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Bioavailability of heavy metals and decontamination of soils by plants

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Abstract—Bioavailability of heavy metals in metal-contaminated soils depends on physical, chemical and biological factors. Physical (structure, penetrability) and chemical factors (Eh, pH, speciation, concentration) give the framework in which biological factors can modify the metal availability by release of oxygen, protons, and organic acids and by association with mycorrhizal fungi. With these conditions in mind, the possibilities of the use of hyperaccumulating higher plants for the decontamination of metal polluted soils, i.e. phytoremediation, are explored.

By small scale experiments it has been demonstrated that at present phytoremediation is only an economically important clean-up technique for slightly contaminated soils. Heavily contaminated soils can only be revegetated using highly metal-resistant plants. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Contaminants such as radionuclides, heavy metals and organic pollutants as well as their mixtures are threatening human health by their impact on water and food quality and ecosystems. Therefore decontamination of soils is a priority topic in environmental legislation. Two approaches have been applied to enhance decontamination of soils: (1) *ex situ*, i.e. removal of the polluted soil, transport to and cleaning in a technical plant procedure; (2) *in situ*, i.e. clean-up at the site itself. The *ex situ* clean-up by conventional technologies is often extremely costly and insufficiently risk reducing (van Gestel *et al.*, 1992). Recently the use of organisms for decontamination of these contaminated sites *in situ* have received increasing interest, namelly biodegradiation, bioremediation and phytoremediation. In particular the breakdown of organic soil pollutants by microorganisms to innocuous compounds, even a full decomposition to CO_2 and H_2O is very promising (Hinchee and Olfenbuttel, 1992; National Research Council, 1993; Alexander, 1994; Freijer, 1994). The situation of radionuclides and heavy metals is quite different from that of the organic pollutants due to their persistence as basic chemical elements and their emission origin as aerial fallout of smelters (Ernst, 1972; Freedman and Hutchinson, 1980; Pilgrim and Hughes, 1994; Barkan *et al.*, 1993; Eklund, 1995), accumulation in river sediments (Foerstner and Wittmann, 1981; Leenaers, 1989; Vernet, 1991) and in sewage sludge (Bingham *et al.*, 1976; Alloway and Jackson, 1991).

In addition to the immobilization of metals in agricultural soils *in situ* (Gworek, 1992; Mench *et al.*, 1994) the use of a "green" approach of soil decontamination (Baker *et al.*, 1994; DOE, 1994) has received a high ranking on the international research agenda. In this contribution several aspects of decontamination of soils by plants, i.e. phytoremediation, will be highlighted.

(1) The bioavailability of heavy metals in contaminated soils.

(2) The possibilities and limits of plants in the process of phytoremediation.

(3) The vegetation and recultivation of heavily metal contaminated soils.

BIOAVAILABILITY OF HEAVY METALS IN CONTAMINATED SOILS

The clean-up of metal-contaminated soils *in situ* by higher plants depends on the bioavailability of the heavy metals, the nutrient and water status of the soils and the capacity of the involved plant species to have access to the heavy metals. Bioavailability, however, is regulated by physical, chemical and biological processes and their interaction.

Physical aspects

The impact of the physical aspects of metal bioavailability varies from soil to soil. Remnants of mining activities have often a very coarse structure. It keeps a great deal of the metal inaccessible to plant roots and water. In addition the physical resistance may demand such a lot of energy that it hampers the penetration of plant roots to deeper soil layers. Lichens which can evolve metal resistance (Ernst, 1974) may enhance the accessibility of metals by promoting the destruction of compact stone structure, but their total impact has not yet been explored. Due to the coarse structure of mining remnants the water storage capacity is often too small to let plant roots survive during dry spells. As soon as soils contain a lot of clay minerals together with a shortage of organic material they may be packed together and hamper penetration of roots and their supply with sufficient oxygen, thus affecting metal speciation.

