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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.

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 (separated by "-")	Rassessment - PHEs - Bioavailability - Bioaccessibility - Bioaccumulation factor

Chapter 10
Risk Assessment of PHEs

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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 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). AU2

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:

$$\mathrm{RCF} = \mathrm{C\ root}/\mathrm{Csoil}$$
$$\mathrm{SCF} = \mathrm{C\ shoot}/\mathrm{Csoil}$$
$$\mathrm{FCF} = \mathrm{Cfruit}/\mathrm{Csoil}$$

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:

$$\mathrm{DI_{PHEs}} = \mathrm{C_{PHEs}} \times \mathrm{C_{factor}} \times \mathrm{V_{intake}}/\mathrm{BW},$$

where DI is the total PHEs daily intake, C_{PHEs} is the total PHEs concentration in vegetables ($mgkg^{-1}$), C_{factor} is a conversion factor from fresh weight of vegetables to dry weight (0.085 following Rattan et al. 2005), V_{intake} is the daily intake of vegetables (0.350 kg $person^{-1}day^{-1}$), and BW is the average body weight (64 kg). AU4

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. 2013). 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. (2013) 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. 2013). 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

t.1 **Table 10.1** Ranking of risk indexes based on hazard quotients and level of disturbance (Adapted from Moreno-Jimenez et al. 2011)

t.2 Hazard quotients	Risk index	Level of disturbance
t.3 <1 (predicted non-effect)	0	Negligible effects
t.4 1–10 (predicted non-effect)	1	Sensitive species
t.5 1–10 (non-observed chronic effects)	2	Standard species
t.6 10–100 (non-observed chronic effects)	3	Community
t.7 >100 (non-observed chronic effects)	4	Ecological structure
t.8 1–10 (50 % lethal acute effects)	5	Standard species
t.9 10–100 (50 % lethal acute effects)	6	Community
t.10 >100 (50 % lethal acute effects)	7	Ecological structure

344 concentrations (i.e. exposure or daily intake) and toxicity values (i.e. reference dose
345 or acute toxic dose). Consistently, a scoring system of 8 risk indexes (RIs) is defined
346 according to the level of disturbance. RIs from 0 to 4 are based on chronic exposure
347 and RIs from 5 to 7 are based on acute exposure (Table 10.1) (see Moreno-Jimenez
348 et al. 2011, for details).
349 The second step evaluates the overall potential impacts of a contaminated site
350 based on the Impact Index (ImI). This is obtained as the sum of the chronic and
351 acute RIs. Finally, the ImI obtained is assigned to five different categories, from
352 negligible to very high impact according to the following criteria:

$$\begin{aligned} \mathrm{RI(HQchronic)} + \mathrm{RI(HQacute)} = \quad & \mathrm{ImI} \leq 1 \quad \text{(negligible impact)} \\ & \mathrm{ImI} \leq 2 \quad \text{(low impact)} \\ & \mathrm{ImI} \leq 7 \quad \text{(moderate impact)} \\ & \mathrm{ImI} \leq 9 \quad \text{(high impact)} \\ & \mathrm{ImI} > 9 \quad \text{(very high impact).} \end{aligned}$$

353 In order to select the ecological receptors and exposure routes, three protection
354 goals are considered: soil organisms (plants, earthworms and microorganisms),
355 aquatic organisms (algae, invertebrates and fish) and terrestrial vertebrates (birds
356 and mammals).
357 The exposure concentration of soil organisms (Csoil) is represented by the metal
358 concentrations measured in soil. The same Csoil values are also taken into account
359 when assessing the exposure of terrestrial vertebrates.
360 For the aquatic compartment, the exposure for aquatic organisms and terrestrial
361 vertebrates (through drinking water) is represented by the metal concentration in
362 the water samples (Cwater).
363 Three main exposure routes are considered for terrestrial vertebrates: oral food
364 ingestion, soil accidental ingestion and drinking water. Unlike to soil and aquatic
365 organisms, exposure levels for terrestrial vertebrates are estimated using exposure
366 models, admitted by different regulations (EC 2002a, b, 2003). The daily dose of
367 metals through oral food ingestion (DDfood) is calculated by the following
368 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 ~~1881~~, 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).

t.1 **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

572 4. *Risk characterization* – Toxic risks refer to the non-carcinogenic harm AU5
573 occurring due to the exposure level (Chon et al. 2011), and the extent of the harm
574 is indicated by US-EPA (1992, 1998) in terms of hazard quotient (HQnc):

$$\mathrm{HQnc} = \mathrm{E}/\mathrm{RfD}.$$

575 The exposure level (E), is the average daily dose (ADD), and the reference dose
576 (RfD) is the daily dosage that enables the exposed individual to sustain this level of
577 exposure over a prolonged time period without experiencing any harmful effect.
578 The hazard index (HI) is the overall toxic risk resulting from the sum of
579 individual toxic risk due to a single PHE. If HI <1.0, the non-carcinogenic adverse
580 effect is considered negligible.
581 The cancer risks refer to the probability one may develop cancer at a given
582 lifetime exposure level. High carcinogenic risk levels are expressed by the follow-
583 ing equation (US-EPA 1998):

$$\mathrm{Risk} = 1 - \exp(-\mathrm{CDI} \times \mathrm{SF}),$$

584 where CDI is the chronic daily intake over 70 years and SF is the slope factor (see
585 above).
586 Chon et al. (2011) proposed a similar calculation of cancer risk, which is
587 determined as the product of the lifetime exposure level (ADDlife) by the slope
588 factor (SF):

$$\text{Cancer risk} = \mathrm{ADDlife} \times \mathrm{SF}.$$

589 The above model has been widely accepted and used, but has been also
590 improved and adapted to specific purposes, combining human health with ecolog-
591 ical risk assessment (Korre et al. 2002).
592 For example, an integrated procedure has been proposed so far by Covello and
593 Merkhofer (1993), which consists of seven steps, and include:

