Soil contamination, risk reduction and remediation

Article *in* Land Contamination & Reclamation · January 1998

3 authors, including:

Enzo Lombi
University of South Australia
335 PUBLICATIONS **26,720** CITATIONS

SEE PROFILE

Walter Wenzel
University of Natural Resources and Life Sciences Vienna
196 PUBLICATIONS **14,488** CITATIONS

SEE PROFILE

Soil contamination, risk reduction and remediation

Enzo Lombi,[a] Walter W. Wenzel,[b] and Domy C. Adriano[c]

a. Department of Soil Sciences, IARC-Rothamsted, Harpenden, UK

b. Institute of Soil Sciences, University of Agricultural Sciences, Vienna, Austria

c. Savannah River Ecology Laboratory, University of Georgia, Aiken SC, USA

Abstract

Soil contamination by trace elements is caused by several processes. The biogeochemical cycles of inorganic pollutants have been gradually accelerated by human activities for several centuries, the Industrial Revolution marked a dramatic increase in the emissions of trace elements to the biosphere. Moreover, locally large concentrations of contaminants may be related to natural phenomena. The public welfare concern over the hazards of soil pollution has led to legislative action aimed at controlling the major pathways of contamination. Land application of sewage sludge, combustion of fossil fuel, smelter activities, etc. have been strictly regulated during recent decades. This paper describes, for some countries, the legislative aspects that regulate the land application of sewage sludge. Particular emphasis is given to the comparison of the legislation in EU and USA The second part of the paper reviews the legislative aspects related to soil remediation and the remediation technologies currently employed. The formulation of legislative guidelines for soil remediation are based on the definition of threshold limits specific to the element and related to land use. Examples of limits based on total and extractable concentrations of trace elements are reported. A general description of the most common reclamation techniques is given.

INTRODUCTION

Soil and environmental contamination as a result of human activity is not a recent phenomenon. About 100 BC, Cicero first related structural damage of buildings and statues in Rome to smoky rains from wood and charcoal burning (Eney and Petzold 1987). Some of the deleterious effects on human health due to mining activities have been recognized for a long time. The Romans used slaves to extract cinnabar (an ore containing Hg) at the Almadén mine (Spain). Due to mercurialism the miners' life expectancy was only three working years (Wren *et al.* 1995).

The public welfare concern over the effects of environmental pollution has increased substantially in the last century with the Industrial Revolution and as a consequence of an enhanced understanding of the risk to human health. The Industrial Revolution started in the mid-1800s and the extensive use of coal to produce energy caused the release of considerable amounts of gases (CO_2, SO_2, NO_x) and fly ashes into the atmosphere (the term 'acid rain' was introduced in 1872 by R. A. Smith). Since then the biogeochemical cycle of potential inorganic pollutants (e.g. heavy metals) naturally present in the environment has been largely accelerated by human activities. The conversion of the world economy from coal to oil, initiated between the two world wars, enlarged the range of pollut-

ants released in the environment to organic compounds (e.g. PAHs). The development of the organic chemistry industry in this century lead to the commercialization of a large number of new substances, some of which were found to be toxic for the environment and animal life (PCBs entered the market in the late 1920s and DDT in the 1940s). In recent decades many xenobiotics have been discovered, produced and released into the biosphere. It has been calculated that about 1000 new compounds are synthetized every year and 60–90 000 chemicals are currently commercialized (Alloway and Ayres 1997). The discovery and utilization of nuclear energy has introduced a large number of radionuclides of potential concern into the environment. After the nuclear detonations that took place from 1945 to 1960s, more recent nuclear testing and three reactor accidents (Windscale – UK, 1957; Three Mile Island Unit – USA 1979; and Chernobyl – Ukraine 1986) are the main sources of radionuclide emission. In recent decades, urbanization and higher standards of living in western countries have led to the production of increasing amounts of waste in urban areas. Today, the pollution problems arising from poor waste disposal practices have become crucial in discussions on environmental sustainability.

The soil is a key component of natural ecosystems because environmental sustainability depends largely on a sustainable soil ecosystem (Adriano *et al.* 1998). Unlike

Table 1. Suspected contaminated sites and estimated treatment costs in selected countries

Country	Suspected contaminated sites	Estimated treatment costs (1993, in billions US$)	Source*
Austria	3300	0.8	a
Belgium	8300	–	b
Denmark	20 000	–	a
Germany	100 000–200 000	6–110	a
Italy	5600	–	b
Norway	25 000	0.2	a
The Netherlands	110 000	28	a
UK	50 000–100 000	14–32	a
USA	35 000	10	a

*Source: (a) Overcash (1996); (b) Eijsackers and Hamers (1993).

other environmental compartments (e.g. atmosphere, water) pollutants have long residence times in soil. Therefore, soil acts as a sink or a filter in which pollutants are accumulated rapidly but depleted slowly. Purves (1972) stated that 'Contamination of soil with respect to copper, lead and zinc appears to be virtually permanent.'

The decontamination of polluted soils is going to become a social problem because of its importance for environmental protection and human health and for its economical relevance; an estimation of contaminated sites and clean-up costs in some countries is presented in Table 1. There are strong indications that the number of contaminated sites, and therefore the treatment costs reported, may be underestimated for some countries.

Public concern related to environmental and soil contamination has led to the promulgation of national and international regulation to reduce pollution and to remediate polluted sites. New technologies based on physical, chemical, and biological processes to reclaim polluted soils have been developed in recent decades.

This paper describes some legislative, scientific, and technological aspects of soil contamination and remediation in relation to inorganic pollutants (i.e. trace elements) in Europe and North America.

SOIL CONTAMINATION
Processes of contamination

Trace elements are ubiquitous in the environment and, in normal condition, they are present in small amounts. Typically, the principal reservoir of trace elements is the geological substrate followed by the oceans, soil, biota and atmosphere (Figure 1). An example of the relative distribution among the environmental compartments is reported for As in Table 2.

Anomalously large concentrations of trace elements in soils are caused by either anthropogenic or natural sources (Figure 1). Natural inputs of trace elements to soil are due to weathering processes, volcanic activities and wood/plant burning. Anthropogenic sources of trace elements of possible environmental concern are a consequence of the Industrial Revolution and urbanization (Adriano *et al.* 1995). These sources are related to human activities such as mining and smelter activities, fossil fuel combustion, waste incineration and disposal, and agricultural practices (fertilizers and pesticides).

The biogeochemical cycles of heavy metals have been greatly accelerated by human activities. Sposito and Page (1984) have calculated that anthropogenic emissions to the atmosphere, for several heavy metals, are one to three orders of magnitude larger than natural fluxes. Shotyk *et al.* (1996) studied peat cores from a Swiss bog and found that As, Sb, and Pb fluxes due to anthropogenic activity have been exceeding natural fluxes for more than 2000 years. They determined present enrichment factors of the order of 20 times for As, 70 for Sb, and 130 for Pb. The modification of the natural cycle of heavy metals has led to a situation in which the inputs of heavy metals in soils generally exceed the removal due to harvests of agricultural crops and the losses by leaching, volatilization, etc. (Van Driel and Smilde 1990; Jones 1991).

Sources of pollutants are also commonly divided in two categories: point sources and nonpoint sources (Hemond and Fechner 1994). Point sources refer to discrete and localized contamination processes. For example, natural point sources are represented by particular pedogenic substrates rich in specific trace elements (i.e. metalliferous soils developed on serpentinitic rocks). Local accumulations of pollutants may also originate from human activities such as mining and smelter processes.
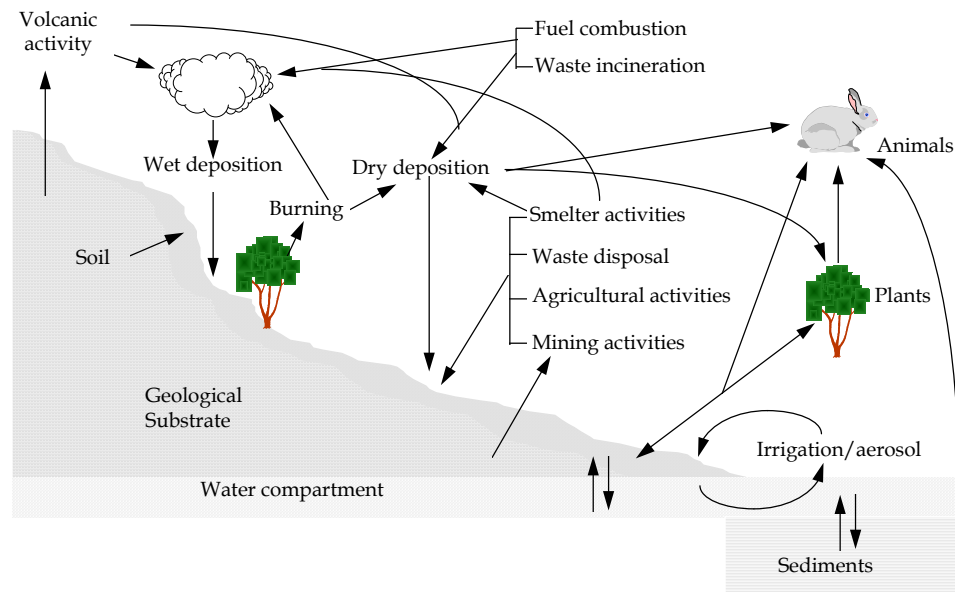
Figure 1. A general biogeochemical cycle of trace elements