Chemical aspects

Chemical processes such as metal speciation and chemical conditions such as soil acidity and oxygen status can widely determine bioavailability of heavy metals. For more than a hundred years soil chemists have tried to find chemical extractants which can simulate metal availability to plants; no extractant, however, can really achieve this goal (Westerman, 1990; Carter, 1993). For metal contaminated soils some sequential extraction can approach those ranges of metal concentrations which are immediately and in the medium term available to plants. Extraction with demineralized water (1:5 soil/water) gives the immediately available metal; addition of chemically cleaned charcoal allows the metal speciation to be elaborated. Its knowledge is necessary for a judgement of phytotoxicity (Ernst, 1968, 1988a; van der Werff, 1981). Extractions with organic solvents such as DTPA–TEA (diethylenetriaminepentaacetic acid–triethanolamine; Lindsay and Norvell, 1978) or NH_4-acetate (Ernst, 1974) give a good indication of the amount of metals available to plant roots over a period of years. As shown in Fig. 1 for cadmium, there is a very good correlation between NH_4–acetate and DTPA–TEA extractable heavy metals, but only a reasonable one between water and DTPA–TEA extractable heavy metals, taking in to consideration that the absolute concentration between these methods differs by a factor of 25 to 100. Dissolution of heavy metals in aqua regia is only interesting for toxicity potential of the soils during hundreds or even thousands of years, but they say nothing about bioavailability.

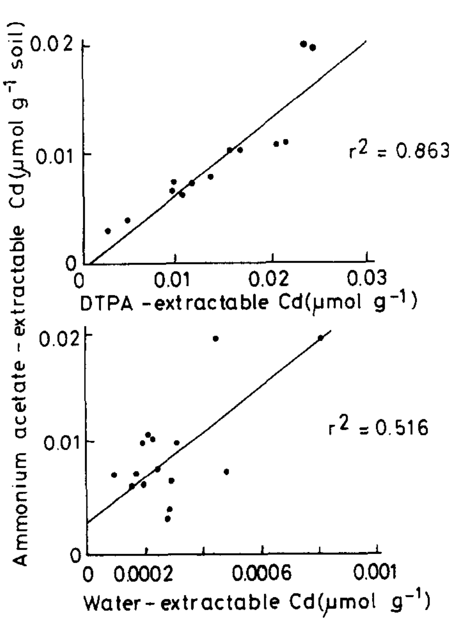

Fig. 1. Relationship between extractable fractions of ammonium acetate, DTPA and water from a metal-contaminated soil in the vicinity of a smelter site in The Netherlands. Soil:solution ratio was 1:5, pH 4.5.

Immobilization procedures for contaminated soils may be helpful. To overcome short-term toxicity in agricultural soils, improving the pH via fertilization with calcium carbonate (Mench *et al.*, 1994) or the addition of metal complexing agents (Chen and Stevenson, 1986) are advised, but owing to plant–microbe interaction they are insufficient on the long-term (Gemmell, 1977).

Biological aspects

Biota, especially bacteria, fungi and higher plants can strongly modify the chemical and physical conditions and processes which determine metal bioavailability. In mining remnants chemolithotrophic bacteria may acidify the soil and thus enhance metal mobility or precipitate the metals as sulfides (Kelley and Tuovinen, 1988). The presence of plasmid bound metal resistance in other bacteria, i.e. *Alcaligenes eutrophus* (Diels *et al.*, 1989) may affect further processes of metal speciation in contaminated soils. Higher plants affect constantly the metal concentration and metal speciation in contaminated soils: by the uptake of metal ions and the simultanous exudation of protons due to an antiport uptake system (Larcher, 1994) they acidify the rhizosphere and enhance metal availability in weakly buffered soils; by the exudation of simple phenolics and other organic acids they change the metal speciation (Kuiters and Mulder, 1993). The impact of these plant-borne organic compounds on the decontamination efficiency in the phytoremediation process is great (see Fig. 2). A very specific organic compound, i.e. the siderophore, not only affects the speciation of iron but also that of other heavy metals (Treeby *et al.*, 1989). In wet soils with a surplus of heavy metals the oxygen release by aerenchyma of flood-resistant plants (Armstrong, 1982) creates morphologically recognizable *pedotubuli*, i.e. small stable soil columns, which build up a strong metal speciation gradient from the root to the non-rooted environment (Otte, 1991). The iron plaque on the root surface can regulate the metal uptake by plants in dependence of their metal loading.

The symbiotic association of plant roots with vesicular–arbuscular (VA) mycorrhizal (Griffioen *et al.*, 1994) and ectomycorrhizal (EM) fungi (Colpaert and van Assche, 1992) in metal contaminated soils gives a new dimension to biologically changed bioavailability by exploiting an essentially greater soil volume than roots can do and by solubilization of heavy metals. VA mycorrhizae can enhance (Dosskey and Adriano, 1993) or diminish (Dueck *et al.*, 1986) metal toxicity in metal contaminated soils. As a consequence of these changes in the chemistry and nutrient availability of the rhizosphere, it may be expected that the whole microflora around the root

