Chapter I-2

Soils

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. Soil functions as a filtering, buffering, storage, and transformation system protect against the effects of trace element pollution. Soil is effective in these functions only as long as its capacity for cation exchange and its biological activity are preserved. The frequent association of trace element pollution with acid deposition (mainly S, NO_x, and HF) greatly complicates the overall effects in the environments.

Soil is the main source of trace elements for plants both as micronutrients and as pollutants. It is also a direct source of these elements to humans due to soil ingestion affected by "pica-soil", geophagia, dust inhalation, and absorption through skin.

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. Thus, the prediction of trace element uptake by plants from a given growth medium should be based on several biotic and abiotic parameters that control their behavior in soil.

Soils contain trace elements of various origins: *(i) lithogenic* – inherited from the lithosphere (parent material), *(ii) pedogenic* – from lithogenic sources but forms changed due to soil-forming processes, and *(iii) anthropogenic* – elements deposited onto and/or into soils as results of human's activities. Soil processes and anthropogenic factors control the behavior of all these elements (Table I-2.1). It has been assumed that the behavior 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 Pendias 2001).

Soils of several regions of the world (and especially of Europe) 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 behavior of trace elements in soils. The impact of soil acidification, alkalization, salinity and losses of SOM on the uptake of trace elements by vegetation, particularly by crop plants, have already become serious issues for the environment and for human health.

Weathering. Weathering, the basic soil-forming process is a complex set of interactions between the lithosphere, atmosphere, and hydrosphere that occur in the biosphere and are powered by solar energy. It can be described chemically as the processes of

Table I-2.1. Influence of origin of trace elements on their behavior in soil

Origin	Association	Phase	Form[a]	Bioavailablity
Lithogenic	Minerals or bound to minerals	Solid	Residual	Very slight
Pedogenic	CM, SOM, and OX	Solid	Fixed by CM, SOM, and OX	Slight
	Simple and complex ions	Aqueous	Free ions and nonionic forms	Easy
Anthropogenic	Minerals, SOM, and PS	Solid	Mainly exchangeable and chelated	Moderate and easy
Pedogenic and anthropogenic	Simple and complexed ions	Aqueous	Free ions and nonionic forms	Easy

Symbols: *CM* – clay fraction, *SOM* – soil organic matter, *OX* – oxides and hydroxides, *PS* – particle surface.

[a] Operational fractions according to the sequential extraction (Tessier et al. 1979).

Table I-2.2. Geochemical classification of trace elements (based on data after Rankama and Sahama *vide* Fairbridge 1972)

Siderophile		Chalcophile		Lithophile	
6	Mo	**5**	(Ta)	**1**	Li, Rb, Cs
7	Re	**6**	(Mo)	**2**	Be, Sr, Ba, Ra
8	Fe, Ru, Os	**8**	Fe, Ru	**3**	Sc, Y, Lanthanides, Actinides
9	Co, R, Ir	**9**	(Co)	**4**	Ti, Zr, Hf
10	Ni, Pd, Pt	**10**	(Ni), (Pd), (Pt)	**5**	V, Nb, Ta
11	Au	**11**	Cu, Ag	**6**	Cr, Mo, W
14	Ge, Sn, (Pb)	**12**	Zn, Cd, Hg	**7**	Mn
15	As	**13**	Ga, In, Tl	**8**	(Fe)
		14	(Ge), (Sn), Pb	**9**	(Co)
		15	As, Sb, Bi	**10**	(Ni)
				12	(Zn), (Cd)
				13	B
				14	(Ge), (Sn), (Pb)
				15	(As)
				17	F, Cl, Br, I

Bold numbers are the Periodic Table's groups. *Symbols in parenthesis* are given for secondary geochemical tendencies of an element.

dissolution, hydration, hydrolysis, oxidation, reduction, and carbonization. All these processes are guided by the rules of enthalpy and entropy, and they lead to the formation of mineral and chemical components that are relatively stable and equilibrated in the particular soil environment (Pédro 1979). The behavior of elements during weathering and pedogenic processes are highly associated with their geochemical properties, which are base for the geochemical classification (Table I-2.2). The majority of elements reveal lithophilic character, which indicates a tendency to form oxygen compounds, as well as silicates, carbonates, phosphates, and sulfates.

Clay minerals, the principal products of weathering and soil formation, are due to water-rock interaction processes. Two types of compounds released by organic matter or organisms are believed to be particularly involved in weathering processes: carbonic acid, formed from the CO_2 released during decay of organic matter, and organic chelates.

Processes of weathering (degradation) and neoformation of minerals as well as formation of amorphous minerals and organo-mineral substances greatly affect the forms and adsorption of trace elements in soil. The affinity of trace elements for soil constituents is strongly influenced by their electrochemical properties and is closely related to the specific surface area and cation exchange capacity (CEC) of the minerals. Some clay minerals, such as montmorillonite, imogolite, vermiculite, and amorphous allophanes reveal the highest sorption capacity (Table I-2.3).

Table I-2.3. Surface area and sorption capacity (CEC) of some soil minerals[a]

Mineral	Total or specific surface (m^2 g^{-1})	Cation exchange capacity (cmol(+)/kg)
Allophane	100 – 880	5 – 350
Kaolinite	7 – 30	3 – 22
Halloysite	10 – 45	3 – 57
Montmorillonite	280 – 800	80 – 150
Illite	65 – 100	20 – 50
Chlorite	25 – 150	10 – 40
Vermiculites[b]	50 – 800	10 – 200
Gibbsite	25 – 58	50[c]
Goethite	41 – 81 (305–412)[d]	160[d]
Mn-oxides	32 – 300	150 – 230
Imogolite	900 – 1 500	30 – 135
Zeolite	720	350 – 615
Palygorskite	5 – 30	–
Sepiolite	20 – 45	21 – 24
Muscovite	60 – 100	10 – 40
Biotite	40 – 100	10 – 40
Quartz	2 – 3	7

[a] Data sources: Baldock and Nelson 2000, Bolt 1979, Brümmer 1986, Kabata-Pendias and Pendias 2001, Tan 1998, Sparks 1995.

[b] Dioctahedral and trioctahedral vermiculites.

[c] Amorphous Al-oxides.

[d] Amorphous Fe-oxides.

Table I-2.4. Behavior of trace elements in various weathering conditions (after Kabata-Pendias and Pendias 2001)

Degree of mobility	Condition	Trace elements
High	Oxidizing and acid	B, Br, and I
	Neutral or alkaline	B, Br, F, I, Li, Mo, Re, Se, U, V, W, and Zn
Medium	Reducing	B, Br, and I
	Oxidized and acid	Li, Cs, Mo, Ra, Rb, Se, Sr, F, Cd, Hg, Cu, Ag, and Zn
Medium	Mainly acid	Ag, Au, Cd, Co, Cu, Hg, and Ni
	Reducing, with variable potential	As, Ba, Cd, Co, Cr, F, Fe, Ge, Li, Mn, Nb, Sb, Sn, Sr, Tl, U, and V
Low	Oxidizing and acid	Ba, Be, Bi, Cs, Fe, Ga, Ge, La, Li, Rb, Si, Th, Ti, and Y
	Neutral or alkaline	Ba, Be, Bi, Co, Cu, Ge, Hf, Mn, Ni, Pb, Si, Ta, Te, and Zr
Very low	Oxidized and acid	Al, Au, Cr, Fe, Ga, Os, Pt, Rh, Ru,Sc, Sn, Ta, Te, Th, Ti, Y, and Zr
	Neutral or alkaline	Ag, Al, Au, Cu, Co, Fe, Ga, Ni, Th, Ti, Y, and Zr
	Reducing	Ag, As, Au, B, Ba, Be, Bi, Cd, Co, Cu, Cs, Ge, Hg, Li, Mo, Ni, Pb, Re, Se, Te, Th, Ti, U, V, Y, Zn, and Zr

Factors controlling the complex set of chemical weathering processes of minerals in rocks and soils are: *(i)* oxidation, *(ii)* reduction, *(iii)* hydrolysis, *(iv)* hydration, *(v)* solution, and *(vi)* chelation. All of these reactions are controlled by chemical equilibria of the particular environment that can be illustrated by the Eh-pH diagrams for the given geochemical reactions (Garrels and Christ 1965). In various weathering environments, the behavior of trace elements differs (Table I-2.4). The electrochemical properties of elements and the stability of host minerals controls the mobility of trace elements. In an arid environment, physical weathering generally occurs, chemical transformation being rather poor due to the lack of water. In a tropical climate with high temperature and humidity, chemical weathering is favored, resulting in the formation of more clay minerals.

Due to the variable charge of both clays and organic particles, different organo-mineral complexes are formed that may greatly influence element mobility in soils (Tan 1998). This author has emphasized that various bindings between microorganisms, like bacteria and fungi, and soil clays and organic matter, may also occur and may have serious environmental importance.

Pedogenic processes. Pedogenic processes cannot be easily distinguished from weathering processes as they take place simultaneously and at the same sites; most often they are closely interrelated. The principal types of these processes include: *(i)* podzolization, *(ii)* alkalization, *(iii)* aluminization, *(iv)* laterization, *(v)* sialization, and *(vi)* hydromorphic processes. All these processes control the distribution and behavior 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.

The main soil parameters governing these processes are: *(i)* pH and Eh values, *(ii)* amount and mineral composition of the fine granulometric fraction (<0.2 mm), *(iii)* amount and kind of organic matter, *(iv)* oxides and hydroxides of Fe, Mn and Al, and *(v)* microorganisms.

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 (Chuang et al. 1996). In some soils, however, redox potentials have a crucial impact on the behavior of some metals, in particular of Co, Cr, Fe and Mn (Bartlett 1999). The diversity of ionic species of trace elements and their various affinities to complex inorganic and organic ligands make possible the dissolution of each element over a relatively wide range of pH and Eh.