Table 2. As distribution among environmental compartments (Mackenzie *et al.* 1979)

Reservoir	Relative amount to soil
Rocks	25 000
Oceans	4
Soil	1
Biota (plants, animals, microorganisms)	0.0005
Atmosphere	0.000001

Nonpoint sources are related to diffuse processes or human activities that cover large areas. Atmospheric transport of volcanic emissions and fossil fuel combustion are among the most common processes that disseminate pollutants in the environment. Agricultural practices represent another example of nonpoint sources of contamination that involve large areas.

Point sources are generally responsible for large pollutant concentrations in small areas, whereas nonpoint sources are influenced by dilution effects. Until the mid-1980s the more serious problems of pollution occurred in developed countries with high population densities (Barth and L'Hermite 1987; Merian 1991; Tolba and El-Kholy 1992). Effects of emissions from nonpoint sources in Europe and the USA have been detected even in remote areas such as Antarctica. Bartnicki (1996) has pointed out that, at a European level, the atmospheric transport of heavy metals is a significant process: 30-90%

of the metals emitted from each European country are deposited in other states.

Since the mid-1980s, pollution levels have been diminishing in highly developed countries. For instance, As and Pb deposition in forests in NW Germany, an area which previously had been heavily impacted by emissions from the Ruhr area, has decreased considerably since 1984 (Figure 2; Schulte *et al.* 1996; Schulte and Gehrmann 1996).
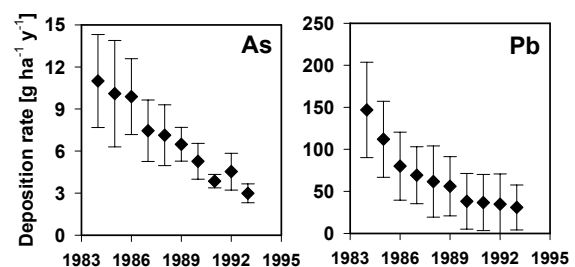

Figure 2. Deposition rate of As and Pb in NW Germany (modified from Schulte et al. 1996; Schulte and Gehrmann 1996).

Legislative aspects

Increasing public concern about the deleterious effects of pollution on environmental and human health has led to legislative actions aimed at controlling and regulating the emission of potential pollutants into the environment. Par-

Table 3. Summary of the EU directive 278/86 relative to the regulation of sewage sludge application in agriculture

	Maximum permitted concentration in soil treated with sludge (mg kg-1)	Maximum permitted concentration in sewage sludge (mg kg^{-1})	Maximum annual loading (kg ha^{-1} year^{-1})
Cd	1–3	20–40	0.15
Cu	50–140	1000–1750	12
Ni	30–75	300–400	3
Pb	50–300	750–1200	15
Zn	150–300	2500–4000	30
Hg	1–1.5	16–25	0.1
Cr	100–150	–	–

ticular attention has been directed to the sustainability of agricultural ecosystems. The conservation of a healthy agricultural ecosystem is a prerequisite for protecting the foodchain from bioaccumulation of hazardous substances, e.g. heavy metals. Inputs of heavy metals into agricultural soils have been gradually raised over past decades due to the increased use of fertilizers and pesticides, the disposal of sewage sludge and augmented atmospheric deposition (Berrow 1986; Sposito and Page 1984; Adriano 1986). On the other hand, there is evidence that during the past 10–15 years, the agricultural input of heavy metals has been reduced in developed countries. The annual production of sewage sludge is increasing as a consequence of the fast growing world population and of stricter regulation of wastewater treatments. A survey by the US EPA revealed that in 1990 the US generated 8.5 million tons per year of sewage sludge and by the year 2000 this amount will have increased to 12 million tons (Hue 1995). The disposal of sewage sludge to agricultural land has been the object of intense discussion. Sewage sludges are potential fertilizers due to their content of N, P, and micronutrients and may be used as a soil conditioner due to their high content of organic matter. Moreover, the increasing cost of sludge incineration and concern over the dumping of sludge in the sea have made the agricultural use of sewage sludge an economically viable option for its disposal. On the other hand, the presence of potential pollutants in sewage sludge has raised concerns over its repeated application on agricultural land. There is evidence that heavy metal concentrations in plants can increase with the addition of large amounts of sewage sludge (e.g. Keefer *et al.* 1986; Chang *et al.* 1987; Lübben and Sauerbeck 1991; Mench *et al.* 1994c).

In order to regulate the land application of sewage sludge the EU, in the directive 278/86, has fixed limit values for concentrations of metals allowed in agricultural soils treated with sewage sludge, the maximum permitted heavy metal concentration in sewage sludge, and the maximum annual loading of heavy metals on agricultural soils. This directive regulates the maximum values permitted by the EU but member states may adopt more restrictive values (Art. 12 of the directive). As a result, the limits in national legislation regulating the use of sewage sludge in agriculture are inconsistent among EU countries.

The amount of sewage sludge applied to agricultural land should be based on crop nutrient requirements (agronomic rate) and must not endanger soil and water quality (Art. 12 of the directive EEC 278/86). Different European countries have regulated the maximum amount applicable to land; for instance Italy has based its legislation on the pH and CEC of the soil on which sewage sludge is applied (Table 4).

Table 4. Soil parameters and maximum annual amount of sewage sludge applicable to soil (Decreto legislativo 99/92)

pH	<5	5–6	6–7.5	>7.5
C.E.C. (meq/100g)	<8	8–15	>15	>15
t of dm ha^{-1} y^{-1}	0	2.5	5	7.5

In the USA, upper limits for the concentration of trace elements in sewage sludge and the maximum pollutant loading of the soil are established in the Standards for the Use or Disposal of Sewage Sludge (*US Federal Register*, Feb. 1993). The basic principle for the application of sewage sludge on land is, as in the European perspective, the 'agronomic rate'. The sewage sludges are divided into two types (Class A and Class B) that relate to pathogen standards, pollutant limits and vector reduction requirements. The maximum concentration of pollutants for Class A and Class B sludge must be below the 'concentration limit' and 'ceiling limit' respectively (limits listed in Table 5). Both classes of sludge can be applied to land but the use of Class B sludge must follow stricter rules. In any case loading limits for given pollutants must not be exceeded.

Table 5. Summary of pollutant limit values from US EPA 40 CFR Part 503

	Concentration limit Class A sludge (mg kg^{-1})	Ceiling concentration Class B sludge (mg kg^{-1})	Maximum annual loading (kg ha^{-1} y^{-1})	Maximum cumulative loading (kg ha^{-1})	Maximum permitted concentration in soil treated with sludge (a) (mg kg^{-1})
As	41	75	2.0	41	20
Cd	39	85	1.9	39	20
Cr	1200	3000	150	3000	1500
Cu	1500	4300	75	1500	750
Pb	300	840	15	300	150
Hg	17	57	0.85	17	8
Mo(b)	18	75	0.90	18	9
Ni	420	420	21	420	210
Se	36	100	5.0	100	50
Zn	2800	7500	140	2800	1400

(a) Calculated from maximum cumulative pollutant loading limits without taking into account background concentration of the elements in soils (McGrath *et al.* 1994).

(b) Mo limits deleted on February 18, 1994 – Reproposal anticipated in 1997 (Forste 1995).

