

Claudio Bini • Jaume Bech

Editors

# PHEs, Environment and Human Health

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

 Springer

*Editors*

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ISBN 978-94-017-8964-6      ISBN 978-94-017-8965-3 (eBook)  
DOI 10.1007/978-94-017-8965-3  
Springer Dordrecht Heidelberg New York London

Library of Congress Control Number: 2014940067

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Printed on acid-free paper

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## Preface

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

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

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

The book provides new insight on the role and function of PHEs in the environmental and human health, following fundamental textbooks (e.g. Ferguson 1990; Adriano 2001; Kabata-Pendias and Mukhejre 2007; Brevik 2013; Alloway 2013) and papers (e.g. Lag 1980, 1984; Nriagu 1988; Nriagu and Pacyna 1988; Thornton 1993; Oliver 1997; Abrahams 2002; Bernard 2008; Steinnes 2009) without forgetting recent thousands of contributions from several scientific domains, not only soil science, but also plant physiology, biology, epidemiology, medicine, and in particular oncology.

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

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

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

University of Venice, Italy  
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Venice, 2014, June

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## Introduction

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

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

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

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

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

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

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

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

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

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

A problem to address thoroughly is the lack of knowledge on residence time of trace elements, i.e. the most probable time period that any element will spend in

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

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

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## References

- Adriano DC (2001) Trace elements in the terrestrial environments, 2nd edn. Springer, New York
- Alloway BJ (2013) Heavy metals in soils, 3rd edn (Environmental pollution series, 22). Springer, Dordrecht, p 615
- Bernard AM (2008) Cadmium and its adverse effects on human health. *Indian J Med Res* 128: 557–564
- Franco R, Sanchez-Olea R, Reyes-Reyes E, Panayiotidis MI (2009) Environmental toxicity, oxidative stress and apoptosis: Ménage à trois. *Mut Res/Genet Toxicol Environ Mutagen* 674: 3–22
- Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to humans. Springer, Heidelberg, p 561
- McGrath S (1995) Behaviour of trace elements in terrestrial ecosystems. In: Prost R (ed) Contaminated soils, 3th ICOBTE, INRA. Paris, pp 35–56
- Steinnes E (2009) Soils and geomedicine. *Environ Geochem Health* 31: 523–535

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## Chapter 7

# Remediation of Potentially Toxic Elements in Contaminated Soils

Jaume Bech, Maria Manuela Abreu, Hyo-Taek Chon, and Núria Roca

**Abstract** This chapter aims to offer an overview of the main remediation methods of potentially toxic elements in contaminated soils, mainly heavy metals, metalloids and radionuclides, focusing on their essential characteristics, advantages and limitations. It consists of two main groups of technologies: the first group dealing with containment and confinement, minimizing their toxicity, mobility and bio-availability. Containment measures include covering, sealing, encapsulation and immobilization through solidification (cement-based, polyethylene and resin binders, bituminization or asphalt batching and vitrification or glassification) and stabilization with inorganic and organic amendments. The second group, remediation with decontamination is based on the removal, clean up and/or destruction of contaminants. This group includes mechanical procedures (excavation, transport and disposal to landfills), physical separations, chemical technologies such as soil washing with leaching or precipitation of potentially toxic elements, soil flushing, thermal treatments (desorption, pyrometallurgical processes and incineration) and electrokinetic technologies (electromigration, electroosmosis, electrophoresis and combinations of electrokinetics with other techniques). There are also two approaches of biological nature: bioremediation (biosorption, bioreduction, biomineralization and bioleaching-with some examples from Korea) and phytoremediation (phytoextraction, including chelate-assisted phytoextraction, phytostabilization, phytoremediation in mining activities -with examples from

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Portugal, Spain, Ecuador, Peru and Chile mainly-, phytovolatilisation and phytomining).

**Keywords** Soil remediation • PTEs • Soil containment • Bioremediation • Phytoremediation

## 1 Introduction

Soils are essential components of the environment, the basis of terrestrial ecosystems and a crossroad for biogeochemical cycles at the lithosphere-hydrosphere-biosphere-atmosphere interface. Therefore, soils are a limited precious and fragile resource, the quality of which should be preserved. The concentration, chemical form and distribution of potentially toxic elements in soils depends on parent rocks, weathering, soil type and soil use. However, their concentration can be altered by mismanagement of industrial and mining activities, energy generation, traffic increase, overuse of agrochemicals, sewage sludge and waste disposal, causing contamination, environmental problems and health concerns.

In contaminated soils metals such as Pb, Cr, Zn, Cd, Cu, Hg and Ni are frequent. Metals such as Ba, Be, Al, V, Ag, Mo and Tl are less frequent. Metalloids such as As, Se and Sb and radionuclides such as U, Th, Pu, Am, Ra,  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ , and Po may also be present.

In general, heavy metals and some metalloids such as As and Sb as well as certain radionuclides are more persistent in the environment than organic pollutants; only Hg and Se can be easily bioremediated. This persistence of the potentially toxic elements hampers the cost/time/efficiency of remediation technologies making them very expensive and difficult. The choice of the most appropriate soil remediation techniques depends on the concentration, nature and distribution (local or diffuse contamination) of the potentially toxic elements, the site characteristics, soil type and soil properties, mainly texture, organic matter, pH and rH values (Wong et al. 1997; Mulligan et al. 2001). Obviously, the optimal election of the remediation technology needs the identification of the soil pollution problem, an applicable site, the end use of the remediated soil, risk assessment, baseline, regulatory limits, threshold and intervention values. Therefore, in the remediation technology for a specific site, not only cost, time and efficiency should be considered, but also the soil protection factor. The remediation process should be as soil protective as possible (Meuser 2013).

This chapter aims to offer an overview of the main remediation methods of potentially toxic elements in contaminated soils, mainly heavy metals, metalloids and radionuclides, focusing on their essential characteristics, advantages and limitations. It consists of two main groups of technologies: the first group dealing with containment and confinement minimizing their toxicity, mobility and bioavailability (Page 1997; FRTR 2002; Khan et al. 2004; Marques et al. 2011). Containment measures include covering, sealing, encapsulation and immobilization through

solidification and stabilization (Sharma 2004). The second group, remediation with decontamination, is based on the removal, clean up and/or destruction of contaminants. This group includes mechanical procedures, physicochemical technologies such as soil washing with leaching or precipitation of potentially toxic elements, soil flushing and thermal and electrokinetic treatments. There are also two approaches of biological nature: bioremediation and phytoremediation.

## 2 Remediation by Containment and Immobilization Measures of Potentially Toxic Elements in Soils

### 2.1 Soil Containment

This is a remediation approach of contaminated soils, impeding their contact with people and the environment and attempts to prevent their migration. It is not a final remediation procedure, but it is adopted to prevent actual exposure of diffusion of contaminants from the site, especially in groundwater under the polluted area. Containment is adopted when remediation is not feasible due to adverse effects of the cleanup (such as the handling of soils and the management of process residuals that may pose hazards i.e. radiation exposure in the case of cleanup of radionuclide contamination) or to excessive costs. The choice of containment is common in cases when a fast response measure is necessary as with radionuclide-contaminated soils. The most used methods in soil containment are: surface cover, side barriers and encapsulation.

#### 2.1.1 Surface Cover

A surface cover or cap is a layer of uncontaminated soil or of synthetic liners such as geomembranes, clays, asphalt, concrete and others, placed over the contaminated soil or landfilled waste. The complexity of the surface cover depends on the hazardousness and concentration of the potentially toxic elements present, soil properties (mainly texture, organic matter and pH value), topography and climatology of the contaminated area.

The goal of surface cover is to keep people and ecosystems from coming into contact with the potentially toxic elements of a contaminated site. Furthermore, the cover stops rain and snow, avoiding harmful elements from being carried to the groundwater. Moreover, it prevents running water from running off and wind erosion that could spread contaminants offsite or into rivers and lakes.

There are three main types of soil cover processes: topsoiling, soil covering or soil capping and sealing.

- Topsoiling or topsoil cover is the most common reclamation method, and uses the natural topsoil cover or a 'vegetative layer' that is a top soil layer planted with grass. This method, which is the most natural and the simplest, consists of using unpolluted or 'clean' soil of the non-contaminated surrounding area. If topsoiling is not possible, there are other similar technologies of 'covering' or 'capping'.
- Soil covering or soil capping: uses a single layer or composite or complex cover with several layers or multilayers. The thickness of the surface cover depends on the nature and concentration of the potentially toxic elements on the site that must be reclaimed, the future use of the area concerned (agricultural, forests, parks, gardens, playgrounds, sport fields, industrial, etc.) and the type of topsoil. It is therefore difficult to recommend a thickness, because this value must correspond to the specific characteristics of the contaminated site. Opinions for different cases differ. Delschen (2000) recommends a thickness of 40 cm and ideally a surface cover of 70 cm to avoid the transfer from soil-plant for certain crops and metals. Monitoring of the topsoil cap is necessary to ensure its protection. A disadvantage is that supplies of topsoil are not available locally. Another disadvantage is that the structure of the original 'clean' soil 'in situ' has deteriorated in its excavation and transport to the contaminated site. The unfavourable changes of the soil's physical properties due to the vulnerability of aggregates can cause soil compaction. Other frequent problems are due to bioturbation created by the activities of earthworms, moles, mice and other edaphofauna species. Their dynamics can mix the clean or uncontaminated soils with the contaminated soils. For these reasons it can be necessary to install complementary groundwater monitoring wells around the covered site and periodical checking of the water composition to determine the possible leaking. Future excavations through the soil cap or mixing of clean and contaminated soil is not allowed. Topsoiling with a natural topsoil or with other materials in a single cover is appropriate for lightly contaminated soils, especially for insoluble contaminants. In case of 'hot spots' of more highly contaminated soils or landfill waste or for soluble potential toxic elements such as  $\text{Cr}^{6+}$ , it is recommended to use complex, composite or multilayer caps (Fig. 7.1).
- Sealing: for highly contaminated areas the complete sealing of the surface with asphalt or concrete can be recommended. In fact, the soil's nature and properties (structure, porosity, edaphon, microbial activity, etc.) are lost. The new artificial surface is a hard slab or pavement layer only useful for roadway paving, parking lots or building slab foundations. Usually the sealed cover structures have a thickness of 10–20 cm. This cap surface must be graded and provided of a drainage system to avoid water ponding.

### 2.1.2 Side Barriers

The soil cover or soil cap only treats the surface of the polluted area which prevents the vertical entry of the rain water into the waste and the possible contact of the

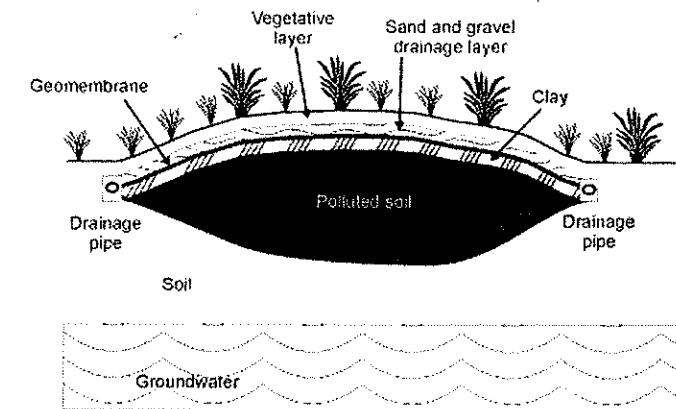


Fig. 7.1 Example of a cover with several layers (Drawing by N. Roca)

potentially harmful elements with people and the ecosystem. It cannot prevent the horizontal flow of ground water through the contaminated soil. For this reason subsurface barriers, especially vertical barriers are focused on the lateral migration of potentially toxic elements. The name used by some authors such as Wuana and Okieimen (2011) is 'vertical engineered barriers' (VEB). These barriers are made with slurry walls, grout walls or geomembrane curtains. Steel, cement and bentonite are also used. In acidic soils (pH 2–3) extreme caution is necessary because the steel can suffer corrosion. Furthermore, sheet pile walls of steel, bored pile walls and rounded piles or soilcrete columns are used. Also slurry trenches, cut-off walls are used as barriers, filled with slurry materials such as cement-water-bentonite mixtures. Horizontal barriers within the soil (trenches or wells) can restrict downward movement of potentially toxic elements by acting as underlying liners without the requirement for excavation. This is frequent in grout injections. Meuser (2013) offers detailed civil engineering methodologies of the subsurface barriers, pp. 175–184 of *Soil Remediation and Rehabilitation*. There have been problems with soil compaction and vertical boreholes that can increase the likelihood of contaminant migration (Mulligan et al. 2001).

### 2.1.3 Encapsulation

Encapsulation or isolation includes soil cover, side barriers as well as bottom sealing. The barrier system in this approach means a complete sealing of the contaminated site. Encapsulation is used when the bottom of the contaminated soil is located underneath the groundwater table or when the distance between the bottom of the contaminated soil and the groundwater is short. The advantage over the other approach of containment is a safer protection. The disadvantages are that it is an expensive technique and it is problematic to verify a complete sealing of the bottom. Moreover, this technique needs a long term monitoring using observation

wells upstream and downstream. Furthermore, although the possibility of gas generation is scarce, it is not impossible (e.g. radon from radionuclides, As, Se and Hg volatilization from organometallic pollutants). Therefore, a gas drainage system is needed to avoid slow gas migration through the walls damaging buildings and posing a threat to humans.

## 2.2 Solidification

Solidification is a containment method for stopping the migration and the bioavailability of potentially toxic elements in contaminated soil by trapping them in a compacted solid mass. The soil nature changes in a monolithic block by means of treatment processes of cementation, using water and binding agents such as Portland cement, pozzolanic materials, fly ash, blast furnace slag, cement kilns, bitumen and polyethylene or thermal energy to melt the soil in the vitrification technique. The solidification is applied mostly to soils contaminated with cationic metals, and is only recommended to a limited extent for soils containing elements forming oxyanions such as Sb, As, Be, Cr, Se and V (Meuser 2013). Mulligan et al. (2001) thought that As,  $\text{Cr}^{6+}$  and Hg were not suitable for this type of treatment. Soils can be treated in situ or ex situ.

### 2.2.1 Cement-Based Solidification

Cement-based solidification reduces the mobility of metals thanks to the formation of immobile hydroxides and carbonates and due to the fixation of the metals into the mineral structure, especially in the lattice of a new hydrous calcium aluminium sulphate format named ettringite. The cement and Portland cement consist of Ca silicates and Ca aluminates, which with the water added during the procedure lead to hydrated Ca aluminosilicates and  $\text{Ca}(\text{OH})_2$ , raising the pH value that favours the precipitation of some heavy metal contaminants (Marques et al. 2011; FRTR 2002). Moreover, the above mentioned  $\text{Ca}(\text{OH})_2$  reacts with  $\text{CO}_2$  and originates  $\text{CaCO}_3$ , which increases the strength of the solidified product (Meuser 2013). The cement-based solidification improves in the presence of fly ash, which is cheaper than Portland cement. It can also be used like fly ash, volcanic tuff, kild dust and blast furnace slag. The potentially toxic elements contaminated soils is mixed with water, alkali additives like cement or CaO and the pozzolanic-based materials. One example of the application of this technology is the Colmix process (Mulligan et al. 2001) that uses slurry including cement, slag-based grout and lime, used to immobilize heavy metals and ammonium in a landfill in Scotland. Guo et al. (2006) used alkaline elements for immobilization of: Cd, Cr, Cu, Pb and Zn; Bhat et al. (2002), cement based solidification to Be contaminated soils. Some disadvantages of this technology are that the fly ash increases the volume of treated soil, that in the long term there is a disintegration of cements with a possible quick metal

leaching (La Grega et al. 2001), and that consequently long term monitoring is necessary.

### 2.2.2 Solidification with Polyethylene and Resine Binders

Authors such as Marques et al. (2011) and Meuser (2013) reported this approach over the use of polyethylene binders for solidification of contaminated soils. The thermoplastic binders are heated previously, applied over dry soil, and then cool and solidify. Different resins are also used for solidification of contaminated soils, such as epoxide, polyester resin and urea resin. They need organic solvents, sometimes with toxic properties for human inhalation. These binders produce a strong solidified product. The period of time necessary to solidify the soil is relatively long. With time, one disadvantage of some of mentioned binders is their potential biodegradation, so a long monitoring period is necessary.

### 2.2.3 Bituminization or Asphalt Batching

Bitumen, derived from oil or asphalt from coal are used heated at 130–230 °C and molten and mixed with the contaminated soil, producing a mixture of extruded soils and bitumen. This mixture cools down and solidifies. This process can be improved by the addition of stabilising agents such fly ash or cement. Bitumen is the cheapest and most common thermoplastic binder (USEPA 1989). The solidified material can be used for roadway paving and car park construction purposes. The potentially toxic elements usually treated are: As, Cd, Cr, Hg, Pb and radionuclides.

### 2.2.4 Vitrification or Glassification

This is usually a in situ technology that uses electric power to heat and melt the contaminated soil and other earthen materials such as dewatered sludge, buried waste and mine tailings. Electric power (4 MW and voltage 12,500–13,500 approx.) is supplied to the graphite electrodes introduced into the soil that heat them until 1,600–2,000 °C. These high temperatures decompose organic contaminants and volatilize some elements such as Hg. The remaining molten soil cools to form a monolithic glass like product that incorporates the potentially toxic non-volatile elements such as metals and radionuclides. This chemically inert glass product has a similar aspect to volcanic obsidian. The vaporized gases are collected by a special 'hood' and passed through an off-gas treatment system (Fig. 7.2). To start the procedure, a conductive mixture of flaked graphite and glass frit is placed just below the polluted soil surface between the electrodes to act as a starter path, since dry soil is usually not electrically conductive.

Vitrification has been used to remediate As, Cr, Sb, Sn, Co, Cu, Ni, Zn, Pb, Be and radionuclide polluted soils. After the vitrification technique, the soil is molten

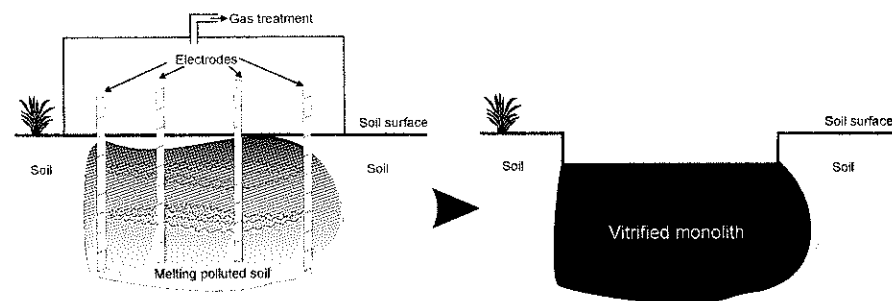


Fig. 7.2 Example of vitrification (drawing by N. Roca)

and very hot, sometimes taking more than 1 year to cool down. A disadvantage of this technique is the high energy intensity required. It is economically wise to keep the treatment zone as dry as possible prior to treatment. Wet soils are more expensive to treat because additional electric energy is needed to evaporate the water. Another disadvantage is the danger of subsidence due to volume reduction of 20–50 % of organic components and volatile metals (e.g. Hg). Moreover, the depth of the treatment of vitrification is currently limited to about 4–5 m. in a single melt. Deeper volumes of contaminated soil may be treated using a combination of staging and in situ treatment (USEPA 1995/540/R-94/520).

### 2.3 Stabilization or Fixation

Stabilization or Fixation is a remediation method that although does not destroy or remove the contaminants, reduces their mobility, toxicity and bioavailability through the use of soil amendments. These amendments can adsorb, complex or coprecipitate the potential toxic elements. This immobilization or fixation usually is in situ immobilization (Guo et al. 2006; Wang et al. 2009). The metals, metalloids and radionuclides of the contaminated soil after this remediation method remain in the soil, but in a form that is much less harmful, and the nature of the soil in contrast to solidification remains more or less intact. In reality, it is a chemical stabilization, a type of assisted natural remediation or attenuation. There are two main groups of amendments or fixing additives: inorganic and organic.