Smith and Huyck (1999) described metal mobility under different environmental conditions. Although it is rather difficult to predict trace element mobility in soils and other terrestrial compartments, the authors referred to the capacity of an element to move with fluids after dissolution in surficial environments. The following conditions and behavior of trace elements were distinguished:

- Oxidizing and acid, pH <3: *(a)* very mobile – Cd, Co, Cu, Ni, and Zn, *(b)* mobile – Hg, Mn, Re, and V, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Oxidizing in the absence of abundant Fe-rich particles, pH >5: *(a)* very mobile – Cd and Zn, *(b)* mobile – Mo, Re, Se, Sr, Te, and V, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Oxidizing with abundant Fe-rich particulates, pH >5: *(a)* very mobile – none, *(b)* mobile – Cd and Zn, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Reducing in the absence of hydrogen sulfide, pH >5: *(a)* very mobile – none, *(b)* mobile – Cd, Cu, Fe, Mn, Pb, Sr, and Zn, and *(c)* somewhat mobile and scarcely mobile – all other metals
- Reducing with hydrogen sulfide, pH >5: *(a)* very mobile – none, *(b)* mobile – Mn and Sr, and *(c)* scarcely mobile to immobile – all other metals

It is evident that Fe/Mn-rich particulates and hydrogen sulfide are most significant among the abiotic factors in controlling trace metal behavior in the terrestrial environment (Sparks 1995; Bartlett 1999). The relationship between Fe contents and some trace metals indicates an impact of soil Fe on the distribution of some trace metals. However, this relationship is significantly high only for Ni (Fig. I-2.1).

All metals that are especially susceptible to redox reactions, e.g., Co, Cr, Fe, and Mn play a significant role in dissolution/precipitation reactions in soil. This is best illustrated by the behavior of Mn:

- The reduction of Mn^{3+} to Mn^{2+} by: Fe^{2+}, Cr^{3+}, Co^{2+}, reduced S, phosphate ligands (e.g., $P_2O_7^{4-}$), phenols, and other easily oxidizing organic compounds
- The oxidation of Mn^{2+} to Mn^{3+} or Mn^{4+} by: any hydroxyl free radicals or atmospheric oxygen
- The Mn^{3+} is an extremely reactive redox species that quickly disappears, either by accepting or by donating an electron

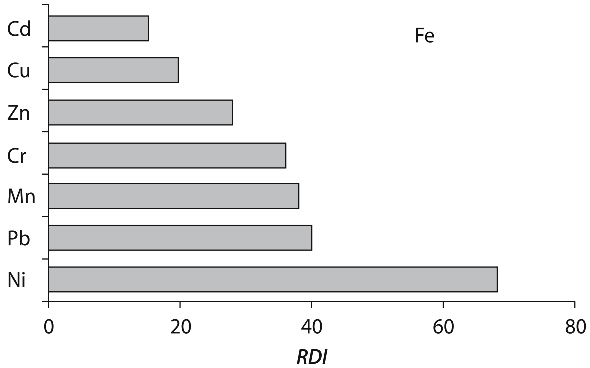

Fig. I-2.1. Relative distribution index (RDI) of statistically-significant relationships between trace metals and Fe content of mineral soils, at the 99% confidence level (after Kabata-Pendias and Pendias 2001)

Other soil minerals such as, carbonates, phosphates, sulfides, sulfates and chlorides may have important influences on the distribution and behavior of trace elements in soils developed under specific geological and climatic conditions (Kabata-Pendias and Sadurski 2004).

Soil biota. Living organisms in soils composed of fauna and flora of various dimensions (macro-, meso-, and micro-) are abundant in soils, especially in surface layers. Functions of living organisms are reflected in biological activity of soils and greatly contribute to bio-physico-chemical processes in soils and soil fertility.

Some species of soil mesofauna (invertebrates) may easily reflect chemical changes in soil and are used as sensitive indicators of the trace metal status of soils (Ma 1987). According to this author the concentration factor (ratio of worms to soil) varies from 0.1 to 190, being the lowest for Pb and the highest for Cd. Depending upon soil properties, this factor is also variable for a given element. Also Edwards et al. (1998) have concluded, based on an earthworm bioassay, that many factors hampered quantitative determination of the degree of metal bioavailability in soil. However, there is always observed a general rule, that Cd is the most available to earthworms (Worms/Soil ratio: 1–37) whereas Cu and Pb are the least available (W/S ratio < 1) (Kabata-Pendias and Pendias 2001).

Trace element contamination causes changes in biochemical parameters of soils such as biomass and species diversity, and microbial activity. Most of these parameters have been used as indices of trace element status of soils, however, there is not always a clear relationship. The impact of soil microorganisms and enzymes on all redox and dissolution/precipitation processes is crucial (Burns and Dick 2002; Naidu et al. 2001; Kostyuk and Bunnenberg 1999). The physicochemical relationship between bacteria and mineral surfaces leads to diverse effects of dissolution and secondary precipitation of trace elements, including changes in their valence and/or conversion into organomineral compounds. The water-extractable F in soils is also positively correlated with the microbial biomass (Tschenko and Kandeler 1997). The microbial activities are associated with following processes:

- uptake or release of an element from a cell
- charge alteration of an ion
- complexation of an element by various produced compounds
- immobilization of an element
- mobilization of an element, often due to the methylation

Biological methylation of some elements, such as As, Hg, Se, Te, Tl, Pb, and In may greatly influence their behavior in soils. Microorganisms reveal a variable and often high sorption capacity to trace elements. Cumulative pools of trace elements in the mass of microbiota has been calculated as follows (g ha^{-1}): Ni, 350; Cu, 310; Zn, 250; Co, 150; Mo, 148; and Pb 8.4, which corresponds to 0.002 to 0.21% of their total abundance in the 20-cm topsoil level (Kovalskiy et al. 1980). Microbioaccumulation of trace elements may be of great importance both in the cycling of elements in soil and in their phytoavailability. Increased levels of trace elements can disturb soil microbial processes. On the other hand, bacterial impact on trace metal behavior may be significant, especially in soil amended with sewage sludge, where bacterial leaching of metals have a practical application (Olson 1986). Apparently, soil microorganisms are more sensitive than other terrestrial organisms to increased levels of metals, thus the assessment of their toxicity has recently become the subject of investigations (Brooks et al. 2005). These authors reported that N fixation in clover is the most sensitive to an excess of Cd and Zn. However, the adverse concentration effects on the potential nitrification rate differs greatly between soils and varied for Cd from 7 to 55 mg kg^{-1} and for Zn from 107 to 1 764 mg kg^{-1}. Increased levels of F (up to 189 mg F kg^{-1}) is reported to decrease microbial activity to 5–20% of those in the uncontaminated soil (Tschenko and Kandeler 1997).

The microbial activity is highly governed by soil properties. As microorganisms are involved in SOM transformations, their activities are associated with organic matter content. Czaban and Wróblewska (2005) observed that microbial transformation of Cd species from the solid phase to species soluble in DTPA was lower in fine-texture soil with low SOM content (1.1% C) than in sandy soil with higher SOM content (4.2% C). Smolders et al. (2004) have suggested that the most significant factor controlling different reactions of microbial processes to increased Zn concentrations is the variable community tolerance. Community level of physiological profiles (CLPPs) of soil microorganisms have not changed under different levels of Cd, Zn, and Pb that indicate their developed tolerance to increased contents of metals (Niklińska et al. 2004).

There are a large number of biologically induced minerals (BIM) especially of Fe and Mn. The major metabolic processes that cause deposition and/or dissolution of Fe and Mn minerals are oxidation and reduction of metal, metal sulfate oxidation, and metal sulfide reduction (Frankel and Bazylinski 2003).

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 (Turnau et al. 1996). The presence of mycorrhizal symbiosis has also been demonstrated in plants, especially hyperaccumulating plants which are being used in the phytoextraction of metals (Skinner et al. 2005; Turnau et al. 2005). Arbuscular mycorrhizal fungi (AMF) exhibit various mechanisms in controlling metal uptake by plants (Biró at al. 2006).

Soil solution. Transfer of trace elements between soil phases should be considered as the main process controlling their behavior and bioavailability. The aqueous phase of the soil (soil solution) is composed of water with a colloidal suspension, free and/or complexed, and dissolved substances of various compounds, including bio-inorganic

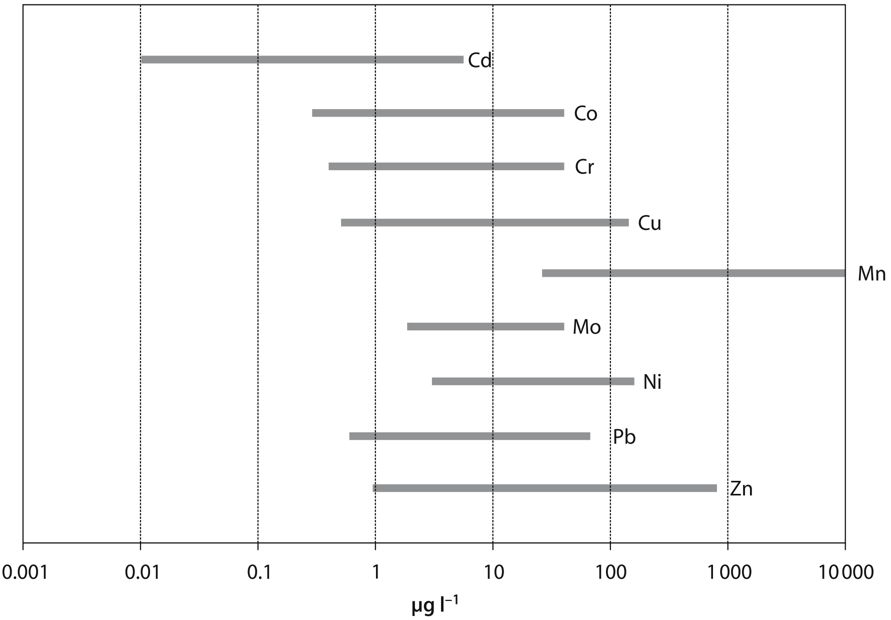

Fig. I-2.2. Common ranges of trace metals in the solution of uncontaminated soils

complexes. Concentrations of trace elements in soil solution are closely correlated with their mobility and availability. However, the soil solution is constantly and rapidly changing in amount and chemical composition of species due to contact with highly diverse soil solid phase and by the uptake of water and ions by plant roots. Data on trace element concentrations in soil solution can be useful for the prediction of their phytoavailability and efficiency/toxicity to crops. Chemistry of the soil solution provides useful information on soil processes that are important to both agricultural and environmental sciences. Mineral particles of biological origin associated with some protists are also found in soil solution (Keller 1997).

Methods used for obtaining soil solution differ widely, and therefore, it is difficult to determine adequate mean contents of trace elements in soil solutions. As Wolt (1994) stated "No one approach to obtain soil solution is appropriate to all applications".