A comparison of Tables 3 and 5 indicates that the limits imposed by EU and US legislation on the concentration of pollutants in sewage sludge (Class A in the case of US) fall in the same range. The European legislation is generally much stricter regarding the maximum annual loading of pollutants and their concentrations in sludge-treated soils. For example, the maximum permitted concentration of Cd in sludge is similar in Europe and the USA (40 and 39 mg kg^{-1} respectively), but the maximum Cd concentration in soils for sludge application is 3 mg kg^{-1} in the EU directive and 20 mg kg^{-1} according to the US rules. Maximum cumulative loadings for Cd are 0.15 and 1.9 kg ha^{-1} year^{-1} in the EU and US, respectively. In the case of Pb the values fixed in the US are close to the generally stricter values defined in Europe. The strict values fixed in the US for Pb go back to several studies in the late 1980s and early 1990s conducted in the USA that identified childhood exposure to Pb as the cause of adverse effects, including deficits in growth and stature, subtle learning disabilities, and hearing impairment (ATSDR 1988; Needleman *et al.* 1990). The differences between US and European legislation can be explained by taking into account the different approaches used to define the limits for heavy metals in soil. The pollutant limits fixed in Part 503 of the US regulations are based on a multi-pathway risk assessment. Each pathway protects a highly exposed individual against a toxicity endpoint and the numerical limit for a pollutant is derived from its most limiting pathway. Therefore, the US regulation is primarily based on human exposure to pollutants (Ryan and Chaney 1997). In the EU and Canada, the zero to minimal risk-oriented policy approach is intended to protect all aspects of the ecosystems.

SOIL REMEDIATION

Legislative aspects

The formulation of legislative guidelines for soil remediation should be based on clear and unequivocal definitions of contamination and pollution, and correct determination of parameters, such as baseline and background levels.

A soil is contaminated when the concentration of one or more contaminants exceeds the baseline level. Essential to this definition is the determination of reliable baseline and background concentrations of contaminants. Baseline concentrations for a contaminant can be defined as the upper limit of the normal range of concentration, in soils unaffected by human activity, on a global scale. These values have been reported in several publications (Adriano 1986; Kabata-Pendias and Pendias 1992; Temmerman *et al.* 1984). Background concentrations refer to the common concentrations of contaminants in soil not affected by anthropogenic contamination, in a defined area. Therefore, background concentrations are related to the parent material and the soil profile. These definitions imply that if the background concentration of a contaminant is higher than the baseline concentration, a soil can be contaminated due to natural sources. For instance, soils developed on serpentinitic parent material display concentrations of Ni and Cr well above the baseline concentration. These soils are therefore contaminated as a result of natural conditions. On the other hand, human activities have generated widespread contamination and, also in pristine areas, the contaminant contents are not necessarily 'natural' (Davies 1992). An example in accordance with the above definition of uncontaminated and contaminated soils is given for As in Figure 3. The geogenically
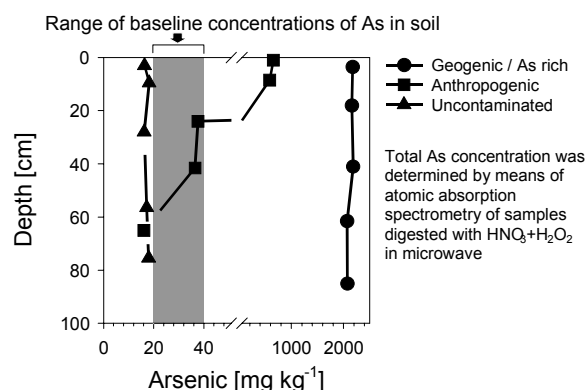
Figure 3. Arsenic concentrations in uncontaminated soil and in geogenically and anthropogenically enriched soil
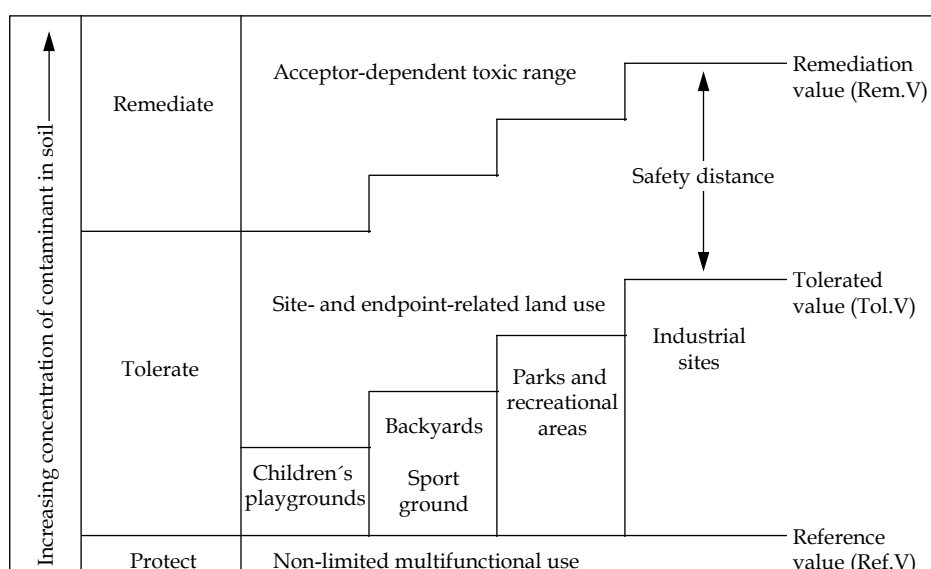

Figure 4. Conceptual description of the threshold limits proposed by Eikmann and Kloke (1991)

contaminated soil is shown as an even As distribution along the profile whereas in the anthropogenically contaminated soil As concentrations exceed the baseline concentration only in the top layers.

A generally accepted definition of pollution can be related to a situation in which the level of contamination as a result of human activity is detrimental to organisms (Adriano *et al.* 1995; Davies 1992). However, this definition may not be satisfactory in specific cases. In fact, soil heavily contaminated by natural sources cannot be classified as polluted, even in the case in which detrimental effects on organisms are evident. Moreover, the response to specific contaminants can vary considerably among different organisms. In accordance with the above definition the soil geogenically enriched in As shown in Figure 3 would be considered contaminated but not polluted even

though leaching of As to fresh water is evident. Arsenic concentration in surface water exceeded the Austrian drinking water standard (30 µg l^{-1}) by over ten times.

In recent years environmental legislation has had to deal with the problem of contaminated or polluted soils and their remediation. The need for soil remediation depends primarily on the nature of the contaminant (toxicology and ecotoxicology) and the land use. However, public perceptions and political considerations can play a key role in the decision-making process in relation to soil remediation. In the absence of national legislation on clean-up levels (remediation levels), many states in the USA have promulgated their own standards. The conceptual backgrounds used to identify such standards are based on different assumptions. Consequently, the clean-up levels for contaminants may vary (Bryda and Sellman 1994).

The situation in Europe is similar: in the absence of concerted recommendations at EU level, individual countries have adopted different clean-up values. One of the most comprehensive collections of threshold values for trace elements in soil was published in Germany by Eikmann and Kloke (1991). The authors define reference, tolerable, and remediation values of trace element concentrations in soil as related to land use (Figure 4). These values can be defined as follows:

Reference values: maximum soil concentration of a specific contaminant that allows non-limited multifunctional use of the land. It can be assimilated to baseline level.

Tolerated values: maximum soil concentration of a specific contaminant in relation to specific site- and endpoint-related land use. Above this value remediation is not immediately required but monitoring or changing the land use is demanded.

Remediation values: threshold values, related to land use, above which risk assessment and subsequent remediation is necessary.

The threshold values proposed by Eikmann and Kloke (1991) are based on the total concentration of trace elements in soil (Table 6).

These values are based on the total content of trace elements and therefore do not take into account the differential mobility and bioavailability of the elements in different soils. Soil characteristics such as pH, CEC, redox potential, texture, the content and type of clays, oxides and organic matter have strong influence on the fate of trace elements in soil. For instance, a soil which is rich in clays, oxides and with a pH over seven will be able to immobilize heavy metals more efficiently than a sandy, acidic soil.

In other legislation the effect of soil type on the mobility of trace elements was considered in determining the threshold values for remediation. In Dutch legislation adopted in 1994, for example, the target and intervention values are dependent on soil type. This is achieved by means of a so-called 'soil type correction formula' that considers soil organic matter and clay content.

In Germany, Pruess (1994, 1997) proposed reference, intervention and threshold values for agricultural soils based on the 1 M NH_4NO_3 – extractable fraction instead of the total amount (Table 7). This recommendation has been accepted as a Deutsche Industrie Norm (DIN 19730). Different endpoints are considered: quality of food and fodder crops, plant growth, microbial activity and water quality (Table 7). The concept here is that pollution can be linked to water quality and not just to detrimental effects on organisms.

