with areas where Se-responsive disorders have been found.

Se is also known to be an antagonist to other heavy metals such as Cd, Hg, Pb (He et al. 2004), and also to have an antioxidative effect on lead-induced oxidative stress, and on oxidative damage in human sperm cell DNA (Chuang et al. 2007).

The geographic distribution of Se is not uniform. Some areas in the world (e.g. part of USA, Colombia, Great Britain) are characterized by large amounts of Se (up to 1,000 mg kg^{-1}) in soils, and vegetation may uptake Se amounts that may pose toxicity problems to living organisms, humans included. Other countries (e.g. Oceania, part of USA and most European countries, including Italy), instead, are characterized by low levels (less than the optimal concentration to avoid deficiency effects: 0.1 mg kg^{-1}) of Se in soils and vegetation (Cottenie 1979). It has been recognized as an essential trace element for humans and animals based on its presence in antioxidant systems and in hormone balance. The major use of Se is in the electronic industry (semiconductors, photovoltaic, solar cells, medical imaging equipments, glass industry). Natural food sources high in Se are cereals (corn, wheat, and rice), nuts, legumes, animal products (beef, chicken, eggs, cheese) (Gbadebo et al 2010). Anthropogenic Se pollution, derived by industrial activities (electronics, photovoltaic, glass, ceramics, paints, rubber, steel, plastics), is limited to the most important urban agglomerates, and does not pose serious environmental problems.

Selenium has a nearly paradoxical behaviour, since a concentration of 0.1 mg kg^{-1}Se in diet is considered essential for mammals, while a concentration of 0.4 mg kg^{-1} presents a noteworthy toxicity. Generally speaking, Se toxicity varies depending on the chemical species, with the organic ones that are more toxic than the inorganic. Moreover, Se toxicity is influenced by interrelations and counteracts with other chemicals (e.g. As, Cu, Hg, Cd), by formation of Hg-Se and Cd-Se complexes that are relatively harmless.

Low Se concentration in soils may lead to low Se uptake, low Se in the food chain, and low Se intake, provoking increasing risk of cardiovascular disease, coronary heart disease and cancer in humans.

The relation between the effects of Se deficiency and toxicity in the soil and health are most clear in some areas in China, where the Se concentration in crops is variable. The first disease associated with Se deficiency was Kashin- Beck disease, an endemic osteoarthropathy (Oliver 1997). It results in chronicle arthritis and deformity of the affected joints in children and teenagers. Muscular weakness is also a characteristic (Steinnes 2009).

Another typical disease associated with Se deficiency in China is Keshan disease, a cardiomyopathy found in young women and children. The symptoms are myocardial necroses, and weakness of the heart muscle (Oliver 1997). Low selenium levels have also been found in many disease states, including various forms of cancer, acute myocardial infarction, severe rheumatoid arthritis, cirrhosis of the liver and conditions exhibiting a compromised health status (Rahman et al. 2000). In addition, deficiency of Se is implicated in the weakening of the immune system, with muscular degeneration, impeded growth, anaemia, liver disease, and with endemic neuropathy and urinary tract tumours (Oliver 1997). Other symptoms of Se deficiency include muscle pain, weakness, and loss of pigments in hair and skin, and whitening of nails beds (Gbadebo et al. 2010).

The disease is likely associated with vitamin E deficiency (WHO 1996): Se deficiency impairs the antioxidant defences of the body, but Se combined with vitamin E act synergistically as antioxidants to restrict tissue damage from oxidative reactions, and in part explain the role of Se deficiency in the pathogenesis of atherosclerosis and multiple sclerosis (MS).

Schalin (1980) observed a clear correlation with the geographical latitude of developed areas, Se deficiency and high prevalence of multiple sclerosis, and suggested the operation of an infective agent. However, it remains unlikely that MS is a disease of predominantly genetic origin since the world distribution suggests the opposite. Another strong argument supporting the hypothetical role of Se in MS is the fact that the only disease with a similar worldwide distribution is cancer of the colon, a disease convincingly related to lack of Se.

The selenium intake is generally through dietary sources, and is frequently below the safe range of 50–200 μg/day recommended daily intake of Se by the US national research Council. Health benefits of Se are partly explained by its antioxidant effect. It may delay or prevent the onset of cancer and also have anti-aging effect. If consumed in overdose, it may have toxic effects (Gbadebo et al. 2010).

Selenium toxicity in humans and animals is a much rarer problem than Se deficiency, but it occurs at sites where high soil Se concentration is combined with high uptake by plants (Alloway 2013).

Symptoms of Se toxicity are fatigue, hair loss, white blotchy nails. Se was found to be an environmental toxin responsible for health problems in livestock grazing on soils with high Se content. Dietary supplementation of 200 μg Se per day significantly reduced lung, prostate and colorectal cancer in humans. Chronic Se toxicity is caused by intakes of 2–4 mg/day or prolonged intakes of 1 mg/day. Chronic symptoms of excessive Se include morphological changes in fingernails, nail brittleness and loss of hair as well as nausea, vomiting and skin lesions.

Selenium is rapidly absorbed by the gastro-intestinal tract, and binds to plasmatic proteins, with albumins and globulins as carriers (Mc Murray and Davidson 1979). Administration of toxic amounts leads to Se accumulation in various organs, with the following order: kidney > liver > lung > heart > muscles > brain. Current knowledge on the metabolic reactions within living organisms is rather fragmentary and not reliable to an organic framework. Many Se compounds follow the same metabolic ways than S compounds, the two elements being isomorphic; for example, a possible metabolic scheme for selenite is the following: Selenite ($Se0_3^-$) reacts with glutathione (GSH) forming derivates such as selenodiglutathione (GS-Se-SG); this is metabolized to form selenidric acid (H_2Se), which is methylated and volatizes, contributing to decreasing Se concentration in organisms (Venugopal and Luckey 1978). A minor pathway of Se elimination is via urinary and faecal systems.

The toxic effects of Se can, at least in part, be explained by formation of Se derivatives of glutathione that function as redox-cycling agents generating reactive oxygen species (ROS). The net effect of Se at excessive levels is therefore not as an antioxidant, but as a strong pro-oxidant (Alloway 2013).

Selenium-Glutathione Peroxidase (GSH-PO), together with vitamin E, plays an important role of protection of biological membranes against damages provoked by Lipid Peroxidation (LPO), reducing peroxides to alcohols (Dini et al. 1981). Toxic amounts of Se, moreover, provoke a noteworthy reduction of GSH, which is an active protector of haemoglobin. Elevated Se doses, furthermore, may interfere with embryo development, since Se is capable to cross the placental filter, reducing oxygen and energy availability.

Selenium carcinogenesis is a very debated problem. Prolonged assumption of small quantities of Se induced hepatic carcinomas and adenomas (Volgarev and Tscherkers 1967); however, recent advances assign to Se a major role in prevention of human neoplasms. Selenium supplementation has been reported to protect against various forms of cancer (prostate, colorectal, lung and liver) in prospective clinical trials from the United States and China (Alloway 2013). These data are consistent with earlier epidemiological studies, especially geographical ones from the United States, showing that mortality from several, but not all forms of cancer, and also from cardiovascular diseases (especially coronary heart disease and hypertension) was negatively correlated to the intake of Se (Alloway 2013).

Selenium poisoning may occur in both acute and chronic forms. Acute forms occur when huge amounts of Se compounds are taken in; symptoms are rapid and weak pulse, shortness of breath, bloating, intense colic pains, diarrhoea, poliuria, respiratory paralysis followed by death. Chronic forms (formerly “alkali disease” originating by excessive consumption of alkaline water) are due to ingestion of Se-contaminated food; symptoms are weight loss, anaemia, joint injury. Selenosis diagnosis is based on blood-Se up to 25 mg kg^{-1} in acute forms, and 2–5 mg kg^{-1} in chronic ones. Arsenic administration in diet is considered effective for chronic selenosis, while no intervention is effective for acute toxicity.

Selenium is known also for its counteracting effect on other metals: high plasma Se concentrations have been shown to decrease lead toxicity (Chuang et al. 2007). Selenium binds with toxic metals, reducing or eliminating their effect (Xie et al. 1998). Animal experiments have shown that Se at high intake levels has a strong protective effect against the toxicity of several calcophilous toxic metals, such as Hg, Cd and Ag (Alloway 2013). Its antioxidant effect may also be an important factor that reduces lead toxicity. Age is a well-established risk for impaired hearing ability, as well as Pb and Se were significantly associated. However, Se concentration was inversely associated with hearing thresholds: it might have a protective function for hearing. No synergistic effect was found (Chuang et al. 2007).

Recent studies and epidemiological observations on HIV progression confirm that Se and GSH directly affect the rate of HIV viral replication in patients. Enhanced oxidative stress (e.g. because of other infections) or impairment of the cellular capacity for antioxidant defence will therefore be a direct cause of progression from AIDS to HIV and mortality (Alloway 2013).

HIV-1 infection most likely occurs in subjects with poor diets; thus, maintaining an optimal Se status in HIV-1 patients may help to increase the enzymatic defence and reduce their risk of hospitalization (Roman et al. 2014). With increasing recognition of the role of antioxidants in disease prevention, the need for accurate determination of selenium status has become more important. Very few papers have been published on the determination of selenium in hair, which allows long-term exposure to be monitored.

2.1.6 Chromium

Among heavy metals, up to now chromium has received little attention in comparison to, for instance, Cd, Pb, As and even Se. The reasons for this lack of interest are diverse. One is that Cr was considered a "local source" contaminant, thus not constituting a widespread environmental problem; nevertheless, because of lax regulatory guidelines, disposal of Cr-containing wastes over large areas has led to the present extensive contamination of soils in many parts of the world. A second reason is that the dominant naturally occurring form of Cr is the trivalent oxide chromite, which has a very stable crystal structure. Consequently, it is very slow to react and is considered essentially immobile in the environment. In contrast, Cr^{VI} is highly mobile and is considered acutely toxic, although its occurrence is rare in nature (Bini et al. 2000). Chromium has been recognized as an essential microelement for animals and humans, potentiating the action of insulin and therefore being effective in carbohydrate and lipid metabolism (Steinnes 2009). On the other hand, recent works point to the severe toxicity of Cr^{VI}, a form utilized in several industrial activities (electroplating, chemicals, varnish, leather tanning), with respect to human health. Indeed, it is known to be a skin irritant and to induce allergic contact dermatitis. In addition, Cr^{VI} has been recently determined to be a potent human carcinogen for which there is adequate evidence of carcinogenic risk (Wang et al 2011). Conversely, the reduced form, Cr^{III}, is considered to have low acute and chronic toxicity, mostly because of the demonstrated low capacity to penetrate animal cell.