The concentrations of some elements measured in the solution obtained by various techniques from uncontaminated soils are (after Kabata-Pendias and Pendias 2001; Wolt 1994), as follows (in µg l^{-1}): As, 0.01; B, 5–800; Be, 0.1; Cd, 0.08–5; Co, 0.08–29; Cr, 0.01–29; Cu, 0.5–135; Mn, 25–8 000; Mo, 0.0004–30; Ni, 0.2–150; Pb, 0.005–63; Se, 0.06; Sn, 0.2; and Zn, 0.1–750. Most commonly reported concentrations of some metals (Co, Cr, Cu, Mo, Ni, and Pb) in soil solution are in the range between 0.05 and 100 µg l^{-1} (Fig. I-2.2).

In general, the total contents of trace elements in solutions of uncontaminated mineral soils range from 1–100 µg l^{-1}, while in contaminated soils these values can be much higher. In both kinds of soils, however, these are negligible portions of the total soil metals. The transfer factor, calculated as ratios of metals in solution of contaminated soils to their contents in solution of the control soils usually decreases in the following order: Cd > Ni > Zn > Cu > Pb > Cr.

Common ion pairs are mainly hydroxides, however several other complexes are also likely to occur in solutions of various soils (Table I-2.5). Ion pairs, specific forms of oppositely charged ions that are thermodynamically stable can occur in solutions as manifold and of variable compositions. Complex compounds of a relatively high stability constant occurring in soils solution are: BeF_2^0, $CdCl_2^0$, $Cd(OH)_2^0$, $CdSO_4^0$, $Co(OH)_2^0$, $Cr(OH)_3^0$, $Cu(OH)_2^0$, $FeCl_2^0$, $FeCl_3^0$, $Hg(OH)_2^0$, $MnSO_4^0$, $Ni(OH)_2^0$, $PbSO_4^0$, $Pb(OH)_2^0$, $VO(OH)_3^0$, $Zn(OH)_2^0$.

Chemistry of the soil solution provides useful information on soil processes that are important to agricultural and environmental sciences. Data on concentrations of trace elements in a "real" soil solution are useful for the prediction of their availability, toxic effects on crops and on biological activities of soils. McBride et al. (1997) have formed an equation for the metal solubility as a function of some soil properties (e.g., pH, SOM, and total metal content). The SOM content was often, but not always, a statistically significant variable in predicting metal solubility, especially Cu. These authors stated that "Although total metal content alone is not generally a good predictor of metal solubility or activity, it assumed great importance when comparing metal solubility in soils having similar pH and organic matter content".

Table I-2.5. Inorganic ionic species of trace elements and iron in soil solutions (after Kabata-Pendias and Sadurski 2004)

Element	Cations	Anions
Ag	Ag^+	$AgCl_2^-$, $AgCl_3^{2-}$, $Ag(SO_4)_2^{3-}$
As	$\mathbf{As^{3+}}$	AsO_2^-, $HAsO_4^{2-}$, $H_2AsO_3^-$
B		$\mathbf{BO_3^{3-}}$, $H_2BO_3^-$, HBO_3^{2-}
Be	Be^{2+}, $BeOH^+$, $Be_5(OH)_7^{3+}$	BeO_2^{2-}, $Be(OH)_3^-$, $Be(CO_3)_2^{2-}$, $Be(OH)_4^{2-}$
Cd	$CdCl^+$, $CdOH^+$, $CdHCO_3^+$, $\mathbf{CdHS^+}$	$CdCl_3^-$, $Cd(OH)_3^-$, $\mathbf{Cd(OH)_4^{2-}}$, $\mathbf{Cd(HS)_4^{2-}}$
Co	Co^{2+}, Co^{3+}, $CoOH^+$	$Co(OH)_3^-$
Cr	Cr^{3+}, $CrOH^{2+}$	$HCrO_3^{2-}$, CrO_4^{2-}, $Cr(OH)_4^-$, $Cr(CO_3)_3^{3-}$, $HCrO_4^-$
Cu	Cu^{2+}, $CuOH^+$, $Cu_2(OH)_2^{2+}$	$Cu(OH)_3^-$, $\mathbf{Cu(OH)_4^{2-}}$, $Cu(CO_3)_2^{2-}$
F	AlF^{2+}, AlF_2^+	F^-, AlF_4^-
Fe	Fe^{2+}, $FeCl^+$, $Fe(OH)_2^+$, $FeH_2PO_4^+$	$Fe(OH)_3^-$, $\mathbf{Fe(OH)_4^{2-}}$, $Fe(SO_4)_2^-$
Hg	Hg_2^{2+}, $HgCl^+$, $HgCH_3^+$	$HgCl_3^-$, $\mathbf{HgS_2^{2-}}$
I		I^-, I_3^-, IO_3^-, $\mathbf{H_4IO_6^-}$
Mn	Mn^{2+}, $MnOH^+$, $MnCl^+$, $MnHCO_3^+$	MnO_4^-, $HMnO_2^-$, $Mn(OH)_3^-$, $\mathbf{Mn(OH)_4^{2-}}$
Mo		MoO_4^{2-}, $HMoO_4^-$
Ni	Ni^{2+}, $NiOH^+$, $NiHCO_3^+$	$HNiO_2^-$, $Ni(OH)_3^-$
Pb	Pb^{2+}, $PbCl^+$, $PbOH^+$	$PbCl_3^-$, $Pb(CO_3)_2^{2-}$
Se		$\mathbf{SeO_3^{2-}}$, SeO_4^{2-}, $\mathbf{HSe^-}$, $HSeO_3^-$
V	VO^{2+}	$H_2VO_4^-$, HVO_4^{2-}, VO_3^-
Zn	Zn^{2+}, $ZnCl^+$, $ZnOH^+$, $ZnHCO_3^+$	ZnO_2^{2-}, $Zn(OH)_3^-$, $ZnCl_3^-$

The symbols given in bold letters indicate the ions occurring only in extreme pH and Eh regimes.

The partitioning of trace elements between the soil and soil solution determines their mobility and bioavailability. However, the prediction of properties of soil solution is rather difficult, and sophisticated techniques must be applied for the extraction of undiluted soil solution as well as special conditions for the storage of soil/sediment samples.

The concentrations of free metal species in soil solution are controlled by several factors of which the most significant are thermodynamic/kinetic parameters. Mathematical approaches to modeling soil solution – solid phase equilibria are broadly described in numerous publications (Sposito et al. 1984; Waite 1991; Wolt 1994; Sparks 1995; Suarez 1999), and several models for calculating activity coefficients for trace metals have been overviewed and discussed. Waite (1991) concluded that: "mathematical modeling clearly has a place in extending the information that can be obtained on trace element species distributed by other methods and will be of practical use in systems for which determination of concentrations of all species of interest is impossible because of sensitivity constraint or other analytical difficulties".

Trace element speciation. As soils consist of heterogeneous mixtures of different organic and organic-mineral substances, clay minerals, oxides and hydroxides of Fe, Mn, and Al, and other solid components as well as a variety of soluble substances, the binding mechanisms for trace elements and forms of their occurrence in soils are manifold and vary with the composition and physical properties of soils.

Great confusion exists in the use of the term "speciation" in environmental sciences. According to Ure et al. (1993), the definition of speciation in the context of soils, sediments and sewage sludge refers to processes of identification and quantification of the different defined species, forms and phases in which an element occurs in investigated materials. However, most often "speciation" also means the description of the amounts and kinds of existing forms of trace elements. Whichever approach is taken, the species, forms or phases are defined: *(i)* functionally, *(ii)* operationally, and/or *(iii)* as specific chemical compounds or oxidation states.

Considerable controversy has developed over selective extraction methods to determine the amounts of trace elements associated with various soil phases and compounds. Determination of various fractions of these elements is broadly used, especially for two purposes: to link with the potential bioavailability, and to predict the mobility affecting their transport within the soil profile and to ground waters. The speciation of trace metals in soils is not stable and relatively easy transformation of their forms in soils is observed.

Various concentrations of different reagents and variable soil/solution ratios over broad pH ranges are used for the selective extraction procedures. In consequence, each method gives operational groups of metals that are not comparable. However, each method gives an approximate fractionation of metals occurring in soils, from easily mobile to strongly sorbed/fixed forms. All these methods are used for the determination of commonly distinguished metal species which are, in general: *(i)* easily exchangeable or water soluble, *(ii)* specifically sorbed, e.g., by carbonates, or phosphates, *(iii)* organically bound, *(iv)* occluded by Fe/Mn oxides and hydroxides, and *(v)* structurally bound in minerals (residual).

Metal species resulting from the partitioning of the total metal content that is associated with various solid soil fractions are usually estimated using specific operational extraction procedures. Comprehensive reviews of methods applied for sequential extraction have been given in several publications (Tessier et al. 1979; Salomons and Förstner 1984; Brümmer 1986, 1986; Kersten and Förstner 1991; Sauvé 2001; Mortvedt et al. 1991; Ure and Davidson 1995).

Some authors distinguish also water-soluble fraction of metals, which actually corresponds to a dilute salt solution extract (Boust and Saas 1981; Mathur and Levésque 1988). Solid phase fractionation methods allow separate additional fractions of metals, such as silicate clays, sulfides, and specifically sorbed or precipitated forms.

Various methods used to evaluate the pool of soluble (phytoavailable) trace elements in soils are based mainly on extraction by various solutions at different concentrations (as described by Houba et al. 1999; McLaughlin 2001):

- Acids: mineral acids at various concentrations
- Chelating agents: e.g., EDTA, DTPA
- Buffered salts: e.g., AAAc
- Neutral salts: $CaCl_2$, $MgCl_2$, NH_4NO_3, $Sr(NO_3)_2$
- Other extractants, like *Coca Cola*, which has been proposed for use in routine soil testing

Several other techniques like electrodialysis, diffusion through membranes, diffusion gradients in thin films as well as bioindicators have also been proposed (Kabata-Pendias and Sadurski 2004).

According to Houba et al. (1999), solutions of a neutral salt, such as $CaCl_2$, are the most suitable for the extraction of bioavailable pools of metals. Karczewska (2002) has reported the highest proportions of metals (up to above 90% of total contents of Cu, Pb, and Mn; and up to above 60% of Zn) to be extracted from surface horizons of polluted soils by the following solutions: 0.02 M EDTA-Na, 1 M HCl, and 0.1 M HCl.

Depending upon the variability in physico-chemical characteristics of metals, their affinity to soil components governs their speciation. Rule (1999) broadly reviewed recent literature on the phase distribution of trace metals in soils, and concluded that the highest proportions of most metals are found either in the residual or in Fe-Mn oxide fractions in both natural and contaminated soils. A high association with the exchangeable fraction was observed only for Cd in a few soils. Cadmium and Zn were also abundant in the carbonate form in some soils. The association of metals with organic matter was generally low for Cd and Ni, and high for Cu. Herbert (1997) found that Cu, Pb, Ni and Zn are bound primarily to cation exchange sites and to organic matter in the reference soil, while in the polluted soils, metal partitioning is dominated by Fe oxide fractions, despite the high organic matter content. However, the proportion of different species is highly variable and depends on elements, soils, and seasons (e.g., climatic conditions).

