11 Use of Soil Amendments to Attenuate Trace Element Exposure: Sustainability, Side Effects, and Failures

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CONTENTS

11.1 INTRODUCTION

The extent of the hazard posed by trace elements in the soil to organisms depends on their concentrations and chemical speciation in the solid, liquid, and gaseous phases. Limiting the exposure pathways will help to decrease acute and chronic risks. Potentially the most cost-effective strategies to achieve this involve the so-called "mild" remediation techniques (Vangronsveld and Cunningham, 1998). Mild remediation options for reducing trace element exposure include deep ploughing, phytoremediation, and chemical immobilization (Osté, 2001). Deep ploughing can work if only the upper soil layer is contaminated and the underlying soil has a sufficient fertility and buffer capacity to function as a topsoil. Phytoextraction uses plants to remove soil contaminants by translocating them into plant tissue. The treatment duration and lack of commercially available plant strains with high biomass currently limit its implementation. Furthermore, in soils contaminated with a number of metals, one or more elements may limit the phytoextraction potential, e.g., high soil Cu content can reduce the growth of *Thlaspi caerulescens*, and thus Zn and Cd phytoextraction. Chemical immobilization, also called *in situ* immobilization, inactivation, or attenuation, comprises several methods that aim at reducing potential exposure via the soil or wastes. Mench et al. (1994), Vangronsveld and Cunningham (1998), and Singh and Osté (2001) provide definitions. In this chapter, *chemical immobilization* is defined as an amendment added to the contaminated soil or waste that renders trace elements less bioavailable by altering chemical forms so that toxicity is reduced via a range of exposure pathways, e.g., the soil solution, the gaseous phase, or the ingested particles. These technologies need to result in suitable conditions for living organisms. At least two options can be adopted. The first option is to promote naturally occurring processes that can alter both speciation and concentration in solid phases and the soil solution. This may be time consuming or even impossible. An alternative option is to introduce one or several compounds via an amendment, leading, for example, to new solid reactive phases or the presence of an essential element for the transformation process. Different mechanisms can be involved, including sorption, acid–base reaction, precipitation, oxidation–reduction and demethylation.

If the bioavailability of contaminants is decreased through attenuation, it may be possible to restore a vegetative cover (i.e., phytostabilization) to the soil with beneficial effects on wind erosion, water transport, and leaching. Alternatively, an increase in biodiversity may be the aim. One challenge is to enhance processes which minimize exposure to nonessential trace elements, without inducing nutrient deficiencies or introducing any further unwanted contaminants (Geebelen, Adriano, Mench et al., 2003). Many short-term experiments have demonstrated that it is possible to use chemical immobilization methods to attenuate the exposure of plant species and other organisms to metals and metalloids (Brown et al., 2000; Lepp et al., 2000; McBride and Martinez, 2000; Mench et al., 2000; Vangronsveld, Ruttens et al., 2000). However long-lasting demonstrations are necessary to gain public acceptance and also to establish the endurance of the remediation techniques. Accordingly, several field experiments and mesocosms have been established to assess the feasibility to use natural and synthetic soil amendments for attenuating trace element exposures. This review will pay special attention to the successes, failures, and side effects indicated by these experiments in relation to the primary production of plant species, metal concentrations in plant parts (especially those consumed by animals and humans), the biodiversity, the presence of genotoxic effects, and the risk of off-site contaminant transport. There is a clear need for long-term attenuation and phytostabilization experiments, to stimulate private initiatives and cofinancing, and to convince the general public and legislators. New soil remediation policy based on risk assessment, bioavailability and risk reduction, and site-specific circumstances, needs to be promoted.

11.2 TYPES OF SOIL AMENDMENTS

A key question for remediation by chemical immobilization is how to select an appropriate amendment. An ideal amendment will rapidly decrease the mobility and bioavailability of the contaminant, preventing leaching, plant uptake, etc. A long lasting, if not permanent, effect is required. Other characteristics to be considered are price, commercial availability, ease of application and safety to workers, lack of disruptive or adverse effects, especially on the soil structure and fertility, compatibility with plants used for revegetation, suitability for several contaminants, and compliance with regulations. Amendment addition should also not result in additional environmental concerns (see the following discussion). The soil amendment should be suitable for combination with other techniques, if possible adaptable to agricultural management, and suitable for different soil types. Osté (2001) stated that the material must have a high metal-binding capacity at common soil pH (about 4 to 8) and needs to be durable under the environmental conditions of the soil. These prerequisites may be overly constraining, as materials such as zerovalent Fe and steelshots have no initial binding capacity, but their alteration in soil can lead to sorption processes or chemical transformations. Aging and crystallization of materials

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TABLE 11.1
Natural and Anthropogenic Soil Amendments That Have Been Used to Attenuate Inorganic Contaminant Exposure

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Alkaline materials	**Fe, Mn, Al oxides/hydroxides**
Calcium, magnesium carbonates	Ferrihydrite
Calcium, magnesium oxides	Hematite
Limed sludges, alkaline biosolids	Lepidocrocite
Fluidised bed coal fly ashes	Magnetite
	Maghemite
Phosphate minerals	Mud from water treatment
Apatites	Fines from ferrous smelter
Hydroxyapatite	Waste from TiO_2 treatment (Fe-rich)
Basic slags	Red mud (bauxite, Al)
Phosphoric acid	Hydrous manganese oxides
Phosphates salts (K, Na, Ca, NH_4, etc.)	Birnessite
Natural phosphates	Chalcophanite
	Iron grit (steelshot)
Alumino-silicates	Zerovalent Fe
Clays (smectites, bentonite, etc.)	
Gravel sludge	**Zeolites**
Coal fly ashes, e.g., beringite	Natural zeolites
	Synthetic zeolites
Organic matter (compost, farmyard manure, etc.)	**Salts** (Cu, FE sulfate, Zn, etc.)

such as Fe oxides, allophanes, and silica gels may increase the attenuation of trace elements.

Numerous materials have been selected for both their lack of negative influences on key aspects of soil health and their efficacy in decreasing the solubility and bioavailability of trace elements in contaminated soils (Knox et al., 2000; McBride and Martinez, 2000; Mench et al., 2000; Osté, 2001) (Table 11.1). Physical and chemical properties of these amendments have been reviewed (Mench et al., 1998; Knox et al., 2000). These materials decrease exposure by one or more processes, e.g., sorption, redox reaction, precipitation, ion exchange, complexation, excesses of competing elements, and humification (Mench et al., 1998).

Materials such as lime, phosphates, and organic matter have been used for a long time in agriculture. Some of the solid phases and processes used for the remediation of metal-contaminated soils are naturally occurring. Amorphous Al, Fe, and Mn oxide minerals are ubiquitous in soils as both discrete particles and surface coatings. Properties of these phases, which contribute significantly to metal attenuation, include high porosity, micropores, high surface area, and a large number of adsorption sites. Intraparticle surface diffusion is a rate-limiting mechanism in the sorption process when metal ions diffuse in hydrated micropores (see Chapter 4). In this chapter, attention is focused on the following materials, which have been tested in long-term field experiments and outdoor mesocosms: lime, zeolites, phosphate compounds, metal oxides, biosolids, and industrial by-products.

Abbreviations used within the text are as follows: Unt (Untreated contaminated material), C (compost), B (beringite), SS (steelshot), Z4A (zeolite 4A), CB (compost and beringite), CSS (compost and steelshot), CBSS (compost combined with beringite and steelshot), and DOM (dissolved organic matter).

11.3 END POINTS FOR TESTING EFFICACY OF ATTENUATION

There are three main routes of exposure to soilborne trace metals. Soluble contaminants migrate with soil water, are taken up from this medium by plants and aquatic organisms, and, in some cases, can be lost from solution through volatilization. The other pathways are direct ingestion and dermal contact with contaminated particulates. Consequently, any thorough evaluation of the overall effectiveness of amendments for chemical immobilization should combine physicochemical and biological methods. For ecotoxicological evaluation, it is important to survey several end points, e.g., biodiversity, bioaccumulation in living organisms, changes in metabolite and protein patterns, as well as genotoxicity, at different trophic levels, with a progression from a well-defined battery of tests to more complex conditions representative of real ecosystems. A combined use of chemical extraction, microbial biosensors, phytotoxicity and zootoxicity tests was reported by Vangronsveld, Mench et al., (2000). However, there is currently no consensus on the battery of tests that should be used to assess the extent of hazard reduction.

11.4 BACKGROUND TO EXPERIMENTAL SITES

Selected long-term field trials, as well as small-scale semifield experiments (i.e., large outdoor mesocosms, which mimic a field trial) in Europe, the U.S., and Australia that feature in this chapter are shown in Table 11.2. Soil characteristics from selected sites in Europe are shown in Table 11.3. One series of long-term field trials not described in this chapter, but important to note, consists of those established in the mid-19th century at Rothamsted Experimental Station in the U.K. Data from these field trials have proven particularly useful in understanding the relationship between land use, acidification, lime use, and metal mobilization (Goulding and Blake, 1998).