The chromium concentration in soils is largely determined by the parent material; the average world Cr concentration in soils is 40 mg kg^{-1}; the highest Cr level (up to 1,800 mg kg^{-1}) is found in serpentine soils, the lowest (<10 mg kg^{-1}) occurring in calcareous soils (Adriano 2001).

Chromium is considered to be a not essential element in plant metabolism, and moreover it is slightly available to plants. The form most available to plants is Cr^{VI}, which is the very unstable form under normal soil conditions (Kabata-Pendias and Mukherjee 2007), and is acutely phytotoxic (Bini et al. 1999). However, it is not easily translocated within plants (Fontana et al. 2011); there is evidence that it is concentrated mainly in roots, that act as a barrier (Bini et al. 2008). Also Cr^{III} seems to be available to plants, accumulating in roots and leaves, where it causes chronic damage to cell structure (Maleci et al. 2014). Visual symptoms of Cr phytotoxicity are stunted growth, poorly developed root system, discoloured leaves (Kabata-Pendias and Mukherjee 2007). However, under normal field conditions phytotoxicity is unlikely to occur.

In contrast to plants, chromium is essential for normal energy metabolism of humans and animals, but above certain concentration levels it is toxic and carcinogenic. It is reported to control the metabolism of glucose and lipids, and affects some of the enzymes that regulate cholesterol synthesis with beneficial impact of Cr on cholesterol fractions (Kabata-Pendias and Mukherjee 2007). Inhalation is the main pathway Cr enters the human body: the respiratory tract is the major target organ for both acute and chronic exposures, which produce nasal ulceration, perforation of septum, bronchitis and other respiratory effects, and ultimately nasal and lung cancer. Oral Cr intake (food ingestion) is another way of exposure, that affects the gastro-intestinal tract; Cr^{VI} is more easily absorbed by the intestinal mucosa than Cr^{III}; however, in the case of Cr^{VI} ingestion, it is almost completely reduced to Cr^{III} by acid gastric juice in the stomach, thus reducing drastically the toxic effects likely provoked by Cr^{VI} (Adriano 2001).

The average daily intake for general population is estimated to be approximately 60–75 μg Cr, depending on age, gender, life style. Excessive doses of Cr intake have been associated with renal dysfunctions (Steinnes 2009), and may result in liver and kidney failure, anemia, muscle breakdown and abnormalities in blood clotting. When an excess of Cr compounds are inhaled, lung, nasal and possible stomach cancer may develop (Kabata-Pendias and Mukherjee 2007). Association between Cr inhalation and mortality due to lung cancer has been found in epidemiological studies; mortality from lung cancer is apparently influenced by cumulative exposure (Steinnes 2009). Chromium dermal absorption also is frequent; Cr is generally considered to be the second most common skin allergen after Ni, and produces increased sensitivity, skin ulceration and allergic contact dermatitis. Instead, increased cholesterol levels, high blood sugar levels, coronary dysfunction, arteriosclerosis and abnormalities of nerve stimulation may occur with Cr deficiency (Steinnes 2009).

In conclusion, as previously stated, Cr^{III} is an essential element to humans and animals, while Cr^{VI} is not, and act as a potent carcinogenic, especially in occupational setting. Thus, Cr^{III} and Cr^{VI} have contrasting relevance in biological systems: the former is an essential nutrient, while the latter is a toxin (Adriano 2001).

2.2 Emerging Harmful Elements

2.2.1 Aluminium

Aluminium is the third abundant element in the earth's crust, being a fundamental component of silicate rocks, where it may attain 8 %. Al-oxide (bauxite) is the most important aluminium ore, widely diffused especially in tropical areas. Aluminium is also an abundant element in soils, where its contents vary commonly between 1 and 4 % (Kabata-Pendias and Mukherjee 2007). Due to its versatile properties, application is current in different industrial sectors, including metallurgical, electrical and chemical, packaging, paper manufacturing, wood preservation and many others.

The total Al content of soils is mostly inherited from parent rocks and from new mineral species formed during pedogenetic processes; its distribution in soil profiles is highly governed by chemical-physical conditions, organic matter, pH, and other soil properties. Only easily mobile and exchangeable fractions of Al play an important role in soil fertility. The mobile Al in acid soils can be taken up by plants and it creates a problem of chemical stress in plants. The most important problem is associated with Al toxicity, as one of the major factors which limits the growth and yield of plants cropped on acid ($pH < 5$) soils. Al toxicity in soils is particularly harmful because it causes shallow rooting, drought susceptibility, and deficient nutrients input (Kabata-Pendias and Mukherjee 2007). Conversely, there is some evidence that low levels of Al may have a beneficial effect on plant growth.

Once considered as a not toxic element for human population, in early 1970s the scientific literature started to consider some toxicity evidences induced by Al as collateral effects of renal dysfunction treatment (dialysis), with intestinal Al absorption up to 500 mg. More recent research indicates Al as one of the factors directly related to neurotoxic disturbances (haedache, epilexy). No definite conclusions have been given on chronic Al exposure; however, aluminium is known to be neurotoxic at high exposure levels, (Steinnes 2009). Indeed, the long-term uptake of aluminium is implicated in the aetiology of neurological disorders such as Alzheimer syndrome (Polizzi et al. 2002) and arteriosclerosis (Nriagu 1988). The World Health Organization (WHO 1996) indicates that an excess A1 also seems to cause softening of bone.

Although there is much debate on Al effects on humans, so far no positive conclusions have been made, and the relation between A1 and Alzheimer's disease is still controversial (Kabata-Pendias and Mukherjee 2007).

Water is the main pathway by which A1 enters the human diet. The WHO (1993) guideline for A1 concentration in drinking water is 0.2 mgL^{-1}. A statistically significant association of Al in drinking water with the incidence of dementia was found (Steinnes 2009), although Al usually contributes a very small proportion (15–20 mg/day) of daily human intake, at the limit value of 1 mg Al kg^{-1} BW (WHO 1993). Yet, the major part of a typical daily intake comes from food (e.g. eggs 0.5–1 mg kg^{-1}; lettuce 5 mg kg^{-1}; meat 1–10 mg kg^{-1}), beverage (beer, tea) and food additives, with possible increase (up to 50 mg/day) due to the use of pans and other kitchen utensils made with aluminium. Considering a daily intake of Al, no risk is expected from eating food cooked in Al-pots and/or Al-foil. A minimal risk level for oral exposure of 2 mg Al kg^{-1} BW per day has been set up in the USA (Kabata-Pendias and Mukherjee 2007).

2.2.2 Antimony

In contrast to arsenic, which belongs to the same periodic group and have the same oxidation states, there is limited understanding of the behaviour, ecotoxicology, and the extent of environmental dispersion of antimony (Liu et al. 2011). Antimony is non-essential for human life, and is completely absent in living organisms; it is found in biological specimens from persons who have been exposed to industrial sources of antimony. Indeed, it is emitted into the environment through human activities such as mining, smelting, alloys, emails, and the combustion of fossil fuels, and its concentration in the environment has increased by 50 % since the early nineteenth century. Although many investigators have highlighted the importance of the environmental chemistry of antimony (and bismuth) (Liu et al. 2011 and references therein), little information is available on how antimony contamination affects exposed populations. Pentavalent antimony is less toxic than trivalent antimony. In humans trivalent antimony is taken up by the red blood cells, whereas pentavalent antimony remains in the plasma and is more easily excreted than the trivalent form (Rahman et al. 2000).

Antimony has been classed as a priority pollutant by the United States Environmental Protection Agency (US EPA). The most likely route in the body from industrial exposure is from inhalation, or from ingestion of drugs containing the element, whose main medicinal use is in the treatment of parasitic diseases (Rahman et al. 2000). A study of industrial occupational exposure in the vicinity of the largest Sb mine in the world, in China reported mean antimony values of 0.05, 0.57 and 0.36 μg/g in hair from locomotive shed workers, industrial welders, and students and office workers, respectively. High antimony concentrations ($\geq$3 μg/g) were found in 80.0 % of children (5–9 years) and 69.6 % of adults aged 41–51 years (Liu et al. 2011).

In France, Sb intake was determined by consumption of goose liver (*foie gras*), achieved administrating to gooses 60 mg kg^{-1} day^{-1}antimony sulphide (today prohibited), which induced liver steatosis, and a Sb concentration up to 100 mg kg^{-1}.

Long-term intake of small amounts of Sb may induce chronic antimony poisoning. Sb exposure has been shown to induce DNA damage and oxidative stress, and generates reactive oxygen species (ROS), causing apoptosis; since Sb geochemical behaviour is similar to As, it is likely that the DNA damage induced by Sb follows similar pathways as those for As (Franco et al. 2009).

Limited information is available as to what level of antimony in hair can be used to estimate whether individuals are suffering from Sb chronic poisoning. Some studies have found that hair As levels are <3 μg/g. Consistently, 3 μg/g have been proposed by Liu et al. (2011) as the normal hair antimony level. Lethal Sb dose for humans (70 kg body burden) is estimated within 100 and 500 mg.

2.2.3 Beryllium

Beryllium is a very rare element (2–10 mg kg^{-1} in the earth crust). It is increasingly used in aircraft and spatial vehicles industry, as a hardening component in Al-Cu alloys, and as neutron source in nuclear reactors. However, the primary environmental source of Be is coal combustion, producing around 180 tonnes year^{-1} (Adriano 2001). Beryllium is recognized as phytotoxic, but its availability in low amounts may have beneficial effects on plants, stimulating growth. It accumulates primarily in roots, and afterwards may translocate to aerial parts and accumulate in leaves. Deleterious effects are antagonism of nutrients such as Ca and Mg, and inhibition of certain enzymes. It may enter the food chain through crop produce contaminated by industrial particulate matter. A second pathway of Be assumption is via drinking water; in three of 96 examined mineral waters a Be concentration above 3.0 μg L^{-1} have been determined (Cerutti, personal communication 2013).