Kernsten and Förstner (1991) presented the affinity of metals for different minerals:

- Sulfides of Fe and Pb are likely to sorb most metals
- Carbonates fix predominantly Cd, Cu, Pb, and Mn
- Fe/Mn nodules (deep-sea) sorb mainly Fe, Mn, Cu, Zn, Ni, and Cr
- Fe crystalline oxides hold, as reducible fractions, Fe, Mn, Cd, and Zn
- Chlorite reveals variable capacity to fix metals, predominantly as reducible and residual fractions

It is necessary to emphasize, however, that during analytical procedures several artifacts can occur and create unreal results.

The speciation of trace metals in soils is related to their biogeochemical reactivity and to several physicochemical soil conditions. The determinations of various fractions of these elements are broadly used especially for two purposes, to link with the potential bioavailability, and to predict the mobility affecting their transport to groundwater. The speciation of metals in soils is not stable, and the transformation of their forms in soil is observed. An example can be the relatively rapid transformation of metals (Cd, Zn, Pb) applied to soils as oxides into exchangeable and carbonate species (Kabata-Pendias and Pendias 2001).

Trace element speciation analysis provides a basis for the description of forms and compounds in which they occur in soils. Other definitions are also used to define the properties of trace elements in soils. The general term "availability" has been recently described as: geoavailability, geochemical availability, biogeochemical availability and bioavailability (Wolt 1994; Smith and Huyck 1999). "Geoavailability" is defined as that portion of the total content of a chemical element or a compound in an earth material that can be liberated to the surficial (soil) environment. "Geochemical availability" is related to that fraction of a chemical element that participates in transport processes affecting the spatial distribution and changes over time. "Biogeochemical availability" is defined as the quantity-intensity factor calculated as a ratio of total content to the concentration of a trace element in soil solution. "Bioavailability" refers to the fraction of a trace element that is or has been available to an organism.

In spite of intensive investigations (sequential extractions and specific extractants) on the prediction of the availability of trace metals, good estimations of general bioavailability of a given trace element are needed. However, based on results of long-term experiments, some specific extractants, as well as weak neutral salt solutions seem to be adequate to assess the impact of trace elements on plants and soil bioactivity.

Trace element interactions. Interactions between chemical elements both micro and macro may have an antagonistic and/or synergistic character. Although most of these interactions are associated with physiological processes in plants some reactions are also related to pedochemical processes. These are mainly impacts of major elements on the distributions and forms of some trace elements in soils. The main antagonistic interactions (or relationships) in soils, often associated with microbiota, are reported by Kabata-Pendias and Pendias (2001) for:

- Ca and B, Ba, Cd, Co, Cr, Cs, Li, Mn, Ni, Pb, Sr, and Zn
- P and As, Cr, Hg, Mo, Mn, Ni, Pb, Rb, Se, and Zn
- Mg and Cr, Mn, Zn, Ni, Co, and Cu
- Fe and Co, Ni, Mn, Mo, Cr, and Zn
- Mn and As, Cr, Cu, Mo, Ni, V, and Zn
- Cu and Mo
- Cd and Zn

Interactions between elements in soils are of multivariant character but may be mainly attributed to the sorption sites of soils particles and also to the surface root cells and to root exudates.

Trace element occurrence. Contents of trace elements in soil materials from natural as well as from contaminated sites show great variability in both the horizontal and vertical dimensions. The heterogeneity of soils, especially at the microscale, creates real problems in representative sampling that have serious impacts on the reproducibility and comparability of analytical data. This is of great concern in the assessment of background (pristine) contents of trace elements in soils. Although a real pristine status of trace elements in soils does not exist nowadays, even in remote regions, some values of trace elements in "uncontaminated" soils are prerequisites as reference values for the evaluation of soil pollution. Several methods were developed to calculate background contents of trace elements in soils. The best-known methods are, as presented (from various sources) by Kabata-Pendias and Pendias (2001):

- GB: Geochemical Baseline
- GD: Index of Geochemical Distribution
- IGL: Index of Geochemical Load
- IPD: Index of Pedogenic Distribution
- PEF: Pedochemical Enrichment Factor
- FSP: Factor of Soil Parameters
- SCV: Spatial Concentration Variability
- GIS and MA: Geographical Information System and Multivariate Analyses

The fine granulometric soil fraction (<0.02 mm) is composed mainly of clay minerals and therefore exhibits a high ability to bind trace ions. Thus, in most soils there is observed a positive correlation between the content of the clay fraction and amounts of trace elements, in particular cations. The highest relationship, more than 50% of relative distribution index (RDI) has been documented for Zn, Fe, Ni and Cr (Fig. I-2.3). This is clearly demonstrated in "background" contents of trace elements in sandy (low content of clay fraction) and loamy (high contents of clay fraction) soils (Table I-2.6). Clay minerals and other aluminosilicates represent several groups of minerals of variable structure, and can be both primary (inherited from parent material) and secondary (formed in soils).

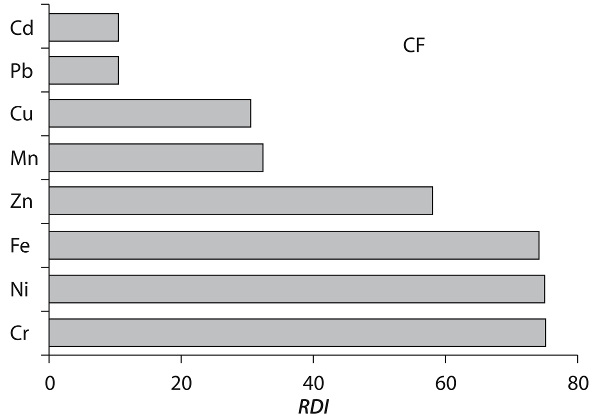

Fig. I-2.3. Relative distribution index (RDI) of statistically-significant relationships between trace metals and content of clay fraction, <0.02 mm (CF) in mineral soils, at the 99% confidence level

Table I-2.6. Mean (arithmetic) and maximum values (mg kg^{-1}) of the background contents of some trace elements[a] in two common soil kinds on the worldwide scale

Element	Podzol, sandy soils (<20% fraction <0.02 mm)		Cambisols, loamy soils (>20% fraction <0.02 mm)	
	Mean	Maximum	Mean	Maximum
As	4.4	30	8.4	27
B	22	134	40	128
Ba	330	1 500	520	1 500
Cd	0.37	2.7	0.45	1.61
Co	5.5	65	10	58
Cr	47	530	51	1 100
Cu	13	70	23	100
F	130	1 100	385	800
Hg	0.05	0.7	0.1	1.1
I	2.3	10	1.7	8.3
Li	22	72	46	130
Mn	270	2 000	525	9 200
Mo	1.3	3.7	2.8	7.2
Ni	13	110	26	110
Pb	22	70	28	70
Sc	5	30	8	20
Se	0.25	1.32	0.34	1.9
Sr	87	1 000	210	1 000
V	67	260	76	330
Zn	45	220	60	362

[a] Related to aqua regia soluble elements or other forms defined as total contents.

Organic matter also plays a significant role in sorption of trace elements. Most kinds of SOM have a relatively high specific surface area and common range of CEC (at pH 8) is calculated to be in the range from 60 to 300 cmol(+) kg^{-1} (Baldock and Nelson 2000). The CEC values of SOM are governed to a great extent by acidity and increase from 36 cmol(+) kg^{-1} at pH 2.5 to 215 cmol(+) kg^{-1} at pH 8 (Sparks 1995). The contribution of SOM to the CEC is significant, and varies from 25 to 90%, depending on soil categories.

In several soils or in some layers of soil horizons, oxides and hydroxides of Fe and Mn play very important roles in the distribution and behavior of trace elements, and may fix great amounts of some trace metals, especially of Co (up to 0.3%) and Ni (up to 0.5%) (see Table II-7.3). The Fe and Mn hydroxides occur in soils as concretions and/or nodules, as well as coatings on soil particles, and as fillings in cracks and veins.

The large database of recent surveys of trace elements in soils allows general estimations to be made of the concentration means in soils of various countries (Table I-2.7). The background populations of trace elements in soils, both uncontaminated and contaminated, seem to be log-normally distributed, though with much higher extremes in contaminated ones.

Many elements are likely to be accumulated in the surface soil layer (SEFcrust > 1). However, some elements, e.g., Te, Se, Pd, Pt, Cd, Ge, Cl, As, Sb, Br, and Hf are significantly enriched in soils as compared to their crustal abundance (SEFcrust from >2 to 16).

The surface soil layer, enriched in organic matter (mainly humus) is an important sink for trace element deposition from the atmosphere. The investigation of trace metals in organic surface soils in Fennoscandia, sampled in 1995, has shown a general impact of long-range transport of pollutants (Steinnes and Rühling 2002). There was observed a much smaller influence of regional differences in geochemistry of the underlying bedrocks than of aerial pollution. The ranges of trace metals were following (in mg kg^{-1}, expressed in range of < and >): As, 0.4–2; Cd, 0.2–1; Cu, 4–12; Fe, 1 000–5 000; Hg, 0.1–0.5; Ni, 2–10; Pb, 10–60; V, 3–15; and Zn, 30–110.

Soil pollution. Both terms, contamination and pollution, are used synonymously. According to the definition given by Knox et al. (1999) trace element contaminated soils are not considered to be polluted unless a threshold concentration exists that begins to affect biochemical and biological processes.