Lommel-Maatheide, the site of one of the oldest field trials on soils contaminated by industrial fallout, is located in Kempen, Limburg Province, Belgium, a region where the Zn industry operated several smelters for more than 100 years. The sandy soil of this region is characterized by an acid pH (4.5 to 6.0), a low organic matter content (<2%), and a low cation exchange capacity (<2 cmol kg^{-1}). In 1990, 3 ha of a highly metal-contaminated soil were treated with a combination of beringite (a type of cyclonic ash, B, 5%) and compost (C, 5%) (Vangronsveld et al. 1995, 1996; Vangronsveld, Ruttens et al., 2000; Vangronsveld, Mench et al., 2000). Field remediation trials and small-scale semifield experiments have also been established at 5 additional sites, i.e., Louis Fargue (France), Jales (Portugal), Overpelt (Belgium), Pyhäsalmi (Finland), and Reppel (Belgium) (Verkleij et al., 1999). Steelshot (SS), AU: Show trials from top down.

TABLE 11.2
Long-Term Field Trials and Outdoor Mesocosms Which Have Used Soil Amendments to Attenuate Trace Element Bioavailability and Mobility

Site	Jales	Reppel	Overpelt	Louis Fargue	Maatheide	Northampton	Staffordshire	South Australia
Country	Portugal	Belgium	Belgium	France	Belgium	UK	UK	Aus
Project	PHY	PHY	PHY	PHY	LUC			
Source	Gold mine	As smelter	Zn/Cd smelter	Sewage sludge	Zn/Pb smelter	Cd oxides	Sewage farm	Fertilizers Cd impurities
Metals	Zn, Cu, Cd, Pb		Zn, Cu, Cd, Pb	Cd, Ni	Zn, Cd, Pb, Cu	Cd	Cd	Cd
Metalloids	As	As						
Set up	1998	1997	1998	1995	1990	1998	1998	
Soil type	Sandy soil	Sandy soil	Sandy soil	Sandy soil	Sandy soil	Loamy soil		Alfisols
Field trial	On site		On site	On site	On site	On site	On site	On site
Outdoor mesocosms	Bordeaux	Bordeaux	Hasselt					
Treatments	C, CB, CBSS, CSS	C, B, SS, BSS	C, B, SS, CB, CSS, CBSS	B, SS	B	L, $FeSO_4$, SS, Z4A	L, Fe-oxide SS, Z4A	Cu, Zn, L Al-WTR $MgCO_3$, FRF, Clay
References[a]	1,2,3	4,5	6	7	8	9	9	10

Note: C: compost (5%), B: cyclonic ashes beringite (5%), SS: iron grit (steelshots), L: lime, Z4A: zeolite 4A, FRF: Fe-rich fines from a ferrous smelter, Al-WTR: alum-based water treatment residual. PHY: Phytorehab, LUC: Limburgs Universitair Centrum.

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[a] 1: Mench et al. (2000), 2: Mench, Bussière et al. (2003), 3: Bleeker et al. (2002), 4: Boisson et al. (1998), 5: Boisson (1999), 6: Ruttens et al. (2003), 7: Mench et al. (2000), 8: Vangronsveld (1998), 9: Lepp et al. (2000), 10: McLaughlin et al. (2000).

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TABLE 11.3
Soil Characteristics of Selected Long-Term Experiments in Europe

Site	pH (water)	OM g kg⁻¹	Org.C g kg⁻¹	CEC cmol kg⁻¹	As	Cd	Cu mg kg⁻¹ dry weight	Pb	Zn	Ni
Jales	4.1		0.4	0.9	1325	3.8	15.2	170	165	<2
Louis Fargue	6.6	18		3.7		29				55
Lommel-Maatheide	4.5–6	19.5		3.3		6–54	206–1393	375–2158	1078–11425	
Northampton	5.3		165		72	47	489	630	1301	87
Overpelt	4.1		1.4	1.3		60	319	756	1620	
Reppel			17.6	3.8	113	1.1		61.8	122	
Staffordshire	6.6				8	16	63	213	225	22

an iron grit containing mainly zerovalent Fe, and beringite (B) were the primary amendments tested, both separately and in combination. Compost (C) was also added to increase soil fertility. The Zn smelter at Overpelt, also located in Limburg province, Belgium, produced 250 tons of Cd waste in 1950, half of which was released as atmospheric emissions (340 kg of Cd d^{1}). The smelter converted to an electrolytic process between 1969 and 1974, but even though emissions were significantly reduced, there were still elevated concentrations of Cd, Pb, and Zn in the local environment. The Jales mine, northeastern Portugal, operated from 1933 to 1993. Metal-enriched mine spoils cover 14.4 ha. The vein contained, besides quartz, FeS_2FeAs, FeS_2, PbS, CuFeS, and sulphur salts of silver and gold (Santos Oliveira and Freira Avila, 1995). Four tons of Jales soil were collected (0 to 0.3 m top soil layer) and transported in January, 1998, to the INRA Bordeaux-Aquitaine Centre (Verkleij et al., 1999). A sandy soil (0 to 0.3 m depth layer) sampled at the INRA Pierroton Centre, Gironde, France, was used as an uncontaminated control soil (Control). Reppel, a village in Limburg province, Belgium, is the site of a former As(III) refinery, which operated from 1910 to 1965. The on-site storage of As and Zn products resulted in high-level contamination of approximately 8 ha of the site. Lysimeters were filled with a soil sampled in the adjacent agricultural area contaminated by fallout from this refinery and placed outside as a small-scale semifield experiment (Boisson, 1999).

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For each experiment described in the following text, time zero is the day on which the amendment was applied. The amount of amendment applied is always expressed as a percentage by soil air-dried weight. Concentrations are all expressed on a dry weight basis.

11.5 CHEMICAL TESTS AND SPECIATION

Soils were sampled at Lommel-Maatheide experiment 5 years following amendment with a mixture of beringite (5%) and compost (5%). Analysis of the treated soil showed a change in pH from acid to slightly alkaline (7.3 to 7.9), together with increases in organic matter content and cation exchange capacity. The ratio of water-extractable vs. total Zn was highest in untreated soils (Table 11.4). This ratio decreased (up to 70 times) in the CB-treated soils, and its value was below that in the control. Similar results were found for Cd. The mechanisms responsible for decreasing metal solubility are considered to be an increase in soil pH, precipitation, and sorption on Ca-phosphates, ferrihydrite, allophanes, and other minerals added in the CB amendment. However, EXAFS and x-ray diffraction indicated that silicates, such as hemimorphite ($Zn_4Si_2O_7(OH)_2.H_2O$) and willemite (Zn_2SiO_4), were also present in the CB-treated soil and could be involved in the attenuation process (Hargé, 1997).

Soluble and exchangeable Cd and Zn fractions in the small-scale Overpelt experiment were assessed 3 years after initial treatment, using a 0.01 *M* $Ca(NO_3)_2$ extraction (Semane, 2001) (Figure 11.1). Soil pH values were as follows: 6.5 (control), 6.4 (C), 6.9 (CB), 6.9 (BSS), 7 (CBSS), and 6.1 (Unt). The lowest Cd concentration among treated soils was found for CBSS (up to 4 times lower than in Unt soil). Despite a similar pH, CBSS more efficiently decreased extractable Cd than CB,

TABLE 11.4
Ratio of Water-Extractable Zn vs. Total Zn Concentration in Soil Measured 5 Years after Soil Treatment at the Lommel-Maatheide Experiment (SD, n = 3)

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Treatments	Total Zn (aqua regia, mg kg^{-1})	Water-Extracted Zn (mg kg^{-1})	Ratio (%)
Uncontaminated garden soil	106 (7)	0.7 (0.06)	0.660
Untreated	11425 (506)	14 (11)	1.234
CB	7639 (455)	2.2 (0.22)	0.029

Note: Standard deviation in parentheses; CB: compost (5%) + beringite (5%). AU: OK?

Source: From Vangronsveld, J., Colpaert, J.V., Van Tichelen, K.K., 1996. *Environ Pollut* 94: 131–140. With permission.

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demonstrating an additional mechanism, probably due to steelshots oxidation. The CBSS and BSS treatments showed the greatest decrease in extractable Zn (4 times compared to the Unt treatment).

As discussed in Chapter 1, attenuation can be assessed by using sequential fractionation techniques to examine metal redistribution between different solid phases. An example of this is shown for data from the small-scale Reppel experiment, 4 years following soil amendment. Zinc redistribution among organic and mineral phases was associated with a decrease in Zn exposure. Comparison of B-treated and Unt soils showed that the percentage of Zn associated with the organic compounds decreased, whereas Zn associated with amorphous minerals and other compounds increased (Figure 11.2) (Pannetier, 2000).