#### 2.3.1 Inorganic Amendments

- Iron compounds: metallic Fe or zerovalent Iron,  $Fe_0$ , is used as amendment in form of iron grit and steel shot for stabilize Cr, Cu and As contaminated soils (Bes and Mench 2008; Kumpiene et al. 2006) and removal soluble arsenate (Melitas et al. 2002). Moreover, the  $Fe_0$  added to contaminated soil form iron

oxides of high specific surface area that favour the trace element sorption (Kumpiene 2010). Fe metal was also used as an amendment for immobilization of As in the reclamation of the closed mine of Salsigne (S. France). Iron Oxides can reduce the mobility of AS, Cd, Cu, Ni, Pb and Zn by sorption, co-precipitation or formation of secondary minerals which contain trace elements (Kumpiene 2010).  $FeSO_4$  and  $Fe_2(SO_4)_3$  reduce As mobility (Hartley et al. 2004). Red mud, an industrial by-product of the aluminium metallurgy that contains Fe and Al is efficient in the immobilisation of Cu, Cr and Zn (Kumpiene 2010).

- Mn oxides: these can bind and immobilize trace elements such as As in form of precipitate of manganese arsenate. Moreover, Mn oxides can immobilize Pb, Cd and Zn (Kumpiene 2010). Likewise, synthetic oxide such birnessite have been used as sorbent of Pb and Cd, as well as of As (Mannig et al. 2002a).
- Al oxides: Al-natural oxides or components of waste by-products such as red mud, beringite and ettringite, derived of aluminium manufacturing (from bauxite ore) have a high adsorption capacity and can immobilise Cd, Cr, Cu, Ni, Pb and Zn in processes in situ and ex situ.
- Liming compounds: liming materials such as lime ( $CaCO_3$ ), quicklime ( $CaO$ ) and  $Ca(OH)_2$ , dolomite  $Ca, Mg(CO_3)_2$  and industrial by-products such as sugar foam (sugar beet lime) rich in  $CaCO_3$ , marble wastes and LSB (lime stabilized biosolid) are applied. These liming agents are effective in the reduction of the mobility of metal cations such as Cd, Cu, Ni, Pb and Zn, but the results are variable for oxyanions such as As and Cr. Moreover, liming increases the soil pH, which favours the oxidation of  $Cr^{3+}$  to the more mobile and toxic  $Cr^{6+}$ . The precipitation of As by carbonates needs more research.
- Gypsum ( $CaSO_4 \cdot 2H_2O$ ) amendments were used in reducing Pb and Cd mobility in contaminated soils (Kumpiene 2010). Pb mobility is reduced because it precipitates as anglesite ( $PbSO_4$ ). Gypsum was used for chemical mitigation of Pb pollution in urban soils (Tahaoun and Abdel-Bary 2000). The immobilization of oxyanions with gypsum is lower than with metal cations. This can be due to increased competitive sorption between  $SO_4^{2-}$  and, for example  $AsO_4^{3-}$  anions. The by-product phosphogypsum is also used to amend contaminated soils. However, the concentration of Cd, U, Th and some other harmful trace elements of the phosphogypsum must be controlled.
- Phosphates: the presence of trace elements in phosphate rock has been studied for some time. These elements are adsorbed and fixed in the lattice of the apatite by exchange and more or less partial replacement of Ca by other metals such as Pb in pyromorphite,  $Pb_5(PO_4)_3Cl$ . This affinity of metal cations to react with phosphates suggested the use of several phosphate amendments for soil remediation purposes. This reaction has been experimented with Cd, Cu, Ni, Pb and Zn. Bes and Mench (2008) assessed the stabilization of Cu-contaminated soils in this way. Chrysochoous et al. (2007) assessed Pb immobilization. Besides, phosphate minerals such as rock phosphate and phosphorites, phosphate-based salts and phosphoric acid have also been investigated. Industrial by-products like phosphatic slag and biogenic phosphate such as bone meal amendments for

remediation of Zn, Pb and Cd soil pollution (Sneddon et al. 2006) have also produced significant results. Phosphate amendments should be avoided when soil is contaminated with oxyanions such as As and Se, because phosphate competition with arsenate for sorption sites may increase As mobility and bioavailability. This technique of remediation must take in account that several phosphorite deposits have significant concentration of hazardous trace elements such Cd, Se, U, Th and others (Bech et al. 2010).

- Aluminosilicates: clays are fine-grained phyllosilicates built up of tetrahedrally (Si, Al, Fe<sup>3+</sup>) and octahedrally (Al, Fe<sup>3+</sup>, Fe<sup>2+</sup>, Mg) sheets or chains. A special combination of sheets forms a layer. Clays are available for sorption of cationic elements and radionuclides due to the mainly negative surface area by ion exchange, chemisorption and surface precipitation. The cation exchange capacity (CEC) of clays ranges from 2 to 130 cmolc · kg<sup>-1</sup> (e.g. kaolinite 2–15, illite 15–40, montmorillonite 80–130). Sepiolites are Mg-rich clays with fibrous texture and chain structure. Their CEC ranges between 4 and 50 cmolc/Kg. Recent studies referred to by Kumpiene (2010) treated the ability of clays for fixing As, Pb, Cd, Cu, Zn, Ni and Mn and radionuclides such as Cs, Sr, U, Th from contaminated soils. Bentonite (commercial name for montmorillonite) was used to fix Pb, Zn, Cu and sepiolites have been used to amend Cd, Cu, Pb, Zn contaminated soils. Kaolinites at low pH can develop a positive charge, and are therefore able to sorb anions, such as arseniate, in acidic soil conditions. The immobilization of As with bentonite to be pH dependent. At pH 4.6 there had been an appreciable fixation, but at pH 3.8 bentonite was shown to become incapable of sorbing As (Kumpiene 2010). A disadvantage of the use of bentonite are the possible problems of swelling by hydration and shrinking by drying. This dynamics can produce cracks which are negative in stabilization approaches.
- Zeolites: zeolites are tectosilicates of a (Al,Si)O<sub>4</sub> tetraedra framework with a robust open structure, pores and cavities, but without swelling and shrinking properties of the majority of clays. Because of the open structure Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> cations occupy these cavities and are exchangeable with ions of the contaminated soils. The immobilization of these potential toxic elements depends on the elements, pH and other properties of the soils and zeolite types (e.g. clinoptilolite). Zeolites have a high selectivity for Cd and Pb, but can also fix Cu, Zn, Tl, Mn, Co and As (reported by Kumpiene 2010). Muhabadi et al. (2007) referred soil Cd stabilization using an Iranian natural zeolite. Neutral pH is unfavourable for As immobilization. It seems that Fe-improved zeolites can be better for As sorption.
- Fly ashes and slags: coal fly ashes consist of ferroaluminosilicates rich in Ca, Mg, Na, K and with several concentrations of trace elements such As, B, Ba, Cd, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V, Zn (Kumpiene 2010; Kumpiene et al. 2008). The pH of fly ash ranges from acidic to alkaline depending on the coal, fuel or wood original composition. Alkaline ashes can improve the pH of acidic soils and mine spoils. Ashes can also improve the texture of sandy soils and actually immobilize potentially toxic elements of contaminated soils and decrease their

bioavailability and harmfulness. Fly ashes can immobilize cationic trace elements such as Cd, Cr, Cu, Ni, Pb and Zn, but not be adequate for the stabilization of oxyanions such as arsenates and chromates. It seems that the fixation of cationic elements is due to an increase in pH that causes their precipitation, and the increase of surface area of the soil promotes the sorption, complexation and cation exchange reactions. The composition of ash varies largely and must be analysed, especially its trace element contents, when used as an amendment for the stabilization of contaminated soils.

### 2.3.2 Organic Amendments

Tables I and III of the work of Guo et al. (2006) summarises the most important immobilizing organic agents used for soil remediation. These are mainly waste components, and their fixation of metals is due to the sorption to oxygen-containing functional groups such as –COOH, phenol and –OH. These groups can dissociate their H<sup>+</sup> ions, which favorise ion exchange, complex formation, and the adsorption and chelation with trace elements. The most spread waste is sewage sludge, by-product of wastewater treatment processes used as “biosolid”. They are also used for fixing potential harmful elements of contaminated soils, domestic refuse, manure compost, poultry and cattle manure, useful to fix Cd, Cu, Pb, Zn. The use of the cited biodegradable wastes however, can give reasons for concern in the release of their own trace elements. But the use of waste as amendments for contaminated soils is a possible option for reclamation because the concentrations of trace elements in domestic biosolids are lower than those found in industrial and mining areas. Other resources of organic amendments for metal immobilization are: straws of cotton, rice and maize and rice hulls used to fix Cd, Cr, Pb, bagasse of sugarcane for Pb, waste water of paper mills for Cd, Cu, Hg, Ni, Pb and Zn and bark and sawdust. The latter are effective because of their high tannin content. The phenolic hydroxyl groups of tannin easily form chelates with metals when ion exchange happens. Both mechanisms can favorise the fixation of Cd, Hg, Cu and Pb of contaminated soils. Peats have a great affinity for Cd, Cu, Pb and Zn (Kumpiene et al. 2008). A disadvantage of peat is its high affinity for water and a tendency to shrink and swell by drying and weeting, producing bad stability. Brown coal had been used as a detoxicant of soils polluted with Pb, Cu and Zn (Shestopalov and Bezuglova 2000).

### 3 Remediation with Decontamination: Remotion, Clean-Up and Destruction of Contaminants

#### 3.1 Physical Separation Techniques

##### 3.1.1 Excavation, Transport and Disposal to Landfills

Excavation and physical removal of the contaminated soil has been the conventional remediation method most used up to now. Excavation of contaminated soil involves digging it for ex-situ treatment using a mobile treatment facility brought to the site. If the soil is treated on site, the soil may be used to fill in the excavated area. Advantages of excavation are: (1) to be a cost-effective approach for small amounts of contaminated soil and (2) the complete removal of the contaminants relatively and a rapid clean up of a contaminate site. Disadvantages: (1) the contaminants are simply moved to a different place, with the exception of the complementary use of a mobile treatment facility, and (2) the excavated soil transport needs safety precautions (e.g. swelling processes, oxidative reactions, spreading prevention, etc.).

##### 3.1.2 Mechanical Separation

Some processes based in the mining industry are used ex-situ to remove smaller more polluted particles, versus the larger ones. Size and density are two decisive factors in separation procedures. Dry conditioning procedures can be combined with particle size separation by using static and vibratory screeners. Air flow or centrifugal force can be used. Air cyclone separators are frequently used. By wet conditions procedures the material can be treated by sedimentation and flotation. Addition of froths and aeration causes the contaminated particles to float (Mulligan et al. 2001). Materials such as ferrous slag are removed by magnetic overhead belts (Meuser 2013).

#### 3.2 Chemical Treatment

The chemical treatments are based on the redox reactions and used to change harmful contaminants into less toxic or less mobile ones.

In situ chemical oxidation or "ISCO" uses "oxidant agents" such as potassium permanganate, persulphate, hydrogen peroxide, hypochlorite, chlorine gas and chloride dioxide. These oxidants are injected into wells and spread into the surrounding contaminated soil and groundwater. One example of oxidation is  $As^{3+}$  toxic to  $As^{5+}$  less toxic. In situ chemical reduction or "ISCR" uses "reducing agents" such as sodium dithionite, sulphur dioxide, sulphite salts, ferrous sulphate

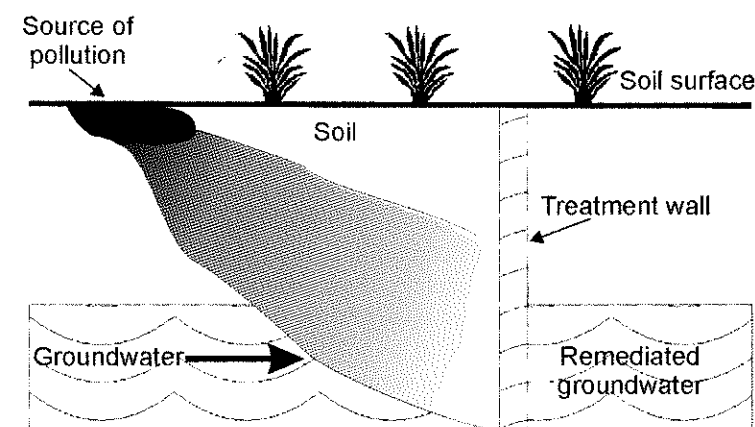


Fig. 7.3 Model of in situ treatment with a PRB (Drawing by N. Roca)

and zero valent metals (e.g. zero valent iron ZVI). These reducing agents change contaminants into their less toxic or less mobile species. ISCR can clean up elements such as  $Cr^{6+}$  that is reduced to  $Cr^{3+}$ , less toxic and less soluble in water. The most usual ways of ISCR (USEPA 2012) are two: (a) direct injection, and (b) the use of a permeable reactive barrier or PRB. Both techniques are in situ treatments, which are advantageous because they avoid excavation, always environmentally drastic and expensive in equipment.

- (a) Direct injection involves mixing the reducing agent with water to create a slurry, which is pumped down holes drilled directly into the contaminated soil.
- (b) A PRB or permeable reactive barrier, also named a permeable treatment wall, is built below ground by digging a trench and filling it with several of the cited reducing agents. Iron filings of ZVI are commonly used. The figure shows the soil and/or groundwater contaminated with  $Cr^{6+}$  flowing through the PRB allowing  $Cr^{6+}$  to react with the reducing Iron ZVI and flowing out the other side with  $Cr^{3+}$ .

ISCR using direct injection can clean up a contaminated soil in a few months, while PRBs may take several years. But the actual clean up time vary from site to site (Fig. 7.3).

#### 3.3 Soil Washing

Soil washing is a minimisation treatment by concentration of heavy metals into a smaller volume of soil by physical separation, usually followed by a chemical extraction (Dermont et al. 2008). It is done mainly ex situ, and less in-situ, without excavation. This technology is widely used in Northern Europe, America and

Japan. A case cited by Meuser (2013), it was the soil remediation process used in the Olympic Park in Stratford, London.

Physical separation processes exploiting differences between particle grain size, density, hydrophobic surface behaviour, magnetic susceptibility and others, to separate harmful trace elements bound preferentially to clay and silt fractions, from the coarse fractions sand and gravel. The techniques used, based in mining and metallurgical industries are: mechanical screening, hydrodynamic classification, gravity concentration, froth flotation, magnetic separation, attrition scrubbing and others. The polluted sludge, mainly associated to the clay and silt fractions, separated and dried, must be passed through filter presses. Finally, the "filter cake" obtained must be decontaminated (e.g. by solidification, thermally, etc.). Chemical extraction or chemical leaching using various solubilising agents such as inorganic acids:  $H_2SO_4$ ,  $HCl$ ,  $HNO_3$  ( $pH < 2$ ), salts: sodium citrate, sodium dithionite, organic acids: acetic, iminodiacetic, citric, malic, oxalic, tartaric ( $pH < 4$ ), bases:  $NaOH$ ,  $Na_2CO_3$ ,  $CaO$  ( $pH > 9$ ), chelating agents: citric acid, tartaric acid, EDTA, DTPA, NTA (Wuana et al. 2010). Some workers had been used  $HCl$  and  $H_2SO_4$  to extract:  $Pb$ ,  $Cu$ ,  $Zn$ ,  $Cr$ ,  $Hg$  and  $As$  (Moutsatsou et al. 2006; Meuser 2013). Others use citric acid, tartaric acid and EDTA for  $Cd$ ,  $Cu$ ,  $Ni$ ,  $Pb$ ,  $Zn$  (Wuana and Okieimen, 2011), EDTA for  $Cd$  and  $Pb$  in Laurion (Karvounis and Kelepertsis 2000), EDTA, DTPA and citric acid (Bricka 1997), citric and fluorosilicic acid for  $Cr$  and citric, fluorosilicic, DTPA and NTA for  $Cd$  and  $Pb$  (Neale 1997). The washing treatment has also been used to separate and concentrate radionuclides such as Plutonium, Americium,  $^{137}Cesium$  and Uranium (Bradbury and Scrivens 1995; Grace et al. 1995). Though less used, we must cite in situ soil washing.

In situ soil washing: is a soil washing approach without excavation. It is a high pressure technique. Steel tubes are arranged with a vibrator and situated until about 10 m deep. A high pressure jet is used to loosen the soil and to form a sludge that is pumped out of the ground (Meuser 2013). This soil-water suspension, with pollutants is treated with a suitable decontaminant. This technological approach is possible in sandy soils. Clayey and humic soils are not adequate to this technique. In general, ex-situ and in-situ soil washing provides a cost effective way of reducing soil contamination, especially at larger sites, but does not destroy the potential harmful elements of contaminated soils. The contaminants are simply moved to a different place, and is therefore not adequate to wash complex waste mixtures of metals and organics.

### 3.4 Soil Flushing

Soil flushing is an in-situ remediation technology that removes the contaminants from the soil with water or water with additives injected at high pressure to enhance contaminant solubility. The flushing solution passes through in place contaminated soils using an injection or infiltration process (Khan et al. 2004). The potentially toxic elements are moved to an area where the flushing wastewater charged with

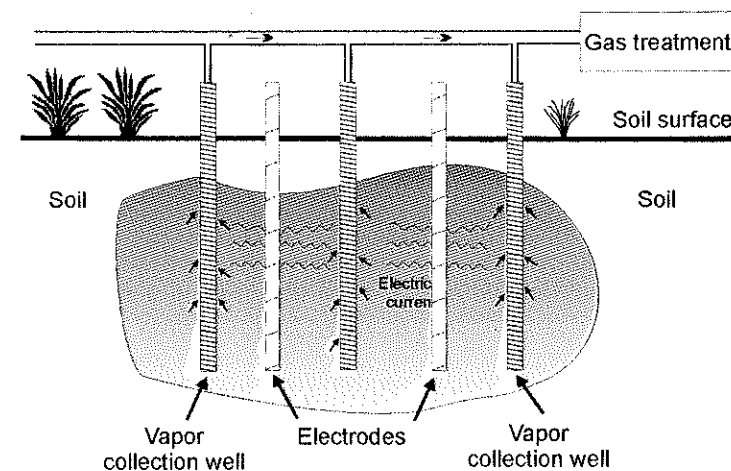


Fig. 7.4 An example of thermal treatment (Drawing by N. Roca)

them is captured and pumped to the surface using groundwater extraction wells. This wastewater must be treated to remove the metals which can be reutilized into the flushing process. The chemical enhanced flushing includes addition of solvents and complexing agents, previously cited in the Soil Washing section. The use of non toxic additives is recommended to minimize soil degradation. Soil flushing is currently used as an in situ soil washing process. Soil flushing can be applied in the remediation of contaminated soils by heavy metals and radionuclides. Some examples are:  $Cd$  (Urlings 1990),  $Cr$  (USEPA 1996),  $Cu$  (Di Palma and Medici 2002; Tsang et al. 2007) and  $Cu$  and  $Zn$  (Swab et al. 2008). Soil flushing is a cost reasonable technique if the contaminated soil has a good permeability ( $> 1.0 \times 10^{-3} \text{ cm} \cdot \text{s}^{-1}$ ). Some limitations are: low permeability of clayey soils, heterogeneity of soil. Deeper groundwater results in higher costs.

### 3.5 Thermal Treatment

This is a physical remediation technology that heats contaminated soil. In situ the heat is applied underground directly to the contaminated area and the potentially toxic chemicals move through the soil toward wells where they are pumped off (Fig. 7.4). Three techniques were mainly used:

1. Steam enhanced extraction (SEE), injects steam underground that heats the contaminated site and mobilises and evaporates contaminants.
2. Microwave heating, shows a high degree of effectiveness for removing organic pollutants from soils with low permeability like clayey soils (Meuser 2013).

3. Thermal conduction heating (TCH) uses heaters located in underground steel pipes.

Ex situ (on site and off site) thermal treatments involve several types such as: thermal desorption, pyrometallurgical processes and incineration.

### 3.5.1 Thermal Desorption

Removes but does not destroy contaminants from soil in a machine called a "thermal desorber", usually a rotary kiln and thermal screw to evaporate the contaminants, mainly organics. It is not generally used to treat metals, but can partially remove some such as Hg and the metalloid As. There are two groups of procedure based on the operating temperature of the desorber: (1) Low temperature Thermal Desorption (LTTD) in which contaminated soil is heated between 90 and 320 °C and High Temperature Desorption (HTTD) in which wastes are heated from 320 to 560 °C (FRTR) or 700 °C according to Chang and Yen (2006). HTTD can eliminate Hg and reduce the concentration of As and Cd of contaminated soils, but without their complete volatilization.