Remediation technologies

Increasing public (and political) concern about environmental pollution and the new findings on pollutant effects on environmental and human health have led to the development of remediation technologies. In the USA, since the Superfund Amendments and Reauthorization Act (SARA) was enacted in 1986, soil remediation technologies have been improved and intensively tested (Iskandar and Adriano 1997; Houthoofd et al. 1991; US EPA 1992a). Once a soil has to be remediated the key issue is 'which is the most appropriate technology to be used?' The US National Contingency Plan (NCP) proposed nine possible criteria to select a remedy (Lafornara 1991):

- the overall protection of human health and the environment;
- compliance with applicable or relevant and appropriate requirements;
- long-term effectiveness and permanence;
- reduction of toxicity, mobility, and volume through treatment;
- short-term effectiveness;
- implementability;
- cost;
- state acceptance;
- community acceptance.

In the UK, three criteria that influence the choice of remediation techniques are considered (Beckett and Cairney 1993):

- cost-effectiveness;
- speed of reclamation;
- flexibility.

These criteria limit the use of technologies such as bio- and phytoremediation that, though well accepted by the community, require more time than well-established engineering technologies.

A general description of the most common reclamation technique follows below. The technologies presented will be grouped according to the underlying processes.

Physico-chemical processes
Physical barriers

Physical processes include containment technologies based on the use of physical barriers to prevent contaminant migration due to groundwater flow. Containment technologies include both surface capping or subsurface barriers (vertical and horizontal) that limit infiltration of uncontaminated surface water, or reduce lateral or vertical migration of contaminated groundwater (Smith et al. 1995). These technologies are used when subsurface con-

Table 6. Land use and endpoint-related orientation value (mg kg^{-1}) for trace elements in soils (Eikmann and Kloke 1991)

Land use	Value	As	Be	Cd	Cr	Cu	Hg	Ni	Pb	Se	Tl	Zn
Multifunctional land use	Ref.V.	20	1	1	50	50	0.5	40	100	1	0,5	150
Children's playgrounds	Tol.V.	20	1	2	50	50	0.5	40	200	5	0,5	300
	Rem.V	50	5	10	250	250	10	200	1000	20	10	2000
Backyards	Tol.V.	40	2	2	100	50	2	80	300	5	5	300
	Rem.V	80	5	5	350	200	20	200	2000	10	20	600
Sports grounds	Tol.V.	35	1	2	150	100	0.5	100	200	5	2	300
	Rem.V	90	2.5	5	350	350	10	250	1000	20	20	2000
Parks and recreational areas; unconsolidated, nonvegetated soils	Tol.V.	40	5	4	150	200	5	100	500	10	5	1000
	Rem.V	80	15	15	600	600	15	250	2000	50	30	3000
Industrial sites and staple grounds (non-paved)	Tol.V.	50	5	10	200	300	10	200	1000	15	10	1000
	Rem.V	150	20	20	800	1000	20	500	2000	70	30	3000
Agricultural soils	Tol.V.	40	10	2	200	50	10	100	500	5	2	300
	Rem.V	50	20	5	500	200	50	200	1000	10	20	600
Non-agricultural ecosystems	Tol.V.	40	10	5	200	50	10	100	1000	5	2	300
	Rem.V	60	20	10	500	200	50	200	2000	10	20	600

Table 7. Proposed values after Pruess (1994). Data in µg kg^{-1}

Element	Reference value[1]	Intervention value[2] / Threshold value[3]					
		Quality of food crops	Quality of fodder crops	Plant growth	Activity of micro-organisms	Water quality topsoil <30cm	Water quality subsoil >30cm
Ag	1.5 / 1.5	•	•	•	5	5	1.5
As	40 / 60	100	100	600	•	100	50
Be	0.4 / 60	•	•	•	•	60	15
Bi	1 / 3	•	•	•	•	•	•
Cd	3 / 80	20 / 30 or 90	20 / 30 or 90	•	•	80	25
Co	20 / 500	•	150	500	•	500	150
Cr	10 / 50	•	•	50	100	100	15
Cu	250 / 400	•	800 / 2500	2000	1000	1000	400
Hg	1 / 1	5	5	•	5	5	1
Mn	3000 / 30 000	•	•	30 000	•	•	•
Mo	10 / 110	•	500	2	•	•	•
Ni	200 / 1000	•	•	1000	•	1000	600
Pb	3 / 3000	300 / 10 000	300 / 10 000	•	•	3000	200
Sb	5 / 40	•	•	•	•	1000	40
Sn	1 / 1	•	•	•	•	•	•
Tl	10 / 50	30 / 100	30 / 100	•	•	•	30
U	3 / 5	•	•	•	•	25	5
V	15 / 40	•	•	•	100	100	30
Zn	100 / 5000	•	5000	10 000	•	5000	1500

1. pH-dependent, only the concentration for the smallest and largest pH value is presented.
2. Limit above which risk assessment is required.
3. Limit above which the concentration in plant products exceeds threshold limits according to the German legislation.
• Impact on specific soil function is not known or is evident only above the largest intervention value.

tamination precludes excavation and removal of the soil.

Separation/concentration processes

These methods aim to concentrate the pollutant in a smaller amount of material that can be eventually treated with other processes to reduce the hazard related to the pollutant or can be reused to recover valuable contaminants. These processes can be classified according to Smith *et al.* (1995) as *in situ* and *ex situ* technologies.

Ex situ technologies

After soil excavation, separation can be achieved by techniques based on the physical properties of the particles. These systems are useful in two situations: (a) when the pollutant is present in the form of discrete particles in soil; (b) when the pollutant is concentrated in specific particle-size fractions, as is common for trace elements in the fine fraction of soil (Helmke *et al.* 1977; Lombi *et al.* 1998).

The costs range between $27 to 180/t according to the technology used (Iskandar and Adriano 1997).

The pollutant-rich fraction physically separated can be processed to recover valuable metals using pyrometallurgical or hydrometallurgical separation techniques. The first is based on high-temperature processes that volatilize elements such as As, Cd, and Pb which can be recovered by filtration. Nonvolatile metals (Ni, Cr) remain in the furnace and are recovered by slagging. Hydrometallurgical processes involve the use of leaching solutions to recover metals.

In situ technologies

These technologies include soil flushing and electrokinetic treatment.

Soil flushing is based on leaching with water, acid or basic aqueous solution, chelating, reducing or complexing agents, and surfactants. The choice of the washing solution has to address the pollutant present in the soil and the possible environmental side effects. The contaminated fluid is collected and pumped to the surface where it can be recirculated, removed, or treated and reinjected. Subsurface barriers may be used to simplify fluid collection and avoid deep percolation. This technique may be employed in *in situ* treatment of soils polluted with organ-

ics, metals and radionuclides. Estimated costs range from $100 to 260 m^3 (US EPA and US Air Force 1993).

Electrokinetic technology is based on the movement of ions due to the application of an electric field. This field is generated by anodes and cathodes placed in the soil. As a consequence, anions migrate to the anodes and cations to the cathodes. The cathode and anode can be equipped with different circulation solution systems in order to maximize the recovery of specific ions. Undesirable effects are associated with the electrolysis of water (Acar and Alshawabkeh 1993). This may lead to the formation of an acid front in the vicinity of the anode due to evolution of oxygen and the production of hydrogen ions. Similarly, the formation of hydrogen gas (which escapes) and hydroxide ions may increase the pH in the cathode zone to above 13 (US EPA 1990*b*).

Soil amendments

Contaminated soils have classically been ameliorated using amendments such as lime, phosphate, and organic matter (Kabata-Pendias and Pendias 1992). The addition of lime generally reduces the bioavailability of heavy metals (Benninger-Traux and Taylor 1993; Marschner *et al.* 1995). In some cases, however, depression of crop yields due to overliming and a long-term increase in the exchangeable amount of Zn were observed (Han and Lee 1996; Chlopecka and Adriano 1996).