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). Ernst (1998b) comprehensively reviewed ancient metal contamination from the Bronze Age to Roman times. Almost all human activities have resulted in increased levels of trace elements in soils. 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 (Ma and Uren 1998; Ramos et al. 1994). Sources of trace inorganic contaminants (TIC) are:

- Industrial activities
  - Mining and smelting of metalliferous ores
  - Brick and pipe manufacture
  - Cement manufacture
  - Others, e.g., ceramic, glass, chemical plants
- Power generation
  - Burning of fossil fuel
  - Nuclear reactors
  - Incineration of municipal wastes
- Agricultural practices
  - Soil amendment with sewage sludge
  - Application of manure
  - Mineral fertilizers
  - Pesticides, fumigation
- Transport and urban-derived pollution
- Long-range transport of pollutants

Energy and mineral consumption by humans is the main cause of contamination of the biosphere. The ratio of mined trace elements to their deposition in contemporary geological sediments may indicate their potential threat to the environment. Based on such calculations, Bowen (1979) has found that the most dangerous to the biosphere are following elements: Ag, Au, Cd, Cr, Cu, Hg, Pb, Sb, Tl, and Zn. Among the

Table I-2.7. Commonly reported mean background contents of trace elements in continental crust and surface soils ($mg\,kg^{-1}$)

Element	Crustal average[a]	A	B	C	D	E	SEFcrust
Antimony, Sb	0.2	0.62	0.25	0.78	–	0.66	2.89
Arsenic, As	1.8	4.7	3.8	–	–	7.2	2.91
Barium, Ba	400	362	608	350	–	580	1.19
Beryllium, Be	3	1.9	1.3	1.4	–	0.92	0.46
Bismuth, Bi	0.2	0.7	0.16	0.33	–	–	1.98
Boron, B	15	–	5.1	–	–	33	1.27
Bromine, Br	2	–	–	–	10.5	0.85	2.84
Cadmium, Cd	0.1	1.1	0.17	0.33	0.18	<0.01–41	4.40
Cerium, Ce	60	49	60	52	89	75	1.08
Cesium, Cs	3	8	1.7	5.4	4.6	–	1.64
Chlorine, Cl	130	380	–	–	–	–	2.92
Chromium, Cr	100	42	22	58	86	54	0.52
Cobalt, Co	10	6.9	7.1	18	17	9.1	1.16
Copper, Cu	55	14	17	48	109	25	0.77
Dysprosium, Dy	3	0.7	4.1	3.9	5.6	–	1.19
Erbium, , Er	2.8	1.6	2.2	2.2	3.1	–	0.81
Europium, Eu	1.2	1.2	0.79	1.2	1.5	–	0.98
Fluorine, F	625	264	–	–	269	430	0.51
Gadolinium, Gd	5.4	2.2	3.4	4.2	5.5	–	0.71
Gallium, Ga	15	1.2	8.9	20	31	17	1.04
Germanium, Ge	1.5	1.2	19	–	1.9	1.2	3.88
Gold, Au	0.004	0.002	<0.005	–	0.002	–	0.75
Hafnium, Hf	3	3	7.6	2.5	12.7	–	2.15
Holmium, Ho	0.8	1.1	0.87	0.73	1	–	1.16
Indium, In	0.06	–	<0.04	0.09	0.11	–	1.33
Iodine, I	0.5	2.4	–	–	13	1.2	11.1
Iridium, Ir	0.0001	–	<0.04	–	–	–	–
Lanthanum, La	30	26	33	23	34	37	1.02
Lead, Pb	14	25	18	24	22	19	1.54
Lithium, Li	20	28	17	13	24	24	1.06
Lutetium, Lu	0.3	0.34	0.39	0.31	0.52	–	1.30
Manganese, Mn	900	418	411	–	535	550	0.53
Mercury, Hg	0.07	0.1	0.043	–	0.053	0.09	1.02
Molybdenum, Mo	1.5	1.8	0.58	1.3	1.6	0.97	0.83
Neodymium, Nd	28	19	29	22	32	46	1.06

Table I-2.7. *Continued*

Element	Crustal average[a]	A	B	C	D	E	SEFcrust
Nickel, Ni	20	18	13	26	25	19	1.01
Niobium, Nb	20	12	12	10	25	11	0.70
Osmium, Os	0.0005	–	–	–	–	–	–
Palladium, Pd	0.004	–	0.04	–	0.003	–	5.38
Platinum, Pt	0.004	–	<0.04	–	0.002	–	5.25
Praseodymium, Pr	8.2	7.6	7.7	5.3	8.4	–	0.88
Rhenium, Re	0.001	–	<0.04	–	–	–	–
Rhodium, Rh	0.001	–	<0.04	–	–	–	–
Rubidium, Rb	90	50	116	70	18	67	0.71
Ruthenium, Ru	0.001	–	<0.04	–	–	–	–
Samarium, Sm	4.7	3.1	4.5	4.4	6.7	–	0.99
Scandium, Sc	11	9.5	10	21	–	8.9	1.12
Selenium, Se	0.05	0.7	0.23	–	0.47	0.39	8.95
Silver, Ag	0.06	0.1	0.11	0.1	0.05	–	1.50
Strontium, Sr	375	147	163	190	–	240	0.49
Tantalum, Ta	2	1.1	1.1	1.7	2.3	–	0.78
Tellurium, Te	0.005	–	<0.08	–	–	–	16.0
Terbium, Tb	0.6	0.4	0.48	0.74	0.9	–	1.05
Thallium, Tl	0.5	0.6	0.23	0.49	0.36	–	0.84
Thorium, Th	7.2	8.2	8.1	9	11	9.4	1.27
Thulium, Tm	0.5	0.46	0.32	0.3	0.5	–	0.79
Tin, Sn	2.5	–	1.8	2.4	–	1.3	0.73
Titanium, Ti	4400	–	3700	–	15480	2900	1.67
Tungsten, W	1.5	1.2	1.3	1.3	1.4	<0.16–0.17	0.71
Uranium, U	2	3.7	4.4	1.9	2.9	2.7	1.56
Vanadium, V	135	60	69	180	320	80	1.05
Ytterbium,Yb	2.2	2.1	2.9	2.1	3.2	3.1	1.22
Yttrium, Y	33	12	27	21	27	25	0.68
Zinc, Zn	70	62	65	89	73	60	1.00
Zirconium, Zr	165	300	308	92	421	230	1.64

[a] Values are compiled from Mason and Moore (*vide* Hedrick 1995) and Reimann and Caritat (1998). Given are mean values for various soils in different countries: *A* – worldwide data after Kabata-Pendias and Pendias (1999, 2001); *B* – agricultural soils of Sweden after Eriksson (2001a); *C* – agricultural soils of Japan, after Takeda (2004); *D* – medians for soils of Parana State, Brazil, after Licht (2005); *E* – data for the U.S. soils, after Burt et al. (2003) and Shacklette and Boerngen (1984); *SEFcrust* – soil enrichment factor in relation to crust mean concentrations (ratio of "grand" mean soil content to upper continental crust content).

Table I-2.8. World mining of the elements in 2000 and 2003 (t, kt, Mt yr^{-1})

Element	2000	2003	Element	2000	2003
Aluminum, Al	139 Mt	148 Mt	Lithium, Li	138 kt	–
Antimony, Sb	130 kt	155 kt	Manganese, Mn	21.38 Mt	24.35 Mt
Arsenic, As	27.9 kt	38.8 kt	Mercury, Hg	2.2 kt[a]	–
Barium, Ba	266 t	–	Molybdenum, Mo	–	127.4 kt
Beryllium, Be,	2.26 t	2.55 t[b]	Nickel, Ni	1.14 Mt	1.2 Mt
Bismuth, Bi	4.28 kt	4.47	Niobium, Nb	–	27 kt
Boron, B	4.2 Mt	4.4 Mt	Palladium, Pd	140 t	230 t
Bromine, Br	540 kt	–	Platinum, Pt,	365 t	–
Cadmium, Cd	19.21 kt	16.87 kt	Rhenium, Re	43 t	39.3 t
Cesium, Cs	5.9 Mt	–	Selenium, Se	–	2.31[d] kt
Chromium, Cr	13.91 Mt	15.83 Mt	Silver, Ag	17.75 kt	18.21 kt
Cobalt, Co	35.6 kt	43.03 kt	Strontium, Sr	320 kt	–
Copper, Cu	13.23 Mt	13.68 Mt	Tantalum, Ta	1.22 kt	–
Fluorine, F	4.4 kt	4.5 kt[c]	Thallium, Tl	15 t	–
Gallium, Ga	70 t	203 t	Tellurium, Te	313 t	243 t
Germanium, Ge	2.4 kt	–	Tin, Sn	247.3 kt	257.7 kt
Gold, Au	–	2.35 kt	Titanium, Ti	4.31 Mt	4.22 Mt
Hafnium, Hf	145 t	335 t	Tungsten, W	35.74 kt	50.0 kt
Indium, In	335 t	–	Uranium, U	34.86 kt	35.37 Kt
Iodine, I	18 kt	–	Vanadium, V	43 kt	–
Iron, Fe	571 Mt	–	Zinc, Zn	8.73 Mt	9.17 Mt
Lead, Pb	3.1 Mt	6.8 Mt	Zirconium, Zr	750 kt	1.1 Mt

t – Metric ton, *kt* – thousand tons, *Mt* – million tons. Sources: WMSY (2004), and USGS (2004).

[a] Data for 1999.

[b] Given as Be-ores.

[c] Given as fluorspar.

[d] Data for 1995, after Reimann and Caritat (1998).

least dangerous elements are: Ga, La, Nb, Sr, Ta, and Zr. Data for the world mining of trace elements differ between 2000 and 2003, and also depend on the source of data (Table I-2.8). The residence time of trace metals in surface soils depends on several soil properties of which pH and Eh parameters are the most significant. As Bowen (1979) has reported, the maximum residence time (in years) may be: *(i)* 1 000 for Cd, Hg, and Be, *(ii)* 3 000 for Zn and As, and *(iii)* 6 000 for Pb.

The natural sources of trace elements are associated mainly with continental and volcanic dust, although some elements easily released from the ocean surface (e.g., I and Se) contribute to their elevated contents in soils of some ecosystems. According to Korzh (1991) the deposition of trace elements from oceans *via* the atmosphere onto soils are at the rate (in t yr^{-1}):

- 10^4–10^6: Li, Rb, Mo, I, Ba, B, Br, F, and Sr
- 10^2–10^3: Cr, Mn, Fe, Cu, Ga, Se, Y, Zr, Cd, W, TI, Ti, V, Ni, Zn, As, Sb, Cs and U
- 1 –10: Be, In, Eu, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, Hf, Ta, Re, Au, Hg, and Pb

Cosmic particles that are deposited on the Earth at rates of 100–1 000 t d^{-1} may also be, though mainly unrecognized, a source of some trace elements (Dodd 1981). However, as indicated by data presented by Kjølholt (1997), the atmospheric deposition of trace metals from natural sources is negligible compared with their loads with products used for soil amendment (Table I-2.9). The highest amounts of trace metals are added to agricultural soils with the application of sewage sludge, compost with biosolids, and fly ash (Table I-2.10). This may change, however, depending on the soil system and on variable factors that affect the trace element status of soils (Fig. I-2.4). Inputs of trace metals to soil on both animal and crop farms may be quite significant, however

Table I-2.9. Loads of trace elements (g ha^{-1} yr^{-1}) from various products applied on Danish agricultural soils and from aerial deposition (after Kjølholt 1997)

Source	Cd	Cr	Cu	Hg	Ni	Pb	Zn
Sewage sludge	2	65	390	2.4	50	96	1 900
Fertilizers (P_2O_5)	0.25	3.3	67	≪0.01	0.61	0.26	4.3
Manure, cattle + pigs	1.9	11	630	<0.4	21	3.8	820
Compost, all	3.2	53	320	0.66	89	140	970
Compost, MSW[a]	3.8	98	320	1.2	150	350	1 200
Liming	0.6	<1	3	0.003	4	<3	13
Irrigation	0.04	0.6	1.2	0.008	3.3	1	21
Emissions from tractors	0.009	0.009	0.043	0.0004	2.7	0.13	0.11
Atmospheric deposition	0.15	10	7	0.07	7	12	4

[a] *MSW* – Municipal Solid Waste.