Be, as well as Ag, As, Cd, Hg, Pb, are good examples of PHEs that have no proven essential functions in humans, and are known to have adverse physiological effects at relatively low concentrations (Abrahams 2002). Indeed, beryllium is highly toxic to living organisms, and affects exposed workers; the target organs are bones, liver, kidney, and lung. Pulmonary diseases that affect Be-workers are particularly serious, and may appear after long time from exposure. Be may induce also rickety, due to the high insolubility of Be-phosphate. Be-induced apoptosis has also been ascribed to ROS generation, but may be prevented by superoxide dismutase (SOD) mimics; Be also induces activation of protein kinase C in a ROS-independent manner (Franco et al. 2009).

Current data on Be effects to humans is lacking; more attention should be paid to this emerging element.

2.2.4 Bismuth

Bismuth is an emerging metal belonging at the same group as As and Sb, and the most common chemical form is sulphide; large ore deposits are found in southern America, Australia and northern Sweden. Its geochemical behaviour may be compared with that of As and Sb. Although little investigated, it is known since ancient times, and the main usage is in easy fusible alloys with Pb and Sn, and in pharmaceutical industry, as substitute for Hg, being less toxic. Currently there is a great interest in some clinics for the monitoring of patients on bismuth drip treatment for peptic ulcer complaints (Rahman et al. 2000).

Industrially it is considered one of the less toxic heavy metals. Yet, the metallic form Bi is not considered toxic and poses minimum threats to the environment. Conversely, Bi compounds generally have very low solubility but they should be handled with care, as there is only limited information on their effects and fate in the environment, and the cautelative principle should apply.

The main routes of Bi entry in the human body are dust inhalation, skin contact and ingestion by food or drinking water. Exposure may cause both acute and chronic effects. The bismuth content in most biological samples is very low, with biological fluids normally containing only a few ng ml^{-1}, while in biological tissues concentrations may range from 10 to 90 ng g^{-1}. Jorgensen et al. (quoted in Liu et al. 2011) reported that bismuth concentrations ranged <0.03 to <0.1 μg/g in mammalian tissues. Hair is the target tissue for assessing Bi poisoning. Park et al. (2007) found a mean bismuth level of 0.04 μg/g in hair samples from 655 children (3–6 years old) from metropolitan and small cities in Korea. High bismuth concentrations (≥0.1 μg/g) were observed in individual groups of various ages affected by bismuth exposure. Children (5–9 years) and adults aged ≥41 years presented higher Bi levels than individuals in other age groups.

Toxic effects, both acute and chronic, have been recorded upon exposure to bismuth and its salts.

Acute effects determined by inhalation are a nuisance dust causing respiratory irritation. Inhalation may cause foul breath, metallic taste and gingivitis. Ingestion may cause nausea, loss of appetite and weight, albuminuria, diarrhoea, skin reactions, stomatitis, headache, fever, sleeplessness, depression, rheumatic pain and a black line may form on guns in the mouth due to deposition of bismuth sulphide. Skin contact and dermal absorption may cause irritation. Exposure to contaminated atmospheric particulate may cause eyes irritation (Lenntech BV – Internal report, 2013, unpublished. Delft, The Netherlands).

Bismuth chronic effects: long-term Bi inhalation may affect the function of liver and kidneys. Ingestion, besides affect the function of liver and kidneys, may cause anaemia, black line on gums and ulcerative stomatitis. Skin contact and dermal absorption may cause dermatitis.

Although little information is available on Bi carcinogenicity, bismuth is not considered a human carcinogenic; nevertheless, it can cause kidney damage. Other toxic results may develop, such as vague feeling or bodily discomfort, presence of albumin or other protein substance in the urine, diarrhea, skin reactions and sometimes serious exodermatitis. Serious and sometimes fatal poisoning may occur from the injection of large doses into closed cavities and from extensive application to burns (in form of soluble bismuth compounds). Administration of large doses can be fatal. It is stated that the administration of Bi should be stopped when gingivitis appears, for otherwise serious ulceration stomatitis is likely to result.

2.2.5 Boron

Boron is a widely diffused light non-metallic element, that is easily available as H_3BO_3 (sassolite) in volcanic fluids in Tuscany (Italy) and as $Na_2B_4O_7.10H_2O$ (borax) in Tibet, Chile and California (USA). Boron compounds usage was recommended at very low dose as food preservative, but is currently prohibited in several countries because of its toxicity at doses of grams; the main industrial use is in glass, email and paints industry, soaps and teeth pasts preparation. As pharmaceutical it is a light antiseptic, and in agriculture, it proved efficient in enhancing flowering of orchards, and particularly the olive groves. Given its ability to form complexes with sugars, B has been implicated in sugar transport across cell membrane. Some plants (sesame, sugar beet) showed B accumulation in leaves as a consequence of passive transport from roots to shoots, *via* xylem, eventually up to a toxic level (Adriano 2001). Boron is essential for plant growth, although the amounts requested for some crops (e.g. alfalfa) may cause damage to other crops (e.g. legumes and cereals). Conversely, B deficiency has been reported in food crops in USA, UK and Australia, without apparent geographic pattern. Concentrations <0.05 μg B mL^{-1} proved to produce deficiency, while 1.0 μg B mL^{-1}proved toxic; 0.50 mg kg^{-1} is likely a safe level, while ranges 0.05–0.10 μg B mL^{-1} look adequate for many plants. For example, sunflower, cotton, celery, cauliflower are more sensitive in comparison to cabbage, broccoli, carrots, clover, radish, olive (semitolerant), and to tolerant plants such as corn, oat, onion, potato. High boron levels in irrigation water may cause a rise of boron levels in the soil to a toxic extent. Tolerant crops may achieve 2.0–4.0 μg B mL^{-1} before presenting toxicity symptoms (e.g. chlorosis), while USEPA has set a limit of 0.75 μg B mL^{-1} for long-term irrigation water.

From plants, B may enter the food chain. To date, there is no sufficient information on the essentiality of B in animal nutrition and human health, and also its toxicity has not been established conclusively (Steinnes 2009). The World Health Organization Committee on Trace Elements in Human Nutrition (WHO 1996) concluded that B is *probably essential*, being beneficial in humans and animals for many life processes as cell membrane function, mineral and hormone metabolisms, and enzyme reactions (Kabata-Pendias and Mukherjee 2007). The only information is that excessive boron intake (4,000 mg day^{-1}) may cause symptoms of boron poisoning, such as gastrointestinal disturbances, skin eruptions, and signs of central nervous system stimulation, followed by depression (WHO 1996).

2.2.6 Copper

Copper is known since the pre-historical times, and gives the name to an epoch of civilization; Greeks and Romans exploited Cu from Cyprus (its Latin name *cuprum* comes from there) and Spain, and commerce flourished with copper, as well as with lead. Native Cu and Cu compounds come from Chile, USA, Russia, Africa; mixed sulphide with Pb, Fe, Zn were exploited until the 1960s of the last century in several countries, including Italy (Bini 2012; see also this volume, Chap. 5). Copper is the most widely used metal in the world, after iron. Its usage is mainly in electrical applications and energy transport (42 %), metallurgy (33 %), agrochemicals (12 %), and others.

Copper is an essential microelement to living organisms, contributing to haematopoietic function and to the formation of bone tissue. Moreover, it is a component of several important enzymes acting in oxidation-reduction processes and in catalysis of enzymatic reactions such as urease, laccase, hydroxylase. Copper is considered slightly toxic; Cu-poisoning may occur as a consequence of excessive Cu intake from the food chain (e.g. from pesticide-contaminated forage, vegetables and particularly vineyards treated with the classic "Bordeaux mixture" based on copper sulphate). Yet copper, unlike lead, is largely absorbed by plants growing on naturally enriched soils or in areas conterminous to industrial plants (smelters) and mines, or spread with sewage sludge and as antiparasitic and fungicide in agriculture.

Copper is essential for man; it forms organic complexes, and metalloproteins, especially haemoglobin. Some function as enzymes in metabolic reactions. Copper aids blood clotting, maturation of connective tissue, development of the bones, and participates in lipid metabolism (Davis and Mertz 1987). The metabolic behaviour of Cu is strictly connected with that of Mo. This metal, indeed, enhances copper elimination from liver, and counteracts, as well as other metals (Fe, Zn, Cd) its absorption in the gastro-intestinal tract, at amounts less than 30 % of the ingested Cu. The ingested copper dissociates and forms new Cu-complexes with amino acid as carriers of active transport crossing the intestinal mucous; within the cells, it binds metallothionein and than enters the circulatory system; in the plasma, it may bind albumins or is distributed in cytoplasm and in different subcellular fractions, where enzymatic synthesis occurs.

Similarly to other essential (and critical) elements, both Cu-deficiency and excess may occur, and the pathways of exposition are inhalation, ingestion and skin contact, the latter being common with workers in agriculture; however, ingestion of contaminated food is the most likely to occur.

An intake of 2 mg Cu day^{-1} is assumed to be adequate for healthy adults, 80 pg day^{-1}for infants and 40 pg day^{-1} for children (Oliver 1997). Deficiency is generally induced by inadequate diet, especially in developing countries. Toxicity from Cu excess is rare: the WHO (1996) suggests a safe upper limit of 12 mg day^{-1} for adults and 150 pg day^{-1} for children.

Copper deficiency in humans is serious and may lead to typical disease symptoms such as anaemia and leukopenia, bone deformations, osteoporosis, lack of colour of the hair and skin, degeneration of the hearing muscle, reduced elasticity of arteries, coronary heart disease, and neurological disorders. Antagonistic effects with Mo are reported (Steinnes 2009). Deficiency is associated with anaemia and neutropenia in premature babies, and with diarrhoea in children (Oliver 1997).

Excessive Cu intake induce acute and chronic toxicity, although with generally mild forms. Acute poisoning may be determined by Cu intake up to 200 mg kg^{-1}; more complex is quantification of chronic poisoning, given the interaction/counteraction with other metals; for example, it is considered to be harmful a diet with a ratio Cu/Mo less than 10:1. If ingested at high amounts, copper acts as a protoplasmatic poison with regard to the gastro-enteric tract mucous. The long-term intake of Cu normal doses may determine metal accumulation in liver, provoking functional and structural alterations symptomatic of incipient poisoning. However, no carcinogenic effects are recorded with copper. Once overcome a certain accumulation level (e.g. 150 mg kg^{-1}), liver releases a huge amount of metal, and possibly oxidant substances in the circulatory system, with red globule membrane damage (LPO), determining haemolytic crisis. Indeed, copper is prone to participate in the formation of ROS, leading to final LPO and cell apoptosis (Franco et al. 2009).