The effect of soil amendments on attenuation of metalloids in soils has also been studied, but considerably fewer data are available compared to metals. In soil solutions sampled from the small-scale Reppel experiment, As(V) was the primary As species present in the (1%) SS-treated soil, both before and after the Fe in this material was oxidized (Boisson, 1999). A range of iron oxide-producing systems, including Fe grit, Fe II sulfate + lime, and Fe III sulfate + lime, and goethite + lime, demonstrated a high sorption affinity for As in solution in three soils originating from northwestern England (Hartley et al., 2001). These selected data provide evidence that the use of amendments can decrease metal or metalloid exposure via the soil solution (soil–plant system–animal pathway) in several different types of contaminated soils. But does a decrease in trace element concentration in the soil solution necessarily indicate a decrease in trace element mobility (leaching) to groundwater?

11.6 LEACHING

Time-dependant changes in metal and As concentrations in water percolating through amended soil layers are reported in some long-term experiments. The small-scale

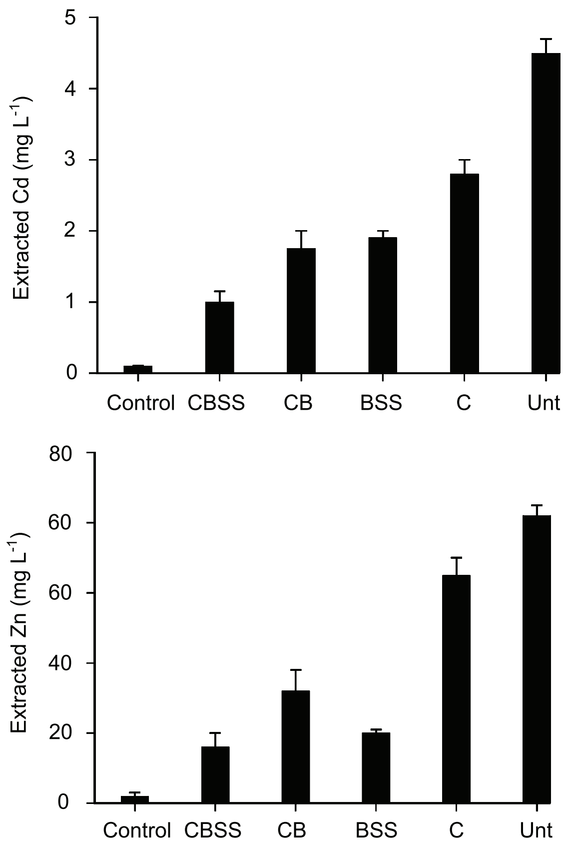

FIGURE 11.1 Cadmium and zinc extracted by 0.1- *M* calcium nitrate in soils sampled at the small-scale Overpelt experiment 3 years after soil treatment (Unt: untreated; Control: control soil; C: compost (5%); CB : C + beringite (5%); BSS: beringite (5%) + steelshot (1%); CBSS: C + beringite (5%) + steelshot (1%). (From Seaman, J.C., Meehan, T., Bertsch, P.M., 2001. *J Environ Qual* 30: 1206–1213. With permission.)

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Overpelt experiment showed that all the amendments decreased the leachability of Cd and Zn in comparison to the control, with the amount of these elements leaching over a 12-month period decreasing in the following order: Unt > C > CB > CBSS (Figure 11.3). However in contrast, compost addition resulted in an increase in Cu and Pb leachability in comparison to the control (Figure 11.3). As discussed in Chapter 6, increases in soil pH and organic matter may change the solid–solution partitioning of the organic matter, increase DOM concentration in the soil solution, and enhance the presence of colloids able to transport metals. An additional approach, e.g., phosphates added in the amendment combination, may solve this side effect when these metals are of primary concern at a contaminated site. The effect of amendment with beringite on metal leachability in a kitchen garden soil from the Lommel-Maatheide site was investigated (Vangronsveld, 1998; Vangronsveld, Mench et al., 2000). The simulated annual amounts of percolated Cd and Zn

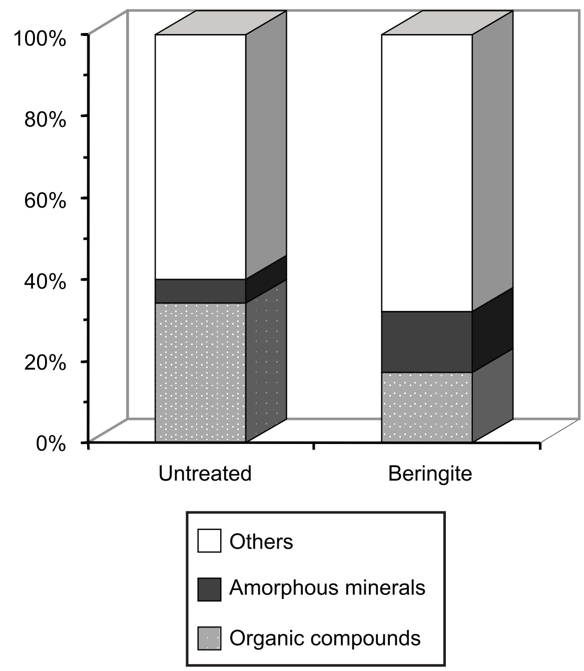

FIGURE 11.2 Distribution of Zn in soil fractions of the beringite-treated and untreated soils at the small-scale Reppel experiment. (From Pannetier, S., 2000. Etude de l'incidence des amendements de béringite sur l'abondance des minéraux amorphes dans les sols: conséquences sur l'immobilisation des cations métalliques. Report, IUP EGID, Bordeaux III. Talence, France. With permission.)

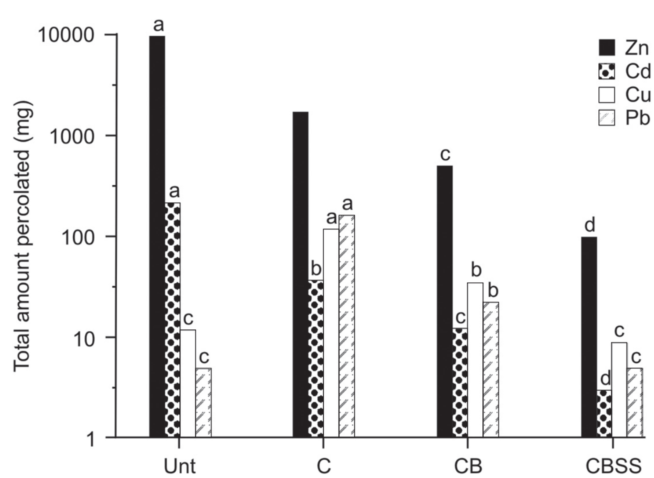

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FIGURE 11.3 Total percolated metal content (mg) at the small-scale Overpelt experiment, during the 8-month period after soil treatment. For each metal, mean values with the same letter are not statistically different at the 5% level.

were found to sharply decrease (i.e., by 90% Cd and 80% Zn) with the beringite treatment (Vangronsveld, 1998). Data for leaching of As, Cd, Cu, Pb, and Zn are available from the small-scale Jales Experiment (Mench, Bussiere et al., 2003). The pH of percolates from the unamended soil was acidic and decreased further over 3 years. An increase in SO_4^{2} concentration in percolated water supported the occurrence of sulfide oxidation. All amendments increased the percolate pH and significantly decreased the leachability of the metals compared to the untreated soil. In contrast, leached As increased more than 50-fold in C- and CB-amended soils compared with the unamended treatment and also increased, but to a lesser extent, in the CBSS and CSS soils (De Koe et al., 1998). Possible mechanisms following compost addition that could trigger the increase in As mobility include the increase in soil pH, As binding to DOM, and competition for solid phase binding sites with DOM or with inorganic anions such as phosphates. Boisson et al. (1998) monitored As leaching over a 9-month period at the small-scale Reppel Experiment. Arsenic concentration in leachates decreased 8.6 times and 12 times in the SS and BSS treatments, respectively, compared with the unamended control. We conclude from the monitoring of small-scale Overpelt, Jales, and Reppel experiments that amendments such as CB, CBSS, and BSS have beneficial effects in decreasing Cd and Zn leaching. Leaching of other cationic metals such as Ni, which has a pH-dependent solubility, would also probably be attenuated. However, the addition of organic carbon may increase leachability of metals such as Cu and Pb, which have a high affinity for organic materials. Attention must be paid to As leaching, and to other trace elements that form anionic species in solution such as Mo, Cr(VI), and Se, as their mobility can be enhanced by the same amendments that attenuate mobility of cationic metals.