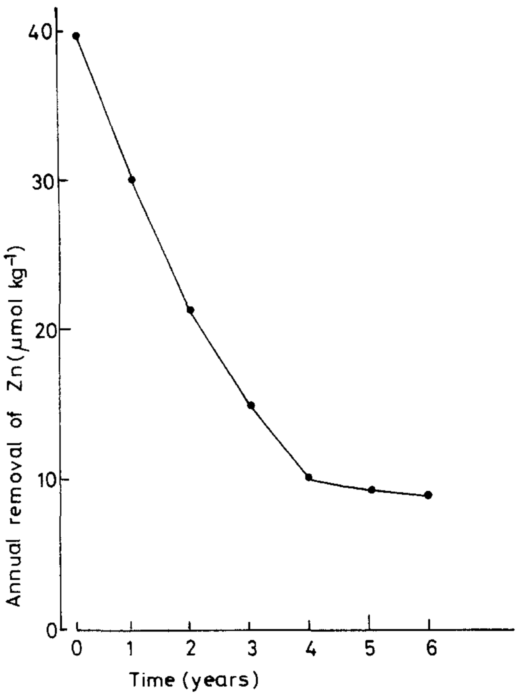

Fig. 2. Annual removal of zinc by harvesting the leaves of the metal-resistant grass *Festuca ovina*, grown for 6 years in the mining remnants of an old zinc–lead mine near Blankenrode, Germany. Owing to the accumulation of organic matter in the top soil the zinc removal decreased drastically during the years. Based on data in Ernst (1995).

may undergo significant changes, once more affecting metal speciation and thus metal bioavailability.

THE POSSIBILITIES AND LIMITS OF PLANTS IN THE PROCESS OF PHYTOREMEDIATION

Owing to the high variety of soil chemistry in metal-contaminated soils and the evolutionary potential of plants to adapt to extreme environments, a number of plant species is able to colonize naturally metal enriched soils and to maintain functional heavy metal ecosystems (Ernst, 1990). The success of phytoremediation can be ensured when these naturally selected and highly adapted plant species can be used economically. The success will depend on three factors: (1) the degree of metal contamination of the soil; (2) the degree of metal bioavailability (its chemical and physical aspects); (3) the capacity of the higher plants to accumulate the metal in the shoots.

As shown earlier (Ernst, 1988b, 1995) soils with a high degree of metal pollution can be revegetated by metal resistant plants, but their decontamination capacity is restricted by their low biomass production, so that decontamination of the soil can not be achieved in a reasonable time, i.e. between 10 and 20 years. In the case of grasses there are no hyperaccumulators. Various grass species such as *Festuca ovina*, *F. rubra*, *Agrostis capillaris*, *A. delicatula* and *A. stolonifera* can evolve high degrees of metal resistance. The potential for phytoremediation is low owing to (1) the uptake of heavy metals and its accumulation in the leaves, as shown for *F. ovina*, grown on the remnants of a zinc factory and harvested annually (Fig. 2), (2) the high production of metal-chelating phenolics; the annual removal of zinc by the grass decreased strongly over the years. Therefore an ecologically and economically acceptable clean-up of these soils is impossible. However, by revegetation of these often bare sites a further dispersal of metals by water and wind erosion and a percolation of the metals to the groundwater can be prevented.

Slightly metal-polluted soils can be decontaminated by enhancing growth of metal resistant and accumulating plants (Ernst, 1988b; Baker *et al.*, 1994). In Europe famous hyperaccumulators are the cruciferous herbs *Cardaminopsis halleri*, *Thlaspi caerulescens* and *T. cepaeifolium*, and *Alyssum* species and the Caryophyllaceae *Silene vulgaris* and *Minuartia verna*. Unfortunately their biomass production is low, the root system with the exception of *S. vulgaris* small and restricted to a tap root, as shown for the zinc hyperaccumulator *T. caerulescens* (Fig. 3). Therefore they lack the agronomic properties for easy harvesting. Nevertheless it has internationally been agreed upon that despite these drawbacks, hyperaccumulators are the only option for phytorernediation of slightly metal-polluted soils, as long as the isolation and transfer of the genes responsible for metal accumulation is not possible (DOE, 1994). Additional problems yet unsolved are the conservation of the germplasm of these hyperaccumulators being often rare and endangered species, the processing of the metal-enriched plant material and its recycling by the metal industries. Pioneer experiments give reasonable perspectives for phytoremediation by hyperaccumulators for zinc and cadmium (Baker *et al.*, 1994).