Acute poisoning symptoms, as for other metals (e.g. Hg, Pb, Tl) are generally vomit, colic pains, diarrhoea with fluid greenish faeces, cardio-circulatory collapse, and death is likely to occur. The lethal dose for humans is considered to be 2.5 g/70 kg body weight.

Similar critical evolution occurs also with chronic poisoning; symptoms are weakness, muscle tremors, haemoglobinuria, jaundice, dyspnea. Liver is generally hypertrophic, kidney presents necrotic tubular alterations, that may induce degenerative phenomena in the brain. Morbidity of chronic poisoning is generally low (<5 %), while mortality is high, with 75 % of subjects dying within 3–4 days.

Chronic poisoning may be assessed by the quantitative estimate of blood-Cu, whose physiological amount is in the range 1–3 mg kg^{-1}. Poisoning prevention may be achieved with equilibrated administration of NH_4-molibdate.

2.2.7 Fluorine

Fluorine is a very reactive element (most of the halogen group) and may combine with several other elements, including inert gases. Fluorite (CaF_2) is the most common commercial source of F. It is used the Al-industry, in the steel industry, and also in plastic, ceramic and glass production and in various chemical processes (Kabata-Pendias and Mukherjee 2007).

Fluoride has long been added to municipal drinking water (at the level of 1.2–1.9 mg L^{-1}) for the prevention of dental caries. It is still added to tooth pastes.

Elemental fluorine does not pose severe poisoning hazard to living organisms, while both organic and inorganic compounds play a significant role in toxicology, being frequent in nature, associated with P-bearing minerals. Soils derived from P-bearing rocks contain huge amounts of F; however, it is not easily translocated to plants, being arrested mostly in roots. The main source of fluorine is from industrial plants such as smelters, foundries, glass factories, aluminium and steel produce, whose emissions (both fumes and dust) are dispersed in conterminous areas, contaminating soils and vegetation. Contamination, therefore, results from the site topography and from wind regime.

Environmental pollution by F in some regions has become of ecological importance. The reactions of plants exposed to F pollution, before any visible toxicity symptom, are retarded growth, inhibited reproduction, and yield reduction. However, the greatest concern with increased F concentrations in plants is related to the toxicity to mammals, including humans (Kabata-Pendias and Mukherjee 2007). The average F contents in mammalian tissues are established as 2–5 mg kg^{-1} in soft tissues and 250 mg kg^{-1} in the skeleton, where F substitutes for (OH) in the mineral structure of teeth and bones. Fluoride ion F^- is able to bind and precipitate the essential ion Ca^{2+}, decreasing its physiological functions, and in particular inhibiting enzymatic activity and arresting cell respiration. Dental fluorosis affects developing teeth with thinning of the layer of enamel and dentin defective mineralization. Bone lesions are a consequence of inadequate formation of bone matrix and subsequent deficient mineralization.

Exposure to fluoride may occur by ingestion, inhalation or by skin absorption; the oral pathway is the prominent, and fluoride absorption by the gastro-intestinal tract is very rapid, although the occurrence of Ca, Al, Mg, Fe, P counteracts F^- absorption. Fluoride distribution in the animal body is mostly in hard tissues (skeleton and teeth) and secondly in kidney, although it has been found in all organs and tissues. Excretion is generally via renal system; by interrupting exposure, F^- depletion occurs very slowly, in several months or even years.

Recently there has been a wide discussion on the health risk associated with increased intake of F. Fluorine toxicity may occur both in acute and chronic form, in relation to ingested amount, exposition, absorption capacity in bones and teeth. Threshold levels are considered to correspond to a daily intake up 40 mg kg^{-1} NaF; however, with only 15 mg kg^{-1} dental alterations may occur. Severe toxicity and bone lesions have been observed within 30 days after intake of 100 mg kg^{-1} NaF; lethal doses are achieved with intake 100 g (Beretta 1984). The intake of 20–70 mg F day^{-1} by adults can cause heartburn symptoms due to displacement of Ca.

Elevated F levels in drinking water can produce both mutagenic and carcinogenic changes in the kidneys. It has been observed that the mortality rate from cancer in the cities using fluorinated water increased significantly as compared with the cities that did not use fluorinated water. Consistently, in several countries, F addition to drinking water has ceased, although in the last century there has been great interest in the fluoridation of water as means of reducing dental caries (Kabata-Pendias and Mukherjee 2007). Dental tissue also shows the earliest sign of toxicity; concentrations of F over 1 mg L^{-1} are likely to produce symptoms, and mottling of the teeth is prevalent when the concentration exceeds 4.5 mg F L^{-1} (WHO 1996). Nearly one million people in rural India suffer for fluorosis, a chronic, incurable, and debilitating affliction (Oliver 1997). Moderate amounts of F are beneficial to dental structure, whereas intake of high amounts may lead to development of dental fluorosis, and in extreme cases skeletal fluorosis.

Although no cases of F deficiency have been reported in humans, some symptoms of low F supply have long be linked to dental decay, osteoporosis, and possible with growth retardation (Steinnes 2009). These symptoms are observed mainly in children <6 year age.

Typical symptoms of intoxication (fluorosis) are mottling of tooth enamel and several skeletal and joint deformation including spinal curvature and knock-knees problems. Some individuals may be especially susceptible to F and its compounds. These include elderly people, persons with deficiencies of Ca, Mg, and vitamin C, as well as people with cardiovascular and kidney problems (Kabata-Pendias and Mukherjee 2007).

Acute fluorine intoxication is characterized initially by gastro-enteric disturbances, vomit, abdominal pains, diarrhoea, as a consequence of gastro-intestinal mucous irritation. Afterwards, muscle tremors, urinary incontinence, cardio-circulatory collapse may occur owing to hypocalcaemia. Respiratory paralysis and heart failure determine lethal consequences.

Chronic intoxication is the most frequent, and is characterized mostly by evident disturbances of skeletal apparatus during a time span ranging from 6 to 12 months. The process starts with scarcely relevant bone lesions, and proceeds with thickening of the long bones of the limbs, calcification, spontaneous fractures. Dental lesions too (e.g. partial enamel loss, teeth erosion) are a sensible index of chronic intoxication, with possible infection of oral cave. Chewing is more and more difficult and painful, and this is reflected on the nutritional state and the growth retardation. Urinary excretion may be accompanied by the reduction of blood levels of goitre hormone, determining hypothyroidism, anaemia, leucocytosis.

An improvement of the fluorosis disease may be obtained by administering in the diet Ca-salts and especially Al-salts, that reduce fluorine bone content by 45 %.

Fluoride tolerance may be augmented by equilibrated assumption of Ca, P, vitamin D.

2.2.8 Iodine

Iodine has an extreme variability in the earth's crust, with the highest content in sedimentary rocks (1.5 mg kg^{-1} in shale), and the lowest in volcanic rocks. Its concentration in surface soils is generally higher than the corresponding parent material, and the suggestion of an atmospheric origin of I seems to be most reasonable. Iodine and its organic compounds are utilized in a number of chemicals and pharmaceutics, both for external and internal applications. Radioactive isotopes are most commonly by-products of atomic reactors and are used in medical diagnosis; being released in various proportion into the environment, they are of growing environmental and health concern (Kabata-Pendias and Mukherjee 2007).

Iodine was the first element to be recognized as essential to human health, in 1846 (Oliver 1997). It has long been known as an essential element for humans and mammals, where it is a component of the thyroid hormone thyroxin (Steinnes 2009). This contains up to 80 % of the total body store of I and is involved in most biological processes (e.g. bone growth, reproduction). Therefore, an adequate level of I in the human body is crucial (Kabata-Pendias and Mukherjee 2007).

The daily requirement of I by adults is around 150–200 μg. Intake below 100 μg day^{-1} has resulted in mild deficiency, and a dose below 20 μg day^{-1} has caused severe deficiency symptoms (Kabata-Pendias and Mukherjee 2007).

Insufficient supply of I (*hyperthyroidism*) may lead to a series of iodine deficiency disorders, the most common being endemic goitre, which was the first endemic disease attributed to the environment. Goitre was first recognized as resulting from I deficiency in areas far from the sea and in the Alps and Himalayas.

Iodine deficiency during pre-natal development and the first year of life can result in endemic cretinism, a disease that causes stunted growth and brain damage. Other consequences of I deficiency include abortions, stillbirths, congenital abnormalities, impaired mental function and reduced thyroid hormones. Of these the most serious disorder is endemic cretinism (Oliver 1997) which is caused by the most severe I deficiency. Goitre occurs when I intake is 50 % of normal (WHO 1996). Hyperthyroidism is generally counteracted administrating more (radioactive) I to patients. The only common side effect of radioactive iodine treatment is underactivity of the thyroid gland. The problem here is that the amount of radioactive iodine given kills too many of the thyroid cells so that the remaining thyroid does not produce enough hormone, a condition called *hypothyroidism.* There is no evidence that radioactive iodine treatment of hyperthyroidism causes cancer of the thyroid gland or other parts of the body, or that it interferes with a woman's chances of becoming pregnant and delivering a healthy baby in the future. It is to note, moreover, that women are more prone to hyperthyroidism than men, and that this disease affects more frequently older individuals than young persons.

2.2.9 Cobalt

Cobalt, as well as manganese (see below) are two heavy metals which have received little attention in comparison to other heavy metals such as lead and cadmium, for example. Their lack of notoriety is a result of their lower potential to exert any toxic properties that they may have and to the lack of appropriate situations, particularly in soils (Alloway 2013). Nevertheless, they play significant roles in soil health, acting as oxidants and Co, in particular, for medical treatments. Indeed, the only known Co function is as a constituent of Vitamin B12, which plays a major part in animal cells; its deficiency in humans causes pernicious anaemia and severe effects on the nervous system.