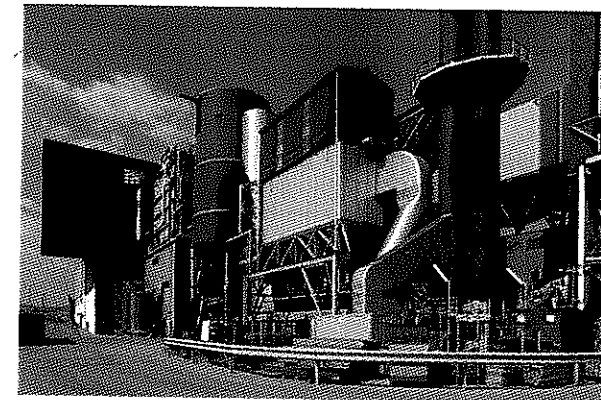
### 3.5.2 Pyrometallurgical Processes

Many installations during the high temperature phase in a second rotary kiln operate without oxygen- pyrolysis-. This is named pyrometallurgical separation, and is used to volatilize metals (Mulligan et al. 2001). Separation of metals is not easy due to their high boiling points (e.g.: Hg, 357; As, 613; Cd, 767; Zn, 907; Pb, 1,740, Cu, 2,395; Cr, 2,599 °C). With the exception of Hg and As, metals cannot usually be treated with this process.

### 3.5.3 Incineration

Is the process of burning hazardous materials at temperatures high enough (970–1,200 °C) to destroy contaminants. The incineration usually operates in presence of oxygen. This technique can eliminate Hg, As, Cd and Zn, but not Cr and Pb. Mulligan et al. (2001) including Pb, Au and Pt between the metals that can be recovered by pyrometallurgical separation, but USEPA (2012) asserts that incineration does not destroy metals such Pb and Cr. For Meuser (2013), incineration causes vitrification of the metals, and at least immobilises them temporarily. An exception was Cr, which in alkaline conditions can generate toxic and mobile chromate ( $\text{Cr}^{6+}$ ) (Fig. 7.5).

Fig. 7.5 Example of offside incinerator (Mataró, NE Spain)



## 3.6 Electrokinetic Remediation

Electrokinetic treatment is mainly an in situ remediation technology (but can also be used ex situ), designed to remove radionuclides and heavy metal contaminants from soil by passing a low intensity electric current between a cathode and an anode embedded in the contaminated soil (Acar et al. 1995). Positively charged metal or metalloid cations such as  $\text{Cr}^{3+}$  and  $\text{As}^{3+}$  migrate to the negatively-charged electrode (cathode), while metal or metalloid anion such chromate ( $\text{CrO}_4^{2-}$ ) and arsenate ( $\text{H}_2\text{AsO}_4^-$ ) move towards the positive charged electrode (anode). Upon their migration to the electrodes the contaminants may be removed by electroplating, precipitation, co-precipitation, pumping near the electrode or complexing with exchange resins. The electroremediation technique can be applied at great soil depths. In most cases, one central cathode is installed surrounded by a number of external anode electrodes. The maximum distance between electrodes should be restricted to 10 m, the usual maximum depth is 12 m and the tensions (voltage) applied vary from 20 to 100  $\text{Vm}^{-1}$ , exceptionally 500  $\text{Vm}^{-1}$  (Meuser 2013). Most soils contain water in the pores between the soil particles and have an inherent electrical conductivity that results from salts present in the soil. Electrokinetic remediation uses the current that mobilizes charged species, particles and ions in the soil. The main strategies used are: electromigration, electroosmosis and electrophoresis (Meuser 2013) (Fig. 7.6).

### 3.6.1 Electromigration

Electromigration is based on the transport of soluble cations, anions and non polar substances, mass flow or advection, dissolved in the pore fluid. It is feasible in different textural classes, but most effective in coarse grained soils. The ion velocities of electromigration are 5–40 times higher than those of the electroosmosis. The water content must correspond to 50–70 % of the field capacity. An



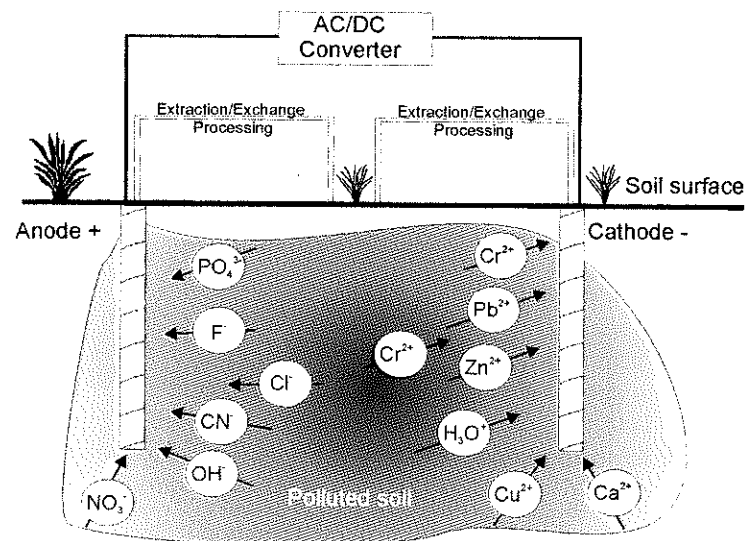


Fig. 7.6 An example of electrokinetic remediation (Drawing by N. Roca)

electrical gradient initiates movement of charged chemical species and follows with their transport to the electrode of opposite charge.

### 3.6.2 Electroosmosis

Electroosmosis is the movement or transport of pore fluid under an electrical gradient from the anode to the cathode that follows the principle of a cation and water film movement through the diffuse double layer of clay minerals. Clay minerals provide diffuse double layers with negatively charged surfaces. The electroosmosis treatment is preferentially applied to silty and clayey soils because the presence of clay minerals is required. This option is advantageous in soils with low permeability difficult to treat by traditional technologies. The suitable water content must be of 80 % of the field capacity.

### 3.6.3 Electrophoresis

Electrophoresis is the transport of charged particles or colloids under the influence of an electric field; contaminants bound to mobile particulate matter can be transported in this manner (Van Cauwenberghe 1997). This charged particle movement under an electric gradient is mostly present in sandy and pebbly soils, coarse-grained soils with a lot of macropores (Meuser 2013). The best water content corresponds to 50–70 % of the field capacity.

### 3.6.4 Factors Affecting Electrokinetic Technology

The efficiency of the electrokinetic treatment is influenced by several factors:

- Contaminant properties: the applicability of electrokinetics to contaminated soil depends of the cation type and concentration, their solubility in the specific soil, their electrical charge and ionic mobility and their location and form in the soil.
- Salinity and cation exchange capacity (CEC): this technology is most efficient when these parameters are low. The electrical conductivity (EC) of the pore water is a decisive factor in determining the efficiency of the electrokinetic process.
- Soil moisture: electrokinetic treatment requires adequate soil moisture. It is possible in saturated and unsaturated soils, but is most applicable to saturated soils. There is a minimum moisture content at which electromigration can take place that corresponds to residual moisture called “immobile water”. For optimum results, it should be less than saturation (Van Cauwenberghe 1997). Therefore, addition of a conducting pore fluid may be required.
- Soil type, grain size and structure: electrokinetic remediation technology is most applicable to homogeneous soils with high permeability, but may also be applicable to low permeable soils such as clayey soils, due to their large surface area which provides numerous sites for reactions necessary for electrokinetic processes.
- pH: the pH gradient influences the movement of the ions. The pH can affect the electrochemical process and cause precipitation of contaminants, reducing soil permeability and inhibiting recovery. The deposition of precipitated solids may be prevented by flushing the cathode with water or a dilute acid (Van Cauwenberghe 1997).

### 3.6.5 Technology Advantages

Electrokinetics can be used either in situ or ex situ and can be very cost-effective in both uses. This technology can be used in saturated or unsaturated soils because of the insertion of pore fluid. This process is an effective method of inducing movement of water through clay soils, of low permeability, which normally are very difficult to treat by traditional technologies such as soil flushing. Electrokinetic remediation may be able to be performed without the addition of chemical agents, such as strong acids that could destroy the soil structure. This technology applied in situ does not require excavation of contaminated soil and can work at great soil depths. Electrokinetics in situ not only avoids excavations that are dangerous adjacent to buildings and difficult areas, but can even be used under buildings.

### 3.6.6 Technology Limitations

The effectiveness of electrokinetic treatment may be limited by a variety of cation type and concentration, soil characteristics such as texture, organic matter, carbonates and pH. Heavy metals in their metallic state have not been successfully dissolved and separated from soil samples. The treatment depth is limited by the depth to which the electrodes can be placed. Heterogeneous soils with large rocks or gravel, or containing technogenic substrates such as building foundations, rubble, buried metallic or insulatic material can interfere with the electrical conductivity of the soil and therefore the voltage gradient, and even short circuit the system. Electroremediation can enhance the soil temperature, eventually reaching more than 60 °C, causing soil drying and a cessation of the fluid flow. Moreover the edaphon will be strongly disturbed.

In situ electroremediation has a detrimental impact on soil microorganisms because at the anode (pH 2) base-tolerant species are killed and at the cathode (pH 12) acid-tolerant species are also destroyed. Several polarization effects can decrease the electric potential and therefore the effectivity of the electrokinetics process. Most of the cations will precipitate at the cathode as oxides, hydroxides and carbonates because the pH 12 favours the precipitation, but a successful decontamination depends on permanent maintenance of the metal solubility. Thus, a high precipitation rate may reduce the effectiveness of the electroremediation, since clogging of the pores may occur resulting in a cessation of the flow.

### 3.6.7 Combining Electrokinetics with Other Techniques

In this section some methods developed by combining electrokinetics with other techniques are cited. There are mainly trademarked or patented commercial processes:

- Extraction and removal by electrodeposition, separation, condensation, precipitation or ion exchange either at the electrodes or in a treatment unit (Electrokinetics, Inc and EPA).
- Use of electrode well for both anodes and cathodes and the management of the pH and electrolyte levels in the electrolyte streams of the anode and the cathode (Patent of Geokinetics International, Inc., GII, 1995).
- Electrokinetic movement and capture of Uranium in contaminate soil (Isotron Corporation).
- Electroacoustical soil decontamination is a technology that combines electrokinetics with sonic or ultrasonic energy to remove metals (Battelle Memorial Institute and EPA 1992).
- Lasagna is an in-situ remediation process, combining electroosmosis and in-situ sorption in treatment zones (Ho et al. 1995).
- Combination of organo-acid leaching of metals of the contaminated soil and electrolysis of the extract, avoiding the deposition of highly contaminated

residue. The leachate thus, can be reused for leaching. This process is applied for soil contaminated with Cu, Pb, Sb and Cd (Thöming and Calmano 1995).

### 3.6.8 Summary of More Cited Treatable Contaminants

The following potential toxic elements have been remediated by electrokinetic treatments in situ at full-scale, pilot scale and bench-scale applications and efficiency reduction range between >74–95 %.: Pb, 14 citations; Cr, 13 cit.; Zn, 11 cit., Cd, 9 cit.; Cu, 8 cit., Ni and Hg, 7 cit., As, 6 cit., Fe, 2 cit.

Between Radionuclides: U, 5 citations, Th, 3 cit., Ra, 2 cit., <sup>90</sup>Sr, 1 citation, <sup>137</sup>Cs, 1 cit. Cr and As have been remediated either such as cations Cr<sup>3+</sup>, Cr<sup>6+</sup>, As<sup>3+</sup>, As<sup>5+</sup> or anions arsenate H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and chromate CrO<sub>4</sub><sup>2-</sup>.

This summary is mainly based on the data reported by: Acar et al. 1995; USEPA 1997; Van Cauwenberghe 1997; Puppala et al. 1997; Sobral and Thoming 1998; Reddy and Chinthamreddy 1999; Mulligan et al. 2001; Virkutyte et al. 2002; Page and Page 2002; Gent et al. 2004; Sharma 2004; Mascia et al. 2007; Beukes et al. 2012; Meuser 2013.

## 3.7 Bioremediation

Conventional physicochemical technologies to remediate heavy metals-contaminated soil and sediment have many problems such as low efficiency, high cost and occurrence of byproducts. Recently bioremediation technology is getting more and more attention. Bioremediation is defined as the use of biological methods to remediate and/or restore the contaminated land. The objectives of bioremediation are to degrade hazardous organic contaminants and to convert hazardous inorganic contaminants to less toxic compounds at safe levels (e.g., Lovley et al. 1989; Lovley and Phillips 1992). The use of bioremediation in the treatment of heavy metals in soils and sediments is a relatively new concept. Bioremediation using microbes has been developed to remove toxic heavy metals from contaminated soils in laboratory scale to the contaminated field sites. Recently, the application of cost-effective and environment-friendly bioremediation technology to the heavy metals-contaminated sites has been gradually carried out in Korea (Lee et al. 2005; Lee et al. 2006; Park et al. 2006; Chon et al. 2011; Kim et al. 2011a).

The merits of bioremediation include low cost, natural process, minimal exposure to the contaminants, and minimum amount of equipment. The limitations of bioremediation are length of remediation, long monitoring time, and sometimes, toxicity of byproducts for especially organic contaminants. From now on, it is necessary to prove the applicability of these technologies to contaminated sites and to establish this highly effective, low-cost and easy bioremediation technology.

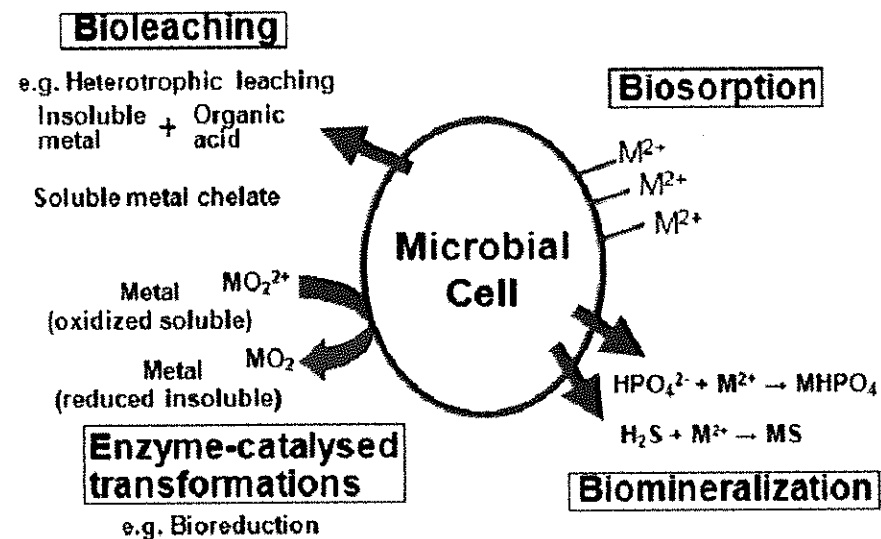


Fig. 7.7 Metal-microbe interactions; biosorption, bioreduction, biomineralization and bioleaching

Four categories of metal-microbe interactions are generally (1) biosorption, (2) bioreduction, (3) biomineralization and (4) bioleaching (Fig. 7.7). In this chapter, some case studies of the above metal-microbe interactions which were published recently in Korean domestic journals and international journals will be introduced and summarized (for example, Kim et al. 2009a, b; Lee et al. 2008a, b; Jang et al. 2009; Kim et al. 2011b; Lee et al. 2011).

### 3.7.1 Biosorption of Heavy Metals in Soils

Bacterial cell walls are negatively charged under circumneutral pH conditions and they can passively adsorb positively charged metal ions. This electrostatic complexation is followed by further deposition of dissolved metals and, then, development of biominerals at the cell surfaces (e.g., Beveridge and Murray, 1980). Some experiments have been designed to determine whether complexation and subsequent mineralization of metals onto microbial cell walls can be explained by surface complexation models as has been applied to inorganic particles (Fein et al. 1997; Warren and Ferris 1998).

Biofilms are microcosms consisting of microorganisms distributed throughout a matrix of fibrous and highly hydrated, extracellular polymeric substances (EPS), which are often exopolysaccharides. By forming biofilms in natural settings, a community of bacteria can better obtain nutrients in oligotrophic environments and protect themselves from a variety of unfavorable conditions such as dehydration, chemical toxicity and predation (Costerton et al. 1995). The local effects of

### • Phylogenetic tree

- Isolated bacteria were identified by 16s ribosomal DNA sequencing
- Bacteria; Firmicutes; Bacilli; Bacillales; Bacillaceae; Bacillus; Bacillus cereus group; *Bacillus thuringiensis*

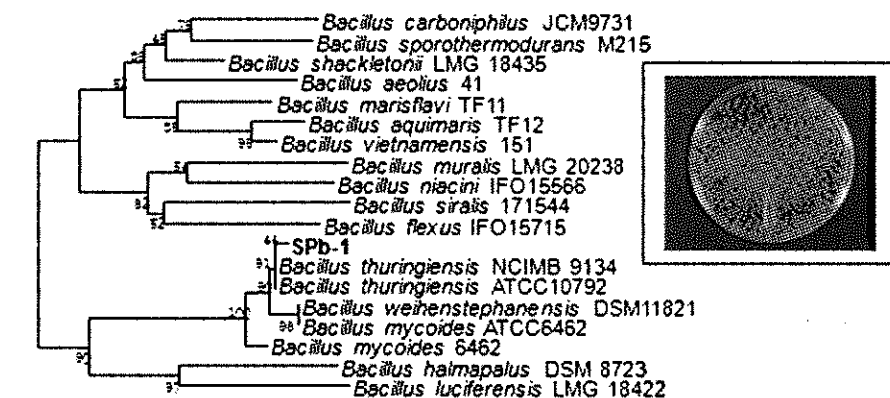


Fig. 7.8 Identification of the isolated bacterium from contaminated soil (SPb-1) (Kim et al. 2009a)

biofilms on geochemical processes, such as redox and pH, could drastically alter the state of metals and metalloids thereby influencing the degree of metal accumulation or mineral dissolution (Lee and Beveridge 2001).

Kim et al. (2009a, b) studied the biosorption of Pb and Cd to apply for the remediation of contaminated sites through the reduction of heavy metal mobility by using indigenous bacteria from the soil, and to evaluate the characteristics of biosorption onto biofilm according to various environmental factors which can affect the sorption of toxic heavy metals. Indigenous bacterium having a tolerance to high Pb ( $353 \text{ mg kg}^{-1}$ ) and Cd ( $3.2 \text{ mg kg}^{-1}$ ) toxicity was isolated from Pb and Cd-contaminated soil which was concomitantly contaminated with TPH (total petroleum hydrocarbons). The bacterium was identified as *Bacillus thuringiensis* by 16 s rRNA sequence analysis and named SPb-1 (Fig. 7.8).

As a result of batch-type biosorption experiments using SPb-1, the highest removal rates of aqueous Pb and Cd were observed with the initial concentration of Pb and Cd less than  $100 \text{ mg L}^{-1}$  and  $5 \text{ mg L}^{-1}$ , respectively (Fig. 7.9). The optimal operating conditions of Pb and Cd biosorption were as follows; culture age of over 16 h to stationary growth phase, biomass amount of more than  $2 \text{ g L}^{-1}$ , pH 5–9, and temperature at  $25^\circ\text{C}$  and  $35^\circ\text{C}$  for Pb and Cd, respectively (Fig. 7.10).

Acrylic columns with dimension of 5 cm diameter and 31 cm height were filled with the contaminated soils and a variety of carbon sources – acetate, lactate and glucose – and deionized water as a control were made to pass through the columns to instigate formation of biofilm. Effluent volume ratio through the columns with acetate, lactate and glucose supply showed 98.5 %, 97.3 %, and 94.7 %, respectively.