Zeolites are hydrated aluminosilicates that have been used as a molecular sieves for water treatment. Zeolites possess a high CEC (Gworek 1992*a,b*; Loizidou *et al.* 1992) and a selective sorption for several heavy metals (Cd, Cu, Pb, Zn). These materials were found able to reduce the amount of heavy metals in plant tissues (Gworek 1992*a,b*; Rebedea and Lepp 1994; Chlopecka and Adriano 1996). Similar effects were achieved with oxy/hydroxides of Al, Mn and Fe (McKenzie 1980; Fu *et al.* 1991; Mench *et al.* 1994*a,b*). Recently, byproducts of industrial processes such as beringite and steel shots have attracted attention for their affordable cost and ability to immobilize heavy metals (Vangronsveld *et al.* 1990, 1995*a,b*; Mench *et al.* 1994*a,b*; Sappin-Didier 1997). Field applications of these materials have already demonstrated their usefulness in reclaiming soil contaminated with heavy metals as a consequence of smelting activities

Table 8. Physical separation techniques based on particle characteristics (modified from Smith *et al.* 1995)

Particle characteristic	Technique	Basic principle
Particle size	Screening	Sieving of the material
Particle density	Sedimentation/thickening	Gravity separation
Surface properties	Froth flotation	Particles are attracted to bubbles due to their surface properties
Magnetic properties	Magnetic separation	Magnetic susceptibility

(Vangronsveld *et al.* 1995*a*,*b*, 1996) and massive applications of sewage sludge (Boisson *et al.* 1998).

Chemical treatments

Chemical treatments aim to reduce the bioavailability/mobility of contaminants upon reaction with specific reagents. The reactions include chemical oxidation, reduction and neutralization. Oxidation treatment can reduce the toxicity of As by transformation of As (III) to the less soluble (Deuel and Swoboda 1972) and toxic (Ferguson and Gavis 1972) As (V). Reduction treatments can target the transformation of Cr (VI) to Cr (III); in this case it is the reduced species that is less toxic and mobile (Peterson and Girling 1981). Neutralization treatments reduce the toxicity of pollutants by adjusting soil pH. This technique is based on the different bioavailability/mobility of pollutants depending on pH condition. For instance, heavy metals are in general more mobile in acidic than in alkaline conditions (Adriano 1986). The choice of the chemical reagents has to take into consideration all possible side effects on the environment (Smith *et al.* 1995).

Solidification/stabilization (S/S) technologies

Polymer microencapsulation

This technology is based on the physical encapsulation of polluted soil in water-insoluble organic resins or asphalt. It involves the mixing of the waste material with the resin at an elevated temperature. The presence of excessive organic pollutants may limit the use of this method. Polymer microencapsulation is particularly suitable for water soluble salts (chlorides, sulphates), As and Cr that are generally difficult to immobilize in cement-based processes (Kalb *et al.* 1993). The costs are in the range of $45-91/t which does not include excavation and backfilling (US EPA 1977; Brenner and Rugg 1982).

Cement-based stabilization technologies

These methods are based on the treatment of contaminated soils with inorganic materials such as cements and siliceous pozzolans. This technology can be employed *in situ* or to excavated material. As a result, the mobility of the contaminant is reduced by physical and chemical processes. Solidification of the polluted substrate with cement restricts its contact with groundwater and air. Cement and siliceous pozzolans react with metals and cause the formation of hydroxides, carbonates, and silicates of very low solubility. This treatment is not efficient for metals that form soluble hydroxides (e.g. Hg) or for anions (US EPA 1990*a*). It should be noticed that the mixing process and the heat generated by cement hydration reaction can increase the vaporization of organic pollutants (Ponder and Schmitt 1991; Shukla *et al.* 1992; Weitzman and Hamel 1990). Depending on the technology considered, the treatment costs may range from $66 to 186/t (Smith *et al.* 1995).

Vitrification technologies

These technologies are appropriate for *in situ* treatment or for vitrification of excavated materials. In either case, the soil is melted and the pollutants are incorporated in a stable vitreous mass. The large amount of glass-forming materials, such as silica, in soil make this substrate ideal for this technology without pre-treatment. In the case of *in situ* processes it is achieved by electric melter technology. Resistance heaters are placed in the soil to initiate the melting process. In *ex situ* treatments the soil is first excavated and then the process of vitrification takes place in a glass melter, heated for example by fossil fuels, or in plasma centrifugal furnaces. Arsenic, lead, selenium, and chlorides are incorporated less efficiently than other inorganic pollutants. The costs in case of vitrification of excavated materials are reported to be in the range of $425-545/t (US EPA 1992*b*); *in situ* vitrification can be expected to cost $325-350/t (US EPA 1992*b*).

Biological processes
Bioremediation
Biological technologies for remediation take advantage of the pathways developed by microorganisms to protect themselves from metals. Common protection mechanisms include oxidation/reduction, sorption and methylation. Biotechnologies that incorporate these mechanisms are in an advanced state of development for the remediation of organic compounds but experience is limited for inorganic contaminants. Processes such as bioleaching, biosorption, biovolatilization, and biological oxidation and reduction may provide *in situ* treatments without the use of environmentally aggressive chemicals. In the case of Se-contaminated soils, Terry and Zayed (1994) showed that volatilisation of Se was primarily localized in the rhizosphere. This process is probably enhanced by bacteria living in the rhizosphere or in the intercellular space inside the roots. A better understanding of the processes involved may open new opportunities for remediation of Se contaminated soils.

Phytoremediation
Based on traditional terminology (Baker *et al.* 1991; Raskin *et al.* 1994), phytoremediation refers to technologies that use green or higher terrestrial plants for treating chemically or radioactively polluted soils.

Basically, there are four fundamental processes by which plants can be used to remediate soil contaminated with trace elements (Salt *et al.* 1995). These processes result in the plant-based containment or removal of the soil pollutant (Wenzel *et al.* in press).

Containment processes:
• Phytoimmobilization processes prevent the movement and transport of dissolved contaminants using plants to decrease the mobility of pollutants in soils. This is a modified view of the definition of phytostabilization as

proposed by Raskin *et al.* (1994) and Cunningham *et al.* (1995).·

- Phytostabilization, as defined here, uses pollutant-tolerant plants to mechanically stabilize polluted soils to prevent bulk erosion and airborne transport to other environments. In addition, leachability of pollutants may be reduced due to higher evapotranspiration rates relative to bare soils.

Removal processes:

- Phytoextraction processes extract both metallic and organic constituents from soil by direct uptake into plants and translocation to above-ground biomass (Salt *et al.* 1995);
- Phytovolatilization processes involve specialized enzymes that can transform and volatilize contaminants in the plant – microbe – soil system (Meagher and Rugh 1996; Schnoor *et al.* 1995).

Because of the plant-microbe interactions involved, such as the association of fungi and bacteria with plant roots, i.e., in the rhizosphere, plant-based clean-up technology has been referred to as a plant-microbe treatment system.

Enhancement of phytoremediation processes may be achieved by improving plant properties, soil conditioning and management practices. Depending on the phytoremediation process and pollutants involved, enhancement of plant properties can focus on modification of the above-ground biomass (e.g. increasing it for phytoextraction) and/or modification of the root/rhizosphere system (e.g. morphology, surface area, microbe associations, root exudates). Plant properties may be improved using breeding or genetic manipulation. The transfer of hyperaccumulating genes from endemic hyperaccumulating species into high biomass plants may be achieved by using somatic hybridization of high biomass / hyperaccumulating plants, or by single gene transfer using modern genetic manipulations. Somatic hybridization between the high biomass crop *Brassica napus* and *Thlaspi perfoliatum*, a close relative of several hyperaccumulating species, has already been demonstrated (Fahleson *et al.* 1994). This infers the feasibility of this approach and indicates that it may be possible to hybridize other high biomass / metal-accumulating species, such as *Brassica juncea* (Kumar *et al.* 1995), with *T. caerulescens*, a known hyperaccumulator of Zn and Ni (Baker and Brooks 1989; Baker *et al.* 1994), to develop effective phytoextractors.

Hyperaccumulator plants generally need elevated levels of essential metals to grow well. This can be due to the fact that their exceptional mechanisms of tolerance are active even at low concentration. Therefore, natural hyperaccumulator plants or genetically engineered plants will be probably confined to the contaminated site and will not become a weed problem (McGrath 1998).

The soil bioavailability of chemical elements, and therefore also pollutants such as heavy metals, is strongly related to pH. Plant roots are able to markedly change the pH in the rhizosphere. Moreover, the rhizosphere pH can be, to some extent, controlled using different N fertilizers. Neng-Chang and Huai-Man (1992) pointed out that Cd extractability in the rhizosphere was controlled by pH, and changes in pH in the rhizosphere were closely related to the balance between the uptake of anions and cations. They suggested the use of alkaline fertilizer to reduce the mobility of toxic metals in the soil. Another important aspect of the rhizosphere is the interaction between mycorrhizal fungi and plant roots. Mycorrhizal plants are of great interest in phytoimmobilization since mycorrhizae can bind metals and limit their translocation to shoots (Leyval *et al.* 1997). Since the management of soil microorganisms, including mycorrhizal fungi, is a prerequisite for the success of future restoration programmes (Haselwandter 1997), more in-depth studies of the relationships between roots and microorganisms in the rhizosphere are urgently required. Release of chelating substances, such as organic acids, is another mechanism that plants use to enhance mobility of elements in the rhizosphere.