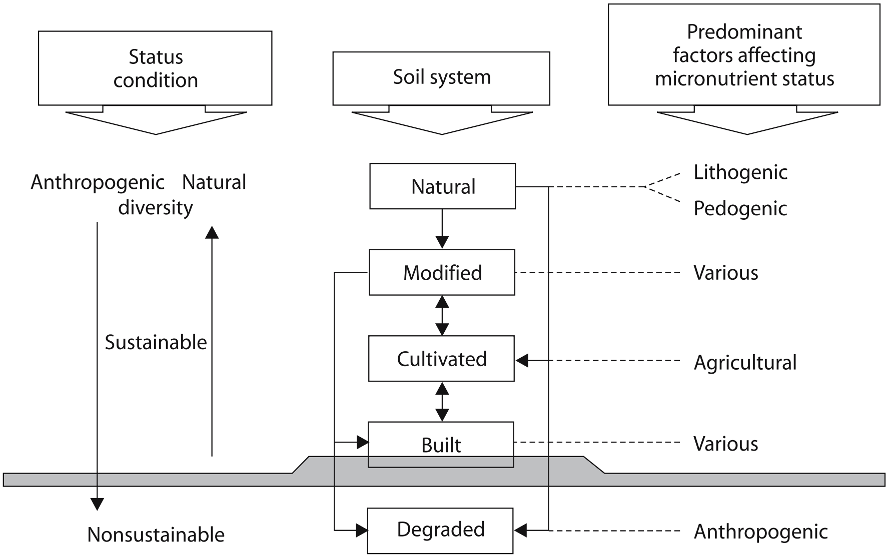

Fig. I-2.4. Factors affecting the trace element status of various soil systems

Table I-2.10. Mean contents of trace elements in fertilizers, sewage sludge, and fly ash (adopted from Eriksson 2001a, unless otherwise stated)

Element	NPK-S[a]	P20[b]	SS[c]	SM[d]	Fly ash[e]
Antimony, Sb	0.031	0.20	2.4	0.16	3.8
Arsenic, As	0.59	9.1	4.7	1.3	60
Barium, Ba	3.3	123	310	72	398
Beryllium, Be	0.066	0.14	<0.6	0.13	11
Bismuth, Bi	0.003	0.06	0.73	0.013	–
Boron, B	24	7.6	61	28	509
Cadmium, Cd	0.05	0.11	1.2	0.25	1.3
Cerium, Ce	27	1027	24	7.1	112
Cesium, Cs	0.073	0.32	0.63	0.14	16.1
Chromium, Cr	8.9	12	33	11	118
Cobalt, Co	0.95	5	6.2	1.1	29.2
Copper, Cu	1.5	109	390	113	71.8
Dysprosium, Dy	2.1	35	1.7	0.33	9.5
Erbium, Er	1	9.1	1	0.18	–
Europium, Eu	0.87	25	0.3	0.11	–
Gadolinium, Gd	3.1	87	2	0.77	–
Gallium, Ga	0.25	0.69	3.5	0.45	10.8
Germanium, Ge	0.019	0.16	4.3	0.05	6.6
Gold, Au	0.001	0.003	0.79	0.002	–
Hafnium, Hf	0.1	0.48	1.3	0.45	–
Holmium, Ho	0.38	0.024	0.4	0.07	–
Indium, In	<0.005	<0.005	0.15	<0.01	–
Iridium, Ir	0.0002	0.001	<0.4	<0.0001	–
Lanthanum, La	12	422	16	4.1	56.5
Lead, Pb	0.53	9.1	33	2	52
Lithium, Li	0.66	3.6	4.3	1.5	235
Lutetium, Lu	0.096	0.56	0.19	0.02	0.7
Manganese, Mn	323	307	280	250	325
Mercury, Hg	0.012	0.024	1.1	0.02	52
Molybdenum, Mo	0.13	0.56	6.7	6.8	14.6
Neodymium, Nd	13	594	11.3	2.9	–
Nickel, Ni	6.2	11	20	6.1	87.9
Niobium, Nb	1.6	0.83	4.5	0.34	–
Palladium, Pd	<0.001	<0.001	0.16	0.01	–
Platinum, Pt	0.006	0.003	<0.04	<0.001	–
Praseodymium, Pr	–	136	2.8	0.8	–
Rhenium, Re	0.0002	0.0007	<0.04	0.0008	–
Rhodium, Rh	<0.001	0.002	0.04	<0.001	–
Rubidium, Rb	<0.001	6.8	15	224	106
Ruthenium, Ru	<0.001	0.003	0.08	<0.001	–
Samarium, Sm	2.6	113	1.8	0.49	–
Scandium, Sc	0.41	3.5	3.2	0.27	–
Selenium, Se	0.041	0.032	1.3	0.89	1.6
Silver, Ag	<0.0005	<0.0005	7.4	0.018	–
Strontium, Sr	53	1720	170	76	720
Tantalum, Ta	0.071	0.011	0.94	0.0026	1.5
Tellurium, Te	<0.0005	<0.0005	0.16	0.006	–
Terbium, Tb	0.42	9.8	0.34	0.066	1.6
Thallium, Tl	0.026	0.11	0.15	0.026	1.4
Thorium, Th	1.9	48	2.4	0.35	22.1
Thulium, Tm	0.13	089	0.21	0.025	–
Tin, Sn	0.075	0.34	22	1.3	8.7
Titanium, Ti	78	259	1800	57	–
Tungsten, W	0.04	0.023	7.9	0.11	4.5
Uranium, U	0.36	9.6	10	2.2	22.9
Vanadium, V	6.7	17	18	6.1	208
Ytterbium, Yb	0.75	5	1.1	0.16	4.8
Yttrium, Y	14	114	11	2.1	43.8
Zinc, Zn	15	54	550	680	221
Zirconium, Zr	3.3	21	53	2.6	194

[a] Fertilizers manufactured by Hydro Agri, Sweden. [b] Phosphorus fertilizer manufactured in Sweden. [c] Sewage sludge produced in Sweden. [d] Solid pig manure. [e] After Llorens et al. (2000).

they vary depending on the farm, the country, and the metal (Table I-2.11). The highest annual net gain has been calculated, among European countries, for Cu and Zn in dairy farms in France. The balance for the same elements was negative in dairy farms of Norway. Crop farms may generate higher inputs, than animal farms, of trace metals to soils. However, there is also observed a great variation between farm types and this depends mostly on crop and soil types. Balances for trace metals in crop-farm soils are presented in the AROMIS database (Eckel et al. 2005) as follows (in $\mathrm{g\,ha^{-1}\,yr^{-1}}$):

- Cd: from −0.3 in Denmark to 4.4 in France
- Cr: from 14 in Denmark to 100 in France
- Cu: from −35 in France to 347 in Germany
- Ni: from −3.3 in Denmark to 33 in France
- Pb: from 1.3 in Norway to 139 in France
- Zn: from −115 in Germany to 838 in France

Table I-2.11. Trace metal balance ($\mathrm{g\,ha^{-1}\,yr^{-1}}$) for livestock farms in some EU countries, selected data from the AROMIS data base (after Eckel et al. 2005)

Country	Farm	Cd	Cr	Cu	Ni	Pb	Zn
Czech Republic							
Input/output	Pigs	2.1/0.9	19/8.5	87/57	25/21	24/6.5	609/389
Balance		1.2	11	30	4	17	220
Finland							
Input/output	Dairy	0.5/0.04	15/0.4	123/6.0	23/2.9	13/0.8	629/36
Balance		0.5	15	117	20	12	593
France							
Input/output	Pigs-1	7.5/0.7	60/7.6	1 556/632	17/21	13/4.3	3 279/1 495
Balance		6.7	53	924	−3.9	8.8	1 784
Input/output	Dairy	6.1/0.4	–	1 066/29	–	17/3.7	2 746/152
Balance		5.7	–	1 037	–	13	2 594
Germany							
Input/output	Pigs	2.0/1.5	43/2.6	408/37	36/15	62/4.4	1 482/206
Balance		0.5	41	371	21	58	1 276
Input/output	Dairy	2.5/0.8	34/1.9	939/31	38/16	40/3.6	959/161
Balance		1.8	32	908	21	36	798
Norway							
Input/output	Dairy	1.5/1.4	250/36	63/201	100/67	32/31	404/535
Balance		0.1	215	−138	32	1.3	−131
United Kingdom							
Input/output	Dairy	3.1/0.1	27/7.9	109/8.6	22/16	59/3.4	393/40
Balance		3.0	19	100	6	55	354

Budgets of trace metals in soils of forest ecosystems are also variable, however, they are more often negative than in agricultural soils. The highest negative balances were calculated (in the 1970s and 1980s) for spruce forest soils (in Sweden) and for Fe and Mn (Tyler, Bergkvist *vide* Kabata-Pendias and Pendias 2001).

Trace element budgets have been calculated for various ecosystems, and the ratio of input/output, show that for the majority of elements, the accumulation rate in surface soils is positive. However, in some European forest soils with a high rate of mobility and leaching of trace metals, a decrease of these elements is observed, even with relatively high inputs to soils. The highest losses, under such conditions, have been reported mainly for Mn (up to 6 100 g ha^{-1} yr^{-1}) and for Fe (up to 11 000 g ha^{-1} yr^{-1}) (Kabata-Pendias and Pendias 2001). It has been estimated, that in most European ecosystems, and in particular in agricultural soils, the input of most metals is higher than their losses. This is especially pronounced for Zn, Pb and Cd. The calculation of Cd budgets for two soils, in Germany and Poland, has indicated that the point source of pollution and long-range transport is about equal to nonpoint source of pollution, which is mainly from agricultural practices. The net gain balances for Cd range (in g ha^{-1} yr^{-1}) between 4.5–7.5 and 1.3–40 for Poland and Germany, respectively (Kabata-Pendias and Brümmer 1991).