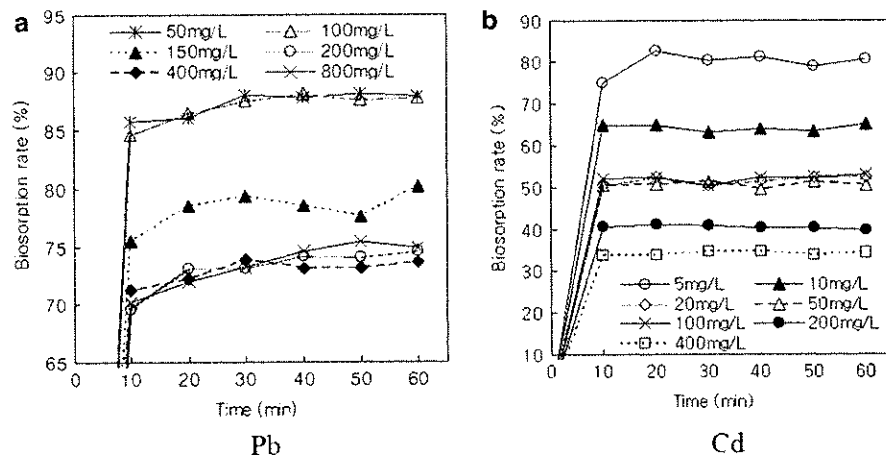


Fig. 7.9 Biosorption rates of Pb and Cd by Spb-1 according to the initial concentration of heavy metals (Kim et al. 2009a)

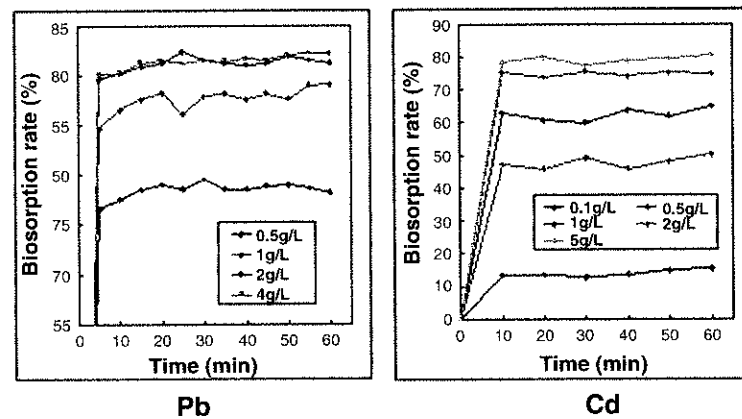


Fig. 7.10 Biosorption rate of Pb and Cd with bacteria concentration (Kim et al. 2009a)

respectively, when compared to deionized water. This was likely due to the biofilm formation in pore and the flow of injected carbon source solution might be limited.

Biofilm developed onto the soil particles through supply with carbon sources adsorbed higher concentrations of heavy metals than control. Maximum removal rate of metals by sorption onto biofilm depended on the type of carbon sources; for example, glucose for Cr and Cd adsorption and acetate for Cu and Zn adsorption (e.g., Fig. 7.11). The results suggest that in-situ stabilization of dissolved toxic

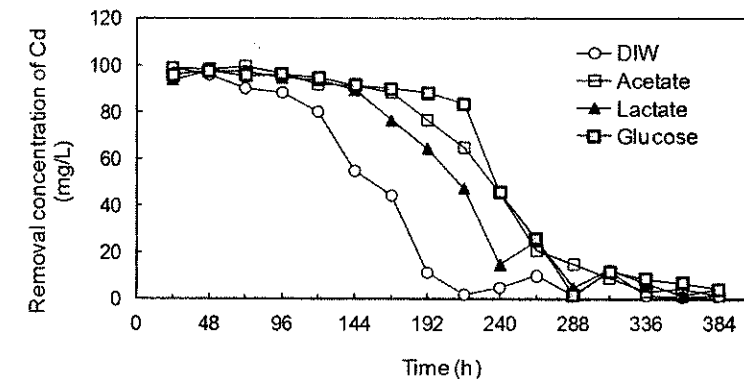
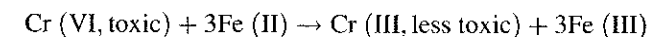


Fig. 7.11 Removal of dissolved Cd by biosorption to biofilm developed onto soil particles (Kim et al. 2009b)

metal ions can be possible and used effectively for the remediation of heavy metals-contaminated soils by biofilm formation.

### 3.7.2 Bioreduction of Cr (VI) to Cr (III) in Sediments

Treatment technologies for removing Cr (VI) is generally ion-exchange, electro-deposition and chemical reduction with iron- and sulphur-containing solutions by precipitation. The problem is that these techniques are quite costly, generate large amounts of secondary waste products due to various reagents used in a series of treatments and require high energy input or large quantities of chemical reagents (Lee 2006). Recently, bioreduction using microorganisms offers an attractive treatment option, because the technology is cost-effective and environmentally compatible. The oxidation-reduction reactions of Cr are controlled in the presence of a strong reducing and oxidizing materials. Reduction of Cr (VI) to Cr (III) can occur in natural systems in the presence of reductants, such as Fe(II) and sulphides.



Microbiological reduction of Cr (VI) by indigenous bacteria in Cr-contaminated sediment with industrial wastes was studied for the first time in Korea (Lee et al. 2006, 2008a, b). Sediment samples were collected in June of 2004 and 2005 from sediment bed in the area of the pigment manufacturing factories in Dongducheon city which is located in the northern part of Seoul, Korea (Fig. 7.12). The average concentration of Cr in sediments by aqua regia digestion was  $708 \text{ mg kg}^{-1}$ . It was found that isolated indigenous bacteria in Cr-contaminated sediment from the pigment manufacturing factories, which can reduce Cr (VI) to Cr (III), were identified as *Rhodococcus erythropolis* (Fig. 7.13).

- **Source of bacteria**
- : **Sediment samples from stream bed in the area of the pigment manufacturing factories, Dongducheon city, Korea**
- **Sampling period : June in 2004 and 2005**

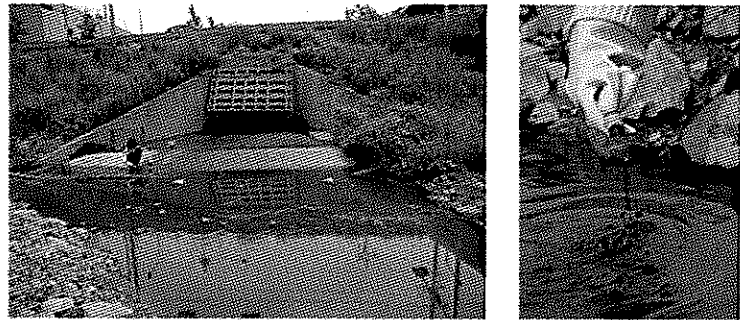


Fig. 7.12 Source of bacteria in Cr-contaminated sediments collected from the area of the pigment manufacturing factories (Lee 2006)

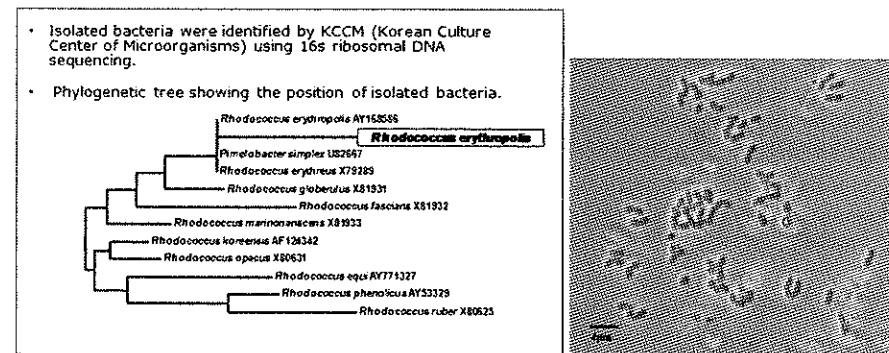


Fig. 7.13 Identification of isolated bacteria, *Rhodococcus erythropolis* (Lee 2006)

The removal efficiency of Cr (VI) by *Rhodococcus erythropolis* increased with time and decreased with an increase of Cr (VI) concentration with mediums of living and heat-killed cells (Fig. 7.14). The reduction rate of Cr (VI) by *Rhodococcus erythropolis* increased with an increase in biomass concentration (Fig. 7.15), while the contact time required for the reduction of Cr (VI) decreased with an increasing biomass concentration. Also Mn-oxides could effect on the behavior of chromium (Fig. 7.16).

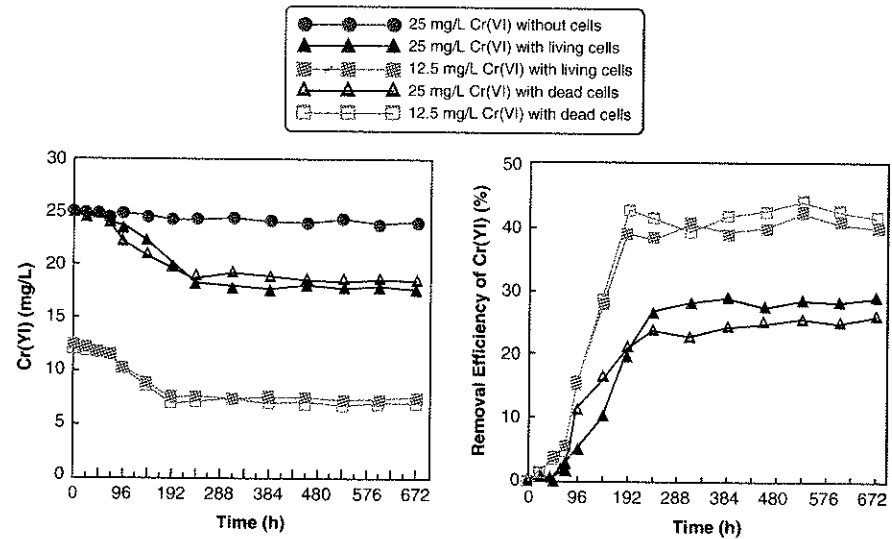


Fig. 7.14 Cr(VI) reduction by *R. erythropolis* in CRB medium

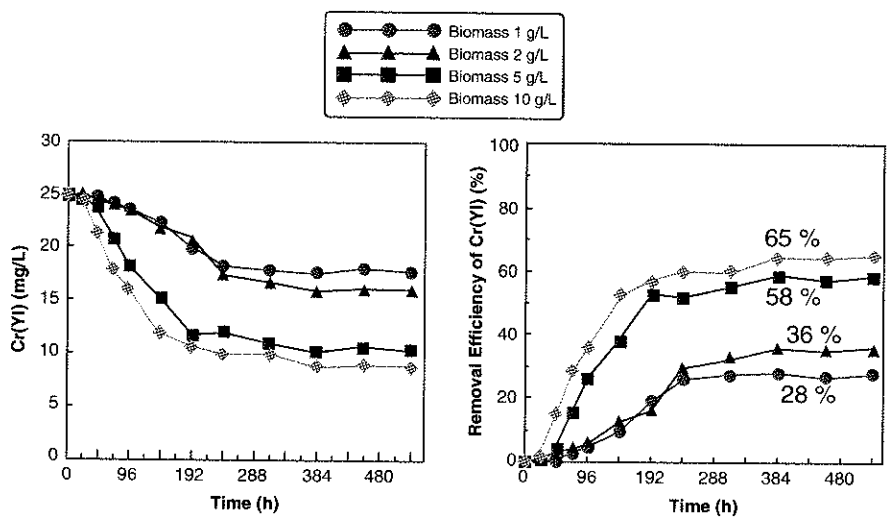


Fig. 7.15 Effect of biomass concentration on Cr (VI) reduction by *R. erythropolis* in CRB medium

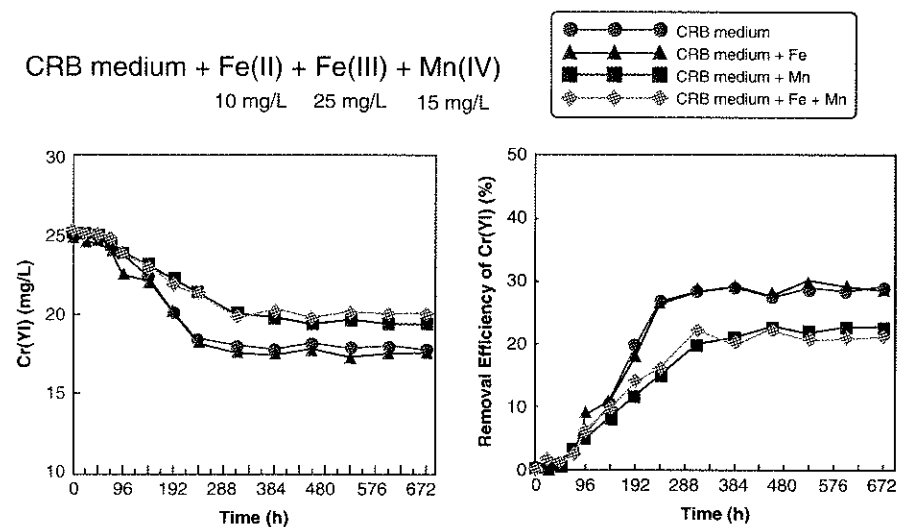


Fig. 7.16 Effects of Fe and Mn on Cr(VI) reduction by *R. erythropolis* in CRB medium

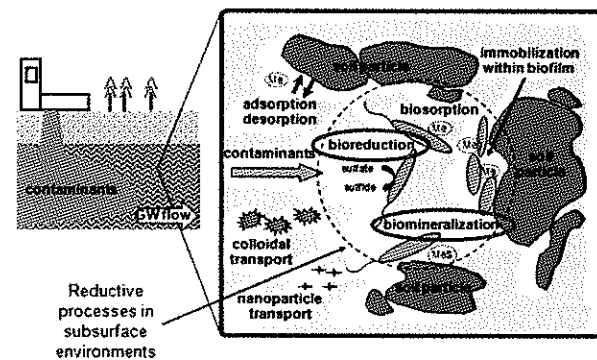


Fig. 7.17 The main reductive processes in subsurface environments are bioreduction and biomineralization

### 3.7.3 Biomineralization (Bioprecipitation): In-Situ Precipitation of As and Heavy Metals in Soils by Microbiological Sulphate Reduction

The main reductive processes in subsurface environments are bioreduction and biomineralization as shown in Fig. 7.17. Microbiological sulphate reduction is the transformation of sulphate to sulphide catalyzed by the activity of sulphate-reducing bacteria using sulphate as an electron acceptor. Low solubility of metal sulphides leads to the precipitation of sulphides (biomineralization) in solution. The applicability of in-situ metal precipitation based on biological sulphate reduction (BSR)

was tested for the immobilization of As and Cu in a more realistic condition and the long-term stability of stabilized As and Cu was evaluated (Jang et al. 2009). Mean concentration of As and Cu in subsurface soil (by *aqua regia* digestion) around the abandoned Songcheon Au mine site in Korea was estimated as 1,311 mg/kg and 146 mg kg<sup>-1</sup>, respectively. Inoculation of indigenous bacteria was extracted from the contaminated mine soils. From sequential extraction test, As exists mainly as Mn-oxide bounds (35 %) and Fe-oxide bound (52 %), and Cu as relatively high sulphide fractions. In batch-type experiments, indigenous sulphate-reducing bacteria rapidly decreased sulphate concentration and redox potential and lead to substantial removal of dissolved As and Cu from solution. More than 98 % of injected As and Cu were removed in the effluents from both microbial and chemical columns designed for metal sulphides to be precipitated. Black precipitates formed in the microbial column during the experiments were identified as iron sulphide and copper sulphide. Arsenic was observed to be adsorbed on the surface of iron sulphide precipitate (Jang et al. 2009) (Figs. 7.18 and 7.19).

### 3.7.4 Bioleaching of As in Contaminated Soils

Bioleaching technique is the increasing mobility of heavy metals and As by metabolism of bacteria. The principle of bioleaching for As is the increasing of As mobility in contaminated soil. Direct metabolism of the bacteria, direct As (V) – reducing bacteria, makes the reduction of As (V) to As (III) which has greater mobility than As(V). Iron (Fe)-reducing bacteria dissolve Fe minerals (e.g. Fe hydroxide) by altering Fe (III) to aqueous Fe (II), and subsequently As associated with Fe mineral (e.g. As adsorbed on Fe hydroxide) in contaminated soil is leached out into solution (Nickson et al. 2000).

A study on the bioleaching As in contaminated soil collected from an old smelting site in Korea was carried out using metal reducing bacteria (Lee et al. 2011). Two types of batch experiments, biostimulation and bioaugmentation, were conducted for 28 days under anaerobic conditions. The biostimulation experiments were performed through activation of indigenous bacteria by supply with glucose or lactate as a carbon source. The results indicated that the maximum concentration of the extracted As was 11.2 mg L<sup>-1</sup> at 4 days from the onset of the experiment when 20 mM glucose supplied, and As removal efficiency was in the range of 60–63 % in the biostimulation experiment (Fig. 7.20).

In the case of bioaugmentation the highest dissolved As concentration was 24.4 mg L<sup>-1</sup> at 2 days though it dramatically decreased over time through readsorption onto soil particles (Lee et al. 2011). This novel technique of bioleaching may be practically applied to remediation of As-contaminated soil after determination of optimum operational conditions such as operation time and proper carbon source and its concentration.

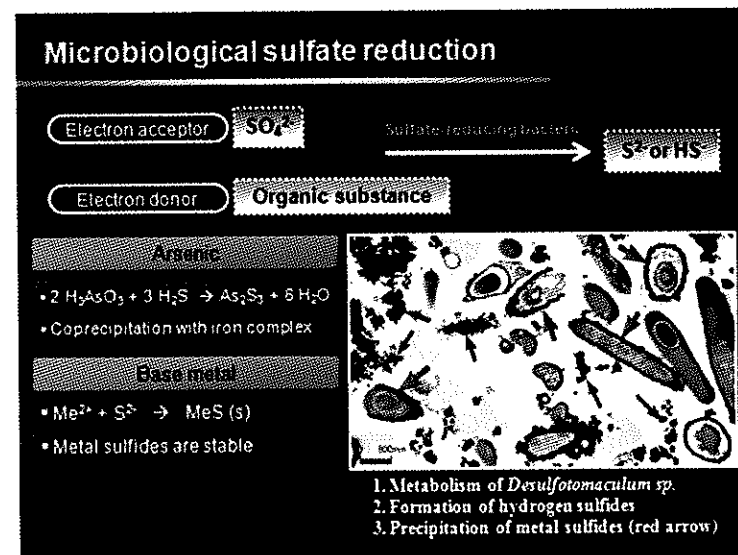
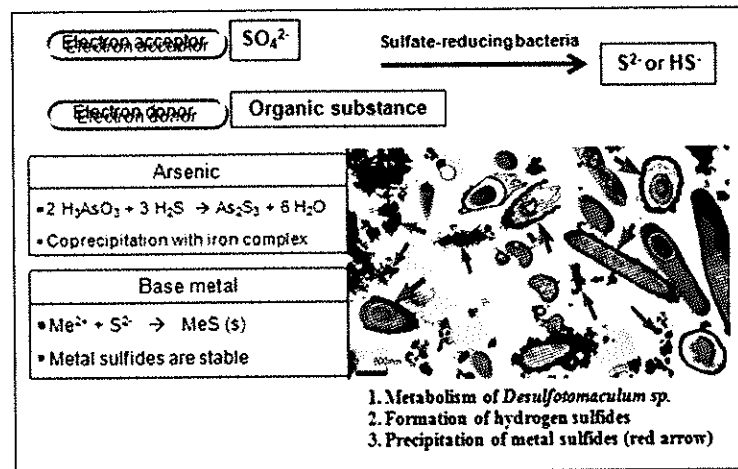


Fig. 7.18 Black precipitates formed in the microbial column and identified as Fe sulfide by SEM-EDS analysis (Jang et al. 2009)

### 3.8 Phytoremediation

The cleanup of contaminated sites with heavy metals is necessary, but environmental remediation strategies are often expensive, energy consuming, lead to  $\text{CO}_2$  emissions and are intrusive (McGrath et al. 1995), so the soil itself can rarely be utilized after the treatment. Thus, it is important to develop low-cost and environmentally friendly strategies. In these conditions, phytoremediation could be the

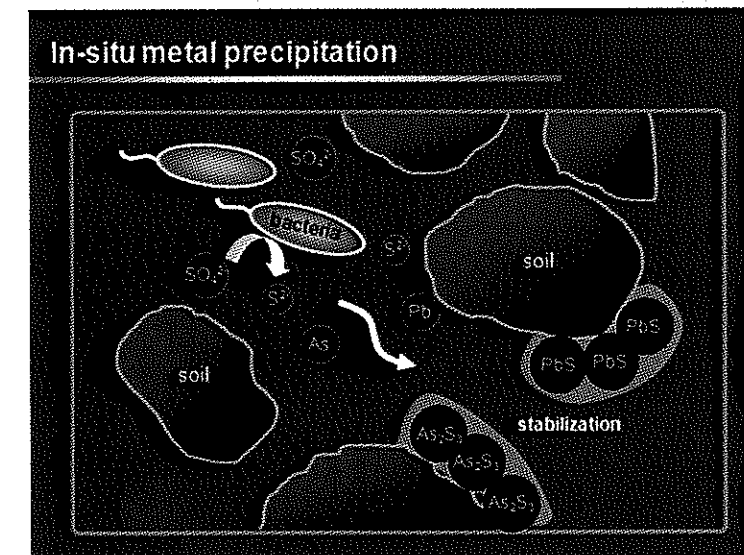
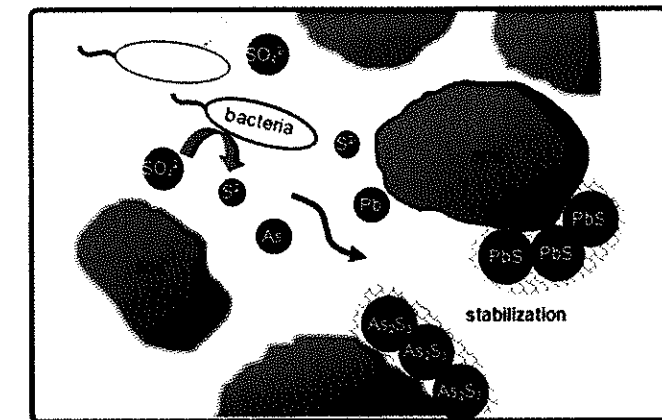


Fig. 7.19 Removal of arsenic with various concentrations of sulfate (Jang et al. 2009)

cheapest and simplest option among the available soil clean-up strategies. USEPA (2000) defines phytoremediation as "the use of plants for containment, degradation or extraction of xenobiotics from water or soil substrates". Thus, phytoremediation takes advantage of the inherent ability of plants to take up water, soluble mineral nutrients and their associated co-contaminants through their roots, to transpire through leaves, and to act as a transformation system to metabolize organic compounds, or to adsorb and bioaccumulate toxic trace elements including heavy metals (Purakayastha and Chhonkar 2010).