Chemical conditioning by adding acids, lime, or organic matter directly alters the soil chemical milieu, e.g. pH, redox and the concentration of complexing / chelating agents in solution and in the soil solid phase. As mentioned, this may influence nutrient bioavailability to plants and microorganisms, but equally important, may directly change the mobility / bioavailability of the pollutants. Materials commonly used for soil conditioning / amelioration are organic matter (peat, sewage sludge, composts of biowaste, etc.), lime, gypsum, clay minerals and occasionally oxides. In addition, inorganic by-products from industrial processes such as from olive oil production (Madrid and Diaz-Barrientos 1994) or flue dust may be considered, although these materials may contain considerable amounts of metals (Carlson and Adriano 1993). Synthetic chelators, e.g. EDTA and DTPA have been applied in micronutrient fertilization and were recently found to increase Cd uptake in *Brassica juncea*, a strong candidate for phytoremediation (Salt *et al.* 1995). Application of 10 mmoles kg^{-1} of EDTA to soil containing 1200 mg kg^{-1} Pb resulted in the accumulation of 16 000 mg kg^{-1} Pb, on a dry weight basis, in *Brassica juncea* shoots (Baylock *et al.* 1997). Lead accumulation in shoots of *Zea mays* L. cv. Fiesta was increased from 40 mg kg^{-1} for the control to 10 600 mg kg^{-1} for the soil treated with 2 g kg^{-1} HEDTA (Huang *et al.* 1997).

One of the main problems related to phytoremediation is the long time required by this technology. McGrath *et al.* (1993) calculated that it would take nine years to reduce Zn concentration in soil from 440 µg g^{-1} to 300 µg g^{-1} using *Thalspi caerulescens*. On the other hand, this technology is well accepted by the public and the costs are deemed to be low (in the range of $80/m^3).

REFERENCES

Acar, Y.B. and Alshawabkeh, A.N. (1993) Principles of electrokinetic remediation. *Environ. Sci. Technol.*, **27**, 2638-2647.

Adriano, D.C. (1986) *Trace Elements in the Terrestrial Environment*. Springer-Verlag, New York.

Adriano, D.C., Chlopecka, A. and Kaplan, K.I. (1998) *Role of Soil Chemistry in Soil Remediation and Ecosystem Conservation*. Soil Sci. Soc. Am. Spec. Public. Madison, WI.

Adriano, D.C., Chlopecka, A., Kaplan, D.I., Clijsters, H. and Vangronsveld, J. (1995) Soil contamination and remediation: philosophy, science and technology. In: *Contaminated Soils*, R. Prost ed. INRA Les olloques, n° 85, Paris. pp. 465-504.

Alloway, B.J. and Ayres, D.C. (1997) *Chemical Principles of Environmental Pollution*. 2nd edition. 4.

ATSDR (1988) *The Nature and Extent of Lead Poisoning in the United States: A Report to Congress*. US Department of Health and Human Services, Atlanta, Georgia.

Baker, A.J.M., and Brooks, R.R. (1989) Terrestrial higher plants which accumulate metallic elements – a review of their distribution, ecology and phytochemistry. *Biorecovery,* **1**, 81-126.

Baker, A.J.M., Reeves, R.D. and McGrath, S.P. (1991) In situ decontamination of heavy metal polluted soils. Using crops of metal-accumulating plants – a feasibility study. In: R.E. Hinchee and R.F. Olfenbuttel (eds.) *In situ Bioreclamation*. Butterworth-Heinemann, Stoneham, MA, USA, pp. 539.

Baker, A.J.M., Reeves, R.D. and Hajar, A.S.M (1994) Heavy metal accumulation and tolerance in British populations of the metallophyte Thlaspi caerulescens J. & C. Presl (Brassicaceae). *New Phytol.*, **127**, 61-68.

Barth, H. and L'Hermite, P. (1987) *Scientific Basis for Soil Protection in the European Community*. Elsevier Scientific Publishers Ltd., Essex, England. p. 630.

Bartnicki, J. (1996) Computing atmospheric transport and deposition of heavy metals over Europe: country budget for 1985. *Water Air and Soil Pollution*, **92**, 343-374.

Baylock, M.J., Salt, D.E., Dushenkov, S., Zakharova, O., Gussman, C., Kapulnik, Y., Ensley, B.D. and Raskin I. (1997) Enhanced accumulation of Pb in indian mustard by soil-applied chelating agents. *Environ. Sci. Techn.*, **31**, 860-865.

Beckett M.J. and Cairney T. (1993) Reclamation option. In: *Contaminated Land: problems and solutions*. T. Cairney (ed.) Blackie Academic & Professional, London. pp. 68-83.

Benninger-Traux, M. and Taylor, D.H. (1993) Municipal sludge metal contamination of old-field ecosystems: do liming and tilling affect remediation? *Environ. Toxicol. Chem.,* **12**, 1931-1943.

Berrow, M.L. (1986) An overview of soil contamination problems. In: Proc. Int. Conf. Chemicals in the Environment. Lester, Perry and Sterrit (eds.) London, Selper, pp. 543-552.

Boisson, J., Mench, M., Sappin-Didier, V., Solda, P. and Vangronsveld, J. (1998) In situ immobilization of Cd and Ni by beringite and steel shots application to long-term sludged plots. *Agronomie* (in press).

Brenner, W. and Rugg, B. (1982) Exploratory studies on the encapsulation of selected hazardous wastes with sulfur-asphalt blends. In: *Proceedings of the 8th Annual Research Symposium on Land Disposal of Hazardous Waste*. Cincinnati, OH.

Bryda, L.K. and Sellman, C.L. (1994) Recent development in cleanup technology. *Remediation* (Autumn), 475-489.

Carlson, C.L., and Adriano, D.C. (1993) Environmental impacts of coal residues. *J. Environ. Qual.*, **22**, 227-247.

Chang, A.C., Page, A.L. and Warneke, J.E. (1987) Long-term sludge applications on cadmium and zinc accumulation in Swiss chard and radish. *J. Environ. Qual.,* **16**, 217-221.

Chlopecka, A. and Adriano, D.C. (1996) Mimicked in situ stabilization of metals in a cropped soil: bioavailability and chemical form of zinc. *Environ. Sci. Technol.*, **30**, 3294-3303.

Cunningham, S.D., Berti, W.R. and Huang, J.W. (1995) Phytoremediation of contaminated soils. *Trends in Biotechnology (TIBTECH),* **13**, 393-397.

Davies, B.E. (1992) Trace elements in the environment: retrospect and prospect. In: *Biogeochemistry of Trace Elements*, D.C. Adriano (ed.). Lewis Publishers. Boca Raton, FL. pp. 1-17.

Decreto legislativo 27 gennaio 1992 n. 99 'Attuazione della direttiva 86/278/CEE, concernente la protezione dell'ambiente, in particolare del suolo, nell'utilizzazione dei fanghi di depurazione in agricoltura'. *Gazzetta Ufficiale della Republica Italiana,* n.38 del 15-2-1992, Parte prima.

Deuel, L.E. and Swoboda, A.R. (1972) Arsenic solubility in a reduced environment. *Soil Sci. Soc. Am. Proc.*, **36**, 276-278.

EC Council Directive 86/278/EEC (1986) On the protection of the environment and in particular of the soil when sewage sludge is used. *Off. J. European Community,* L181 (Annex A). 6-12.

Eijsackers, H.J.P. and Hamers, T. eds. (1993) Integrated soil and sediments research: a basis for protection. Kluwer Academic Pub., Dordrecht, The Netherlands. p. 763.

Eikmann, Th. and Kloke, A. (1991) Nutzungs- und Schutzgutbezogene Orientierungswerte für (Schad-) stoffe in Böden. In: Rosenkranz, D., Bachmann, G., Einsele, G. and Harreß, H.M. (eds.) *Bodenschutz. Ergänzbares Handbuch der Maßnahmen und Empfehlungen für Schutz, Pflege und Sanierung von Böden, Landschaft und Grundwasser*. Erich Schmidt Verlag, Berlin.