11.7 EFFECTS OF DIFFERENT AMENDMENTS ON PLANT GROWTH AND CONTAMINANT UPTAKE

11.7.1 Biosolids Combined with Liming

Use of biosolids and similar organic wastes (e.g., papermill sludge) alone and in combination with other materials, such as limestone and cyclonic ashes that display a high calcium carbonate equivalent, is a long-standing practice by which many contaminated sites have been restored (Sopper, 1993). Applications of this type provide the organic matter necessary to improve soil physical properties, water infiltration and water holding capacity. They deliver micro- and macronutrients necessary for plant growth, and decrease bulk density. Several experiments have investigated the efficacy of biosolids and calcium carbonate mixtures to restore a vegetative cover.

11.7.1.1 Pronto Mine Experiment, Canada

Rio Algom's Pronto Waste Management Area, near Elliot Lake, Ontario, was a former uranium mine, in operation until 1960, where Cu ore was processed until

1970 (Tisch et al., 2000). Factors contributing to the lack of vegetation establishment on the fine-grained Cu tailings (23 ha) included low existing pH and continued acid generation, high levels of soluble metals, compaction, erosion, poor nutritional status, lack of organic matter, and a high water table. Test plots were constructed on these tailings using papermill sludge in combination with lime as a cover material, with and without a capillary barrier (gravel and blast furnace slag), or through direct incorporation. Over a 3-year period, only cover materials incorporated directly led to acceptable establishment of vegetation. Elemental concentrations in the grass shoots were similar to values listed for vegetation growing on Ontario background soils.

11.7.1.2 Leadville Experiment, Colorado

Pyrite-rich wastes from historic Pb and Zn mine tailing piles entered the Arkansas River and contaminated areas along an 18-km stretch. Oxidation of the pyrite has resulted in acidic soil pH (1.5 to 4.5) (Compton et al., 2001). Several contaminated areas were amended with a mixture of municipal biosolids and agricultural limestone, and then seeded with a mixture of native grasses or annual rye grass. In year 1, the amendment increased pH from 3.9 up to 6.4. Calcium nitrate-extractable Cd, Pb, and Zn decreased significantly in the surface horizon. Metal concentrations in annual rye grass also decreased. Initial results indicate that the amendment was effective in restoring a plant cover, but metal concentrations in plant tissues remained too high to prevent animal exposure. Chemical and biological parameters measured over time suggest that ecosystem function has been restored to the amended tailings, but that these systems are not yet in equilibrium (Brown et al., 2005).

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11.7.1.3 Bunker Hill Experiment, Idaho

Mining and smelting of Pb and Zn ores resulted in extensive metal contamination of the surrounding hillsides and waterways, leaving more than 500 ha barren of vegetation. Surface application of biosolids (112 Mt ha^{1}) in 1997, in combination with wood ash (220 Mt ha^{1}) and log yard debris (20% by volume), was able to restore a vegetative cover on the metal-contaminated materials for 3 years (Brown et al., 2000, 2001). Metal concentrations in plant tissues were within "normal" concentration ranges for all treatments during the 3-year period. In a wetland located at the same site, surface applications of a biosolid compost (60% DW) and wood ash (40% DW) to a depth of 15 cm were sufficient to enable a volunteer plant community to reestablish in the treated area. In this case, metal concentrations of reeds (*Typha latifoli*) were within the normal range.

11.7.1.4 Palmerton Experiment, Pennsylvania

The Palmerton Zinc Superfund site surrounds a former Zn smelting facility located in Palmerton, PA, which operated from 1898 until 1980. The site has been treated on a large scale with biosolids and coal fly ash. Amendments were initially tested from 1988 to 1990. At Blue Mountain, application of high-Fe and high-lime sewage sludge compost into the soil decreased Zn toxicity to grasses. The metal-attenuating effect of the biosolids-compost soil treatment remained stable over 6 years (Li et al., 2000).

11.7.2 Cyclonic Ashes (Beringite): Lommel-Maatheide and Overpelt Experiments, Belgium

Data for the following experiments as well as those described in the following subsections, summarizing the degree of soil contamination and application rates used for the soil amendments, are shown in Table 11.2 and Table 11.3.

Cyclonic ashes (beringite) were found to decrease plant exposure to metals and to restore vegetative cover. Twelve years after the CB treatment (5% C + 5% B) the vegetation (mainly *Agrostis capillaris* and *Festuca rubra*) was found to be healthy and regenerating by both vegetative means and seeds at the Lommel-Maatheide experiment (Vangronsveld et al., 1996; Vangronsveld, 1998). On untreated soils, growth of test plants (e.g., *Phaseolus vulgaris*) was strongly inhibited (Vangronsveld, 1998). Contaminated soil in the playground area of the Lommel school was also treated with CB. The vegetation immediately recovered and was still developing after 3 years (Vangronsveld, Ruttens et al., 2000; Vangronsveld, Mench et at., 2000). Following evidence of metal attenuation in the small-scale Overpelt experiment at Limburgs Universitair Centrum (LUC), a field experiment was established at Overpelt. In year 3, vegetation was well established in the B-, SS-, CSS-, and CBSS-treated plots. Plant biomass production was highest in the CBSS plots.

The efficacy of beringite amendments in decreasing Cd and Zn uptake in vegetables was investigated. Test plots in 10 kitchen gardens, which consisted of sandy soils contaminated by aerial deposition from the former Lommel-Maatheide zinc smelter, were treated with beringite (100 ton ha^{1}). Comparison of Cd contents in edible parts of plants grown on both untreated and B-treated plots showed marked (2 to 4 times) reductions in Cd content in plants from the beringite-treated plots.

11.7.3 Metal Oxides

Three field trials in the U.K. were established to investigate the efficacy of Fe oxide as an immobilizing agent for As (Alloway et al., 2001). These were an agricultural field adjacent to a derelict As smelter in Cornwall, long-term sludge-spreading plots at a sewage works in Northampton, and a domestic garden in St Helens, Merseyside. Ferrous sulfate (commercial grade), which would be oxidized to Fe oxide in the soil, was applied as a single treatment before the first crops were planted with no further amendment for the duration of the trial. Lime was also added to compensate for the acidifying effect of the sulfate. Treatments with 0.2% Fe caused a significant decrease in As transfer to calabrese leaf, cauliflower, and radish at the Cornwall site. However, the amendment had an inconsistent effect with potato. There were no significant treatment responses found at either the Northampton or Merseyside sites. Results from these trials illustrate the problems of using prescriptive amendments to reduce As mobility across widely differing sites.

TABLE 11.5
Yield DM and Shoot Metal Concentrations in Lettuce Cultivated at the Louis Fargue Experiment, 6 Years after Soil Treatment

		Untreated	Beringite	Steelshots	Uncontaminated
Yield	Mg ha^{1}	37.2 ± 7.9	27.2	49.4	63.9
Cd	mg kg^{-1}	56.9 ± 10.4	68.8	34.7	1.6
Cu	mg kg^{-1}	8.0 ± 0.4	5.4	8.3	9.3
Mn	mg kg^{-1}	8.7 ± 1.6	9.5	26.2	40.1
Ni	mg kg^{-1}	15.5 ± 3.4	7.6	6.7	1.6
Pb	mg kg^{-1}	0.33 ± 0.11	0.37	0.43	0.88
Zn	mg kg^{-1}	70.5 ± 2.4	71.8	55.8	82.1
P	g kg^{-1}	8.0 ± 0.2	5.6	5.6	8.6

Note: Beringite (5%), steelshot (1%).

11.7.4 Zerovalent Fe-Related Compounds Combined with Cyclonic Ashes

11.7.4.1 Louis Fargue Experiment, Domaine INRA de Couhins, France

Sewage sludges were applied to a coarse sandy soil from 1976 to 1980. In 1995, one block was amended with beringite (5%) and another one with steelshot (1%) (Mench et al., 2000). Corn ears were better filled in the SS plot, whereas those from the B-treated plots showed poor filling, and a corresponding yield decrease, due to Mn deficiency, which resulted from Mn attenuation by beringite in the sandy soil. The SS addition resulted in a sustained decrease in Cd phytoavailability to maize. In 2000, Cd concentration in corn grain from the SS plot was approximately 40% lower than concentrations found from 1980 to 1994 before the soil was treated. The data indicated increased amelioration over time, suggesting that Cd was becoming occluded in the newly formed Fe oxides. Both SS and B amendments resulted in a sustained decrease in Ni concentration in corn grain, probably from an increase in soil pH. In 2001 (year 6 after soil treatment), metal toxicity to and metal uptake by lettuce was investigated. Dry matter yield showed a beneficial effect of SS amendment (+32% compared with Unt), whereas a detrimental effect of B (27%) was again observed (Table 11.5). Lettuce shoots revealed elevated Cd and Ni and low Mn when the untreated plots were compared with the uncontaminated plots. Lettuce grown on the SS plots showed decreases in Cd (40%), Ni (57%), Zn (21%), and P (30%) concentrations, and elevated Mn concentration (Table 11.5). Copper and Pb concentrations were not affected by SS amendment.