Phytoremediation can be practiced in order to scavenge both organic and inorganic pollutants present in solid substrates (e.g. soil), liquid substrates

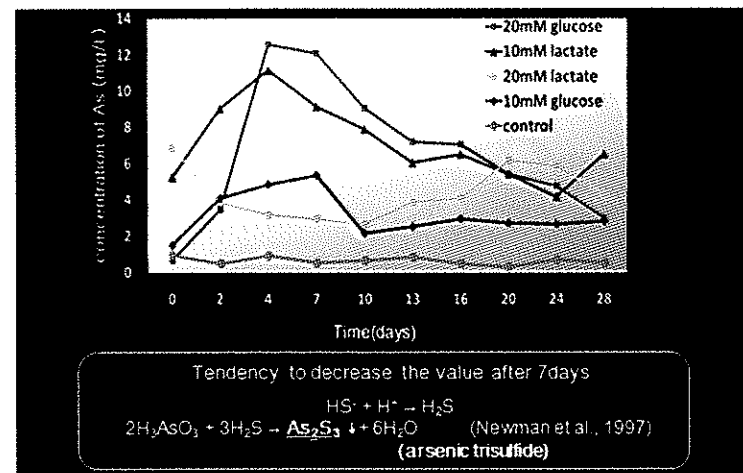


Fig. 7.20 Leaching of As with various concentration of carbon sources in biostimulation batch experiment (Lee et al. 2011)

(e.g. water) and the air. There are various phytoremediation approaches that can be employed:

- Phytoextraction, accumulator plants are planted on contaminated soil to absorb, translocate and concentrate hazardous compounds, particularly heavy metals, in aboveground biomass and later harvested in order to remove these hazardous compounds from the soil.
- Rhizofiltration, roots of accumulating plants absorb concentrate, and/or precipitate hazardous compounds, particularly heavy metals or radionuclides, from polluted effluents and are later harvested to diminish the metals in the effluent.
- Phytodegradation, plants and associated microorganisms degrade organic pollutants into less toxic forms or render them immobile in order to prevent their entry into the food chain or environment.
- Phytostabilization, metal-tolerant plants are used to reduce the mobility of hazardous compounds, particularly heavy metals. Thus, the pollutants are stabilized in the substrate.
- Phytovolatilization, plants are used to volatilize pollutants.

Phytodegradation can only be of use in the case of degradable wastes. Plants and associated microorganisms degrade organic pollutants into less toxic forms, and thus it has limited applicability to the remediation of heavy metal contaminated soils (Purakayastha and Chhonkar 2010). Rhizofiltration can only occur in water bodies and aqueous waste streams. The advantages associated with rhizofiltration are the ability to use both terrestrial and aquatic plants. Another advantage is that contaminants do not have to be translocated to the shoots. Although several publications have shown the ability of aquatic plants for heavy metal removal, the majority of them have been performed under laboratory conditions (Olguín and

Sánchez-Galván 2012). These metal uptake capacities may be entirely different when plants are under natural conditions with environmental factors less favourable (Lu et al. 2011). Therefore, specific remediation of soil trace elements (hereafter, heavy metals) by plant species includes (Ghosh and Singh 2005): phytoextraction, phytostabilization, and phytovolatilization.

### 3.8.1 Phytoextraction

Phytoextraction seems to be most attractive due to its versatility in usage; however it depends heavily on the efficiency of the metal accumulating plants used. Robinson et al. (2006) list the potential limitations in using phytoextraction to remediate contaminated sites: (i) long period required for cleanup; (ii) limited number of target metals which can be phytoextracted; (iii) limited depth that can be accessed by roots; (iv) difficulty in producing a high biomass crop of the desired species; (v) potential of plant metals to enter environmental food chains, and (vi) inevitable leaching of metals if chelators are added to induce phytoextraction. Thus, it is important to develop the research on various plant species in relation to the phytoextraction of metal from contaminated soils.

Up to now, more than 450 angiosperm species that can accumulate high concentration of metals (As, Cd, Co, Cu, Mn, Ni, Pb, Sb, Se, Tl, Zn,) into their aboveground have been reported (Rascio and Navari-Izzo 2011). These plants include trees, vegetable crops, grasses and weeds. Metal hyperaccumulation occurs in approximately 0.2 % of all known species and is particularly well represented in the Brassicaceae (Krämer 2010). About 25 % of discovered hyperaccumulators belong to the family of Brassicaceae (Bini et al. 2012; Marchiol et al. 2004) and in particular to genera *Thlaspi* and *Alyssum*. However, new reports of this kind of plants continue to accrue, so that it is conceivable that many yet unidentified hyperaccumulators may occur in nature. *Arabidopsis halleri* and *Sedum alfredii*, together with *Thlaspi caerulescens* and *Thlaspi praecox*, are the four recognized species that besides Zn, hyperaccumulate Cd (Rascio and Navari-Izzo 2011). Sun et al. (2008) noticed *Solanum nigrum* (Solanaceae) as the fifth Cd hyperaccumulator. The first As hyperaccumulator described was *Pteris vittata*, which accumulated up to 7,500 mg As kg in its fronds at an As-contaminated site containing 18–1,600 mg kg total As in the soil (Ma et al. 2001).

Plants that accumulate very high concentrations of metals in any aboveground tissue in their natural habitat are called hyperaccumulators (Baker 1981). A metal hyperaccumulator is defined as a plant that is able to accumulate about 100–1,000 times the metal concentrations as compared to normal plants growing in soils with background metal concentrations and about 10–100 times that of most other plants growing in metal-contaminated soils (McGrath and Zhao 2003). Therefore, the criteria to define hyperaccumulation of As, Co, Cu, Cr, Ni, Pb and Se is a concentration of 1,000 mg kg<sup>-1</sup> or greater, on a dry leaf basis, whereas the threshold value for Zn and Mn hyperaccumulation is 10,000 mg kg<sup>-1</sup> (Baker and Brooks 1989; Kabata-Pendias and Mukherjee 2007). Additionally,



hyperaccumulation for Cd is defined as values larger or equal to  $100 \text{ mg kg}^{-1}$  (Baker and Brooks 1989).

Hyperaccumulators are also characterized by a shoot to root metal concentration ratio (i.e., the translocation factor (TF)) of more than 1, whereas non-hyperaccumulator plants usually have greater metal concentrations in the roots than in the shoots. Several authors (Baker 1981, Baker et al. Baker et al. 1994; Krämer et al. 1996; Sun et al. 2008) included the bioaccumulation factor (BF) as an element for classification as a hyperaccumulator species. The BF refers to the plant metal concentration and the soil metal concentration ratio. This ratio should be greater than one for inclusion into the hyperaccumulator category. Besides, plants with bioaccumulation factor greater than one and translocation factor less than one ( $\text{BF} > 1$  and  $\text{TF} < 1$ ) have the potential for phytostabilization (Yoon et al. 2006).

The hyperaccumulators should be vigorous herbaceous perennial plant with a high rate of biomass production and with broad ecological amplitude, especially in disturbed areas. For example, *Thlaspi caerulescens* was identified as a hyperaccumulator of Zn and Cd due to more  $40,000 \text{ mg Zn kg}^{-1}$  accumulated in shoots in some of its ecotypes; however, the slow growth rate and small size is a great limitation for phytoremediation. Recent evidence suggests that moderately accumulating high-biomass species such as Indian mustard (*Brassica juncea*) can accumulate four times more Zn than *T. caerulescens* (Purakayastha and Chlonkar 2010). For these reasons research on phytoextraction has focused on crops such as maize (*Zea mays*), tobacco (*Nicotiana tabacum*), Indian mustard (*Brassica juncea*), oat (*Avena sativa*), barley (*Hordeum vulgare*), pea (*Pisum sativa*), poplar (*Populus sp.*) and sunflower (*Helianthus annuus*).

The use of native plants for phytoremediation can be a useful option, because these plants are better adapted to the environmental conditions of the region than plants introduced from other environments (Antonsiewicz et al. 2008; Yoon et al. 2006). There has been a continuing interest in searching for native plants that are tolerant to heavy metals (e.g. Bech et al. 2012a, b; González and González-Chávez 2006; Lorestani et al. 2011; Shu et al. 2002). For example, the common dandelion (*Taraxacum officinale* Web) is a very common species, widely diffused in Central and Southern Europe, greatly adaptable to every substrate and capable of uptaking and storing heavy metals (Bini et al. 2012). Heavy metals can cause severe phytotoxicity, and may act as powerful force for the evolution of tolerant plant populations.

### 3.8.2 Chelate-Assisted Phytoextraction

The availability of metals for plant uptake is greatly restricted by their adsorption to solid soil fractions. The degree of availability for uptake is affected by numerous soil factors, such as cation exchange capacity (CEC), pH and organic matter content. In addition, the speciation of the metal, which is correlated to the factors mentioned above, and the metal species itself, play an important role. Regardless of

the plants used, availability of heavy metals to plant roots is considered the key factor limiting the efficiency of phytoextraction (Evangelou et al. 2007). The addition of chelating agents and the consequent formation of metal-chelate complexes prevents precipitation and sorption of the metals in the soil, thereby maintaining their availability for plant uptake (Marques et al. 2009) and translocation to harvestable above-ground parts of high biomass crops (Meers et al. 2008).

In the last decade, the use of persistent aminopolycarboxylic acids (APCAs) such as ethylene diamine tetraacetic acid (EDTA) have been used in various phytoextraction experiments. Compared to EDTA far fewer studies investigating the enhanced mobilisation and uptake capability of others APCAs have been published. Different synthetic APCAs are hydroxyethylene diamine tetraacetic acid (HEDTA), diethylene triamino pentaacetic acid (DTPA), trans-1,2-cyclohexylene dinitrilo tetraacetic acid (CDTA), ethylene bis[oxymethylenetrinitrilo] tetraacetic acid (EGTA), ethylenediamine-N,N0bis(o-hydroxyphenyl)acetic acid (EDDHA), N-(2-hydroxyethyl)iminodiacetic acid (HEIDA), and N,N0-di(2-hydroxybenzyl) ethylene diamine N,N0-diacetic acid (HBED). Recently, the biodegradable APCAs, ethylene diamine disuccinate (EDDS), iminodisuccinic acid (IDSA), methylglycinediacetic acid (MGDA) and nitrilo triacetic acid (NTA) have been proposed as an alternative to EDTA and other persistent APCAs (Grčman et al. 2003). Several experiments using low molecular weight organic acids (LMWOA) have also been performed as chelating agents (Evangelou et al. 2007). The population density and composition of symbiotic and non-infecting microorganisms in the rhizosphere can enhance root exudation and the concentration of organic acids, for example malic and citric acids, chelators and acid phosphatases released as ectoenzymes from roots, or form microorganisms including arbuscular mycorrhizal fungi as microbial metabolites (Khan et al. 2000), increasing the effectiveness of metal mobilization.

Despite the possible usefulness of this technology, some concerns have been expressed regarding the potential inherent risk of leaching of metals to groundwater. Increased metal solubility could also affect soil microbial communities due to metal toxicity (Grčman et al. 2001). Environmentally- persistent chelates can also cause eutrophication due to their nitrogen-rich composition (Carsten and Heinz-Jurgen 2004). Some chelates, such as EDTA, are also toxic to photosynthetic organisms, inhibiting cell division, chlorophyll synthesis and production of biomass (Oviedo and Rodriguez 2003). Although EDTA has been shown in several publications to be effective in enhancing phytoextraction, heavy metals amounts mobilised in the soil are higher than the uptake. Chen et al. (2004) and Grčman et al. (2001) observed that Cu, Pb and Zn were leached down the soil profiles during EDTA treatment. Kos and Leštan (2003) found that  $2.5\text{--}10 \text{ mmol} \cdot \text{kg}^{-1}$  of EDTA caused the leaching of a large portion of the total Pb initially present in soil, and suggested that uncontrolled EDTA treatments may not be acceptable for environmentally safe phytoextraction. Svenson et al. (1989) reported that the half lifetimes of DTPA and EDTA iron complexes in aqueous solution were 8 and 11 minutes, respectively. Means et al. (1980) also demonstrated that DTPA is more rapidly degraded than EDTA.

To avoid these environmental risks, the use of biodegradable chelates (EDDS, ISDA, NTA and MGDA) has been suggested. These chelates have short half-life (days), in comparison with the conventional chelates whose persistence in the environment endures for years (Tandy et al. 2004). In case of EDDS no toxicity to microorganisms has been observed. Similar to EDTA, EDDS increased the uptake of heavy metals, but as in the case of EDTA only a fraction of the mobilised metals are effectively absorbed by the plant and subsequently translocated to the shoot (according to Komarek et al. (2010) up to a 65-fold increase). In studies by Meers et al. (2005) and Luo et al. (2005) the uptake of Cu and Zn was more enhanced by the addition of EDDS than by the addition of EDTA, whereas Cd and Pb were more explicitly mobilised by EDTA than by EDDS. In comparison to synthetic APCAs, NTA was more effective than HEIDA, HEDTA, EDTA, EGTA, CDTA and DTPA in the extraction of As and Zn from soil (Chiu et al. 2005). However, heavy metal leaching cannot be omitted during the process. González et al. (2011) evaluated the effects of MGDA on Cu increase phytoextraction by *Oenothera picensis* and the minimal leaching of Cu through the soil.

The solubilisation of metals through the application of natural chelating agents on the soil may be attractive due to the mitigation of adverse effects related to synthetic chelates. Citric acid has been one of the most studied natural chelates for phytoextraction. In comparison to EDTA, citric acid is more readily biodegradable but less effective in the removal of metals due to its complexation with other cations (Evangelou et al. 2007). In fact, Gheju and Stelescu (2013) reported that EDTA was found to be the most efficient chelating amendment among the three chelants tested EDTA, disodium oxalate (OX) and trisodium citrate (CI). The less effective uptake of Zn by plants for CI and OX was attributed to the neutral or slightly alkaline pH of these two chelates. On the other hand, the results obtained by Pérez-Esteban et al. (2013) showed that higher concentrations of organic acids increased metal desorption, and citric acid was more effective at facilitating metal desorption than tartaric acid. Freitas et al. (2013) noticed that the use of citric acid in phytoremediation of soils contaminated by battery recycling activities substantially increase the uptake and translocation of Pb to the shoots.

Luo et al. (2008) hypothesized that the root exudates from one crop such as barley (*Hordeum vulgare* L.) in one mixed culture system of peas and barley played an important role in the process of solubilizing metals in soil and facilitating the uptake of metals by peas. Although the improved efficiency from these experiments was relatively low, it may indicate a potential approach to the remediation of metal-contaminated soils in a naturally enhanced way. In Quartacci et al. (2009) the growth of the spontaneous metallophilous populations of *Pinus pinaster*, *Plantago lanceolata* and *Silene paradoxa* increased the extractable metal levels in the soil, which resulted in a higher accumulation of metals in the above-ground parts of *Brassica carinata* in comparison with the same plants grown in soil not previously planted. The fact that accumulation of metals is similar to that shown by *B. carinata* following amendments with biodegradable chelants such as NTA and EDDS, indicates a possible approach to naturally enhanced phytoremediation of multiple metal-contaminated soils.

### 3.8.3 Phytostabilization

Phytoestabilization is a site stabilization technique that reduces the mobility and bioavailability of pollutants in the environment either by immobilization or by prevention of migration (Vangronsveld et al. 1995). Converting the pollutant, especially heavy metals, into less soluble forms will likely diminish the leaching of the metal through the soil profile, and the chances of any biological interactions with humans, animals or plants. For example, the reduction of  $\text{Cr}^{6+}$ , which poses an environmental risk, to  $\text{Cr}^{3+}$ , which is highly insoluble and not demonstrated to pose an environmental risk, by deep rooted plants can be very effective. Chemical species of Pb in soil are usually bioavailable if the soil is ingested by children, livestock or wildlife, whereas a Pb phosphate mineral, chloropyromorphite, is both extremely insoluble and non-bioavailable. In the case of Pb phytoextraction, there are another two major limitations: the low Pb bioavailability in soil and the poor translocation of Pb from roots to shoots (Pulford and Watson 2003). Therefore, phytostabilization appears to have a high potential for these two toxic elements, Cr and Pb.

In this technique, the soil surface is covered with plants to prevent or reduce the dispersion of metal contaminated particles by water and wind erosion and reduce water percolation (Zanuzzi and Faz 2010). The choice of plants is a crucial aspect for the practical use of phytostabilization (Freitas et al. 2004). Plants should develop an extensive root system and a large amount of biomass in presence of high concentrations of heavy metals while keeping the translocation of metals from roots to stems and leaves as low as possible (Rizzi et al. 2004). Possible mechanisms of phytostabilization might include sequestering the contaminant in or on cell wall ligning (lignification), absorption of contaminants to soil humus, via plant or microbial enzymes (humification), or other mechanisms whereby the contaminant is sequestered in the soil, e.g. by binding to organic matter (Prasad 2004).

Phytostabilization of metals using trees is often promoted, although the influence of different tree species on the mobilization of metals is not yet clear. Trees can potentially be very well suited for phytostabilization purposes due to their extensive root systems and high transpiration capacity (Pulford and Watson 2003), especially when it is uneconomic to use other treatments or there is no time pressure on the reuse of the land (Riddell-Black 1993). On the other hand, tree growth might enhance metal leaching because of soil acidification and production of dissolved organic matter (Mayer 1998). Hence, with respect to risk control, it is very important to select tree species for phytostabilization purposes that cause low soil acidification and a minimal translocation of metals to their leaves (Mertens et al. 2007). Van Nevel et al. (2007) identified three main risks associated with the accumulation of metals in aboveground plant parts: (i) metals entering the food chain through herbivores, (ii) dispersion of contaminated plant material to adjacent environments and (iii) accumulation of metals in the topsoil. Furthermore, on highly contaminated soils, or on mining wastes, tree establishment may be inhibited by high concentrations of heavy metals. Under such conditions root immobilisation

may not be able to prevent toxic amounts of metal being translocated to the aerial parts of the plant (Pulford and Watson 2003). In less-contaminated soils, other factors may limit plant growth; such as macronutrient deficiencies and physical conditions, especially those properties leading to poor water holding, aeration and root penetration (Mullins 1991).

The potentiality of Salicaceae, such as poplars and willows, for the remediation of soil and water from metal pollution has been highlighted (Kuzovkina and Quigley 2005; Meers et al. 2007). Poplars are characterised by high variability and adaptability to environmental constraints, in addition to having an extended root system and a low impact on trophic chains. Poplars also grow relatively fast, and they are widely used in agroforestry because of their high biomass production, which can be used to generate heat or electric power. The possibility of obtaining both ecological benefits (i.e. remediation and energy production) has recently been proposed for Salicaceae (Witters et al. 2009). Fernández et al. (2012) expose the great capacity of Zn accumulation especially in roots and the milder alterations occurred in the development of plants biomass, structural parameters and photosynthetic activity of *Populus deltoides x maximowiczii* – clone Eridano.