Eney, A.B. and Petzold, D.E. (1987) The problem of acid rain: an overview. *Environmentalist*, **7**, 95.

Fahleson, J., Eriksson, I., Landgren, M., Stymne, S. and Glimelius, K. (1994) Intertribal somatic hybrids between Brassica napus and Thlaspi perfoliatum with high content of the T. perfoliatum-specific nervonic acid. *Theor. Appl. Genet.*, **87**, 795-804.

Ferguson, J.F. and Gavis, J. (1972). A review of the arsenic cycle in natural waters. *Water Res.*, **6**, 1259-1274.

Forste, J.B. (1995) Biosolid processing, production, and use. In: *Agricultural Uses of By-products and Waste*s. J. E. Rochcigl and H.C. Hackinnon (eds.). ACS Symposium Series 668. Washington D.C. p. 56.

Fu, G., Allen, H.E. and Cowan, C.E. (1991) Adsorption of cadmium and copper by manganese oxide. *Soil Sci.*, **152**, 72-81.

Gworek, B. (1992*a*) Inactivation of cadmium in contaminated soils using synthetic zeolites. *Environ. Pollut.*, **75**, 269-271.

Gworek, B. (1992*b*) Lead inactivation in soils by zeolites. *Plant and Soil*, **143**, 71-74.

Han, D.H. and Lee, J.H. (1996) Effects of liming on uptake of lead and cadmium by Raphanus sativa. *Archives of Environmental Contamination and Toxicology*, **31**, 488-493.

Haselwandter, K. (1997) Soil microorganisms, mycorrhiza, and restoration ecology. In: Urbanska *et al.* (eds.) *Restoration Ecology and Sustainable Development*. Cambridge University Press, Cambridge.

Helmke, P.A., Koons, R.D., Schonberg, P.J. and Iskandar, I.K. (1977) Determination of trace contamination of sediments by multi-element analysis of clay-size fraction. *Environ. Sci. Techn.*, **11**, 984-989.

Hemond, F.H. and Fechner, E. J. (1994) *Chemical Fate and Transport in the Environment*. Academic Press, San Diego, CA. pp. 53-55.

Houthoofd, J.M., McCready, J.H. and Roulier, M.H. (1991) Soil heating technologies for in situ soil treatment: a review. In: *Remedial Action, Treatment and Disposal of Hazardous Waste: Proceedings of the 7th annual RREL Hazardous Waste Research Symposium*. 190-203.

Huang, J.W., Chen, J., Berti, W.B., Cunningham, S.D. (1997) Phytoremediation of lead-contaminated soils: Role of synthetic chelates in lead phytoextraction. *Environ. Sci. Tech.*, **31**, 800-805.

Hue, N.U. (1995) *Soil Amendments and Environmental Quality*, J. E. Rochcigl (ed.) Agriculture and Environment Series. Lewis Publishers, Boca Raton, FL. pp. 199-247.

Iskandar, I.K. and Adriano, D.C. (1997) Remediation of soils contaminated with metals – a review of current practices in the USA. In: *Remediation of Soils Contaminated with Metals*. I.K. Iskandar and D.C. Adriano (eds.) Advances in Environmental Sciences. Science Reviews, Northwood, England. pp. 1-26.

Jones, K.C. (1991) Contaminant trends in soil and crops. *Environ. Pollut.*, **69**, 311-325.

Kabata-Pendias, A. and Pendias, H. (1992) *Trace Elements in Soils and Plants*. CRC Press, Boca Raton, FL, USA.

Kalb, P.D., Burns, H.H. and Meyer, M. (1993) Thermoplastic encapsulation treatability study for a mixed waste incinerator off-gas scrubbing solution. In: T.M. Gilliam ed. *Third International Symposium Stabilization/Solidification of Hazardous, Radioactive and Mixed Wastes*. ASTM STP 1240. America Society for Testing and Materials, Philadelphia.

Keefer, R.F., Singh, R.N. and Horvath, D.J. (1986) Chemical composition of vegetables grown on an agricultural soil amended with sewage sludge. *J. Environ. Qual.*, **15**, 146-152.

Kumar, P.B.A.N., Dushenkov, S., Motto, H. and Raskin, I. (1995) Phytoextraction: the use of plants to remove heavy metals from soils. *Environmental Science and Technology,* **29**, 1232-1238.

Lafornara, P. (1991) Assessing the risk of remedial alternatives at superfund sites: implications for technology demonstration. In: *Remedial Action, Treatment, and Disposal of Hazardous Waste*. Proceedings of 7th Annual RREL Hazardous Waste Research Symposium US EPA Report 600/9-91/002. Cincinnati OH.

Leyval C., Turnau, K. and Haselwandter, K. (1997) Effect of heavy metal pollution on mycorrhizal colonization and function: physiological, ecological and applied aspects. *Mycorrhiza*, 7, 139-153.

Loizidou, M., Haralambous, K.J., Loukatos, A. and Dimitrakopoulou, D. (1992) Natural zeolites and their ion exchange behaviour towards chromium. *J. Env. Sci. & Health*, **A27**, 1759-1769.

Lombi, E., Sletten, R.S. and Wenzel, W.W. (1998) Arsenic sequentially extracted in sand, silt, and clay of contaminated soils. Submitted.

Lubben, S., and Sauerbeck, D. (1991) The uptake and distribution of heavy metals by spring wheat. *Water, Air and Soil Pollution*, **57**, 239-247.

Mackenzie, F.T., Lantzy, R.J. and Paterson, V. (1979) Global trace metal cycle and predictions. *J. Int. Assoc. Math. Geol.*, **11**, 99-142.

Madrid, L., and Diaz-Barrientos, E. (1994) Retention of heavy metals by soils in the presence of a residue from the olive-oil industry. *Europ. J. Soil Sci.*, **45**, 71-77.

Marschner, B., Henke, U. and Wessolek, G. (1995) Effects of ameliorative additives on the adsorption and binding of heavy metals in a contaminated topsoil from a former sewage farm. Z. Pflanzenernähr. *Bodenk.*, **158**, 9-14.

McGrath, S.P. (1998) Phytoextraction for soil remediation. In: *Plants That Hyperaccumulate Heavy Metals*. R.R. Brooks (ed.) CAB International, Wallingford, UK. pp. 261-288.

McGrath, S.P., Chang, A.C., Page, A.L. and Witter, E. (1994) Land application of sewage sludge: scientific perspectives of heavy metal loading limits in Europe and United States. *Environ. Rev.*, **2**, 108-118.

McGrath, S.P., Sidoli, C.M.D., Baker, A.J.M. and Reeves, R.D. (1993) The potential for the use of metal-accumulating plants for the in situ decontamination of metal-polluted soils. In: H.J.P. Eijsackers and T. Hamers (eds.) *Integrated Soil and Sediment Research: a Basis for Proper Prediction*. Kluwer Academic Publishers, Dordrecht. pp. 673-676.

McKenzie, R.M. (1980) The adsorption of lead and other heavy metals on oxides of manganese and iron. *Aust. J. Soil Res.,* **18**, 61-73.

Meagher, R.B., and Rugh, C. (1996) Phytoremediation of mercury and methyl mercury pollution using modified bacterial genes. IBC Conference 5/8/96. Abstract and Outline.

Mench, M., Didier, V., Löffler, M., Gomez, A. and Masson, P. (1994*a*) Evaluation of metal mobility, plant availability and immobilization by chemical agents in a limed-silty soil. *J. Environ. Qual.*, **23**, 58-63.

Mench, M., Vangronsveld, J., Didier, V. and Clijsters, H. (1994*b*) A mimicked in situ remediation study of metal contaminated soils with emphasis on cadmium and lead. *Environ. Poll.* **86**, 279-286.

Mench, M., Martin, E. and Solda, P. (1994*c*) After effects of metals derived from a highly metal-polluted sludge on maize (Zea mays L.). *Water, Air and Soil Pollution*, **75**, 277-291.

Merian, E. (ed.) (1991) *Metals and their Compounds in the Environment*. VCH Publishers, Weinheim, Germany. p. 1438.

Needleman, H.L., Schell, A., Bellinger, D., Leviton, A. and Allred, E.N. (1990) The long-term effects of exposure to low doses of lead in childhood. An 11-years follow-up report. *N. Engl. J. Med.*, **322**, 83-88.

Neng-Chang, C. and Huai-Man, C. (1992) Chemical behavior of cadmium in wheat rhizosphere. *Pedosphere*, **2**, 363-371.