Cobalt occurs in all mammalian tissues and its contents vary from 5.5 to 230 μg kg^{-1}, with the highest value in the liver and the lowest in the brain. Although inorganic Co is present in several organs and tissues, its possible other physiological functions are unknown. Cobalt is likely to be bound by some proteins and to replace other divalent cations (e.g., Zn, Mn) in various enzymes, without any effects. Some organic Co compounds are apparently involved in processes of stabilizing the DNA structure (Kabata-Pendias and Mukherjee 2007). Co has also been observed to induce ROS and apoptosis in different cell lines, leading to oxidative DNA damage via OH^- formation (Franco et al 2009).

Cobalt deficiency in living organisms refers to the scarcity of Co in soils (0.30 mg kg^{-1} in severely Co-deficient areas, according to Adriano 2001) and may affect the animals' health, when pasture concentration falls below 0.08 mg kg^{-1}. Conversely, the occurrence of Co contamination of soils is rare (up to 1,000 mg kg^{-1} in serpentine soils), as well as Co toxicity, except in particular circumstances.

The deficiency of Co may affect anaemia and anorexia. The excessive ingestion of Co may cause polycythemia (increased red blood cells), cardiomyopathy, hypothyroidism, pancreas failure, bone marrow hyperplasia, and some types of cancer.

Human dietary intakes vary from 5 to 40 μg day^{-1} and is mainly from the ingestion of foods, particularly from livers and meet products (Kabata-Pendias and Mukherjee 2007).

2.2.10 Manganese

Manganese, as well as Co (see above) is an heavy metal which has received little notoriety in comparison to other heavy metals such as lead and cadmium, for example. The lack of notoriety is a result of its low potential to exert any toxic properties, and to the lack of appropriate situations, particularly in soils. Nevertheless, the ability of Mn oxides to absorb preferentially heavy metals and to act as oxidants means that it plays a significant role in soil health (Alloway 2013).

Both Mn deficiency and toxicity occur in plants and Mn may be of environmental concern in a few situations associated with water quality and the mining of Mn ores.

Mn is an essential element for humans and is considered an element of low toxicity. Its physiological function is closely associated with some enzyme activities, (e.g. superoxidase, dismutase, arginase) and with metallothionein. It is also known that Mn^{2+} is involved in gene expression processes and stabilizes the DNA structure (Kabata-Pendias and Mukherjee 2007).

In general, Mn is an activator of different enzymes that control the metabolisms of carbohydrates, proteins and lipids (including cholesterol), and nitrogen metabolism. Moreover, it affects the functioning of other enzymes which are involved in bone formation.

The most common Mn deficiency symptoms in livestock are impaired reproduction, skeletal deformities and shortened tendons in the newborn; in humans it can also cause impaired insulin production, lipoprotein metabolism, oxidant defence and growth factor metabolism (Alloway 2013), and neurological disturbances (Iregren 1990).

A great proportion (over 50 %) of Mn in the human body is located in the hepatocyte nuclei of liver, likely indicating some functions of this metal in genetic regulation (Kabata-Pendias and Mukherjee 2007, and references therein). The Mn contents in human tissues, especially in bones, decrease with age; this can be associated with skeletal deformities and bone fractures (osteoporosis), dermatitis and hypocholesterolemia. Moreover, testicular dysfunctions can result from a Mn deficiency.

Manganese deficiency in humans has also been associated with the incidence of esophageal and other types of cancer (Steinnes 2009). However, symptoms of Mn deficiency in humans are very rare.

The adequate daily intake of Mn by adults was previously given to be between 2 and 6 mg day^{-1} whereas the recent USEPA recommendation is up to 10 mg day^{-1} for a 70 kg body weight.

Of the three pathways of Mn exposure, the most harmful is inhalation. Oral Mn poisoning has not been recorded often and is mainly related to drinking water. The ingestion of excess Mn by food may result in liver cirrhosis. The inhalation of Mn-rich dust by humans can increase susceptibility of the respiratory tract to infection and can induce Mn-pneumonitis and some neurobehavioral impairment (Kabata-Pendias and Mukherjee 2007). Mn, together with As, has also been suggested as ototoxin affecting hearing (Chuang et al. 2007).

2.2.11 Molybdenum

Molybdenum occurs at relatively low concentrations in most rocks and soils, but in relatively high concentrations in soils developed on black shales (Abrahams 2002). It is most mobile and plant available in alkaline conditions. It is primarily used in metallurgy for producing various alloy steels and stainless steel, aircraft and automobile components, cutting tools, support wires for filaments in incandescent light bulbs, catalysts, lubricants, pigments and other uses (Alloway 2013).

Concentrations of Mo in soils are generally the lowest of all the essential trace elements for plants (B, Cl, Cu, Fe, Mn, Mo, Ni and Zn). Sewage sludges commonly contain 5–50 mg Mo kg^{-1}and if high Mo sludges are applied to pastures they could cause *molybdenosis* problems in livestock. Yet, molybdenum-induced copper deficiency is a serious problem on Mo-rich pasture soils in several countries.

Besides its known essential role of micronutrient for plants, Mo has recently proved an essential element for both animals and humans. Normal Mo concentrations in plant leaves are 1 mg kg^{-1} or less; plants growing on contaminated soils have been reported to contain <200 mg Mo kg^{-1} (Steinnes 2009). On a global scale, deficiency of Mo in crops is more important than potential excesses from contamination because it is essential to plants. Nevertheless, deficiencies can occur in *Brassicaceae*, legumes, wheat, sunflower and some other crops in many parts of the world, mainly on acid and sandy soils (Alloway 2013).

In animals, Mo is required for the functioning of several enzymes involved in transformations of C, N and S. In grazing livestock, a close connection between Mo, Cu and S is involved in molybdenosis, which is a Mo-induced Cu deficiency. (Alloway 2013). However, deficiency cases are rare. The only people known to have Mo deficiency are those with a genetic defect which prevents the synthesis of sulphite oxidase and causes severe illness except when Mo is administered. Symptoms included tachycardia, headache, nausea and vomiting (Kabata-Pendias and Mukherjee 2007). Sulphite oxidase is very important in humans because it is involved in the metabolism of S-containing amino acids and bisulphite preservative in foods (Alloway 2013).

The main dietary sources of Mo are legumes, nuts and grain products. Tissue concentrations of 0.03–0.15 mg kg^{-1} (dry weight) are considered to be adequate for nutritional requirements (Steinnes 2009). The excess Mo in the human diet influences its accumulation in serum, urea, and hair. With excess amounts, it may exert an antagonistic effect on Cu, causing a secondary copper deficiency.

Molybdenum is not considered as a carcinogenic element. However, there is still inconclusive epidemiological evidence that low Mo intakes may be associated with the occurrence of oesophageal cancer in humans. Apparently, it is also related to cancer of the stomach (Kabata-Pendias and Mukherjee 2007).

2.2.12 Nickel

Nickel is a transition element with a broad range of applications in modern industry, being used in everything from coins to automobiles to jewellery (Alloway 2013). The largest Ni use is by far stainless steel manufacturing. Moreover, Ni is an excellent catalyst for many reactions and so it is used for a large number of industrial and research applications alone or in combination with other metals.

Ni is well known as an essential trace element for plants and domestic animals, but has not yet proven to be essential to humans. Nickel in plants ranges generally from 0.05 to10 mg kg^{-1} dry matter. Nickel deficiency is very rarely found in plants, due to the very small amount needed for normal metabolism; symptoms of Ni deficiency, such as leaf tip and vein necroses, and patchy necrosis of younger leaves may occur (Gonnelli and Renella 2013).

With increasing Ni contamination, excess Ni is more commonly found in these organisms, and toxicity symptoms may occur. With regard to Ni toxicity to plants, threshold concentrations are commonly reported to be less than 100 mg g^{-1}. Responses to toxicity differ significantly according to plant species, growth stage, soil Ni concentration and exposure time. In general, critical toxicity levels are >10 mg g^{-1} dry matter in sensitive species, and >50 mg g^{-1}(dry matter) in moderately tolerant species (Alloway 2013). Among the toxic effects due to high Ni concentrations in plants, retardation of germination, inhibition of growth, reduction of yield, induction of leaf chlorosis and wilting, disturbance of photosynthesis (Gonnelli and Renella 2013) are the most common symptoms. However, there exist Ni-accumulator plants (e.g. the well known *Alyssum bertoloni*, a typical endemic of serpentine soils) that apparently do not show evidence of toxicity symptoms.

Ni-beneficial effects have been recorded in experiments with Ni-deprived animals. Nickel seems to be a bioactive element with some beneficial functions. Ni deprivation affects reproductive function in goats and rats, and changes carbohydrate and lipid metabolism. Nickel has beneficial effects in bone and may also alleviate Vitamin B12 deficiency (Gonnelli and Renella 2013).

Nickel is scarcely absorbed by human organism, with the exception of the respiratory tract in metal industry workers, since it may be released by Ni- bearing alloys (e.g. special steel widely used in food industry).

The Ni deficiency seems unlikely to occur in humans. However, Ni requirements by adults have been established as 25–35 μg day^{-1} (Kabata-Pendias and Mukherjee 2007). Lower Ni intake can induce some dysfunction of lipid metabolism, but human diets generally contain sufficient amounts of Ni. The usual Ni daily intake, comprehensive of the three pathways, is within the range 0.3–0.6 mg $day^{-1}$for humans (70 kg body weight). Legumes contain the highest Ni amounts (up to 1.60 mg kg^{-1} in peas), whilst it is nearly absent in milk, eggs and cattle meat. Normally, food assumption does not induce toxic effects. The optimum Ni intake should probably be <100 mg day^{-1}. and the average Ni intake by inhalation is calculated to range from 0.1 to 1 μg day^{-1}. Smokers inhale from 2 to 12 μg of this metal, for each pack of cigarettes (ATSDR 2002).

The toxicity of Ni is relatively low, but Ni allergy is a significant problem in humans, even at low exposure doses (Steinnes 2009). Instead, the toxicity and carcinogenicity of high doses of Ni are well documented and depend mainly on its potential to damage proteins and nucleic acids. Yet, Ni is known as producer of ROS (e.g. OH^-), lipid peroxidation (LPO) and oxidative DNA damage and, in addition, has been shown to induce NO production (Franco et al. 2009).

Investigations on the toxicity of Ni have indicated various effects of its excess, among which the most important are developmental, genotoxic, neurological, reproductive, and carcinogenic (Kabata-Pendias and Mukherjee 2007). Slightly soluble Ni compounds, in particular, are likely to be carcinogenic at the site of deposition (ATSDR 2002). Toxicology concerns nearly exclusively the incidence of lung and respiratory tract cancer as professional disease of nickel refinery workers.