However, Van Nevel et al. (2011) demonstrate an accumulation of total Cd and Zn concentrations in the topsoil under aspen trees, only after 10 years of tree growth. The topsoil is particularly vulnerable as it is the biologically most active part of the soil system and biological activity has been shown to be highly sensitive to metal pollution (Bergkvist et al. 1989). In general, aspen and *Populus* species should be avoided for afforesting Cd and Zn contaminated lands because they translocate high amounts of Cd and Zn into the foliage (Van Nevel et al. 2011). On the other hand, the higher pH and CEC values in the topsoils of this species reduce the bioavailable of Cd and Zn concentrations. This indicates that in more acid conditions the accumulated Cd and Zn in the topsoil will yet become more mobile and thus bioavailable. This could be a problem if the aspen trees would be harvested and replaced by more acidifying species (Van Nevel et al. 2011).

### 3.8.4 Phytoremediation in Mining Activities

There are a large number of sites worldwide polluted with trace elements as a result of human activities. Extraction of metals from sulphide minerals usually results in large amounts of tailings which often contain elevated concentrations of potentially harmful metals such as Cd, Cu, Pb and Zn. Tailings usually provide an unfavourable substrate for plant growth because of their extreme pH, low organic matter and nutrients, high concentrations of trace elements and physical disturbance, such as bad soil structure, and low water availability (Mullins 1991). Heavy metal contamination has also been one serious problem in the vicinity of mine sites due to the discharge and dispersion of mine-waste materials into the ecosystem (Jung and Thornton 1996; Navarro et al. 2008). The presence of vegetation reduces water and wind erosion, which may decrease the downward migration of contaminants into the groundwater and improve aesthetical aspects (Wong 2003).

Therefore, the use of plants to remediate hazardous soils is considered as a highly promising approach for improving the environmental quality of the tailings.

Plants growing on naturally metal-enriched soils are of particular interest in this perspective, since they are genetically tolerant to high metal concentrations, have an excellent adaptation to this multi-stress environment (Ernst 1989; Barceló and Poschenrieder, 2003). Bech et al. (2012d) observed that the native mine spoil ecotype of *Agrostis capillaris* plants can grow on these acid soils with high burdens of potentially toxic trace elements due to efficient restriction of uptake and translocation of Sb, As, Pb and Cu. In contrast, a commercially *A. capillaris* variety that has not evolved under these extreme soil conditions is unable to prospect because of the high accumulation of these trace elements in roots and shoots. Therefore, the conservation of the genetic diversity of these metallophytes is of enormous importance for the future development of efficient plant for phytoremediation purposes.

Several authors have developed important studies. In the case of Caveira and Sao Domingos (Portugal) mine areas, Abreu et al. (2012a) analysed the behaviour (trace elements uptake, accumulation and translocation from roots to shoots) of different populations of *Cistus salvifolius* plants growing spontaneously in these contaminated mines. *Cistus salvifolius*, plants included in Mediterranean communities, showed tolerance for moderate acid soils developed on different waste materials, presenting relatively small fertility and great total concentrations of trace elements. Although the populations of *Cistus salvifolius* L. plants were no considered hyperaccumulators, all the plants stored up phytotoxic elements (As, Sb and Pb) in roots, as a possible mechanism of exclusion. Similar behavior was observed for *Cistus populifolius* L. and hybrid, *Cistus x hybridus* Pourr. (Abreu et al. 2012b).

South American countries are rich in valuable ore deposits and mining activities that have quickly developed all over the continent. In general, the environmental impact of mines in Europe and North America has been evaluated in detail, for example Conesa and Schulin (2010) and Conesa et al. (2006). In contrast, data on impact assessment of the mining activities in South America countries are still very poor. Frequently, native farmers, living downstream of the copper mine, had observed unidentified toxic effects in natural vegetation and crop plants and some health problems of inhabitants and cattle in zone downstream of the mines (Bech et al. 1997). There are 172 hyperaccumulator species described in the literature for Latin America (Ginocchio and Baker 2004).

In 2002, Bech et al. reported the first results of the screening of plant species from three mining areas (Canchaque district of Piura department in the Western Andes, Mina San Bartolomé in Ecuador, Mina El Teniente in Chile) in South America (Figs. 7.21 and 7.22). The different plant species collected on the polluted soils exhibited large differences in shoot accumulation of heavy metals and As. Among the grass species (Poaceae), the highest shoot As concentration were found in *Paspalum sp.* (>1,000 µg/g) and *Eriochola ramosa* (460 µg/g) from the Cu mine in Peru and in *Holcus lanatus* and *Pennisetum clandestinum* (>200 µg/g) from the silver mine in Ecuador. *Paspalum racemosum* also accumulated considerable concentration of Cu and Zn. The species from the genus *Bidens* (Asteraceae) were able not only to accumulate high shoot As concentrations (>1,000 µg/g in

**Fig. 7.21** *Cortaderia nitida*, a Cu-Pb-Zn accumulator plant from San Bartolomé mine in Ecuador (Photo by J. Bech)



*B. cynapiifolia* from Peru) but also considerable amounts of Pb (*B. humilis* from Chile). The highest Cu shoot concentrations were found in *Mullinum spinosum* (870  $\mu\text{g/g}$ ) and in *B. cynapiifolia* (620  $\mu\text{g/g}$ ). The shoot accumulation of Zn was highest in *Baccharis amdatensis* (>1,900  $\mu\text{g/g}$ ) and in *Rumex crispus* (1,300  $\mu\text{g/g}$ ) from the Ag mine in Ecuador.

Bech et al. 2012a also proposed *Plantago orbignyana* Steinheil as Pb hyperaccumulator, due to its ability to accumulate more than 1,000 mg Pb  $\text{kg}^{-1}$  in the shoots, with TF and BF values greater than one. This species can also accumulate Zn in the shoots and had a TF greater than one, but the BF was smaller than one. These results are of great interest because Pb is considered a target metal when undertaking soil remediation, because it is usually quite immobile and not readily accumulated in upper plant parts (Fig. 7.23). Moreover, Bech et al. (2012b) also remark the potentiality of *Bidens triplinervia* L. for phytostabilization due to its capacity to restrict the accumulation of elevated amounts of Pb and Zn in the shoots. Flores-Tavizón et al. (2003) reported that *Eleocharis sp.* absorbed up to 301 mg  $\text{kg}^{-1}$  of As and It is apparently an accumulator species. Plant metal analysis in El Bote mine near to Zacatecas city (Mexico) revealed that most species did not translocate metals to their shoots. However, *Polygonum aviculare* accumulated Zn at

**Fig. 7.22** *Chenopodium ambrosioides*, a Cu-accumulator plant from El Teniente mine in Chile (Photo by J. Bech)



**Fig. 7.23** *Plantago orbignyana* Steinheil has been proposed as Pb hyperaccumulator (Photo by J. Bech)



**Fig. 7.24** *Moricandia moricandioides* growing naturally around lead mining in Bellmunt (Spain) (photo by J. Bech)



concentrations near to the criteria for hyperaccumulator plants ( $9,236 \text{ mg kg}^{-1}$ ). *Jatropha dioica* also accumulated high Zn ( $6,249 \text{ mg kg}^{-1}$ ) concentrations (González and González-Chávez 2006).

Much less information is available on metal uptake by natural vegetation in neutral to alkaline abandoned mining sites with high metal burdens (Conesa et al. 2006; Martínez-Sánchez et al. 2012; Poschenrieder et al. 2001). Investigations on the natural vegetation simultaneously adapted to high soil carbonate and high metal availability can be important for both the fundamental knowledge on metal uptake and tolerance mechanisms and for the characterization of germplasm for phytoremediation of large areas of near neutral to alkaline mine spoils (McCabe and Otte 2000; Schroeder et al. 2005). Poschenreider et al. (2012) propose *S. aspera* for phytostabilization of metal contaminated soils in Mediterranean area due to its efficiency in metal exclusion of Cd, Pb and Zn from leaves. Bech et al. (2012c) highlighted that all analysed plants growing naturally around lead mining in Bellmunt (Spain) showed enhanced root and shoot concentrations of Cu, Pb, Zn, and Sb when growing on the more polluted soils. Except for one, they all restricted the translocation of metals from roots to shoots exhibiting shoot/root concentration ratios lower or close to unity. A notable exception was *Moricandia moricandioides* (Boiss.) Heyw [M. ramburii Webb] where shoot/root Zn concentration ratios up to 5.5 were observed. This metal accumulation pattern was only observed for Zn (Fig. 7.24).

### 3.8.5 Phytovolatilisation

This method is a specialized form of phytoextraction that can be used only for a small number of contaminants that are highly volatile. Pollutant trace elements like mercury (Hg) or selenium (Se), once taken up by the plant roots, can be converted

into nontoxic forms (Prasad 2004). However, instead of accumulating inside the plant, the trace element is enzymatically transformed and volatilized into the atmosphere from the roots, shoots or leaves. Phytovolatilization has been primarily used for the removal of mercury (Hg), the mercuric ion is transformed into less toxic elemental mercury. The disadvantage is that mercury released into the atmosphere is likely to be recycled by precipitation and then redeposited back into ecosystem, repeating the production of methyl-mercury by anaerobic bacteria (USEPA 2000).

Wang et al. (2012) carried out an extensive review of Hg phytovolatilisation. Much of the following text is based on that review. Very few studies have reported the use of plants for the phytovolatilization of Hg, because Hg emission from leaf tissues is strongly affected by environmental parameters such as light intensity and air temperature (Leonard et al. 1998a). Leonard et al. (1998a, b) presented the higher mercury emission rate ( $92.6 \text{ ng m}^{-2} \text{ h}^{-1}$ ) in the daytime for *Caulanthus sp.* An interesting proposed approach is the use of transgenic plants that volatilize Hg (for example: Bizily et al. 2000; Meagher and Heaton 2005). However, genetically modified organisms are not allowed by European laws (Davison 2010). Genetic engineering can integrate genes from other organisms to enhance the phytovolatilization capabilities of plants. Of the known bacterial mercury resistance systems, the Mer (mercuric ion resistance) determinant is unique in terms of the orientation of the mercury transporter it encodes (Sasaki et al. 2006). Mercuric reductase, which is encoded by the *merA* gene, can reduce mercuric ions ( $\text{Hg}^{2+}$ ) to the less toxic and volatile elemental mercury form (Fox and Walsh 1982). Unfortunately, the *MerA* gene fails to protect against organic-mercury, more toxic and environmentally relevant (Wang et al. 2012). Another important enzyme-organomercurial lyase (*MerB*) catalyzes the protonolysis of the carbon-mercury bond. The products of this reaction are a less toxic inorganic species and a reduced carbon compound (Bizily et al. 1999). Both the *MerA* and the *MerB* genes are needed to protect cells from organic-mercury (Ruiz and Daniell, 2009). Hussein et al. (2007) reported that transgenic tobacco plants engineered with *MerA* and *MerB* genes via the chloroplast can accelerate the plant uptake of mercury from the substrate.

Alternatively, studies have been conducted to increase Hg availability for plant uptake by the application of soil additives. Among them, interesting results have been obtained using thioligands (Moreno et al. 2005; Pedron et al. 2013) and halogen salts (Wang et al. 2003), which are nontoxic chemicals commonly used in agriculture for their fertilizing properties. In this case, caution must be taken with the metal leaching into deeper soil horizons. Moreover, Hg volatilization does not appear to occur in assisted Hg phytoextraction using *Brassica juncea* plants and ammonium thiosulfate (TS) as soil amendment (Moreno et al. 2005). Cassina et al. (2012) provides evidence that the combination of cytokinins and ammonium thiosulfate contributes favourably to enhancing Hg phytoextraction in the tested crops. This study shows that Hg-volatilization related issues are of no concern, since they did not observe any evidence of Hg loss by phytovolatilization.

In the natural environment Se occurs primarily in two forms – selenate ( $\text{SeO}_4^{2-}$ ) and selenite ( $\text{SeO}_3^{2-}$ ) (Adriano 2001). Organic Se may also be present in soil

solutions (Abrams et al. 1990). The concentration and bioavailability of different forms of Se depend on soil properties such as pH, organic matter content, texture, microbiological activity and the presence of competing ions and organic compounds (Dhillon et al. 2010). Selenate is generally the toxic form in soils (Bisbjerg and Gissel-Nielsen 1969), whereas selenite can be toxic to plants grown in solution culture (Spencer and Siegel 1978). Volatilisation rates for selenite are generally two- to three-fold higher than those for selenate. Thus, selenate reduction seems to be a rate-limiting step for selenium volatilization by plants. In soil, the redox reactions of Se are mediated by soil microorganisms. Soil microbes have the capacity to remove Se from a contaminated medium with or without plants, by metabolizing it into a non-toxic volatile gas form like dimethyl selenide or dimethyl diselenide (Zhang and Moore 1997). Plants volatilise relatively low amounts of selenate or selenite in the absence of bacteria; though the mechanisms are not clear (Terry et al. 2000). Volatile Se can be recovered in recyclable forms free from other metals, salts, and organic matters using a gas trapping process. However, such a hypothetical process has not been practically established because microbial Se volatilization is generally too slow for industrial processing (Kagami et al. 2013).

Selenium can be taken up by plants of the Brassica genus and other wetland plants. For example, Bañuelos (2000) and other earlier research demonstrated that planting certain *Brassica* species, led to reductions of total soil Se up to 40 % under greenhouse conditions and up to 20 % under field conditions after one growing season. Brassica species have high affinity for sulphur (S) and its apparent inability to discriminate between absorbing Se and S species from the soil (Anderson and Scarf 1983). Most of the Se was removed by plants, although there may have been biological volatilization of Se. Understanding and then promoting the natural pathway of Se methylation with plants will increase the efficacy of phytoremediation of Se (Bañuelos 2006). Pilon-Smits et al. (1998) working with the poplar hybrid *Populus tremula x alba* reported that almost 70 % of the SeMet that was taken up by poplar was volatilised compared with 3 and 4.5 % for selenite and selenate. These authors stated that poplar volatilisation rates and biomass productivity were comparable with those of cattail, making it an attractive species for phytoremediation. Dhillon et al. (2010) reported that application of organic manures and fresh plant material helped in increasing the rate of Se volatilization from the seleniferous soil. Organic Se forms constitute an important pool which regulates the availability of Se to plants as well as Se volatilization.

The complexities of Se behavior in soil-plant systems arise because of the several different valence states of the element that can occur and because of the potential significance of volatilization from both soils and plants. Pérez-Sánchez et al. (2012) proposed a simplified model has been developed that represents the annual cycle of soil hydrology and estimates the effects of that annual cycle on the transport of Se-79 in soil and its uptake by plants. Furthermore, the model incorporates the effects of plant growth, cropping and the transfer of Se-79 from plant residues to organic matter in soils from whence it can be released by mineralisation reactions.

### 3.8.6 Phytomining

Phytomining involves the use of the plant biomass as an alternative ore with monetary value (Chaney et al. 2010). The process involves growing repeated crops of a hyperaccumulator on a polluted area. The plant material would be burnt to produce a 'bio-ore'. This metal-rich ash, typically only 7 % of the weight of the dried plant material, could be stored in a safe area or conceivably even be sold as feedstock to a smelter to recoup some of the cost of the operation (Robinson et al. 1997). The economics of phytomining basically depends on the metal content in the soil, metal uptake by the plant, plant biomass and most importantly the price of the metal. The principal advantage of phytomining is its low cost relative to conventional mining methods, allowing economic exploitation of mineralised soil, mill tailings, overburdens or low-grade ores that is too metal-poor for direct mining operations (Nedelkoska and Doran 2000). The best candidates for phytomining are Au, Th, Co and Ni due to their high cost and high metal concentration in hyperaccumulator biomass. Although metal prices of U are comparatively high, its reported metal concentration ( $100 \text{ mg} \cdot \text{kg}^{-1}$ ) in biomass ( $10,000 \text{ kg} \cdot \text{ha}^{-1}$ ) is low, which makes it uneconomical for phytomining (Sheoran et al. 2009). Since the initial proposal by Chaney (1983), intensive trials were designed specifically to study phytomining. However, the majority of the research has been conducted on laboratory scale and in relatively controlled conditions for a short period of time; the true potential of phytomining is yet to be established (Sheoran et al. 2009).

Gold has been suggested as a candidate for phytomining. However, plants do not normally accumulate gold; the metal must be made soluble before uptake can occur. Background levels of gold in plants are usually very low, rarely exceeding  $10 \text{ ng} \cdot \text{g}^{-1}$  dry weight. Some plants exude natural lixivants that can mobilize gold in a soil. Therefore, hyperaccumulation can be induced by adding a chemical amendment. Anderson et al. (1998a) have proposed that hyperaccumulation of gold in plants be represented by  $1,000 \text{ ng} \cdot \text{g}^{-1}$  ( $1 \mu\text{g} \cdot \text{g}^{-1}$ ) in dry mass.

In an induced hyperaccumulation operation of gold, the geochemistry of the substrate will dictate the choice of the solubilizing agent necessary to affect the uptake of the gold. For low-pH sulphide tailings, gold is made soluble by thiocyanate, and for high-pH unoxidised sulphide tailings gold is soluble with thiosulphate (Anderson et al. 1999). Thiocyanates have low toxicity over cyanides. The toxicity of thiosulphate is even lower and is about equal to that of common salt (Anderson et al. 1998b). Use of thiocyanate would have to be strictly controlled to prevent leaching into ground and surface waters if these chemicals and its associated metals are not taken up by plants. It might also be possible to use transgenic plants expressing a bacterial thiocyanate degrading system in order to extract Au from auriferous substrates. Such an approach would solve the problem of thiocyanate toxicity to plants and perhaps allow them to extract more Au, but not non target metals (Anderson et al. 1998b).

Induced hyperaccumulation of Au appears to be relatively independent of plant species, so it should be possible to use plants such as chicory (Lamb et al. 2001),

that might be easy to grow on mine tailings (Anderson et al. 1998a). However, according with Anderson et al. (2005) *Brassica juncea* (Indian mustard) showed the best ability to concentrate gold induced with sodium cyanide and thiocyanate grown on oxidized ore pile containing  $0.6 \text{ mg} \cdot \text{kg}^{-1}$  gold. Gold phytomining has also been reported by Msuya et al. (2000) with five root crops (carrot, red beet, onion and two cultivars of radish) grown in artificial substrate consisting of  $3.8 \text{ mg} \cdot \text{kg}^{-1}$  of Au. The carrot roots yield  $1.45 \text{ Au kg} \cdot \text{ha}^{-1}$  of final worth \$US 7,550. Phytomining not only produces gold ingots but more important are gold nanoparticles with in plant cells (crystallite or primary particles measuring less than 100 nm in size), which has great importance for rapidly expanding nanoparticle market (Reeves and Baker 2000; Harris and Bali 2008).

Moreover, the plants growing on soils affected by mining activities can also be used to generate useful products or ecosystem services. Ruíz-Olivares et al. (2013) results consistently, contrary to published information, showed that *Ricinus communis* L. had low metal shoot concentrations, high root metal concentrations, low metal translocation factors and in consequence this plant is participating in metal stabilization (phytostabilization). Moreover, this plant could be an energetic crop due to plants naturally growing in mine tailings with high concentrations of Cd, Pb and Zn had high oil yields (41–64 %). Currently, about 1 Mt of castor bean is harvested annually for oil production, with India, China and Brazil being the mayor producers (Mutlu and Meier 2010). Rajkumar and Freitas (2008) also mentioned that this plant is a crop with multiple non-food uses (industrial, medical and cosmetic products derived thereof) and is an excellent rotation and companion crop. Ruíz-Olivares et al. (2013) was the first report regarding combined oil production and a phytostabilization role for *Ricinus* plants in metal mine tailings and may give a new value to suitable metal-polluted areas.