11.7.4.2 Jales Experiments

Previous attempts to establish vegetative cover on the fine-grained spoil at the former Jales gold mine, northeastern Portugal, were unsuccessful. Colonization by plants

TABLE 11.6
Arsenate (μmol g⁻¹ DW) in Above-Ground Biomass of *Holcus lanatus, Agrostis castellana, Cytisus striatus* and *Betula alba* Grown on Untreated Soil (Unt) and Soil Treated with Steelshot (SS, 1%), Organic Matter (C, 5%) and/or Beringite (B, 5%) in Presence and Absence of P

	H. lanatus			*A. castellana*		*C. striatus*	*B. alba*
	Green	*Green* Fertilized	*Senescent* Fertilized	*Green*	*Green* Fertilized	*Green*	*Green*
Unt	n.g.	1.39 ± 0.12	2.11 ± 0.23	n.g.	0.63 ± 0.10	n.g.	0.90 ± 0.15
SS	n.g.	0.89 ± 0.15	1.73 ± 0.12	n.g.	0.36 ± 0.04	0.38 ± 0.04	0.91 ± 0.28
SSB	0.47 ± 0.05	0.34 ± 0.09	0.81 ± 0.08	0.27 ± 0.05	0.43 ± 0.05	0.27 ± 0.02	1.34 ± 0.16
CSS	0.39 ± 0.03	0.23 ± 0.02	0.76 ± 0.06	0.25 ± 0.01	0.28 ± 0.01	0.32 ± 0.03	0.94 ± 0.15
CSSB	0.34 ± 0.03	0.25 ± 0.01	0.72 ± 0.06	0.17 ± 0.04	0.28 ± 0.05	0.19 ± 0.02	1.18 ± 0.10
CB	0.38 ± 0.05	0.33 ± 0.01	0.89 ± 0.07	0.29 ± 0.03	0.30 ± 0.05	0.21 ± 0.01	1.35 ± 0.43
C	1.06 ± 0.04	0.54 ± 0.03	1.27 ± 0.09	0.50 ± 0.12	0.50 ± 0.16	0.32 ± 0.01	1.44 ± 0.14
B	0.61 ± 0.04	0.44 ± 0.06	1.20 ± 0.09	0.59 ± 0.03	0.40 ± 0.07	0.34 ± 0.03	0.86 ± 0.06

Note: n = 8 (+SE); n.g. indicates no plant growth.

Source: From Bleeker, P.M., Assunção, G.L., Teiga, P.M., de Koe, T., Verkleij, J.A.C., 2002. *Sci Total Environ* 300: 1–13. With permission.

was limited to a few isolated spots. The grasses *Holcus lanatus*, *Agrostis castellana,* and *A. delicatula* were the sole colonizers, growing in small isolated tufts (De Koe, 1994). The effectiveness of the following amendments in promoting plant growth was assessed in eight plots established on one of the Jales spoil terraces: Unt, B (5%), SS (1%), C (commercial garden compost, 5%), BSS, CSS, CB, and CBSS, with and without P fertilization (Bleeker et al., 2002). Material was incorporated into the top 30 cm of the soil. Despite a small pH increase in SS and CSS treatments, water-soluble As was similar to Unt. In contrast, the CBSS treatment resulted in a threefold higher water-soluble As concentrations compared to the control. The use of tolerant grasses in combination with soil treatments resulted in a rapid and effective revegetation of the contaminated soils. Colonization and reproduction of both *H. lanatus* and *Agrostis castellana* were most successful when additives were combined and soil supplemented with P fertilizer (Bleeker et al., 2002). Lowest As concentrations in *H. lanatus* and *A. castellana* were found in CBSS, CSS, CB, and BSS (Table 11.6).

11.7.4.3 Small-Scale Reppel Experiment

In this contaminated agricultural soil, incorporation of B and BSS soil amendments had sustained beneficial effects on yield of corn, lettuce, and radish (Table 11.7). A decrease in tissue concentrations of Cd and Zn was found for the B and BSS treatment (Table 11.8). Only the BSS treatment resulted in a decrease in plant concentrations of As and Pb (Table 11.8). The SS treatment either had no effect or

AU: Footnotes needed for a,b,c, following numbers? (Lettering should begin with “c,” as “a” and “b” are in table column heads as per CRC style.)

TABLE 11.7
Plant Biomass and Soil pH at the Small-Scale Reppel Experiment, Bordeaux, France

Year	Corn Ear[a] 4	Soil pH 5	Lettuce Shoot[b] 5	Radish Whole Plant[b] 5
Control soil	204[a]	4.9	113[a]	6.1[ab]
Unt	157[a]	4.9	168[a]	5.7[a]
SS	230[ab]	5.15	246[ab]	8.5b[c]
B	264[b]	6.35	283[c]	7.9[b]
BSS	249[b]	6.9	293[bc]	10.5[c]

[a] g DW ear[1].
[b] g FW plant[1].

TABLE 11.8
Trace Element Concentrations (mg kg^{-1}) in Corn Third-Leaf at the Small-Scale Reppel Experiment 4 Years after Soil Treatment

AU: a,b,c,d following numbers need footnote.

	As	Zn	Cd	Cu	Pb
Control soil	<0.5[a]	69[b]	0.065[a]	<3[a]	0.41[c]
Unt	2.16[c]	69[bc]	0.668[d]	4.6[b]	0.28[a]
SS	2.16[c]	86[c]	0.705[d]	8.2[d]	0.51[d]
B	1.97[c]	43[a]	0.315[c]	5.2[c]	0.38[b]
BSS	1.09[b]	48[a]	0.233[b]	5.5[c]	0.28[a]

increased the plant concentrations of metals compared to Unt. The concentration of Cu was increased in all amended soils compared to Unt; however, the concentrations of Cu were not at the phytotoxic level for corn. Soil CEC increased from 3.8 to 5.3 cmol kg^{-1} in B-treated soils, which was higher than expected, based on the 22 cmol kg^{-1} CEC of beringite. This may be due to the formation of minerals. Chemical extractions inferred that B addition induced *de novo* formation of ferrihydrite and allophane in Reppel soil and that the proportion of Cu, Mn, and Zn associated with amorphous minerals increased (Pannetier, 2000).

11.7.5 Zeolites

Field trials were established at Northampton and Staffordshire to evaluate the efficacy of soil amendments, including zeolite, in decreasing Cd transfer from soil to vegetable crops (Lepp et al., 2000). The application of sewage sludge resulted in elevated soil Cd at the Northampton site (mean total Cd content 47 mg kg^{-1}). At the Staffordshire site (mean total Cd content 16 mg kg^{-1}), deposition of Cd oxide particles from an adjacent pigment manufacturer had contaminated the soil of a domestic garden.

The Staffordshire site was only Cd contaminated, whereas the Northampton soil contained elevated contents of other metals and As. Plots were treated in 1998 with the following amendments: $FeSO_4$ 1% (equal to 1% Fe_2O_3 plus 5.7% lime), iron grit 1%, lime 3% and zeolite 4A 1%. The results demonstrated that although transfer of both As and Cd from soils to crops (lettuce, spinach, radish, and red beet) was generally low, incorporation of a range of amendments, including zeolite, had little further influence on reducing risk associated with this transfer.

11.7.6 Red Muds

Red mud is a by-product of the alumina industry that is alkaline and rich in Al/Fe-oxides. Several pot experiments have demonstrated its efficacy for remediation of metal-contaminated soils over relatively long time periods (Mench et al., 2000). Red mud (1%) performed well in a 15-month pot study carried out by Friesl et al. (2001). Müller and Pluquet (1998), who used red mud to treat a harbor dredging site contaminated with Cd and Zn, also showed that red mud could reduce metal mobility and availability.

11.7.7 Phosphate Compounds

Phosphates react with many metals, metalloids, and radionuclides. Precipitates formed can be stable over a wide range of geochemical conditions. In particular, conversion of soil Pb to pyromorphite, an insoluble lead phosphate [$Pb_5(PO_4)_3$(OH, Cl, F, …)], could immobilize soil Pb, decrease its bioavailability, especially in the gastrointestinal tract (Yang et al., 2002), and decrease Pb leaching in soil. A range of compounds has been evaluated including mineral apatite, synthetic hydroxyapatite, phosphoric acid and diammonium phosphate materials.