594 (a) problem formulation;
595 (b) hazard identification;
596 (c) release assessment;
597 (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 $mgkg^{-1}day^{-1}$ (Petts et al. 1997), and AERIS (Aid for Evaluating the redevelopment of Industrial Sites) proposes 0.0035 $mgkg^{-1}day^{-1}$ (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:

$$SI = 1 - CDImin/CDImax$$

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 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:

$$\text{CDI ingestion} = (\text{C} \times \text{IR} \times \text{EF} \times \text{ED/BW} \times \text{AT}) \times 10^{-6}$$
$$\text{CDI inhalation} = \text{C} \times \text{EF} \times \text{ET} \times \text{ED/PEF} \times 24 \times \text{AT}$$
$$\text{CDI dermal} = (\text{C} \times \text{SA} \times \text{AF} \times \text{ABS} \times \text{EF} \times \text{ED/BW} \times \text{AT}) \times 10^{-6}$$
(see Luo et al.2012, for details)

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):

$$\text{CDIingestion} = (\text{C} \times \text{IR} \times \text{EF/AT}) \times 10^{-6}$$
$$\text{CDI inhalation} = (\text{C} \times \text{EF} \times \text{ET} \times \text{ED/PEF} \times 24 \times \text{AT}) \times 10^{3}$$
$$\text{CDI dermal} = (\text{C} \times \text{ABS} \times \text{EF} \times \text{DFS/AT}) \times 10^{-6}$$
$$\text{DFS} = \text{soil dermal contact factor-age-adjusted.}$$

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 (HI = $\sum$ 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 2013) 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); agricultural soils suffer for large use of fertilizers and herbicides (Simon 2013); mine soils are naturally enriched in PHEs that might pose serious problems to human health (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:

$$\log\mathrm{Metal(crop)} = \mathrm{a} + \mathrm{b} \times \log\mathrm{Metal(soil)} + \mathrm{c} \times \mathrm{pH\ soil},$$

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

t.1 **Table 10.3** PHEs concentrations at various sites and guidelines values for different land uses

t.2 Location	Land use	Cd	Cr	Cu	Ni	Pb	Zn
t.3 China (21 cities)	Residential	0.39	69	40	25	55	109
t.4 Europe	Agricultural	0.79	53	195	27	39	68
t.5 Europe (34 cities)	Residential	0.95	59	46	22	102	130
t.6 Canadian guidelines	Agricultural	14	64	63	50	70	200
t.7 Canadian guidelines	Residential	10	64	63	50	140	200
t.8 Canadian guidelines	Industrial	22	87	91	50	600	360
t.9 UK guidelines	Residential	10	100	36	130	85	140
t.10 UK guidelines	Industrial	230	–	–	1,800	–	–
t.11 US-EPA soil screening level	Residential	70	120	3,100	1,500	400	23,000
t.12 US-EPA soil screening level	Industrial	800	1,500	41,000	20,000	800	31,000
t.13 Italy	Mine soils	33	95	412	54	306	657

780 of local residents in the investigated area was in the range 24.10 (highest exposure)
781 −1.87 (lowest exposure) μg/L, as reported by Wang et al. (2011).
782 The modelling proposed (Zhao et al. 2012) provides a reasonable assessment of
783 human health risk by integrating a spatial analysis of contaminant concentrations
784 and land use.
785 Other approaches have become common in the last decade in the Environmental
786 Risk Assessment. One of these is based on the Weight of Evidence (WoE), a system
787 which allows determination of environmental risks by weighting multiple Lines of
788 Evidence (LoEs) that report the quality, extent, and congruence of data
789 (e.g. chemical analyses) that pertain to important aspects of the environment
790 (Smith et al. 2002). Another approach is the Sediment Quality Triad (SQT),
791 which is based on a standard combination of three LoEs, namely Sediment chem-
792 istry, Sediment toxicity and Benthic community structure. Each LoE provides
793 distinct and complementary information about the investigated environment. More-
794 over, the latter is the assessment endpoint that changes in response to exposure to a
795 certain stressor: the model is widely used, and is continuously improved (Chapman
796 et al. 2002).

797 8 Biomonitoring

798 As previously stated, it is difficult to attribute the incidence of a disturbance at any
799 environmental compartment, or some adverse effects to humans, to a particular
800 industrial activity or a chemical substance (Nieuwenhuijsen et al. 2006), as is the
801 case of arbitrary waste disposal on the land (e.g. chromium-rich effluents from
802 leather industry, see f.i. Bini et al. 2008), or emissions in the atmosphere (see
803 Chap. 1, this volume). This is further complicated by other factors such as the fate
804 of chemicals (Alloway 1995), their pattern of dispersion, or the influence of local
805 geological, hydrological and meteorological conditions (Dall'Aglio et al. 1966).
806 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. 2013). 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. 2013). 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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Author Queries

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AU2	AU: References "Menzies (2007), Kabata-Pendias (2011), UK-EA (2003), EC (1881), Commission's White Paper (2001), European Thematic Strategy for Soil Protection (2006), REACH regulatory (2013), US-EPA (2006, 2009)" are cited in text but not given in the reference list. Please provide.	done when necessary some achronims refer to internal reports
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