The transport of dissolved trace elements may take place through the soil solution (diffusion) and with the moving soil solution (mass flow, leaching). In soils formed under a humid and cool climate, the leaching of elements downward through the profiles is greater than their accumulation, unless there is a higher input of these elements into the soils. In warm and dry climates, and to some extent in humid hot climates, upward translocation of trace elements in the soil profiles is relatively common. Several soil properties control leaching processes, of which the most important may be considered soil texture and the Eh-pH system.

Radionuclide contamination. Nuclear power generation has been utilized since the mid-1950s. As Fuge (2005) has described, accidental leakage and permitted effluence have released some radionuclides, mainly to the immediate environment of the nuclear installations. The explosion at the Chernobyl nuclear station (presently in Ukraine) in April 1986 caused widespread contamination that seriously affected some European countries and several other parts of the world.

More important radioactive isotopes released by the Chernobyl accident, according to Becker-Heidmann and Scharpensel (1990), are as follows:

- Short half-life time (days): ^{141}Ce, ^{132}Te, ^{133}Xe, ^{131}I, ^{99}Mo, ^{95}Zr, and ^{89}Sr
- Longer half-life time (years): ^{134}Cs, ^{85}Kr, ^{137}Cs, ^{103}Ru, and ^{90}Sr
- Long half-life time (hundreds of years): $^{238-240}$Pu, and ^{241}Am

The artificial radioactivity of soils is caused by settling of the released radionuclides. The fallout of Chernobyl's isotopes varied greatly and the nonhomogenous distribution is partly associated with the wet precipitation (rainfall) during that period.

The behavior of isotopes in soil depends on several soil properties, as well as on the specific behavior of each radionuclide. The distribution, fate, and phytoavailability of ^{137}Cs (half-life 30 years) have been investigated most frequently (Sheppard 2003).

The highest radioactive contamination of surface soils of Poland, after the Chernobyl explosion was observed in the southwestern part of the country. The concentrations of ^{137}Cs in soils of those regions were at the range 5–13 kBq m^{-2}. During the period 1988–2001 the country average concentration of this isotope diminished from about 4.6 to 3.2 kBq m^{-2} (Biernacka et al. 2004).

Urban soils. Contamination of urban soils has recently become the subject of several studies (Kasimov 1995; de Miquel et al. 1997; Kabata-Pendias and Krakowiak 1998; Umfitseva and Terekhina 2005). Recently reported levels of some trace metals in various soils, e.g., in China may be a real hazard to the environment and health (Table I-2.12).

There are several sources of trace element pollution in the urban environment, among which roadside dust may be a significant one, due to their increased contents in fuels and road materials (Table I-2.13).

Based on investigations of soil pollution in Oslo and Madrid, some trace metals have been distinguished as so-called "urban" contaminants: Ba, Cd, Pb, Sb, Ti, and Zn (de Miquel et al. 1997). However, the pollution of cities is specific and varies with local conditions. The trace elements increased in soils of some cities as compared with surrounding soils are reported as follows:

- Berlin: Cd, Cu, Hg, Ni, Pb, Sn, Th, Tl (Birke and Rauch 1994)
- Minsk: Cd, Pb, and Zn (Pietukhova et al. 1996)
- Novosibirsk: As, Br, Cd, Cu, Hg, Mo, Pb, Zn, and Zr (Ilyin 1997)
- Sankt-Petersburg: Ba, Cr, Cu, Pb, V, W, and Zn (Umfitseva and Terekhina 2005)
- Toronto, increase in house dust against street dust: Cd, Cu, Hg, Pb, Sn (Rasmussen et al. 2001)
- Warsaw: Ba, Cd, Cr, Cu, Li, Ni, Pb, Sr, and Zn (Kabata-Pendias and Krakowiak 1998)

Table I-2.12. Concentrations (the highest reported contents) of some trace elements in soils contaminated from industrial sources in selected countries (mg kg^{-1}) (various sources, as compiled by Kabata-Pendias and Pendias 2001, unless otherwise indicated)

Element	Canada	China[a]	Japan	Poland	UK	USA
As	2000	2500	2470	2000	900	2000
Cd	36	800	88	270	468	1500
Co	127	300	–	–	67	85
Cu	3700	>2000	206	620	2000	–
Hg	5.7	100	–	–	3.4	40
Pb	12123	>10000	2100	8000	4563	13000
Mo	–	100	–	–	–	–
Ni	26000	8000	–	–	1150	–
Zn	1397	>10000	5400	13800	4500	80000

[a] Chinese soils polluted either from parent material or from industrial sources; after He et al. (2005).

Table I-2.13. Trace metals in samples contributing to roadside dust (after Ozaki et al. 2004). Samples collected during the period 2001–2002 in Japan

Sample	Cd	Hg	Cu	As	Sb	Pb	V	Cr	Ni	Zn
	$\mu g\ kg^{-1}$		$mg\ kg^{-1}$							
Exhausted soot (bus)	49.5	13	29.7	7.5	1.1	10.5	346	32.5	5.3	1 450
Road marking (white)	510	4.3	2.2	2.5	0.6	7.4	5.9	2.7	1.2	20.8
Road marking (yellow)	413	7.2	1.5	0.9	2.1	12 000	26	820	0.5	8.4
Road marking (red)	365	20	1.9	6.7	10.2	5 290	53.6	561	1.6	13.6
Asphalt	50	11.3	9.8	3.1	0.5	6.9	38.4	38.4	27.5	4
Auto tire	4 040	ND	0.8	0.7	2.2	2.2	10.4	0.9	0.4	12 700
	$\mu g\ kg^{-1}$						$mg\ kg^{-1}$			
Regular gasoline	240	15	193	54	43	295	ND	ND	3.5	13
Premium gasoline	347	47	246	ND	5.4	173	ND	ND	4.6	13.6
Gas oil	266	0.7	179	11	16	13	ND	ND	2.9	4.4
Kerosene	171	2.7	18.6	11	18	7	ND	ND	1.2	2.5

ND – Not detected.

As reported by Umfitseva and Terekhina (2005), most of other trace elements also are increased in urban soils as compared with soils of surrounding areas (Table I-2.14). Increased levels of some trace metals in house dust as compared with both street dust and garden soils may be a significant source of metallic pollutants, and may pose a risk especially to children.

Soil remediation. The remediation of soils refers to practices of either removing contaminants or converting them into to less mobile species – that is, into less bioavailable forms. Remediation methods are based on physical, chemical and biological approaches. The selection of a method is generally based on the nature of the contaminants, the soil type, the characteristics of the contaminated site (e.g., chemical and physical soil properties, and the length of the soil contamination period). Also remediation costs and regulations of the country are involved in remediation projects (Alloway 1995; Mukherjee 2001).

Methods for remediating metal-polluted soils have been recently widely investigated and discussed (Sparks 1995; Adriano et al. 1998; Cunningham and Berti 2000; Iskandar 2001; Knox et al. 2000). The remediation of soils and sites contaminated with radionuclides is of special concern. Several techniques, *in situ* and non-*in situ* are applied to clean up soils contaminated with trace metals. Due to the complexity of soils and the presence of multiple contaminants, only a few of these techniques have been applied successfully in practice and some of them are quite costly. Most commonly used remediation technologies (in-situ and non-in-situ methods) are:

Table I-2.14.
Trace elements and iron in soils of central Sankt-Petersburg and of the surrounding region (mg kg^{-1}) (after Umfitseva and Terekhina 2005)

Element	Surrounding region		Down town	
	Mean	Maximum	Mean	Maximum
Ag	<0.1	0.1	0.4	30
As	2.6	6	5.7	–
Ba	202	300	533	50 000
Cd	0.2	0.6	1.5	190
Co	4.1	7	11.5	500
Cr	12.5	30	92.2	30 000
Cu	18	30	120	15 000
Fe[a]	13.9	50	38	200
Hg	<0.1	0.1	0.8	53.5
Mo	1.1	1.5	3.2	500
Mn	118	300	323	7 000
Ni	15.3	30	47.7	5 000
Pb	19.1	44	223	29 448
Sn	1.4	3	15	2 000
Sr	162	283	117	3 000
Ti	1 522	5 000	3 011	30 000
V	16.2	30	24.4	5 000
W	1	1	9	1 500
Y	17	50	20	70
Zn	43	70	774	X[b]
Zr	140	300	155	1 500

[a] Fe content in g kg^{-1}.
[b] Maximum Zn concentration not established due to extremely high values.

- Leaching/washing/flushing – soil with water or surfactant (a surface active substance), not very commonly practiced, limited due to the need for large quantities of water, results depend strongly on physical soil parameters
- Solidification/stabilization/immobilization – soil amendments with materials having a high capacity to bind metals in possible slightly mobile fractions and/or immobilize by keeping a neutral soil pH, for effectiveness required site-specific data, relatively low cost
- Biodegradation – substances containing trace metals are decomposed due to microbial degradation, trace pollutants are mobilized and washed-out, long-term effects, practiced in specific sites
- Vitrification – pollutants are immobilized with an electric current, seldom used, very costly
- Isolation/containment – minimizing downward migration of pollutants by installing subsurface barriers: e.g., clay layer, organo-clay layer, plastic liner
- Encapsulation – covering small sites with a layer of material of a low permeability (e.g., clay) to prevent water percolation and wind-blown dust

- Immobilization of trace metals, e.g., by steel shots, containing mainly Fe oxides, which adsorb or occlude several trace metals, by phosphoric compounds which decrease the mobility of most metals
- Phytoremediation – the phytoextraction techniques provide an adequate method under reasonable yield of plants that hyperaccumulate metals, promising in practice, needs development of technology, relatively low cost
- Removal – the contaminated soil is exposed to chemical extraction and/or thermal treatment to remove volatile elements or compounds, and to other leaching or immobilizing processes, high costs
- Excavation – the contaminated soil is removed and disposed elsewhere (e.g., in prepared landfills), high cost and possible problem with groundwater contamination

The problem of concern in soil remediation actions is the cost. Phytoremediation techniques are likely to be less costly than those based on conventional technologies. At present, an urgent requirement for phytoextraction is to increase the yield of plants that hyperaccumulate metals from soils, and to develop adequate technologies for the utilization of the plant materials.