Therefore, Ni should be used with great precautions in industry since it is exceedingly toxic when inhaled. Moreover, sensitivity from Ni may occur also with dermal absorption (e.g. by bracelets and other fittings), causing allergenic dermatitis.

2.2.13 Thallium

Thallium is an actual poisonous heavy metal, and is a US Environmental Protection Agency (USEPA) priority pollutant. It was discovered in 1861 in Pb-bearing mud with which it has somewhat chemical affinity but, while being a highly toxic element, has been studied to a much lesser degree than other toxic elements such as cadmium or mercury, probably because classical analytical methods have less sensitivity for Tl than for other elements.

Besides current industrial uses in semiconductors, electronics, NMR, glasses etc., over 150 uses and potential applications for thallium and its compounds are recorded. In the past (since 1883), thallium was extensively used for medical purpose: in the treatment of venereal diseases, tuberculosis and malaria, to produce hair loss in the treatment of children ringworm (Peter and Viraraghavan 2005). The use of thallium salts as poisons for rodents and later as insecticides began in 1920 and for the next 45 years remained the principal use for this element (Nriagu 1988).

Thallium is normally associated with sulphide minerals and is often found in mineralized areas interspersed with sulphide deposits. Thallium pollution, therefore, is manmade; the most important anthropogenic sources of thallium are emissions and solid wastes from coal combustion and ferrous and non-ferrous smelting (Oliver 1997).

The ecotoxicological importance of thallium is derived from its high acute toxicity on living organisms, comparable to that of lead and mercury (Peter and Viraraghavan 2005). The major pathway of Tl exposure for animals and humans is the ingestion of plants grown in Tl-contaminated soils (Alloway 2013). A concentration range of 0.17–0.22 μg g^{-1}in garden soils, in Canada, and a range of 0.2–2.8 μg g^{-1}on various soils in the USA were reported (Ferguson 1990). In soils originating from a mining area southwest Guizhou, China, Tl concentrations ranged from 40 to 124 mg kg^{-1}, and from 1.5 to 6.9 mg kg^{-1} in undisturbed natural soils (Peter and Viraraghavan 2005).

The most widely documented case (Alloway 1995) was in West Germany near to a cement works, where Tl was deposited on the soil from the atmosphere. Crops grown on the contaminated soil showed significant amounts of Tl, and the people living there were poisoned by eating them. Many inhabitants suffered ill health, such as depression, insomnia and various nervous disorders (Alloway 1995). Following that episode, in Germany, 1 mg kg^{-1} Tl in soils has been established as the tolerance level for agricultural use (Alloway 2013).

The contents of Tl in most mammalian tissues is reported to be <200 μg kg^{-1}, with level increasing at 500 μg kg^{-1} in skin (Kabata-Pendias and Mukherjee 2007). Mean Tl concentrations in human tissues and fluids range from <1–9 μg kg^{-1} and 0.2–0.4 μg L^{-1}, respectively. The median contents of Tl in kidneys and hair of healthy unexposed individuals have been reported as 0.5 and <1 μg kg^{-1}, respectively (Kabata-Pendias and Mukherjee 2007).

Although several hundred cases of acute and chronic thallium poisoning in man have been recorded, only a few cases resulting from industrial exposures have been reported. Intoxication mainly resulted from skin contact, since it is easily absorbed not only through the gastrointestinal tract but also through the skin. Exposure via inhalation may occur in the extraction of the metal, in the manufacture of thallium-containing rodenticides and thallium-containing lenses, and in the separation of industrial diamonds (Peter and Viraraghavan 2005).

Considering that exposure to high levels of thallium can result in harmful health effects for workers and general people, several World Organizations (e.g. OSHA, ACGIH, NIOSH) and Governments (e.g. in Canada, Russia, Switzerland, USA) have proposed a threshold limit value (TLV) of 0.1 mg/m^3 for thallium in work place air. Yet, a study on chronic health effect of workers exposed to Tl over several years reported nervous system effects, such as numbness of fingers and toes, from breathing thallium. Based on previous studies, the National Institute for Occupational Safety and Health (NIOSH) has recommended that 15 mg/m^3 of thallium be considered immediately dangerous to life and health. However, some studies indicated that there is no thallium mutagenicity or teratogenicity (Peter and Viraraghavan 2005).

Ingested Tl is also harmful to organisms. General exposure occurs through the food chain, especially from fruits and vegetables grown on contaminated soils (Kabata-Pendias and Mukherjee 2007). Accordingly, Swiss and Canadian Governments, established the maximum admissible level of thallium in agricultural soil at 1 mg/kg dry weight.

The toxicity of Tl has not been greatly studied, but its harmful impact has been observed in both humans and animals; moreover, Tl does not play any role in their metabolisms. It has been reported also that Tl is more acutely toxic than Hg, Cd, Pb, Zn and Cu in mammals (Peter and Viraraghavan 2005).

Initial thallium poisoning symptoms in humans are palmar erythema, acne, loss of hair and hallucinations. The principal features of acute thallium poisoning are gastroenteritis, polyneuropathy and alopecia (Kazantzis 1986, 2000). With acute intoxication, there is usually an initial hypotension and bradycardia, followed by hypertension and tachycardia. The central and peripheral nervous system is the main critical organ in thallium intoxication. Major symptoms of Tl poisoning include anorexia, headache, pains in abdomen, upper arms and thighs and even in the whole body. In extreme cases, alopecia, blindness and even death may be caused (Peter and Viraraghavan 2005, and references therein).

The mechanism of Tl poisoning is not very clear but, similarly to other trace metals, Tl binds sulfhydryl groups of proteins and mitochondrial membranes, thereby inhibiting a range of enzyme reactions and leading to a generalized poisoning (Kabata-Pendias and Mukherjee 2007). Possible toxic mechanisms of thallium include ligand formation with proteins, inhibition of cellular respiration, interaction with riboflavin (Vitamin B2), and distribution of calcium homeostasis (Peter and Viraraghavan 2005).

Thallium is excreted mainly through the urine. Thallium excretion via the kidney can be increased upon dosage of potassium chloride, potassium ferricyanoferrate (Prussian Blue) or employment of diuretics (Ghezzi and Marrubini 1979; Hoffman 2003). Hemodialysis and forced diuresis can be an effective means of decreasing the Tl body burden. Polyneuritic symptoms, sleep disorders, headache, fatigue and other signs of psychasthenia were found to be the major health effects associated with increased thallium levels in urine and hair (Peter and Viraraghavan 2005).

2.2.14 Tin

Tin (Sn) is one of the metals of antiquity and its use with copper in the alloy bronze contributed to a major development in human history since the Bronze Age (Alloway 2013).

The distribution of Sn in the Earth's crust averages at 2.5 mg kg^{-1} crustal abundance with two oxidation states (II and IV), of which Sn^{IV} is prevalent in both inorganic and organic compounds; yet, it is a component of few minerals, of which only cassiterite (SnO_2) is commercially important (Adriano 2001). Organometallic complexes with Sn are prevalent in aquatic systems (see this volume, Chap. 2), and contribute to its enrichment in biolites (Alloway 2013).

Malaysia is the main Sn producer in the world, with about 50 % of the total Sn produced. Major uses of Sn are in alloys with Zn and Cd (tinplate and bronze), in vehicle and aerospace industry, and as protective coating agent; organic complexes (e.g. tributyltin, TBT) are used mostly as biocides in agriculture and as antifouling agent in paints, with significant environmental effects (Adriano 2001). Organotins are more ubiquitous sources of Sn in the environment than inorganic forms, and are added to soil by atmospheric dust deposition, fungicidal sprays and sewage sludge spread on agricultural land, constituting the greatest ecotoxicity hazard.

In uncontaminated soils, Sn is largely derived from its content in the bedrocks, and occurs with a range between 1 and 10 mg kg^{-1}. In polluted sites, however, its concentration may be highly elevated, as near smelter areas, where it may achieve up to 1,000 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007). Significant differences in Sn concentrations in soils among various countries have been recorded (0.89 mg kg^{-1} in USA; 2 mg kg^{-1} in andisols of Japan; 1.8 mg kg^{-1} in Swedish topsoils, with a range 0.4–8.6 mg kg^{-1}; 3 mg kg^{-1} in tea soils of Nyasaland (Adriano 2001; Kabata-Pendias and Mukherjee 2007, and references therein).

Tin is fairly immobile in typical arable soils, and is considered a non essential element in plant nutrition; conversely, it is considered as toxic to both higher plants and fungi. Hence, plants tend to accumulate tin in roots when it occurs in easily available forms in soils, and it is poorly translocated to shoots and leaves. Yet, as reported by Tyler (2005), the biological absorption coefficient (BAC = metal in root /metal in soil) for tin is about 0.10. Common ranges of Sn in food plants and cereal grains are reported to be between 0.01 and 0.12 mg kg^{-1} (Kabata-Pendias and Pendias 2001). Conversely, plants growing in mineralized or contaminated soils accumulate Sn to high levels (up to 2,000 mg kg^{-1} in vegetation near Sn-smelters) (Kabata-Pendias and Mukherjee 2007).

The organic tin compounds (OTCs), and particularly TBT, are regarded as contaminants in the environment, with particular reference to the aquatic systems. High contamination of ports and marinas waters has been reported, and TBT residues have been recorded in fish and marine mammals living in contaminated waters, with TBT concentrations up to 2,000 ng g^{-1} in dolphin liver in the Mediterranean sea (Adriano 2001). Given the recognized toxicological importance of OTCs to aquatic biota, the recent detection of TBT in human blood points to its potential effect on human health. Indeed, as stated by Alloway (2013), OTCs behave as enzyme disruptors in many animal species and there is concern about their possible impact on human health.

Recent findings indicate that Sn is likely to be an essential trace element (micronutrient) for mammals, with low mammalian toxicity (Alloway 2013 and references therein). It is reported that mammalian tissues contain Sn in the range 0.1–0.85 mg kg^{-1}, with liver and kidney being the target organs (Kabata-Pendias and Mukherjee 2007). Tin in the inorganic forms is considered as being relatively non-toxic because of their low solubility, whereas some OTCs are considered to be toxic, although information on OTC contents to in human tissues is quite rare.