A field trial was installed in a vacant city lot at Joplin, MO, in 1997 to evaluate different techniques for Pb inactivation in contaminated soils. Lead was mainly present as Pb carbonates. The efficacy of TSP, rock phosphate, phosphoric acid, compost, and an Fe-rich by-product from titanium processing was compared (Berti et al., 1998; Brown et al., 1999). Lime was also added to each plot to bring the pH to 7. Seed (K31 tall fescue) was hand-scattered over the plot surface. The relative plant uptake of Pb in relation to total soil Pb was calculated. This ratio ranged from 0.0013 (3.2% P) to 0.0085 (2.5% Fe + 1% P). Lead availability measured by both relative plant Pb uptake and *in vitro* accessible Pb indicated 3.2% P as the most effective amendment. Reductions in Pb availability were also evident with 10% compost + 0.32% P and 2.5% Fe + 0.32% P.

11.7.8 Clays

Addition of clay to soil can produce physical and chemical changes that could affect contaminant fate and transport. These include increased cation exchange capacity, increased mineral surface area, and sorption within the clay interlayer. Illitic materials may be effective stabilizing agents for Cs^+ because of their ability to fix this cation under a range of moisture conditions (Seaman et al., 2001).

Gravel sludge, a waste product of the gravel industry, contains illite (29%), calcite (30%), and quartz (18%). Its efficacy as an *in situ* immobilizing additive was investigated at two application rates in three field trials with sandy loam soils at Dottikon, Rafz, and Giornico, Switzerland, contaminated by Cd, Cu, and Zn (Krebs et al., 1999). Gravel sludge application increased pH in all three topsoils by up to 0.6 units. In the Dottikon soil, Cu and Zn concentrations in ryegrass were reduced by more than 35%. Lettuce Cd and Zn tissue concentrations decreased by 22 to 48% at Giornico and Dottikon, whereas no effect was found at Rafz. The efficacy of gravel sludge in attenuating metal bioavailability was highest in soils with high $NaNO_3$-extractable metals, and higher for ryegrass than for lettuce.

11.7.9 Competitive Uptake at the Root Surface and Competitive Transfer into Plant Parts

One mechanism for attenuation of trace element exposure may be a decrease in uptake at the biological membrane due to competition with other ions or competition during internal transfer to organs (McLaughlin et al., 2000). There are several examples of this type of interaction, e.g., Cd/Zn, Cu/Fe, and As/P (Oliver et al., 1994; Boisson, 1999), and these may be of use in treating contaminated agricultural soils. Several amendments, i.e., natural clay, alum-based water treatment residuals (Alum WTR, 15 t ha^{1}), lime (15 t ha^{1}), magnesite ($MgCO_3$, 15 t ha^{1}), clay, Fe-rich fines from a ferrous smelter (FRF), zinc sulphate (25 kg ha^{1}), and copper sulphate (10 to 50 kg ha^{1}), were evaluated under field conditions at 3 sites in Australia established on Alfisols (clay mineralogy dominated by kaolinite) with pH values between 5 and 7 (McLaughlin et al., 2000). Cadmium concentrations in potato tubers grown on soils amended with a mixture of Cu/Zn salts and with natural clay were lower (18%) than those amended with lime. All other treatments at all sites were ineffective in decreasing Cd concentrations in tubers. However, results were not sufficiently large to warrant recommendation of the use of Cu/Zn salt application to decrease crop Cd concentrations.

11.8 IMPACTS ON AND UPTAKE BY OTHER ORGANISMS

11.8.1 Soil Microorganisms

The presence and behavior of microbial communities are one bottleneck in the process of restoring soil functions that enhance phytostabilization. Metal exposure to microorganisms was assessed at the Louis Fargue experiment using a biosensor kit (Biomet™) (Van der Lelie et al., 2000). In this assay, bacterial luminescence intensity is related to metal exposure in the soil. The Cd/Zn specific indicator strain of *Ralstonia metallidurans* CH34 showed a decrease in Cd exposure in B- and SS-treated soils in both the farmyard manure and 300 Mg ha^{1} sewage sludge plots. For the 50 Mg ha^{1} plots, Cd exposure to microorganisms was slightly decreased in the B-treated soil. The Ni strain showed a general decrease in Ni exposure for both B- and SS-amended soils compared with the Unt soil. Lowest Ni exposures occurred in SS-treated soils in the farmyard manure and 50-Mg sewage sludge ha^{1} plots.

Consequently, a beneficial effect on microbial communities was likely to be expected in either B- treated or SS-treated soils. Accordingly, soils were sampled at one long-term experiment, Louis Fargue (year 7), and two small-scale experiments, Reppel (year 6), and Jales (year 5). At Louis Fargue, both SS and B treatments restored enzyme activities inhibited in the 50 Mg ha[1] sludged soil, SS being the most efficient soil treatment (Renella et al., 2005). Soils were potted, inoculated with a bean rhizospheric solution, and then cultivated with dwarf bean. *Rhizobium* nodules on roots were enumerated (Mench, Solda et al., 2003). The number of *Rhizobium* nodules was enhanced from 15% to 50% (100% based on control soil) by SS amendment in the 50 Mg ha[1] Louis Fargue sludged plot. Unexpectedly, beringite addition did not result in restoration of symbiosis. *Rhizobium* symbiosis was inhibited in all Jales and Reppel soils, except for a 33% restoration in the BSS-Reppel soil.

An As Biomet strain was used to quantify As exposure in treated and untreated soils from the small-scale Jales experiment, but no luminescence was found for all soils (Corbisier, personal communication). The As exposure may not be toxic for this strain, despite the As contamination in this soil and increase in water-soluble As after CB and C addition into the soil.

AU: Not cited in reference list.

11.8.2 Earthworms and Mites

Earthworms are thought to be highly exposed to soil metals as their diet consists of organic material in soil. Toxicity testing using earthworms is a well-developed method for studying bioavailability and toxicity of soil contaminants. Amendments (B, SS, and BSS) were found to decrease the toxicity of the Reppel soil to earthworms (*Lumbricus terrestris*), but the As, Cd, and Zn concentrations in depurated earthworms were not decreased (Mench, Solda et al., 2003). Consequently, this may be a route of metal exposure for biota that consume earthworms.

Soil ecosystem development on four vegetated tailings sites at Copper Cliff, Ontario, 0, 8, 20, and 40 years after rehabilitation, was assessed in terms of mite (Acari) populations and compared with those from four control sites (John et al., 2002). Mite density on older and more botanically diverse tailings sites was similar to that on control sites, but species richness of oribatids and mesostigmatics was lower. Species richness and diversity on tailings were lower at less botanically diverse sites regardless of age. The similarity of tailings mite communities to control-site communities increased with age, but it was always less than 60%. A few colonizing species dominated mite assemblages on tailings, whereas control sites had a diverse assemblage of species.

11.8.3 Mammals and Birds

Potential pathways of animal exposure to metals from contaminated soils include “soil to flora to animal” (herbivore exposure), “soil to fauna to animal” (carnivore, insectivore exposure), and “soil to animal” (direct ingestion of soil and dermal contact). The effect of soil amendments on each of these pathways needs to be considered in terms of assessing the overall effectiveness of any chemical immobilization treatments for soil remediation. For example, if the remediation treatment results in greater survival of earthworms and other soil fauna in the contaminated soils, then insectivorous mammals can inadvertently be exposed to a greater risk than if the fauna was unable to survive in the soil (Brown et al., 2002). To date, there has been very little full-scale ecosystem monitoring at remediated sites.

Direct soil ingestion by grazing animals or by children, resulting from hand-to-mouth actions can be a significant soil contaminant exposure pathway (Basta, Gradwohl et al., 2001; Basta, Armstong et al., 2001). Human dosing to establish the efficacy of amendments in decreasing exposure through this route is not feasible, but batch tests can deliver some information. One such test used to predict metal availability is the so-called *in vitro* physiologically based extraction test (PBET) (Ruby et al. 1996).

A number of studies have been conducted to assess PBET-extractable As and Pb in treated soils in pot trials (Geebelen, 2002; Geebelen, Adriano et al., 2003; Hettiarachchi et al., 2001). The results of these studies demonstrate that metal and As exposure via soil ingestion, can be decreased by application of different types of amendments to contaminated soils.