## References

- Abrams MM, Shenan C, Zasoski RJ, Burau RG (1990) Selenomethionine uptake by wheat seedlings. *Agronomy J* 82:1127–1130
- Abreu MM, Santos ES, Ferreira M, Magalhães MCF (2012a) *Cistus salvifolius* a promising species for mine wastes remediation. *J Geochem Explor* 113:86–93
- Abreu MM, Santos ES, Magalhães MCF, Fernandes E (2012b) Trace elements tolerance, accumulation and translocation in *Cistus populifolius*, *Cistus salvifolius* and their hybrid growing in polymetallic contaminated mine areas. *J Geochem Explor* 123:52–60
- Acar YB, Gale RJ, Alshawabkeh RE, Marks S, Puppala M, Bricka M, Parker R (1995) Electrokinetic remediation: basics and technology status. *J Hazard Mater* 40:117–137
- Adriano DC (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability and risk of metals. Springer, New York
- Anderson JW, Scarf AR (1983) Selenium and plant metabolism. In: Robb DA, Pierpoint WS (eds) Metals and micronutrients: uptake and utilization by plants. Academic, New York, pp 241–275
- Anderson CWN, Brooks RR, Stewart RB, Simcock R (1998a) Harvesting a crop of gold in plants. *Nature* 395:553–554
- Anderson CWN, Brooks RR, Stewart RB, Simcock R (1998b) Gold uptake by plants. *Gold Bull* 32 (2):48–51
- Anderson CWN, Brooks RR, Chiarucci A, LaCoste CJ, Leblanc M, Robinson BH, Simcock R, Stewart RB (1999) Phytomining for nickel, thallium and gold. *J Geochem Explor* 67:407–415
- Anderson CWN, Moreno F, Meech J (2005) A field demonstration of gold phytoextraction technology. *Miner Eng* 18:385–392
- Antonsiewicz DM, Escude-Duran C, Wierzbowska E, Skłodowska A (2008) Indigenous plant species with potential for the phytoremediation of arsenic and metal contaminated soil. *Water Air Soil Pollut* 19:197–210
- Baker AJM (1981) Accumulators and excluders: strategies in the response of plants to heavy metals. *J Plant Nutr* 3:643–654
- Baker AJM, Brooks RR (1989) Terrestrial higher plants which hyperaccumulate metallic elements – a review of their distribution, ecology and phytochemistry. *Biorecovery* 1:811–826
- Baker AJM, McGrath SP, Sidoli CMD, Reeves RD (1994) The possibility of in-situ heavy-metal decontamination of polluted soils using crops of metal-accumulating plants. *Resour Conserv Recycl* 11:41–49
- Bañuelos GS (2000) Factors influencing field phytoremediation of selenium-laden soils. In: Terry N, Bañuelos GS (eds) Phytoremediation of trace elements in soils and waters. CRC Press, Inc., Boca Raton, pp 41–60
- Bañuelos GS (2006) Phyto-products may be essential for sustainability and implementation of phytoremediation. *Environ Pollut* 144:19–23
- Barceló J, Poschenrieder C (2003) Phytoremediation: principles and perspectives. *Contrib Sci* 2:333–344
- Battelle Memorial Institute and EPA (1992) In situ electroacoustic soil decontamination, superfund innovative technology evaluation program, EPA, Technology Profiles, 7th edn, Columbus, pp 248–249
- Bech J, Poschenrieder CH, Llugany M, Barceló J, Tume P, Tobías FJ, Barranzuela JL, Vásquez ER (1997) Arsenic and heavy metal contamination of soil and vegetation around a copper mine in Northern Peru. *Sci Total Environ* 203:83–91
- Bech J, Poschenrieder C, Barceló J, Lansac A (2002) Plants from mine spoils in the South American area as potential sources of germplasm, for phytoremediation technologies. *Acta Biotechnol* 22(1–2):5–11
- Bech J, Suarez M, Reverter F, Tume P, Sanchez P, Roca N, Lansac A (2010) Selenium and other trace element in phosphorites: a comparison between those of bayovar-sechura and other provenances. *J Geochem Explor* 167:146–160
- Bech J, Duran P, Roca N, Poma W, Sánchez I, Barceló J, Boluda R, Roca-Pérez L, Poschenrieder C (2012a) Shoot accumulation of several trace elements in native plant species from contaminated soils in the Peruvian Andes. *J Geochem Explor* 113:106–111
- Bech J, Duran P, Roca N, Poma W, Sánchez I, Barceló J, Boluda R, Roca-Pérez L, Poschenrieder C (2012b) Accumulation of Pb and Zn in *Bidens triplinervia* and *Senecio sp.* Spontaneous species from mine spoils in Peru and their potential use in phytoremediation. *J Geochem Explor* 123:109–113
- Bech J, Roca N, Barceló J, Duran P, Tume P, Poschenrieder C (2012c) Soil and plant contamination by lead mining in Bellmunt (Western Mediterranean Area). *J Geochem Explor* 113:94–99
- Bech J, Corrales I, Tume P, Barceló J, Duran P, Roca N, Poschenrieder C (2012d) Accumulation of antimony and other potentially toxic elements in plant around a former antimony mine located in the Ribes Valley (eastern Pyrenees). *J Geochem Explor* 113:100–105
- Bergkvist B, Folkesson L, Berggren D (1989) Fluxes of Cu, Zn, Pb, Cr and Ni in temperate forest ecosystems – a literature review. *Water Air Soil Pollut* 47:217–286
- Bes C, Mench M (2008) Remediation of copper-contaminated topsoils from a wood treatment facility using in situ stabilization. *Environ Pollut* 156:1128–1138

- Beukes JP, Van Zyl PG, Ras M (2012) Treatment of Cr(VI)-containing wastes in the South African ferrochrome industry- a review of currently applied methods. *J S Afr Inst Mining Metallurgy* 112:347-352
- Beveridge TJ, Murray RGE (1980) Sites of metal deposition in the cell wall of *Bacillus subtilis*. *J Bacteriol* 141:876-887
- Bhat PN, Gosh DK, Desai MVN (2002) Immobilisation of beryllium in solid waste (red-mud) by fixation and vitrification. *Waste Manag* 22:549-556
- Bini C, Wahsha M, Fontana S, Maleci L (2012) Effects of heavy metals on morphological characteristics of *Taraxacum officinale* Web growing on mine soils in NE Italy. *J Geochem Explor* 123:101-108
- Bisbjerg B, Gissel-Nielsen G (1969) The uptake of applied selenium by agricultural plants. 1. The influence of soil type and plant species. *Plant and Soil* 31:287-291
- Bizily SP, Rugh CL, Summers AO, Meagher RB (1999) Phytoremediation of methylmercury pollution: merB expression in *Arabidopsis thaliana* confers resistance to organomercurials. *Proc Natl Acad Sci USA* 96, pp 6808-6813
- Bizily SP, Rugh CL, Meagher RB (2000) Phytodetoxification of hazardous organomercurials by genetically engineered plants. *Nat Biotechnol* 18:213-217
- Bradbury D, Scrivens S (1995) Remediation of radioactive and heavy metal contaminated soils and groundwater using the ACT<sup>DE</sup>CON<sup>SM</sup> and MAG<sup>SEP</sup>SM processes. *Contam Soil* 95:1161-1162
- Bricka RM (1997) An overview of remediation technologies for treating military heavy metal contaminated soils. In: Proceedings of the 4th international conference on biogeochemistry of trace elements, Berkeley, 23-25 June 1997
- Carsten S, Heinz-Jurgen B (2004) Impact of aminopolycarboxylates on aquatic organisms and eutrophication: overview of available data. *Environ Toxicol* 19:620-637
- Cassina L, Tassi E, Pedron F, Petruzzelli G, Ambrosini P, Barbaferi M (2012) Using a plant hormone and a thioligand to improve phytoremediation of Hg-contaminated soil from a petrochemical plant. *J Hazard Mater* 231-232:36-42
- Chaney RL (1983) Plant uptake of inorganic waste constituents. In: Parr JF (ed) Land treatment of hazardous wastes. Noyes Data Corp, Park Ridge, pp 50-76
- Chaney RL, Broadhurst CL, Centofanti T (2010) Phytoremediation of soil trace elements. In: Hooda PS (ed) Trace elements in soils. Wiley, Chichester
- Chang TC, Yen JH (2006) On site mercury contaminated soils remediation by using thermal desorption technology. *J Hazard Mater* B128:208-217
- Chen Y, Li X, Shen Z (2004) Leaching and uptake of heavy metals by ten different species of plants during an EDTA-assisted phytoextraction process. *Chemosphere* 57:187-196
- Chiu KK, Ye ZH, Wong MH (2005) Enhanced uptake of As, Zn, and Cu by *Vetiveria zizanioides* and *Zea mays* using chelating agents. *Chemosphere* 60:1365-1375
- Chon HT, Lee JS, Lee JU (2011) Heavy metal contamination of soil, its risk assessment and bioremediation. *Geosyst Eng* 14:191-206
- Chrysochoos M, Dermatas D, Grubb D (2007) Phosphate application to firing range soils for Pb immobilization: the unclear role of phosphate. *J Hazard Mater* 144:1-14
- Conesa HM, Faz A, Arnaldos R (2006) Heavy metal accumulation and tolerance in plants from mine tailings of the semiarid Cartagena-La Unión mining district (SE Spain). *Sci Total Environ* 366:1-11
- Conesa HM, Schulin R (2010) The Cartagena-La Unión mining district (SE Spain): a review of environmental problems and emerging phytoremediation solutions after fifteen years research. *J Environ Monit* 12:1225-1233
- Costerton JW, Lewandowski Z, Caldwell DE, Korber DR, Lappin-Scott H (1995) Microbial biofilms. *Annu Rev Microbiol* 49:711-745
- Davison J (2010) GM plants: science, politics and EC regulations. *Plant Sci* 178:94-98

- Delschen T (2000) Soil covering as remediation technique for heavy metal contamination gardens. In: First international conference on soils of urban, industrial, traffic and mining areas. Proceedings vol III. Essen, Germany, pp 789-794
- Dermont G, Bergeron M, Mercier G, Richer-Lafleche M (2008) Soil washing for metal removal: a review of physical/chemical technologies and field applications. *J Hazard Mater* 152(1):1-31
- Dhillon KS, Dhillon SK, Dogra R (2010) Selenium accumulation by forage and grain crops and volatilization from seleniferous soils amended with different organic materials. *Chemosphere* 78:548-556
- Di Palma L, Medici F (2002) Recovery of copper from contaminated soil by flushing. *Waste Manag* 22:883-886
- Ernst WHO (1989) Mine vegetation in Europe. In: Shaw AJ (ed) Heavy metal tolerance in plants: evolutionary aspects. CRC Press, Inc., Boca Raton, pp 21-37
- Evangelou MWH, Ebel M, Schaeffer A (2007) Chelate assisted phytoextraction of heavy metals from soil. Effect, mechanism, toxicity, and fate of chelating agents, review. *Chemosphere* 68:989-1003
- Fein JB, Daughney CJ, Yee N, Davis T (1997) A chemical equilibrium model for metal adsorption onto bacterial surfaces. *Geochim Cosmochim Acta* 61:3319-3328
- Fernández J, Zacchini M, Isabel Fleck I (2012) Photosynthetic and growth responses of *Populus* clones Eridano and I-214 submitted to elevated Zn concentrations. *J Geochem Explor* 123:77-86
- Flores-Tavizón E, Alarcón-Herrera MT, González Elizondo S, Olguin EJ (2003) Arsenic tolerating plants from mine sites and hot springs in the semiarid region of Chihuahua, México. *Acta Biotechnol* 23:113-119
- Fox B, Walsh CT (1982) Mercuric reductase. Purification and characterization of a transposon-encoded flavoprotein containing an oxidation-reduction-active disulphide. *J Biol Chem* 257:2498-2503
- Freitas H, Prasad MNV, Pratas J (2004) Plant community tolerant to trace elements growing on the degraded soils of São Domingos mine in the south east of Portugal: environmental implications. *Environ Int* 30:65-72
- Freitas EV, Nascimento CW, Souza A, Silva FB (2013) Citric acid-assisted phytoextraction of lead: a field experiment. *Chemosphere* 92:213-217
- FRTR, Federal Remediation Technologies Roundtable (2002) Remediation technologies screening matrix and reference guide (ath ed). <http://www.ftrr.Gov/matrix2/section1/toc.html>
- Gent DB, Bricka RM, Alshawabkeh AN, Larsom SL, Fabian G, Granade S (2004) Bench and field scale extraction by electrokinetics. *J Hazard Mater* 110:53-62
- Gheju M, Stelescu I (2013) Chelant-assisted phytoextraction and accumulation of Zn by *Zea mays*. *J Environ Manage* 128:631-636
- Ghosh M, Singh SP (2005) A review on phytoremediation of heavy metals and utilization of its byproducts. *Appl Ecol Environ Res* 3:1-18
- Ginocchio R, Baker A (2004) Metallophytes in Latin America: a remarkable biological and genetic resource scarcely known and studied in the region. *Rev Chil Hist Nat* 77(1):185-194
- González RC, González-Chávez MCA (2006) Metal accumulation in wild plants surrounding mining wastes. *Environ Pollut* 144:84-92
- González I, Cortes A, Neaman A, Rubio P (2011) Biodegradable chelate enhances the phytoextraction of Cu by *Oenothera picensis* grown in Cu-contaminated acid soils. *Chemosphere* 84:490-496
- Grace S, Harris M, Roushey W (1995) Results of treatability studies for the remediation of plutonium and americium from surface soils at the rocky flats superfund site. *Contam Soil* 95:1221-1222
- Grčman H, Velikonja-Bolta S, Vodnik D, Kos B, Leštan D (2001) EDTA enhanced heavy metal phytoextraction: metal accumulation, leaching, and toxicity. *Plant and Soil* 235:105-114
- Grčman H, Vodnik D, Velikonja-Bolta S, Leštan D (2003) Ethylenediamine disuccinate as a new chelate for environmentally safe enhanced lead phytoextraction. *J Environ Qual* 32:500-506



- Guo G, Zhou Q, Ma LQ (2006) Availability and assessment of fixing additives for the in situ remediation of heavy metal contaminated soils: a review. *Environ Monit Assess* 116 (1):513–528
- Harris AT, Bali R (2008) On the formation and extent of uptake of silver nanoparticles by live plants. *J Nanopart Res* 10:691–695
- Hartley W, Edwards R, Lepp NW (2004) Arsenic and heavy metal mobility in iron-oxide amended contaminated soils as evaluated by short and long-term leaching tests. *Environ Pollut* 131 (3):495–504
- Ho SV, Sheridan PW, Athmer CJ, Heitkamp MA, Brackin JM, Weber D, Brodsky PH (1995) Integrated in situ soil remediation technology: the lasagna process. *Environ Sci Technol* 29:2528–2534
- Hussein HS, Ruiz ON, Terry N, Daniell H (2007) Phytoremediation of mercury and organomercurials in chloroplast transgenic plants: enhanced root uptake, translocation to shoots, and volatilization. *Environ Sci Technol* 41:8439–8446
- Jang HY, Chon HT, Lee JU (2009) In-situ precipitation of arsenic and copper in soil by microbiological sulfate reduction. *Econ Environ Geol* 42:445–455 (Korean with English abstract)
- Jung MC, Thornton I (1996) Heavy metal contamination of soils and plants in the vicinity of a lead–zinc mine, Korea. *Appl Geochem* 11:53–59
- Kabata-Pendias A, Mukherjee AB (2007) Trace elements from soil to human. Springer, Berlin/New York
- Kagami T, Narita T, Kuroda M, Notaguchi E, Yamashita M, Sei K, Soda S, Ike M (2013) Effective selenium volatilization under aerobic conditions and recovery from the aqueous phase by *Pseudomonas stutzeri* NT-I. *Water Res* 47:1361–1368
- Karvounis Y, Kelepertsis A (2000) Chemical clean up and properties of soils polluted with heavy metals near mining areas. In: First international conference on soils of urban, industrial, traffic and mining areas. Proceedings vol III. Essen, Germany, pp 799–804
- Khan AG, Kuek C, Chaudhry TM, Khoo CS, Hayes WJ (2000) Role of plants, mycorrhizae and phytochelators in heavy metal contaminated land remediation. *Chemosphere* 41:197–207
- Khan FI, Husain T, Hejazi R (2004) An overview and analysis of site remediation technologies. *J Environ Manage* 71:95–122
- Kim SH, Chon HT, Lee JU (2009a) Biosorption of Pb and Cd by indigenous bacteria isolated from soil contaminated with oil and heavy metals. *Econ Environ Geol* 42:427–434 (Korean with English abstract)
- Kim SH, Chon HT, Lee JU (2009b) Removal of dissolved heavy metals through biosorption onto indigenous bacterial biofilm developed in soil. *Econ Environ Geol* 42:435–444 (Korean with English abstract)
- Kim SH, Lee JU, Ko MS, Yun YH, Lee JS, Hong SJ (2011a) The effects of carbon sources supply to contaminated soil in the vicinity of Pungjeong mine on geomicrobiological behavior of heavy metals and arsenic. *J Korean Soc Geosyst Eng* 48:584–597 (Korean with English abstract)
- Kim YS, Chon HT, Lee JU (2011b) Bioremediation of heavy metals and arsenic in contaminated soil by microbiological sulfur oxidation. *J Korean Soc Geosyst Eng* 48:294–308 (Korean with English abstract)
- Komárek M, Vaněk A, Mrnka L, Sudová R, Száková J, Tejnecký V, Chrastný V (2010) Potential and drawbacks of EDDS-enhanced phytoextraction of copper from contaminated soils. *Environ Pollut* 158:2428–2438
- Kos B, Leštan D (2003) Influence of a biodegradable ([S, S]-EDDS) and nondegradable (EDTA) chelate and hydrogel modified soil water sorption capacity on Pb phytoextraction and leaching. *Plant and Soil* 251:403–411
- Krämer U (2010) Metal hyperaccumulation in plants. *Annu Rev Plant Biol* 61:517–534
- Krämer U, Cotter-Howells JD, Charnock JM, Baker AJM, Smith JAC (1996) Free histidine as a metal chelator in plants that accumulate nickel. *Nature* 379:635–638

- Kumpiene J (2010) Trace element immobilization in soil using amendments. In: Hooda P (ed) Trace elements in soils. Wiley-Blackwell, Chichester, pp 353–380
- Kumpiene J, Lagerkvist A, Maurice C (2008) Stabilization of Pb and Cu contaminated soils using coal fly ash and peat. *Environ Pollut* 145:365–373
- Kumpiene J, Ore S, Renella G, Mench M, Lagerkvist A, Maurice C (2006) Assessment of zerovalent iron for stabilization of chromium, copper, and arsenic in soil. *Environ Pollut* 144:62–69
- Kuzovkina YA, Quigley MF (2005) Willows beyond wetlands: uses of *Salix L.* species for environmental projects. *Water Air Soil Pollut* 162:183–204
- La Grega MD, Buckinham PL, Evnas JC (2001) Hazardous waste management. McGraw-Hill, New York
- Lamb AE, Anderson CWN, Haverkamp RG (2001) The extraction of gold from plants and its applications to phytomining. *Chem N Z* 3:1–33
- Lee SE (2006) Geomicrobiological characteristics and bioremediation of Cr(VI) by indigenous bacteria in Cr-contaminated sediment. PhD thesis, Seoul National University
- Lee JU, Beveridge TJ (2001) Interaction between iron and *Pseudomonas aeruginosa* biofilms attached to Sepharose surfaces. *Chem Geol* 180:67–80
- Lee SE, Lee JS, Chon HT (2005) Environmental contamination of heavy metals and effects of sediment bacteria on the cadmium speciation in the vicinity of the Hwacheon mine. *Key Eng Mater* 277–279:438–444
- Lee SE, Lee J-U, Lee JS, Chon HT (2006) Effects of indigenous bacteria on Cr(VI) reduction in Cr-contaminated sediment with industrial wastes. *J Geochem Explor* 88:41–44
- Lee SE, Lee JU, Chon HT, Lee JS (2008a) Reduction of Cr(VI) by indigenous bacteria in Cr-contaminated sediment under aerobic condition. *J Geochem Explor* 96:144–147
- Lee SE, Lee JU, Chon HT, Lee JS (2008b) Microbiological reduction of hexavalent chromium by indigenous chromium-resistant bacteria in sand column experiments. *Environ Geochem Health* 30:141–145
- Lee SR, Chon HT, Lee JU (2011) Bioremediation of As in contaminated soils using metal-reducing bacteria. *J Korean Soc Geosyst Eng* 48:420–429 (Korean with English abstract)
- Leonard TL, Taylor GE, Gustin MS, Fernandez GCJ (1998a) Mercury and plants in contaminated soils: 1. Uptake, partitioning, and emission to the atmosphere. *Environ Toxicol Chem* 17:2063–2071
- Leonard TL, Taylor GE, Gustin MS, Fernandez GCJ (1998b) Mercury and plants in contaminated soils: 2. Environmental and physiological factors governing mercury flux to the atmosphere. *Environ Toxicol Chem* 17:2072–2079
- Lorestani B, Cheraghi M, Yousefi N (2011) Phytoremediation potential of native plants growing on a heavy metals contaminated soils of copper mine in Iran. *World Acad Sci Eng Technol* 53:377–382
- Lovley DR, Phillips EJP (1992) Bioremediation of uranium contamination with enzymatic uranium reduction. *Environ Sci Technol* 26:2228–2234
- Lovley DR, Baedecker MJ, Lonergan DJ, Cozzarelli IM, Phillips EJP, Siegel DI (1989) Oxidation of aromatic contaminants coupled to microbial iron reduction. *Nature* 339:297–299
- Lu Q, He ZL, Graetz DA, Stoffella PJ, Yang X (2011) Uptake and distribution of metals by water lettuce (*Pistia stratiotes L.*). *Environ Sci Pollut Res Int* 18(6):978–986
- Luo C, Shen Z, Li X (2005) Enhanced phytoextraction of Cu, Pb, Zn and Cd with EDTA and EDDS. *Chemosphere* 59:1–11
- Luo CL, Shen ZG, Li XD (2008) Root exudates increase metal accumulation in mixed cultures: implications for naturally enhanced phytoextraction. *Water Air Soil Pollut* 193:147–154
- Ma LQ, Komar KM, Tu C, Zhang W, Cai Y (2001) A fern that hyperaccumulates arsenic. *Nature* 409:579
- Manning BA, Fendorf SE, Bostick B, Suarez DL (2002a) Arsenic (III) and arsenic (V) adsorption reactions on synthetic birnessite. *Environ Sci Technol* 36:976–981