Overcash, M. (1996) European soil remediation research: 1992-94. *Crit. Rev. Environ. Sci. Techn.*, **26**, 337-368.

Peterson, P.J. and Girling, C.A. (1981) Other trace metals. In: *Effect of Heavy Metal Pollution on Plants*. Vol.1. Effects of trace metals on plant function. N.W. Lepp ed. Applied Science Publishers, London. pp. 222-229.

Ponder, T.G. and Schmitt (1991) Field assessment of air emission from hazardous waste stabilization operation. EPA/600/9-91/002. *Proc. of the 17th Ann. Hazard. Waste Res. Sym.* Cincinnati, OH.

Pruess, A. (1994) Einstufung mobiler Spurenelemente in Böden. In: D. Rosenkranz, G. Bachmann, G. Einsele and H.M. Harreß (Hrsg.), *Bodenschutz. Ergänzbares Handbuch der Maßnahmen und Empfehlungen für Schutz, Pflege und Sanierung von Böden, Landschaft und Grundwasser*. Erich Schmidt Verlag, Berlin.

Pruess, A. (1997) Action values for mobile (NH4NO3-extractable) trace elements in soils based on the German national standard DIN 19730. In: *Contaminated Soil*. R. Prost (ed.) INRA, Paris. pp. 415-432.

Purves, D. (1972) Consequences of trace-element contamination of soils. *Environ. Pollut.*, **3**, 17-24.

Raskin, I., Kumar, P.B.A.N., Dushenkow, S. and Salt, D.E. (1994) Bioconcentration of heavy metals by plants. *Current Opinion in Biotechnology*, **5**, 285-290.

Rebedea, I. and Lepp, N.W. (1994) The use of synthetic zeolites to reduce plant metal uptake and phytotoxicity in two polluted soils. In: *Biogeochemistry of Trace Elements* (D.C. Adriano, Z.S. Chen, S.S. Yang eds.) Science and Technology Letters, Northwood, UK. pp. 81-87.

Ryan, J.A. and Chaney, R.L. (1997) Issue of risk assessment and in situ utility in development of soil standard: the 503 methodology an example. In: *Contaminated Soil*. R. Prost (ed.) INRA, Paris. 394-413.

Salt, D.E., Blaylock, M., Kumar, N.P.B.A., Dushenkov, V., Ensley, B.D., Chet, I. and Raskin, I. (1995) Phytoremediation: A novel strategy for the removal of toxic metals from the environment using plants. *Biotechnology*, **13**, 468-474.

Sappin-Didier, V.L., Mench, M., Gomez, A., Tremel, A., Cambier, P., Manceau, A. and Donard, O.F.X. (1997) Steel shots, a compound that decrease the mobility and bioavailability of metals in polluted soils: benefits and limits. In: *Abstr. Fourth International Conference on the Biogeochemistry of Trace Elements* (I.K. Iskandar, S.E. Hardy, A.C. Chang, G.M. Pierzynski eds.) USA. pp. 445-456.

Schnoor, J.L., Licht, L.A., McCutcheon, S.C., Wolfe, N.L. and Carreira, L.H. (1995) Phytoremediation of organic and nutrient contaminants. *Environ. Sci. Technol.*, **29**, 318-323.

Schulte, A. and Gehrmann, J. (1996) Development of heavy-metal deposition by precipitation in West Germany. 1. Arsenic, chromium, cobalt, and nickel. *Z. Pflanzen. Bodenk.* **159**, 385-390.

Schulte, A., Balazs, A., Block, J. and Gehrmann, J. (1996) Development of heavy-metal deposition by precipitation in West Germany. 1. Lead and cadmium. *Z. Pflanzen. Bodenk.* **159**, 377-384.

Shotyk, W., Cheburkin, A.K., Appleby, P.G., Fankhauser, A. and Kramers, J.D. (1996) Two thousand years of atmospheric arsenic, antimony, and lead deposition recorded in an ombrotrophic peat bog profile, Jura Mountains, Switzerland. *Earth and Planetary Science Letters*, **145**, E1-E7.

Shukla S.S., Shukla A.S. and Lee K.C. (1992). Solidification/stabilization study for the disposal of pentachlorophenol. *J. Hazardous Matter*, **30**, 317-331.

Smith, L.A. *et al.* (1995) *Remedial Options for Metals-contaminated Sites*. L.A. Smith *et al.* (eds.) CRC Lewis Publishers, Boca Raton, FL.

Sposito, G.G. and Page, A.L. (1984) Cycling of metal ions in the soil environment. In: H. Sigel (ed.) *Metal Ions in Biological Systems*. Vol. 18, Circulation of metals in the environment. Marcel Dekker, New York.

Temmerman, L.O., Hoenig, M. and Scokart, P.O. (1984) Determination of 'normal' levels and upper limit values of trace elements in soils. *Z. Pflanzen. Bodenk.*, **147**, 687-694.

Terry N. and Zayed A.M. (1994) Selenium volatilization in plants. In: W.T. Frankenberger Jr. and S. Benson (eds.) *Selenium in the Environment*. Marcel Dekker, New York. pp. 343-367.

Tolba, M.K. and El-Kholy, O.A. (1992) *The World Environment, 1972-1992*. Chapman & Hall, London. 884.

US EPA (1977) *Development of a Polymeric Cementing and Encapsulating Process for Managing Hazardous Wastes by TRW System Group*. US EPA Report-600/2-77-045.

US EPA (1990*a*) *Final Best Demonstrated Available Technology (BDAT) Background Document for Mercury-containing Wastes D009, K106, P092, and U151*. EPA/530-SW-90-059Q; PB90-234170. Report prepared for the US EPA Office of Solid Waste.

US EPA (1990*b*) *Handbook on in situ Treatment of Hazardous-waste Containing Soils*. EPA/540/2-90/002. Risk Reduction Engineering laboratory, Cincinnati.

US EPA (1992*a*) *Federal Remediation Technologies Roundtable: Synopses of Federal Demonstration of Innovative Soil Remediation Technologies*. US EPA report 542/B-92/003.

US EPA (1992*b*) *Handbook: Vitrification Technologies for Treatment of Hazardous and Radioactive Waste*. EPA/625/R-92/002. Office of Research and Development. Washington D.C.

US EPA (1993) Standard for the use of sewage sludge. *Fed. Regist.*, **58**, 9248-9415.

US EPA and US Air Force (1993) *Remediation technology matrix – Reference Guide*. Joint Project of the US EPA Technology Innovation Office (Washington DC) and the US Air Force (Tyndal Air Force Base, FL).

Van Driel, W. and Smilde, K.W. (1990) Micronutrients and heavy metals in Dutch agriculture. *Fert. Res.*, **25**, 115-126.

Vangronsveld, J., Van Assche, F. and Clijsters (1990) Immobilization of heavy metals in polluted soils by application of a mod-ified alumino-silicate: Biological evaluation. In: *Proc. Int. Conf. Environmental Contamination* (J. Barcelo ed.) CEP Consultants, Edinburgh, UK. pp. 283-285.

Vangronsveld, J., Stercks, J., Van Assche, F. and Clijsters (1995*a*) Rehabilitation studies on an old non-ferrous waste dumping ground: effects of revegetation and metal immobilization by beringite. *Geochem Expl.*, **52**, 221-229.

Vangronsveld, J., Van Assche, F. and Clijsters (1995*b*) Reclamation of a bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation. *Environ. Poll.* **87**, 51-59.

Vangronsveld, J., Colpaert, J. and Van Tichelen, K. (1996) Reclamation of a bare industrial area contaminated by non-ferrous metals: Physico-chemical and biological evaluation of the durability of soil treatment and revegetation. *Environ. Poll.*, **94**, 131-140.

Weitzman, L. and Hamel, L.E. (1990) Volatile emissions from stabilized waste. In: *Proc. 15th Annu. Res. Symp*. EPA/600/9-90/006. Cincinnati, OH.

Wenzel, W.W., Salt, D., Adriano, D.C. and Smith, R. (1998) Phytoremediation: a plant-microbe-based remediation system. In: D.C. Adriano *et al.* (eds.) *Soil Remediation*. SSSA Monographs, Madison. In press.

Wren, C.D., Harris, S. and Harttrup, N. (1995) Ecotoxicology of mercury and cadmium. In: *Handbook of Ecotoxicology.* D.J. Hoffman, B.A. Rattner, G.A. Burton and J. Cairns (eds.) Lewis Publishers, Boca Raton, FL. pp. 392-423.