11.9 BIODIVERSITY AND GENETIC ADAPTATION OF ORGANISMS

There is little information available on the effect of amendment applications to contaminated soils on biodiversity. This aspect was however investigated at Lommel-Maatheide experiment. Diversity of higher plant species and saprophytic fungi was extremely low in the untreated soil because of the high soil toxicity and the absence of metal-tolerant ecotypes of plants and fungi (Table 11.9) (Vangronsveld, 1998). Only one plant species was prevalent (*Agrostis capillaris*), the frequency of the two other species present (*Betula pendula*, *Stelleria media*) being less than 1%. In contrast, two plant species (*A. capillaris, Festuca rubra*) were mainly present in the CB-treated plots, and several non-metal-tolerant perennial forbs colonized the remediated area (e.g., *Cerastium fontanum*, *Centaurium erythraea*, *Plantago media*) (Table 11.9). Most of these species belong to mycotrophic families; so the presence of a mycorrhizal network in the soil promotes their establishment. In Unt plots, the arbuscular mycorrhiza (AM) infection percentage of grass roots ranged from 0 to 42% (Table 11.10). This percentage was greatly increased in treated soils, ranging from 37 to 81%, even though total metal concentrations in soils were similar or even higher than the Unt plots. Also, the functional diversity of soil bacterial populations, measured as the capacity to metabolize a number of different substrates, almost doubled after soil treatment (Bouwman et al., 2001).

In treated soils of the small-scale Jales experiment, volunteer plant species established themselves from year 2 onwards. These included trees (*Salix caprea* L.), vascular plants (*Erigeron canadensis* L.), and bryophytes (*Funaria hygrometrica* Hedw). *Salix caprea* colonized the CBSS, CSS, and C, but not the Unt, uncontaminated control, or CB soil. Birch (*Betula* sp.) was present on CBSS, and maple (*Acer negundon* L.) on CB, C, and CBSS. *Gnaphalium sp.* was identified on B soil and *E. canadensis* grew well in the CBSS, CSS, and C soils. Fungi (i.e., *Coprinus*)

AU: Table reconstructed for clarity and to omit nonfunctional cells and repetition.

AU: Frequency of what?

AU: Meaning?

AU: This suggested entry substituted for "Number of plant species" which is indicated in table title already. Better wording? Same as substituted for "Presence" in Lommel entry?

TABLE 11.9
Increase in Number of Plant Species Diversity at the Lommel–Maatheide Experiment and the Small-Scale Jales Experiment

	Soil Treatments					Untreated	
Experiments	**CB**	**CBSS**	**CSS**	**CB**	**C**	**Soil**	**Control**
Lommel–Maatheide							
Frequency in the vegetated quadrats (%)							
90	2						
1–10	3					1	
<1	8						
Presence	13					2	
Jales							
Soil not covered by *H. lanatus*		8	5	5	5	1	4
Soil covered by *H. lanatus*[a]		249	399	499	432	32	100

[a] Expressed in percentage compared with the control soil.

Source: From Vangronsveld, J., Colpaert, J.V., Van Tichelen, K.K., 1996. *Environ Pollut* 94: 131–140. With permission. Mench (unpublished data).

TABLE 11.10
AM Infection Percentages in the Roots of Grasses along the Transect Lines in the Beringite-Treated and Untreated Areas at the Lommel-Maatheide Experiment

Distance (m)	AM Infection (%)	pH	Zn	Cd	Cu (mg kg^{-1})
		CB-Treated			
50	81	7.3	12750	18	475
100	69	7.9	3600	12	895
150	76	7.4	1168	8	206
200	38	7.6	9875	53	495
250	37	7.9	13250	55	765
300	65	7.6	4750	15	1393
		Untreated			
25	0	4.5	2400	16	160
108	0	5.1	2080	8	80
150	3	5.5	2720	14	400
200	42	5.7	4960	61	395
250	24	5.9	4160	56	405
300	14	5.9	800	12	80

Note: pH and total concentrations of Zn, Cd, and Cu in the corresponding soil cores.

developed in year 2 on CBSS- and CB-treated soils. From year 3 onward, carpophores of ectomycorrhizal fungi, e.g., *Rhizopogon roseolus* (Corda) Th. M. Fries associated with *P. pinaster,* were observed in the CSS and CBSS soils (Mench, Guinberteau et al., 2003). *Hebeloma leucosarx* Orton and *Hebeloma mesophaeum* (Fries) Quélet developed in association with *S. caprea* in the CBSS soils.

11.10 FAILURES, SIDE EFFECTS, AND LIMITATIONS OF CHEMICAL IMMOBILIZATION METHODS FOR SOIL REMEDIATION

11.10.1 Failures

Data from the 5- to 12-year-old experiments described earlier demonstrate that attenuation can be sustained, but that a given amendment can give different responses in different soils. The methods used to apply and incorporate the amendment can be very important for the attenuation process. For example, in the Northampton experiment described earlier, Fe grit was applied to the soil surface, but not immediately mixed with the soil. A lack of clear effects of this material on plant Cd uptake in this experiment may have been due to the fact that the surface of Fe grit oxidizes very rapidly, and newly formed oxides may not have been appropriately located to immediately react with Cd in the soil solution.

We have learned that quantifying attenuation in laboratory simulations is necessary, but field demonstrations are also required. For example, a decrease with time in the efficacy of both B and SS amendments for attenuating As exposure was observed in the small-scale Reppel experiment. Similarly, amendments to reduce Cd bioavailability (i.e., lime, clay, Fe-rich fines, Cu and Zn sulfate, and alum-water treatment residuals) performed poorly under field conditions in three Cd-contaminated agricultural soils in South Australia, despite good results obtained in the laboratory (McLaughlin et al., 2000). The application rate of the amendment is also very important. A continuing decrease in 0.01 M $Ca(NO_3)_2$-extractable Cd, Ni, and Zn was observed with increasing application rates of SS from 0.1 up to 10% (Sappin-Didier, 1995). However, the 10% application rate was expensive and produced undesirable side effects; e.g., sorption of P increased Mn exposure.

There is a lack of information on the potential of attenuated sites to revert to their preattenuated soil chemistry, particularly under field conditions. Long-term degradation, weathering processes, acidification, and reducing conditions can influence attenuation, potentially resulting in enhanced transport and exposure (Hamon et al., 2002). Consequences of soil acidification on amended soils have been investigated in laboratory-based batch experiments. Biosolids-induced metal immobilization became destabilized as acidic soil conditions developed ($pH < 6$) (Basta, Gradwohl et al., 2001; Basta, Armstrong et al., 2001). Immobilization products of rock phosphates (i.e., metal pyromorphites) were more stable as soils acidified ($pH < 5$), even though they have less effect on metal extractability and phytoavailability compared with biosolids. Use of carbonate-rich materials (e.g., ground limestone) has had some success in decreasing solubility and crop uptake of Cd and Zn in acid soils, but because of leaching, these responses are often not sustainable. For example, it was noted in the Pronto experiment described earlier that applied limestone has been more or less consumed as a result of oxidation of the Cu tailings and associated soil acidification. It would be interesting to follow the consequences for established vegetation and microbial communities if additional lime is not administered.

11.10.2 Side Effects

Among potential unwanted side effects of soil amendments, the following aspects should be considered (Osté, 2001):

1. Toxicity of the amendment material
2. Toxicity of contaminants in the amendments
3. Imbalance in nutrients as a result of reactions induced by the amendments, either amendment-induced nutrient deficiency, or excess fertility as in the case of P or biosolids addition
4. Negative effects due to changes in soil conditions, such as release of trace elements through amendment-induced dissolution of different phases
5. Negative effects due to impact on soil structure and soil organic matter

Some examples of these aspects are as follows. In the Reppel soil, a transient adverse effect was found on bacteria and earthworms following the rapid oxidation of steelshot in soil and the release of Fe and Mn to soil-pore water before the newly formed Fe and Mn oxides. Several potentially useful amendments such as incinerator ashes, coal fly ashes, biosolids, and Fe-rich muds can contain either inorganic or organic contaminants. Many coal fly ashes contain high concentrations of boron and SO_4 that may rapidly affect plant growth. The sodicity or radioactivity of red muds can be an immediate problem. Steelshot contain Ni, which raised the Ni content of maize grain in the Louis Fargue experiment upon application.

The amendment application can decrease solubility of essential trace elements and macronutrients. Maintaining sufficient P is sometimes difficult because of P fixation by Fe oxides present in soil amendments such as red muds. Phosphate fixation can be counteracted by adjusting the application rate and by repeated application, but competition with As and induction of As leaching must also be considered in soils co-contaminated with As. Beringite was effective in decreasing plant exposure to Ni in the Louis Fargue experiment. Over time, however, Mn deficiency and low P availability developed, both affecting plant yield (Mench et al., 2000). Attenuation of Mn availability induced by beringite addition to the soil was also observed at both the small-scale Jales and Reppel experiments. This could be a frequently occurring side effect using this material, especially in sandy soils.