Human exposure pathways to Sn are mainly from seafood ingestion, with an exception of industrial areas where its concentrations in water and air are elevated; inhalation, and dermal adsorption are minor pathways. Therefore, there is considerable concern about the risk to people consuming a large amount of seafood due to the accumulation of tributyltin (TBT) in marine ecosystems, where up to 78 μg kg^{-1}OTCs in tissues of people from Japan have been reported (Kabata-Pendias and Mukherjee 2007). Mammalian toxicity of OTCs is likely due to their lipophilic character that enables them to penetrate and damage cell membranes, mitochondria, and DNA (Alloway 2013 and references therein).

The typical dietary intake of total Sn in humans is 1–40 mg day^{-1} (Alloway 2013), and the free-hazard inorganic Sn intake has been proposed not to overcome 2 mg kg^{-1} body weight. Canned foods, especially fruits and vegetable products, are considered to be the main source of Sn in the diet. Some canned fruits and juice may contain Sn at the range from 141 to 2,000 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007; Alloway 2013). Higher levels of Sn may be found in some processed food due to the addition of Sn-based preservatives and stabilizers such as stannous chloride (Kabata-Pendias and Mukherjee 2007).

Increased Sn concentration in food may cause acute gastric irritation, impaired reproductivity, and bone strength failure. It is also considered to be genotoxic. Some organotins are highly dermal irritants (Kabata-Pendias and Mukherjee 2007).

As in the case of other elements (e.g. Mo, Se), a dietary deficiency of Sn is likely to induce some disturbances in humans, as hair loss, depressed growth, response to sound, feed efficiency, synergic decrease of other elements in various organs (e.g. Fe in kidney, muscle and spleen) (Alloway 2013).

2.2.15 Tungsten

Tungsten (W) is an emerging PHE about which there is little information, although it is an important strategic element with a wide range of applications in modern science and technology (e.g. metallurgy, lamp filaments and x-ray tubes), and military applications as substitute for the toxic Pb in ammunition (Alloway 2013 and references therein).

It occurs naturally in small concentrations (1–2 mg kg^{-1}) in granitic and sedimentary rocks, while in soils it ranges from 0.5 (in USA) to 85 mg kg^{-1} (in China, that is the biggest utilizer), with even 100–200 mg kg^{-1} in the vicinity of ore-processing plants (Kabata-Pendias and Mukherjee 2007).

There are confusing reports on the phytoavailability of W, but plant uptake and accumulation of W is apparently related to the soil content (Alloway 2013). The common range of W in terrestrial plants is generally very low, being established at the range of $<$1–150 μg kg^{-1}, with concentrations in mosses up to 2,500 μg kg^{-1} (Reimann and de Caritat 1998).

There is some evidence that W, similarly to Mo, might have a biological function in plants, since the behaviour of Mo and W is similar in biochemical processes (Alloway 2013). However, W displays competitive inhibition of Mo, reducing the enzyme catalytic activity. Moreover, some observations on the antagonistic interactions between W and Mo have been recorded, and some substitution by W for Mo has been reported (Kabata-Pendias and Pendias 2001).

The biological functions of tungsten are not well known. Information on adverse and stimulating effects of W in animals and humans are confusing and need more studies. The only available (and contradictory) data for human fluids indicate concentrations of W as follows: 1–390 ng L^{-1} in blood, and 5–320 ng L^{-1}in urine. The reference value for W in urine has been estimated as 860 ng L^{-1}, and the intake of W by individual animals is estimated as 13 μg day^{-1} (Kabata-Pendias and Mukherjee 2007).

It appears that the toxicity of W depends on the solubility of its compounds, and is the highest for polytungstates. Easily soluble W (e.g., from sodium tungstate, Na_2WO_4) is also easily absorbed and is harmful to the nervous system. Dust inhalation is a major exposure pathway for tool-manufacturing workers. The reference value for W in atmospheric dust in Germany has been set at 1 mg m^{-3} for soluble W compounds (Kabata-Pendias and Mukherjee 2007).

The potential environmental effects of W are essentially unknown and not yet thoroughly investigated, but adverse toxicological effects of W (e.g. growth enhancement and moderate toxicity to certain plants and animal species associated with the presence of W) have been recorded recently (Alloway 2013). Fibrotic lung changes are observed in animals under exposure to tungsten-carbide dust

(Kabata-Pendias and Mukherjee 2007). Therefore, its designation as a non-toxic and environmentally friendly metal should be reconsidered.

2.2.16 Vanadium

Vanadium is a polyvalent element, with various oxidation states and a tendency to form oxyanions, a property it shares with Mo, As, W, and P (Adriano 2001). It is ubiquitous in the lithosphere, with some prevalence in igneous rocks (135 mg kg^{-1} on average) and shale (130 mg kg^{-1}), and is widely distributed in nature. Vanadium is largely used in manufacturing steel (80 %), in ceramics, in some alloys with Sn, in chemical industry. Vanadium is the major trace metal in petroleum products. Combustion of coals and oils represents the major source of environmental V enrichment. Industrial activities and anthropogenic emissions have increased significantly V concentrations in soils: the world median is 90 mg kg^{-1}; the range 3–500 mg kg^{-1} (Reimann and de Caritat 1998). Therefore, its potential to enter the food chain is significant, and the number of people exposed to V pollution is increasing (Alloway 2013).

Vanadium is not considered to be an essential element for higher plants; however, some evidence exists that it may be essential to bacteria, fungi and algae as *Azotobacter*, *Aspergillus* and *Scenedesmus* (Adriano 2001). Its content in plants vary broadly: from 10 to 700 mg kg^{-1} (Kabata-Pendias and Mukherjee 2007). Trace concentrations of V have been reported to benefit plant growth, while higher concentrations are toxic (Alloway 2013). Adriano (2001) reports a mean V content of 1 mg kg^{-1} in plants growing on not contaminated soils, with roots having more V than the aerial tissues; no significant correlation was observed between V in soils and in plants, and it is concluded that soils having high V contents should not pose any risk for V bioaccumulation in the food chain.

Vanadium toxicity has proven virtually not existent for plants; however, excess V seems to interfere with chlorophyll synthesis, photosynthetic electron transport, inhibit the plasma membrane ATPase and acid phosphatase (Adriano 2001). Elevated V content in plants is of a great significance since V^{5+} is recognized as a potent inhibitor of several enzymes (Kabata-Pendias and Mukherjee 2007).

Conversely, V is an essential element for some marine organisms, and has long been suspected to have a biological function in humans and domestic animals as well (Steinnes 2009); this explains the increasing interest for V content in plant material.

The critical level of V for livestock has been established at 25 mg kg^{-1} of total diet; if it would be exceeded, the environmental concern about V is primarily due to the air pollution aspect (Adriano 2001; see also this volume, Chap. 1). Although information on the environmental biogeochemistry of V is nearly insignificant, and little is known on the toxicological effects of V in aquatic systems, it is known to have low toxicity to fish (this volume, Chap. 2).

The common pathways of V exposure for the general population are ingestion of food, and dust inhalation during everyday activities; soils containing increased levels of V may result in their increased V exposure. Airborne V can cause irritation of eyes and respiratory track. The threshold level for V toxicity to humans is established at 10–20 mg day^{-1}; requirement is probably less than 2 mg day^{-1} (Alloway 2013).

In humans and animals, V appears to have insulin-like actions at the cellular level, stimulating cellular proliferation and differentiation. Lipids level in blood and abnormalities in bone mineralization have also been reported with V deficiency, suggesting it to play a role in the formation and function of bone and connective tissue (Alloway 2013). Vanadium is easily reduced to V(IV), leading to accumulation of ROS which induce lipid peroxidation, oxidative DNA damage and apoptosis (Franco et al. 2009). Highly oxidized species of V are toxic, especially to nervous system and digestion processes (Kabata-Pendias and Mukherjee 2007).

The USEPA has not listed V as a pollutant requiring urgent research and legislation, because *"there is no evidence that the general population is at risk, either through deficiency of, or overexposure to vanadium"* (USEPA 1991).

2.2.17 Zinc

Among trace elements, zinc is a micronutrient for all biota, and is one of the most important contributors to human health, being essential for the functioning of a great number of enzymes. It is an important component of the earth's crust (24th element in the ranking of abundance), where it is present in rocks and soils in amounts ranging from 40 mg kg^{-1} in acid rocks (granite and gneiss) to 110 mg kg^{-1} in basalts. The average content of soils worldwide is 55 mg kg^{-1}, with typical background concentrations 10–300 mg Zn kg^{-1} (Kabata-Pendias and Mukherjee 2007). Significant differences, up to hundreds of mg Zn kg^{-1} can be recorded at several sites, reflecting the high Zn soil parent material, the presence of mining areas and the anthropic contribution (sewage sludge application, fertilizers, atmospheric emissions from industries and smelters). Yet, besides the limited metal utilization by Romans, and until last century, Zn occurred naturally in soils with the above reported range, and it was only from the middle of nineteenth century that Zn production started to increase dramatically, and has been almost doubled in the last 20 years. The main utilization (50 %) of Zn produced worldwide (11×10^6 tons) is in the galvanic industry, followed by Zn alloys, tyres and rubber (Alloway 2013).

The increased Zn production has released consistent industrial Zn emissions in the atmosphere, and the subsequent deposition onto soil and water determined environmental contamination, with possible ecotoxicological effects. Yet, elevated Zn concentrations can cause toxic effects to plants, soil organisms and microorganisms, and to wildlife, and these ecotoxicological effects precede possible effects on humans. Therefore, risk assessment on Zn should be focuses on the effects to soil biota and soil functioning, before considering human risk.

Zinc in waters is not very toxic to the biota, however, concentrations above 240 μg l^{-1} may have adverse effects on some sensitive organisms, as for example salmons (Kabata-Pendias and Mukherjee 2007 and references therein).

Zinc has essential functions in the metabolism of carbohydrates, proteins, and phosphate in plants; moreover, it is an active component of a variety of enzymes and also influences the permeability of membranes and stabilizes cellular components (Kabata-Pendias and Mukherjee 2007). Therefore, plant response to Zn content, as well as several other trace elements (e.g. Cu, Mo, Se), relies to both excess and deficient Zn levels.