- Marchiol L, Sacco P, Assolari S, Zerbi G (2004) Reclamation of polluted soils: phytoremediation potential of crop-related Brassica species. *Water Air Soil Pollut* 158(1):345–356
- Marques APGC, Rangel AOSS, Castro PML (2009) Remediation of heavy metal contaminated soils: phytoremediation as a potentially promising clean-up technology. *Crit Rev Environ Sci Technol* 39:622–654
- Marques APGC, Rangel AOSS, Castro PML (2011) Remediation of heavy metal contaminated soils: an overview of site remediation techniques. *Crit Rev Environ Sci Technol* 41:879–914
- Martínez-Sánchez MJ, García-Lorenzo ML, Pérez-Sirvent C, Bech J (2012) Trace element accumulation in plants from an arid area affected by mining activities. *J Geochem Explor* 123:8–12
- Mascia M, Palmas S, Polcaro AM, Vacca A, Muntoni A (2007) Experimental study and mathematical model on remediation of Cd spiked kaolinite by electrokinetics. *Electrochim Acta* 52:3360–3365
- Mayer R (1998) Soil acidification and cycling of metal elements: cause–effect relationships with regard to forestry practices and climatic changes. *Agr Ecosyst Environ* 67:145–152
- McCabe OM, Otte ML (2000) The wetland grass *Glyceria fluitans* for revegetation of mine tailings. *Wetlands* 20:548–559
- McGrath SP, Zhao FJ (2003) Phytoextraction of metals and metalloids from contaminated soils. *Curr Opin Biotechnol* 14:1–6
- McGrath SP, Chaudri AM, Giller KE (1995) Long-term effects of metals in sewage sludge on soils, microorganisms and plants. *J Ind Microbiol* 14:94–104
- Meagher RB, Heaton ACP (2005) Strategies for the engineered phytoremediation of toxic element pollution: mercury and arsenic. *J Ind Microbiol Biotechnol* 32:502–513
- Means JL, Kucak T, Cerar DA (1980) Relative degradation rates of NTA, EDTA and DTPA and environmental implications. *Environ Pollut Ser B* 1:45–60
- Meers E, Ruttens A, Hopgood MJ, Samson D, Tack FMG (2005) Comparison of EDTA and EDDS as potential soil amendments for enhanced phytoextraction of heavy metals. *Chemosphere* 58:1011–1022
- Meers E, Vandecasteele B, Ruttens A, Vangronsveld J, Tack FMG (2007) Potential of five willow species (*Salix spp.*) for phytoextraction of heavy metals. *Environ Exp Bot* 60:57–68
- Meers E, Tack FMG, Verloo MG (2008) Degradability of ethylenediamine disuccinic acid (EDDS) in metal contaminated soils: implications for its use in soil remediation. *Chemosphere* 70:358–363
- Melitas N, Wang J, Conklin M, O'Day P, Farrell J (2002) Understanding soluble arsenate removal kinetics of zerovalent iron media. *Environ Sci Technol* 36:2074–2081
- Mertens J, Van Nevel L, De Schrijver A, Piesschaert F, Oosterbaan A, Tack FMG, Verheyen K (2007) Tree species effect on the redistribution of soil metals. *Environ Pollut* 149:173–181
- Meuser H (2013) *Soil remediation and rehabilitation*. Springer, Dordrecht/New York, p 406
- Moreno FN, Anderson CWN, Stewart RB, Robinson BH, Nomura R, Ghomshei M, Meech JA (2005) Effect of thioligands on plant-Hg accumulation and volatilisation from mercury-contaminated mine tailings. *Plant and Soil* 275:233–246
- Moutsatsou A, Gregou M, Matsas D, Protonotarios V (2006) Washing as a remediation technology applicable in soils heavily polluted by mining-metallurgical activities. *Chemosphere* 63:1632–1640
- Msuya FA, Brooks RR, Anderson CWN (2000) Chemically-induced uptake of gold by root crops: its significance for phytomining. *Gold Bull* 33(4):134–137
- Muhabadi AA, Hajabbasi MA, Khademi H, Kazemian H (2007) Soil cadmium stabilization using an Iranian natural zeolite. *Geoderma* 137:388–393
- Mulligan CN, Yong RN, Gibbs BF (2001) *Engin*. *Geology* 60:193–207
- Mullins CE (1991) Physical properties of soils in urban areas. In: Bullock P, Gregory PJ (eds) *Soils in the urban environment*. Blackwell, Oxford, pp 87–118
- Mutlu H, Meier MAR (2010) Castor oil as a renewable resource for the chemical industry. *Eur J Lipid Sci Technol* 112:10–30

- Navarro MC, Pérez-Sirvent C, Martínez-Sánchez MJ, Vidal J, Tovar PJ, Bech J (2008) Abandoned mine sites as a source of contamination by heavy metals: a case study in a semi-arid zone. *J Geochem Explor* 96:183–193
- Neale N (1997) Development of extraction techniques for the removal heavy metals from contaminated soils. In: *Fourth international conference on the biogeochemistry of trace elements*, Berkeley, California
- Nedelkoska TV, Doran PM (2000) Characteristics of heavy metal uptake by plant species with potential for phytoremediation and phytomining. *Miner Eng* 13(5):549–561
- Nickson RT, McArthur JM, Ravenscroft P, Burgess WG, Ahmed KM (2000) Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. *Appl Geochem* 15:403–413
- Olguín EJ, Sánchez-Galván G (2012) Heavy metal removal in phytofiltration and phycoremediation: the need to differentiate between bioadsorption and bioaccumulation. *N Biotechnol* 30(1):3–8
- Oviedo C, Rodríguez J (2003) EDTA: the chelating agent under environmental scrutiny. *Quimica Nova* 26:901–905
- Page GW (1997) *Contaminated sites and environmental cleanup*. Academic, San Diego, p 212
- Page MM, Page CL (2002) Electroremediation of contaminated soils. *J Environ Eng* 128(3):208–219
- Park JM, Lee JS, Lee JU, Chon HT, Jung MC (2006) Microbial effects on geochemical behavior of arsenic in as-contaminated sediments. *J Geochem Explor* 88:134–138
- Pedron F, Petruzzelli G, Barbaferi M, Tassi E (2013) Remediation of a mercury-contaminated industrial soil using bioavailable contaminant stripping. *Pedosphere* 23(1):104–110
- Pérez-Sánchez D, Thorne MC, Limer LMC (2012) A mathematical model for the behaviour of Se-79 in soils and plants that takes account of seasonal variations in soil hydrology. *J Radiol Prot* 32:11–37
- Pérez-Esteban J, Escolástico C, Moliner A, Masaguer A (2013) Chemical speciation and mobilization of copper and zinc in naturally contaminated mine soils with citric and tartaric acids. *Chemosphere* 90:276–283
- Pilon-Smits EAH, de Souza MP, Lytle CM, Shang C, Lgo T, Terry N (1998) Selenium volatilization and assimilation by hybrid poplar (*Populus tremula x alba*). *J Exp Bot* 49:1889–1892
- Poschenrieder C, Bech J, Llugany M, Pace A, Fenés E, Barceló J (2001) Copper in plant species in a copper gradient in Catalonia (North East Spain) and their potential for phytoremediation. *Plant and Soil* 230:247–256
- Poschenrieder C, Llugany M, Lombini A, Dinelli E, Bech J, Barceló J (2012) *Smilax aspera* L. an evergreen Mediterranean climber for phytoremediation. *J Geochem Explor* 123:41–44
- Prasad MNV (2004) Phytoremediation of metals and radionuclides in the environment: the case of natural hyperaccumulators, metal transporters, soil-amending chelators and transgenic plants. In: Prasad (ed) *Heavy metal stress in plants from biomolecules to ecosystems*, 2nd edn. Springer, Berlin Heidelberg, pp 345–391
- Pulford ID, Watson C (2003) Phytoremediation of heavy metal-contaminated land by trees – a review. *Environ Int* 29(4):529–540
- Puppala SK, Alshawabkeh AN, Acar YB, Gale RJ, Bricka M (1997) Enhanced electrokinetic remediation of high sorption capacity soil. *J Hazard Mater* 55:203–220
- Purakayastha TJ, Chhonkar PK (2010) Phytoremediation of heavy metal contaminated soils. In: Sherameti I, Varma A (eds) *Soil heavy metals*. Springer, Heidelberg
- Quartacci MF, Irtelli B, Gonnelli C, Gabbriellini R, Navari-Izzo F (2009) Naturally-assisted metal phytoextraction by *Brassica carinata*: role of root exudates. *Environ Pollut* 157:2697–2703
- Rajkumar M, Freitas SH (2008) Influence of metal resistant-plant growthpromoting bacteria on the growth of *Ricinus communis* soil contaminated with heavy metals. *Chemosphere* 71:834–842
- Rascio N, Navari-Izzo F (2011) Heavy metal hyperaccumulating plants: how and why do they do it? And what makes them so interesting? *Plant Sci* 180:169–181
- Reddy K, Chinthamreddy S (1999) Electrokinetics remediation of heavy metal contaminated soils under reducing environments. *Waste Manag* 19:269–282

- Reeves RD, Baker AJM (2000) Metal accumulating plants. In: Raskin I, Ensley ED (eds) Phytoremediation of toxic metals: using plants to clean up the environment. Wiley, New York, pp 193–229
- Riddell-Black D (1993) A review of the potential for the use of trees in the rehabilitation of contaminated land. WRc report CO 3467. Water Research Centre, Medmenham
- Rizzi L, Petruzzelli G, Poggio G, Vigna Guidi G (2004) Soil physical changes and plant availability of Zn and Pb in a treatability test of phytostabilization. *Chemosphere* 57:1039–1046
- Robinson BH, Brooks RR, Howes AW, Kirkman JH, Gregg PEH (1997) The potential of the high-biomass nickel hyperaccumulator *Berkheya coddii* for phytoremediation and phytomining. *J Geochem Explor* 60:115–126
- Robinson B, Schulin R, Nowack B, Roulier S, Menon M, Clothier B, Green S, Mills T (2006) Phytoremediation for the management of metal flux in contaminated sites. *For Snow Landsc Res* 80(2):221–234
- Ruiz ON, Daniell H (2009) Genetic engineering to enhance mercury phytoremediation. *Curr Opin Chem Biol* 20:213–219
- Ruiz-Olivares A, Carrillo-González R, González-Chávez MCA, Soto Hernández RM (2013) Potential of castor bean (*Ricinus communis* L.) for phytoremediation of mine tailings and oil production. *J Environ Manage* 114:316–323
- Sasaki Y, Hayakawa T, Inoue C, Miyazaki A, Silver S, Kusano T (2006) Generation of mercury-hyperaccumulating plants through transgenic expression of the bacterial mercury membrane transport protein MerC. *Transgenic Res* 15:615–625
- Schroeder K, Rufaut CG, Smith C, Mains D, Craw D (2005) Rapid plant-cover establishment on gold mine tailings in Southern New Zealand: glasshouse screening trials. *Int J Phytoremediation* 7:307–322
- Sharma HD (2004) Geoenvironmental engineering: site remediation, waste containment and emerging waste management technologies. Wiley, Hoboken
- Sheoran V, Sheora AS, Pooni P (2009) Phytomining: a review. *Miner Eng* 22:1007–1019
- Shestopalov A, Bezuglova O (2000) The remediation technique for polluted soils with heavy metals. In: First international conference on soils of urban, industrial, traffic and mining areas. Proceedings vol III. Essen, Germany, pp 795–798
- Shu WS, Ye ZH, Lan CY, Zhang ZQ, Wong MH (2002) Lead, zinc and copper accumulation and tolerance in populations of *Paspalum distichum* and *Cynodon dactylon*. *Environ Pollut* 120:445–453
- Sneddon I, Orueetxebarria M, Hodson M, Schofield P, Valsami-Jones E (2006) Use of bone meal amendments to immobilize Pb, Zn and Cd in soil: a leaching column study. *Environ Pollut* 144:816–825
- Sobral L, Thoming J (1998) Remediation of contaminate Residue from the chlor-alkali industry, with elemental mercury, by using an electrolytic process. In: Contaminated soil '98, vol II. Edinburgh, UK, pp 1133–1134
- Spencer NE, Siege SM (1978) Effects of sulfur and selenium oxyanions on Hg toxicity in turnip seed germination. *Water Air Soil Pollut* 9:423–427
- Sun Y, Zhou Q, Diao C (2008) Effects of cadmium and arsenic on growth and metal accumulation of Cd-hyperaccumulator *Solanum nigrum* L. *Bioresour Technol* 99:1103–1110
- Swab M, Zilka M, Mullerova M, Koci V, Muller V (2008) Semi-empirical approach to modelling of soil flushing: model development, application to soil polluted by zinc and copper. *Sci Total Environ* 392:187–197
- Svenson A, Kaj L, Björndal H (1989) Aqueous photolysis of the iron (III) complexes of NTA, EDTA and DTPA. *Chemosphere* 18:1805–1808
- Tahaoun SA, Abdel-Bary E.S.A. (2000) Chemical mitigation of lead pollution in urban soils. In: First international conference on soils of urban, industrial, traffic and mining areas. Proceedings vol III. Essen, Germany, pp 783–788

- Tandy S, Bossart K, Mueller R, Ritschel J, Hauser L, Schulin R, Nowack B (2004) Extraction of heavy metals from soils using biodegradable chelating agents. *Environ Sci Tech* 38:937–944
- Terry N, Zayed AM, de Souza MP, Tarun AS (2000) Selenium in higher plants. *Annu Rev Plant Physiol Plant Mol Biol* 51:401–432
- Thöming J, Calmano W (1995) Remediation of heavy metal contaminated soils by acid leaching and electrolytic metal separation. In: Contaminated soil '95, vol II. Kluwer, Ac. Publ. Dordrecht, The Netherlands, pp 895–902
- Tsang DCW, Zhang W, Lo IMC (2007) Copper extraction effectiveness and soil dissolution issues of EDTA-flushing of artificially contaminated soils. *Chemosphere* 68:234–243
- Urlings LGCM (1990) In situ cadmium removal- full scale remedial action of contaminate soil. In: International symposium hazard waste treatment: treatment of contaminated soil, air and waste association and USEPA Risk Education Laboratory, Cincinnati, Ohio, 5–8 Feb
- USEPA (1989) Stabilization/Solidification of CERCLA and RCRA wastes. Technical report EPA/625/6-89/022. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH
- USEPA (1995) Technical report EPA/540/R-94/520. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH
- USEPA (1996) Engineering bulletin: technology alternatives for the remediation of soils contaminated with arsenic, cadmium, chromium, mercury and lead. U.S. Environmental Protection Agency, Office of Emergency and Remedial Response, Cincinnati
- USEPA (1997) Technical alternatives for the remediation of soils contaminated with As, Cd, Cr, Hg, and Pb EPA/540/S-97/500. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH
- USEPA (2000) Introduction to phytoremediation. EPA 600/R-99/107. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH.
- USEPA (2012) Technical EPA 542-F-12.012. United States Environmental Protection Agency, Office of Research and Development, Cincinnati, OH
- Van Cauwenberghe L (1997) Electrokinetics. GWRTAC. Series technology overview report. TO-97-03. [http://www.gwrtac.org/pdf/electro\\_o.pdf](http://www.gwrtac.org/pdf/electro_o.pdf)
- Van Nevel L, Mertens J, Oorts K, Verheyen K (2007) Phytoextraction of metals from soils: how far from practice? *Environ Pollut* 150:34–40
- Van Nevel L, Mertens J, Staelens J, De Schrijver A, Tack FMG, De Neve S, Meers E, Verheyen K (2011) Elevated Cd and Zn uptake by aspen limits the phytostabilization potential compared to five other tree species. *Ecol Eng* 37(7):1072–1080
- Vangronsveld J, van Assche F, Clijsters H (1995) Reclamation of a bare industrial area contaminated by non-ferrous metals: in situ metal immobilization and revegetation. *Environ Pollut* 87:51–59
- Virkutyte J, Sillanpää M, Latostenmaa P (2002) Electrokinetic soil remediation- critical overview. *Sci Tot Environ* 289:97–121
- Wang D, Shi X, Wei S (2003) Accumulation and transformation of atmospheric mercury in soil. *Sci Total Environ* 304:209–214
- Wang LQ, Luo L, Ma YB, Wei DP, Hua L (2009) In situ immobilization remediation of heavy metals- contaminated soils: a review. *Chin J Appl Ecol* 20(5):1214–1222
- Wang J, Fenga X, Anderson CWN, Xing Y, Shang L (2012) Remediation of mercury contaminated sites – a review. *J Hazard Mater* 221–222:1–18
- Warren LA, Ferris FG (1998) Continuum between sorption and precipitation of Fe (III) on microbial surfaces. *Environ Sci Technol* 32:2331–2337
- Witters N, Van Slycken S, Ruttens A, Adriaensen K, Meers E, Meiresonne L, Tack FMG, Thewys T, Laes E, Vangronsveld J (2009) Short-rotation coppice of willow for phytoremediation of a metal-contaminated agricultural area: a sustainability assessment. *Bioenerg Res* 2:144–152
- Wong MH (2003) Ecological restoration of mine degraded soils, with emphasis on metal contaminated soils. *Chemosphere* 50:775–780

- Wong JHC, Lim CH, Nolen GL (1997) Design of remediation systems. CRC. Lewis Publication, Boca Raton, p 263
- Wuana RA, Okieimen FQ (2011) Heavy metals in contaminated soils: a review of sources, chemistry, risks and best available strategies for remediation. International Scholarly Research Network ISRN Ecology, vol 2011. Article ID 402647, 20 pp
- Wuana RA, Okieimen FE, Imborvungu JA (2010) Removal of heavy metals from a contaminated soil using organic chelating acids. Environmental Pollution. Int J Environ Sci Technol 7 (3):485–496
- Yoon J, Cao X, Zhou Q, Ma LQ (2006) Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ 368:456–464
- Zanuzzi A, Faz A (2010) Phytostabilization of lead-polluted sites by native plants. In: Sherameti I, Varma A (eds) Soil heavy metals. Springer, Heidelberg, pp 329–337
- Zhang YQ, Moore JN (1997) Environmental conditions controlling selenium volatilization from a wetland system. Environ Sci Technol 31(2):511–519

## Chapter 8

### Potential Hazardous Elements Fluxes from Soil to Plants and the Food Chain

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**Abstract** Chemical elements exist naturally in the environment with different concentrations. However, human activities can increase these concentrations, what represent a serious threat to ecosystems and to the human health. In soil, the chemical elements are distributed in different physicochemical forms; inorganic species, organic complexes, adsorbed on solid phases or as constituents of solid phases with different solubility degrees. Plants can absorb only the elements present in the so-called available fraction, which is associated to the exchange complexes and soluble fractions in the soil solution. Absorption, translocation and accumulation of the elements in the plants depend on the species and ecotype as well as on the plant organ, climatic conditions and season of the year. Usually, essential elements (macro and micro-nutrients) are absorbed and translocated to the aerial part of the plant, while toxic elements are retained in the roots, however some hazardous elements are also transported to shoots. High concentrations of toxic elements in the plants can affect their biological processes and/or trigger different physiological

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