Increasing the soil fertility is often necessary to enable establishment of a vegetation cover in contaminated soils with low nutrient and water-retentive capacity. This can be achieved using compost. The increase in dissolved organic matter from this source may result in reaction with solid phases or an elevated labile pool of contaminants. In the small-scale Jales experiment, compost increased As leaching and plant exposure, and addition of other materials such as beringite was unable to counterbalance this side effect. Higher leaching and organism exposure to Cu and Pb can also occur after organic matter application. Arsenic mobility can increase after hydroxyapatite addition, as was observed in the Overpelt soil (Boisson et al., 1999). Increased soil pH, resulting from alkaline amendments and manganese oxide amendments (K-birnessite), can increase leaching of nonessential metals because of increases in dissolved organic matter (McBride and Martinez, 2000; Chapter 6). Some long-term experiments therefore recommend caution in the use of combinations of fly ash and biosolids (Bhumbla et al., 2001). DTPA-extractable Cu, Fe, Mn, Pb, and Zn were higher in acidic mine soils receiving fly ash and biosolid mixtures. Alkaline additives poor in Ca, such as some zeolites, can strongly increase the dissolved organic matter concentration, resulting in increased metal leaching (Osté, 2001).

Reducing conditions may occur with high-volume applications of biologically active amendments such as sewage sludge (biosolids). Several trace elements, e.g., As, Cr, Hg, Mo, Se, and V may change their oxidation state and hence toxicity within the range of redox conditions commonly encountered in soils (Chapter 8). In addition, redox reactions may induce changes in the mineral composition, structure, and stability of soil solid phases. Labile organic acids produced during the anaerobic decomposition of organic matter may form metal complexes, increasing metal concentration in the soil solution. Newly formed solid phases such as Fe(III) and Mn(IV) oxy-hydroxides, resulting from the oxidation of steelshot or related zerovalent Fe compounds, may undergo reductive dissolution and release adsorbed and coprecipitated trace elements in the soil solution under reducing conditions. For example, the reductive dissolution of birnessite by oxidizable organic ligands such as catechol was rapid, independent of pH, and essentially complete within seconds under conditions of excess of catechol at pH 4 to 6 (Matocha et al., 2001).

High application rates of some additives can affect soil properties. Synthetic zeolite in Na form can damage the soil structure (Osté, 2001). High application rates of steelshot (over 10% soil weight) reduced the soil porosity (Sappin-Didier, 1995). When papermill waste was incorporated into tailings, a good ground cover did not establish. This was probably due to salt accumulation at the surface, which created an osmotic environment unfavorable for the establishment of glycophyte seedlings, although seedlings of volunteer halophytes did start to colonize the area (Tisch et al., 2000).

11.10.3 Limitations

At polluted sites, soils are usually contaminated with several trace elements. For effective remediation, the amendments used need to be able to attenuate the range of elements present, but this is often not possible. For example, MnO_2 can bind metals such as As, Cd, Pb, and Zn but appears less effective in Cu-contaminated soils (McBride and Martinez, 2000). Calplus (clay-aluminum hydroxides) was found effective for Cu and Zn but not for Cd (Osté, 2001). Synthetic zeolites can have a high affinity for Ca; hence, addition to calcareous soils may decrease their metal binding capacity and increase leaching of organic matter (Osté, 2001). Beringite combined with compost decreases Cd and Zn exposure, whereas it can increase As exposure and leaching (Mench, Bussiere et al., 2003).

In the majority of sites where chemical immobilization has been used, treatments have been confined to the uppermost regions of the soil; however, contamination, and plant roots, may extend to some depth especially when trees are used for revegetation. Experience from the Lommel-Maatheide experiment showed that trees died as their roots came into contact with soil solution from untreated contaminated lower soil layers.

11.11 CONCLUSIONS

Soil amendments that can enhance natural attenuation of trace elements and lead to a decrease in trace element exposure are available.

Several current small-scale semifield trials and field experiments show that successful attenuation and phytostabilization can be sustained for over a decade for a range of contaminated soils (Table 11.11). Successful phytostabilization, equally protective of human health and the environment, is frequently based on a combination of several additives. Some materials such as steelshot combined with cyclonic ashes (beringite) have proven effective over time. The oldest field experiments confirm that enhanced attenuation can be a cost-effective technique to initiate a healthy and diverse ecosystem in contaminated soils.

Preselection of additives in laboratory experiments is useful but may not forecast some long-term effects. Materials found to be promising under laboratory or glasshouse conditions can be less effective in the field. A decrease in effectiveness can occur over time. Failures and side effects such as induced deficiencies can arise and tend to be site specific. To avoid failures, a thorough evaluation of materials must be conducted, preferably in field lysimeters or in plots at each site. Year-to-year variation in the concentrations of trace elements in crops generally occurs (McGrath and Johnston, 2001). This prevents clear trends from being detected with short-term experiments. A long-term monitoring program to examine changes in speciation, leaching, and ecotoxicity should be conducted prior to implementation of any large-scale site treatment

Because of the lack of biogeochemical models for amendments, the sustainability of attenuation is not currently predictable. Environmental models are needed to help identify the limiting factors, which can be biotic or abiotic. Rapid and reliable exposure tests, for example using biosensors, are needed for routine low-cost site monitoring. A range of biosensors, specific for different key contaminants need to be developed. The monitoring program should take into account attenuation in different exposure pathways, e.g., soil solution, direct ingestion, and the gaseous phase. It should assure human health and environmental protection. Most studies to date have focused on the effects of chemical immobilization treatments on plant contamination via the soil solution and contaminant mobility to the groundwater. More long-term studies dealing with soil ingestion, dermal contact, and consumption of trace element enriched–products are needed. As discussed in Chapter 7, microorganisms may influence metal attenuation; hence, their activity deserves further consideration. Concerns about the long-term effectiveness of amendments in attenuating contaminants can be addressed by ensuring that monitoring will provide protection and that alternative remedies will be implemented as needed (Swindoll and Firth, 1998).

Regulatory acceptance of enhanced natural attenuation as a strategy for risk reduction in contaminated sites is related to the evolving scientific and social consensus

TABLE 11.11
Summary of Beneficial and Side Effects Induced by Soil Amendments Demonstrated in Field Trials and Outdoor Mesocosms

Sites	**Jales**	**Reppel**	**Overpelt**	**Louis Fargue**	**Maatheide**	**Northampton**	**Stafford-shire**	**Corn-wall**
Monitoring duration	4	5	5	7	12	3	3	3
Most effective treatments	CSS	CBSS	CBSS	SS	CB	Z4A		
		CBSS						
				Beneficial Effects				
Decrease in metal exposure	+	+	+	+	+			
Decrease in As exposure	+	+		+				+
Decrease in leaching	+	+	+		+			
Increase in plant growth	+	+	+	+	+			
Increase in plant diversity	+		+		+			
Decrease in metal content in plants	+	+	+	+	+			
Promote microbial communities	+	+		+	+			
Decrease in animal exposure					+			
				Side Effects				
Induced deficiency	+			+				
Enhanced metal leaching	+							
Enhanced As leaching	+							
Increase in As exposure	+							
Increase in Ni exposure				+				
Increase in metal exposure								+

Note: C: compost (5%); B: cyclonic ashes, beringite (5%); SS: steelshot (iron grit); Z4A: zeolite 4A.

over how bioavailability should be measured and which organisms we specifically seek to model. Present environmental regulations for trace element-contaminated soils are frequently based on total contaminant concentrations. However, from ecological, toxicological, and health viewpoints, the bioavailable fraction in exposure pathways should be considered. Although attenuation may be attractive in some locations, it should not be viewed as an exclusive remedial strategy. It may be combined with other options, in particular, with the use of tolerant plant species to help decrease the risk of off-site contaminant transport through erosion or leaching processes (phytostabilization). Most phytostabilization experiments currently involve crops that could directly enter food chains. However to minimize consumer exposure, it would be necessary to demonstrate the effectiveness of alternative crops that represent a sustainable, low-hazard economic use for remediated sites. These may include plants used for fuel, fiber, oil, and construction materials. Woody and herbaceous plant materials that fall on the surface can be removed to accelerate the remediation. Knox et al. (2001) proposed the use of a mineral-containing mat (geomat) deployed at the ground surface for immobilizing contaminants released from decomposing plant materials.. Among several materials tested in the geomat, metallic iron and an Fe oxide waste were the most efficient for lowering the aqueous Ba, Co, Cr, Eu, Hg, Pb, and U concentrations. Unterköfler et al. (2001) have investigated the immobilization of metals leached from fallen leaves and OM (surface layer) from *Salix caprea*, *Populus tremula,* and *Betula pendula,* on-site using a 2-cm layer of vermiculite. This material was able to adsorb and immobilize more than 99% of the leached metals.

Enhancing natural attenuation of trace elements using soil amendments and phytostabilization of contaminated sites remains a matter for further experimentation. Facing the challenge to attenuate trace element exposure, to restore a vegetation cover and a microbial community, or to reestablish the foodstuff compliance mean recognizing that each site has its own unique problem and potential solutions. "Adapt, not adopt," commented Peters (1995).

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