Zinc toxicity and Zn tolerance in plants have been of concern because of the prolonged use of Zn fertilizers, the application of sewage sludge, and other pollution sources, that enhances Zn content of surface soils. Although Zn content of plants vary considerably, Zn uptake and translocation from soil to the aerial parts seems to be effectively limited by a barrier root. Notwithstanding, phytotoxicity is reported relatively often, although no apparent signs of toxicity are present. Typical Zn concentrations in healthy plants are 60 mg Zn kg^{-1}, although an yield reduction is likely to occur at 100–500 mg Zn kg^{-1} (Alloway 2013). The toxicity limit for Zn depends on the plants species and genotypes, as well as on the growth stage. Kabata-Pendias and Mukherjee (2007) report that sensitive terrestrial plants die when soil Zn concentration exceeds 100 mg kg^{-1}, and photosynthesis is stopped when the content is more than 178 mg Zn kg^{-1}. Conversely, some species (e.g. *Thlaspi caerulescens*) are known to hyperaccumulate Zn above 10,000 mg kg^{-1}, without showing any toxic symptoms (McGrath 1995).

The opposite concern is the Zn deficiency in soils and, accordingly, in plants, which is a worldwide problem and is reflected also on human health. Approximately one third of land all over the world, most of which in developing countries (central Africa, middle and far East, southern America), is Zn-deficient. Zinc deficient soils produce food crops that are low in Zn (e.g. below 15 mg kg^{-1} in wheat grains), and consequently Zn deficiency may affect human population residing in that areas and consuming deficient food; consistently, it has been estimated that approximately 1/3 of the world population may be affected. Zinc deficiency in plants is generally observed when the plant contains less than 20 mg $kg^{-1}$of this metal. As previously stated, Zn is not readily translocated from roots to the aerial parts of plant; generally, deficiency occurs firstly in younger leaves. Deficiency symptoms are plant shortness and underdevelopment as the result of an inadequate supply of the growth hormone (Kabata-Pendias and Mukherjee (2007); large yield losses, due to Zn deficiency, have been reported for various crops in USA and Australia.

Zinc is actually essential for mammals, and must be supplied continuously with the diet; indeed, the main pathway of Zn intake is by food ingestion. The required amounts of Zn vary highly (10–200 mg kg^{-1}), and are generally achieved with normal feeding; few cases of Zn deficiency have been reported. Symptoms of Zn deficiency, such as decreased growth, testicular atrophy, alopecia, and dermal lesions have been observed mainly in young animals, as reported by Kabata-Pendias and Mukherjee (2007).

Farm animals are rather tolerant to high Zn levels in the diet. Horses are the most sensitive to the Zn excess, with symptoms as lameness, osteoporosis, and lymphoid hyperplasia; lethal dose is 10 mg Zn kg^{-1} body weight.

Zinc plays a fundamental role in human health, and is regarded as second only to iron in importance; it is a structural component of several enzymes, and participates in the genetic expression as well. It is important during pregnancy, for brain growth in infants, and in immunocompetence (Steinnes 2009). Deficiency of Zn in the human diet was suspected first in 1961 in some Iranian males with a syndrome that includes hypogonadism, dwarfism, hepatosplenomegaly, geophagia and anaemia (Oliver 1997). Other symptoms include skin lesions, increased susceptibility to infections, growth retardation, delayed sexual and skeletal maturation, anorexia, and behavioral effects. Moderate Zn deficiency has been cited as a major aetiological factor in the adolescent nutritional dwarfism syndrome in the Middle East. Yet, in many Central Asian and Middle Eastern countries wheat provides 50 % of the daily energy intake, and the proportion can exceed 70 % in rural areas. A daily portion of 400 g rice for subsistence farmers contributes less than 10 mg Zn day^{-1}, an amount that counteracts a daily consumption of 250 g meat and 500 g dairy products that contributes >20 mg Zn in normal diet (Alloway 2013).

Opposite to deficiency, zinc can also accumulate in human diets to the point of toxicity. Its intake from food varies highly and depends on several factors, but often on interactions with other metals. Important antagonistic relationship is between Zn-Cd and Zn-Cu. Also increased levels of Ca and Mg in food inhibit its availability (Kabata-Pendias and Pendias 2001). The safe recommended intake of Zn is 15 μg day^{-1}(Oliver 1997), while the average content in tissues of the reference man (40–60 years, 70 kg body weight) is 33 mg kg^{-1}. The ingestion or inhalation of larger doses of Zn, especially in forms of inorganic compounds, can be harmful to individuals. It can damage alimentary tracts, and affect diarrhoea and fever (Kabata-Pendias and Mukherjee 2007); the lethal dose for humans is expected to be less than 3 g kg^{-1} body weight.

3 Conclusions

The flux of elements from the soil/plant system to humans through the food chain is rather well known since the early research papers of the last century (see Oliver 1997 and references therein). The effects of most trace metals on human health seem to be less well understood, partly because of the interactions between them, and partly because of the complex metabolic reactions in the human body, although there are several well-documented case studies.

Despite the copious research addressed to this topic, with thousands of papers published in the last decades, there is still a paucity of quantitative information on the relations between elements in soils and human health. Much is known about the functions of most elements in human body, but there is increasing evidence that the interactions among them are more complex than originally thought. Uncertainty is still prevailing, particularly with non essential elements that are “suspected” to be harmful to humans. The non essential elements As, Cd, Hg, Pb have attracted most attention worldwide, due to their toxicity towards living organisms (Adriano 2001).

Other elements (Al, Be, Bi, Sb, Sn, Tl, V, W) are likely harmful, but may play some beneficial functions not yet well known, and should be more investigated.

Among essential elements, Cu, Fe and Zn are of considerable interest. Iron and zinc deficiencies in humans are rather common, and their effects already known. Other essential elements (B, Co, Cr, F, I, Mn, Mo, Ni, Se) have received less attention.

Potentially (and actually) harmful elements are responsible for some of the main threats to human health. Arsenic is a silent killer, that takes 8–14 years to develop arsenicosis, an As-poisoning that affects more than 20 millions people exposed to As through drinking water (Adriano 2001). Skin pigmentation, diarrhoea, and ulcers are the effects appearing during the initial stage. In the most severe cases, arsenicosis causes liver and renal deficiencies or cancer that may lead to death. Dozen of death induced by skin cancer have been reported in recent years.

Cadmium toxicity is considered among the worst human diseases. Epidemiological studies indicate that renal dysfunctions are caused by Cd poisoning, followed by development of osteomalacia. Once in the body, the elimination of Cd is very slow, with a biological half-life of 20 year. The kidney is considered as the critical target organ for Cd-induced cancer in the general population.

Inorganic Hg is effectively absorbed via the lungs, passing through the blood-brain barrier, and subsequently bioaccumulating in the brain, provoking the Minamata disease (mercurialism). Hg is distributed to all tissues within a short time (ca 4 days), its toxic effects are selective to the nervous system (central system and peripheral nerves). Hg bioaccumulates and biomagnifies in the aquatic food chain, that constitutes the predominant pathway of human exposure to Hg.

Lead enters the human body mainly via inhalation and ingestion. The pronounced toxic effects of Pb (plumbism) are manifested as dysfunction in the nervous system. The neurological effects on children of the slow (chronic) accumulation of Pb should be a matter of immediate concern: US EPA recommends that all children up to 6 year of age be screened for Pb at least once yearly. In short, Pb is the greatest cause of global public health concern.

Deficiency in the soil is implicated in selenium disease (selenosis). Shortage of Se in China soils induce Keshan disease. Evidently soils are deficient in Se, as well as the general population diet. Selenium deficiency is also considered to be implicated in the incidence of cancer and heart disease.

Potential toxicity in humans from chronic exposure to Tl, Sn, V, and Sb has also been reported. Also, there is a current question nowadays: does free Al in poor acid soil contribute to Alzheimer's disease? Yes, it does! and soil acidification is a current process today.

As Oliver pointed out (Oliver 1997), "if people were able to optimize their intake of trace elements, then their health might benefit in the same way as it has done through the controlling of infectious diseases during this century". On this roadmap, epidemiological research is providing increasing evidences that cancer is largely a man-made disorder and that it should be susceptible to preventive intervention. The causes appear to be connected largely with our life-style, that is, smoking and eating habits, rather than with specific industrial factors. The major actions are:

- excessive tobacco usage continues to be the principal challenge in the area of lung cancer prevention;
- heavy alcohol intake enhances the risk of upper alimentary and upper respiratory tract cancer among smokers;
- the greater Mn content in soils, the smaller cancer incidence;
- the cancer incidence is raised by a high Zn/Cu ratio;
- The tissue-damaging activity of the rheumatoid arthritis is accelerated by deficient intake of copper, zinc and/or selenium;
- a deficiency of Mn and Se, as well as an abundance of Zn, has a carcinogenic effect?

In conclusion, the role of geochemical factors in the aetiology of human diseases should be deepened, in combination with epidemiologists, soil scientists, social statisticians and other specialists. It has been observed since the 1980s (Lag 1980, 1984, 1987) that there are considerable geographical variations in the distribution of human diseases, and these variations depend on metal distribution, which, in turn, depends on several factors: geology, soils, climate, etc. Arsenicosis is diffused mainly in the Indian region, diabetes and cardiac infarctions are not found among Eskimoes, as well as the rare occurrence of autoimmune diseases such as rheumatoid arthritis, multiple sclerosis and psoriasis, and the cancer pattern is quite different from the EU one. Most diseases (cardiac-infarction, rheumatoid arthritis, multiple sclerosis, psoriasis) in Nordic Baltic are under the influence of Se-supply. People inhabiting coastal areas proved to have higher dietary intake of aquatic foodstuff, to which correspond higher Hg levels in blood and hair.

Epidemiological studies have not revealed any single factor that could account for differences in breast cancer incidence. Rather, a combination of factors (environmental, genetic, behavioral etc.) is likely the triggering cause for the onset of cancer.

Anomalous situations (geochemical hotspots) may occur in the vicinity of mining areas or close to industrial activities, where the metal burden of humans may be augmented through foodstuffs ingestion, drinking water, dust and air inhalation.

If the soil, or food crop, is not contaminated, human exposure through food consumption is substantially below the provisional tolerable intake guideline for the FAO/WHO (WHO 1996), and this is what people should achieve for a sustainable environmental and human life quality.

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