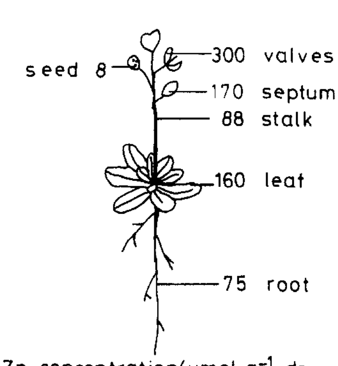

Fig. 3. Zinc concentration in various tissues of the metal hyperaccumulator *Thlaspi caerulescens*, collected on a soil in the vicinity of an ore outcrop near Aachen, Germany. The tap root system is weakly developed and can therefore only exploit a small soil volume. Based on data in Ernst (1974, 1995).

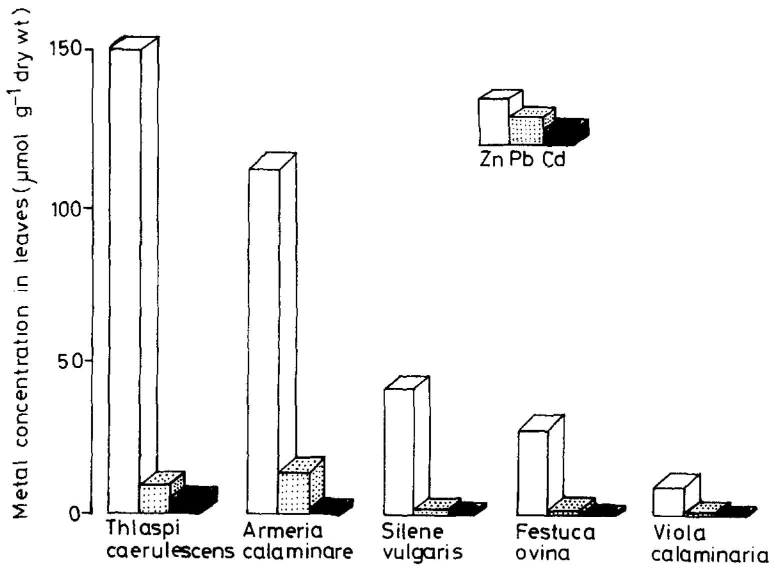

Fig. 4. Metal-specific accumulation of zinc, lead and cadmium in the leaves of metal-resistant plants, growing on a soil near an ore outcrop at Breinigerberg, Aachen, Germany. All plants were harvested in autumn. *Thlaspi caerulescens* and *Armeria calaminare* are characteristic hyperaccumulator plants for zinc. Based on data in Ernst (1982).

REVEGETATION AND RECULTIVATION OF HEAVILY METAL-CONTAMINATED SOILS

At sites with a high burden of soil metals decontamination by biological means lasts too long (Ernst, 1974) and does only remove less than 1% of the metal in a century (Ernst, 1988b). One reasonable solution to control heavily metal-contaminated sites is the revegetation and/or recultivation at a later development stage. The plant material for revegetation has to be selected after the chemical determination of the dominant bioavailable metals, the acidity and water capacity of the soil. By sowing metal-resistant grasses, amended with metal-resistant VA mycorrhizal fungi (Griffioen *et al.*, 1994; Weissenhorn, 1994) and by addition of a small amount of fertilizers a rapid establishment of the grass cover can be achieved, as long as the soil is not too acid. By introducing metal-resistant herbs the revegetated metal-contaminated soil can even achieve a very aesthetic state in the landscape.

A great danger remains for man and cattle. This grassland is a dangerous green, if it is consumed (MAGS, 1975). Although the metal concentration in grasses (*F. ovina* in Fig. 4) is lower than that of most herbs it is still toxic because the concentration of zinc is above the advised daily intake. In contrast to the grasses the metal toxicity of the herbs will remain at high levels for an essentially longer period because they can exploit deeper soil layers and their metal accumulation is structurally higher than that of the grasses (Fig. 4). Therefore regulation of access to the phytoremediated site on the long-term has to be considered as an essential process in revegetation.

CONCLUSION

The evolution of metal-hyperaccumulating plant species opens the possibility for their use in decontamination of metal-polluted soils. The morphological structure of most of these hyperaccumulator is not yet sufficient for their practical application on large areas. The techniques of plant molecular biology and biochemistry have to be applied to these hyperaccumulators so that the improvement of their biomass production can finally result in an effective, low-cost technology to clean-up metal-contaminated soils. There is still a long way to go from the potential small-scale (Brown *et al.*, 1994) to a realistic large-scale approach (DOE, 1994).

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