Agricultural practices have also been applied to soil remediation. Most commonly, the uptake of metals by plants is diminished by keeping a neutral soil pH and by amendments with materials having a high capacity to bind metals in possibly slightly

Table I-2.15. Mean (arithmetic) contents of trace elements in street dust, garden soils and house dust of Ottawa, Canada (mg kg^{-1}) (after Rasmussen et al. 2001; samples collected in 1993)

Element	Street dust	Garden soil	House dust
Ag	0.22	0.31	2.5
As	1.3	3.0	7.3
Ba	576	766	492
Bi	0.05	0.08	1.67
Cd	0.37	0.3	6.46
Co	8.31	8.36	8.92
Cr	43.3	44.8.	86.7
Cu	65.84	13.19	206.08
Hg	0.03	0.11	3.63
Li	7.4	11.3	6.3
Mn	431.5	525.3	269.3
Mo	1.39	0.64	3.16
Ni	15.2	16.3	62.9
Rb	37.2	52.0	25.3
Se	0.5	0.7	1.2
Sn	3.02	1.65	54.84
Sr	459	360	255
Te	0.08	0.04	0.08
Tl	0.21	0.29	0.14
U	0.82	1.17	0.58
V	34.0	46.8	24.8
Zn	112.5	113.7	716.9

mobile fractions. Various materials are used for soil amendments and remediation. These are mainly: lime, phosphate fertilizers, zeolites, montmorillonite clays, humic (organic) matter, and biosolids. The beneficial effects of these treatments are broadly discussed by some authors (Adriano et al. 1995; Cunningham and Berti 2000; Iskandar 2001; Pierzynski et al. 2000).

In general, the phytotoxicity of trace metals are severe at low pH, thus liming is a very common practice to prevent their phytoavailability. However, site effects of liming are a decreased mobility of other metal micronutrients. This has been clearly demonstrated by Siebielec and Chaney (2006) who found Mn deficiency in plants grown in soil limed to remediate Ni-phytotoxicity.

According to Adriano et al. (2004), using agricultural chemicals (e.g., lime, phosphate compounds, organic compounds) metals may be immobilized in soils. Such a natural attenuation has been reported by several authors to be very effective in reducing of the bioavailability of metals (Knox et al. 2000a,b; Basta et al. 2001; Naidu et al. 2006).

The Maximum Allowable Concentrations (MAC) for trace metals, differ greatly between countries (Table I-2.16). Generally, lower concentrations are for light sandy soils and for low range of soil pH 5–6. In most countries, the permissible value for soil Pb is 100 mg kg^{-1}, whereas in the UK, it is 300 mg kg^{-1}. In the Netherlands, the permissible value of soil Cd is reported to be 0.8 mg kg^{-1}, but in other European countries this value is 3 mg kg^{-1} (McGrath 1992; Gzyl 1995).

Table I-2.16. Ranges of Maximum Allowable Concentrations (MAC) and Trigger Action Value (TAV) for trace metals in agricultural soils (mg kg^{-1})

Metal	MAC[a]	TAV[b]
Ag	–	2 – 40
As	15 – 20	10 – 65
Ba	–	400 – 600
Be	10	10 – 300
Cd	1 – 5	2 – 10
Co	20 – 50	30 – 100
Cr_{total}	50 – 200	50 – 450
Cr^{6+}	–	3 – 25
Cu	60 – 150	60 – 500
Hg	0.5 – 5	1.5 – 10
Mo	4 – 10	5 – 20
Ni	20 – 60	75 – 150
Pb	20 – 300	50 – 300
Sb	10	10 – 20
Se	–	3 – 10
Sn	–	35 – 50
V	150	100 – 340
Zn	100 – 300	200 – 1 500

[a] Values reported most commonly in the literature, compiled from Kabata-Pendias and Sadurski (2004) and Chen (1999).

[b] Values proposed in some European countries, compiled from various reports, documents and internet data.

Phytoremediation. Phytoremediation is an environmental cleanup strategy in which plants and their root-bound microbial community are used to absorb and remove trace elements in the contaminated soil and to translocate them to plant tissues (Robinson et al. 2003).

Field trails of accumulation of Ni and Zn in wild plants grown in metal contaminated sludge confirmed the feasibility of phytoextraction. In this process, plants act as bio-pumps to remove contaminants and water from growth media. These processes can be divided into three following sections:

- Phytostabilization – binding of trace metals (metalloids) in an aerobic environment in the root zone
- Phytoextraction – increased uptake of trace metals, mainly by hyperaccumulating plants, process that should be continued for several seasons to obtain an effect
- Phytofiltration/rhizofiltration – absorption of metals (metalloids) in root tissues due to chelation and surface absorption from both soil and groundwater

Recently, several papers have been published on this topic (Baker et al. 1994; Cunningham et al. 1995; McGrath et al. 2001; Fitz and Wenzel 2002; Wenzel et al. 2003; Prasad 2004b, 2006; Chaney et al. 1997).

Hyperaccumulators are plants and/or genotypes that accumulate metals much above common concentrations. At present, there are about 400 species that are known as hyperaccumulator plants (Robinson et al. 2003). As Greger (1999) showed, based on a literature review, hyperaccumulators may contain trace metals in leaves above the following levels (in mg kg^{-1}):

- 100 – Cd
- 1 000 – Co, Cu, Ni, and Pb
- 10 000 – Mn and Zn

Various wild plants species are known as hyperaccumulators, depending on growth conditions and contaminant. Most commonly *Alyssum*, *Thlaspi*, and *Astragalus* species are proposed for the phytoextraction of Ni, Zn, and Se, respectively. These plants, however, usually give a low yield and this limits their effectiveness. Thus, a number of cereal crops, such as wheat, rice, rye, oats, barley, corn, and sorghum, have been recently proposed to be used for phytoremediation, since they can tolerate relatively high concentrations of metals (Huang and Cunningham 1996; Kashem and Singh 2001; Schmidt 2003; Shtangeeva et al. 2001).

The application of phytoremediation procedures for the clean up of highly contaminated soils has been widely discussed (Shtangeeva 2006). Calculated amounts of trace elements that are removed with plant yield are relatively small. Even accumulator plants withdraw, mainly from topsoils, about 10% of Cd, the most readily available metal (Table I-2.17). The utilization of crops enriched in metals is a serious problem that has to be always included in the application of any phytoremediation methods. Such biomass could be used for the production of ethanol and straw (of corn and cereals) and can be burned for the production of heat and electricity. Seeds of sunflower, which is quite effective in the accumulation of Cu and Pb from contaminated soils, can be

Table I-2.17. Trace element removal with plants from soils (after Kabata-Pendias 1994)

Element	Content of soil ($kg\ ha^{-1}$)	Output with plant yield			
		Reference plant		Accumulator plant	
		($g\ ha^{-1}$)	(%)[a]	($g\ ha^{-1}$)	(%)[a]
Mn	810	1 000	0.1	5 000	0.6
Cr	150	50	0.03	500	0.3
Zn	135	100	0.3	1 500	1
B	90	100	0.1	2 500	2
Cu	45	100	0.2	500	1
Ni	39	50	0.1	100	0.3
Mo	6	30	0.5	250	4
Cd	1.5	1	0.06	100	10

[a] Percentage of the total content of topsoil.

used for the production of bio-fuels (Kayser et al. 2000). Any yield of biomass that contains elevated amounts of metals is a hazardous waste which needs specific technologies to be utilized for the production of heat and energy or other secondary products. The ash from biomass power plants containing metals (e.g., Zn and Cd) can be recycled to recover these metals (MacDougall et al. 1997).

Some plants reveal a special capability to accumulate a specific element. For example, ladder brake (*Pteris vittata* L.), a terrestrial fern, can contain large amounts of As, up to 23 000 mg kg^{-1} (Ma et al. 2001). The unique properties of Chinese brake fern has great importance in the clearing of As contaminated soils by the phytoremediation process. The laboratory study conducted by Tu et al. (2002) indicated that this plant might take up to 7 230 mg As kg^{-1} within 20 weeks. Tu and Ma (2003) reported that the addition of phosphates is an important strategy in improving the removal of As from contaminated soils by use of Chinese brake.

The phytovolatilization method can be applied for elements which are highly volatile, such as Se, As and Hg. It is not clear whether or not terrestrial plants can volatilize As in significant quantities. However, volatilization of As may occur by the rhizospheric bacteria of terrestrial plants (Salt et al. 1998). It is also reported that transgenic plants (*Arabidopsis*) are very effective for volatilization of Hg (Watanabe 1997). Rugh et al. (1996) suggested a molecular genetic approach to the transfer of Hg resistance genes to plant species as a potential means of phytovolatilization of Hg^0. According to these authors this technique may be useful to remove Hg from contaminated soils. In addition, it is possible to manipulate the transfer of Hg^0 in plant shoot tissue to Hg^{2+} that may be another option for the Hg phytoremediation. Some plants may convert Se into dimethyl selenium that is nontoxic and may volatilized from plant tissues.

Phytovolatilization mechanisms are not yet fully understood. There are observations that some commercial vegetables (e.g., broccoli, cabbage) and rice are quite effective in the phytovolatilization. These processes, however, are controlled by soil factors, such as sulfates and salinity of soils.

Economic aspects are very significant in phytoremediation practices (Thewys 2006). There is not much information in this field, as well as on farmers' approaches to this problem. Lewandowski et al. (2005) have recently studied this topic in Germany and widely discussed the income expected from cleaned up areas and the length of period the area can be used for the production of food crops. This information is quite valuable for farmers and landowners. The authors have distinguished important parameters, such as: *(i)* length of time needed for remediation and *(ii)* time for production of crops after remediation.

The cost of and socio-economic aspects of phytoremediation has been recently discussed and two alternative crops have been considered: rape and willow (Thewys 2006). However, using the biomass as a source of energy, especially rape oil for biodiesel creates a risk of uncontrolled emission of trace inorganic pollutants.

According to Chaney et al. (1999b), hyperaccumulator plants offer a new sustainable economic system based on the use of biomass from the phytoremediation for power generation factories. There is a belief that phytoremediation processes may be economically acceptable in about 10 years time. However, possible risks of food and forage chain contamination and the reaction of plants when overloaded with metallic pollutants, have become open questions (Keller 2006).

The effectiveness of some plants in the extraction of metals from constructed wetland purification systems have recently become widely investigated in both laboratory and field conditions (Ofelder et al. 2006; Marmiroli et al. 2006). Some plants (e.g., *Phragmites*, *Salix*, and *Populus*) may remove more than 50% of metals (Ba, Cd, Cu, Ni, Pb, Sr) from the growth media (Samecka-Cymerman et al. 2004).