ABSTRACT

For heavy metal–contaminated agricultural land, low-cost, plant-based phytoextraction measures can be a key element for a new land management strategy. When agents are applied into the soil, the solubility of heavy metals and their subsequent accumulation by plants can be increased, and, therefore, phytoextraction enhanced. An overview is given of the state of the art of enhancing heavy metal solubility in soils, increasing the heavy metal accumulation of several high-biomass-yielding and metal-tolerant plants, and the effect of these measures on the risk of heavy metal leaching. Several organic as well as inorganic agents can effectively and specifically increase solubility and, therefore, accumulation of heavy metals by several plant species. Crops like willow (Salix viminalis L.), Indian mustard (Brassica juncea Czern.), corn (Zea mays L.), and sunflower (Helianthus annuus L.) show high tolerance to heavy metals and are, therefore, to a certain extent able to use the surpluses that originate from soil manipulation. More than 100-fold increases of lead concentrations in the biomass of crops were reported, when ethylenediaminetetraacetic acid (EDTA) was applied to contaminated soils. Uranium concentrations could be strongly increased when citric acid was applied. Cadmium and zinc concentrations could be enhanced by inorganic agents like elemental sulfur or ammonium sulfate. However, leaching of heavy metals due to increased mobility in soils cannot be excluded. Thus, implementation on the field scale must consider measures to minimize leaching. So, the application of more than 1 g EDTA kg⁻¹ becomes inefficient as lead concentration in crops is not enhanced and leaching rate increases. Moreover, for large-scale applications, agricultural measures as placement of agents, dosage splitting, the kind and amount of agents applied, and the soil properties are important factors governing plant growth, heavy metal concentrations, and leaching rates. Effective prevention of leaching, breeding of new plant material, and use of the contaminated biomass (e.g., as biofuels) will be crucial for the acceptance and the economic breakthrough of enhanced phytoextraction.

Large areas of agricultural soils are contaminated by heavy metals that mainly originate from former or current mining activities, industrial emissions, or the application of sewage sludge. Elevated heavy metal concentrations in the soil can lead to enhanced crop uptake. Excessive metals in human nutrition can be toxic and can cause acute and chronic diseases (Geldmacher, 1984). Cadmium and Zn, for example, can lead to acute gastrointestinal and respiratory damage and acute heart, brain, and kidney damage. Chronic diseases have been reported in humans exposed to long-term heavy metal uptake including local effects on skin and mucous membranes and various systemic effects on the intestines (Friberg et al., 1986).

Elevated heavy metal concentrations in the soil can also negatively affect crop growth. At higher concentrations, they interfere with metabolic processes and inhibit growth, sometimes leading to plant death (Baker et al., 1976; Hoffmann, 1983; Schaller and Diez, 1991). Consequently, quality standards were established that determine thresholds of maximum heavy metal concentrations allowed in plant tissue. In the European Union, maximum concentrations of lead (Pb) and cadmium (Cd) allowed in several agricultural crops were recently enacted into law (Commission of the European Communities, 2002).

The transfer of heavy metals from soils to plants is dependent on three factors: the total amount of potentially available elements (quantity factor), the activity as well as the ionic ratios of elements in the soil solution (intensity factor), and the rate of element transfer from solid to liquid phases and to plant roots (reaction kinetics) (Brümmer et al., 1986). Because correlations were found between the soluble heavy metal concentrations in the soil and the heavy metal concentrations in plants, several countries passed legislation establishing quality standards based on soluble heavy metal concentrations in the soil. These concentrations must be reduced below maximum threshold levels to avoid reduced plant growth or nutritional quality. Moreover, the leaching of metals into the ground water must be minimized.

Conventional methods to remediate metal-contaminated soils (landfilling or excavation and extraction) can be used at highly contaminated sites but are not applicable to large areas. These remediation methods require high energy input and expensive machinery (Cunningham and Ow, 1996; Schnoor, 1997). At the same time they destroy soil structure and decrease soil productivity (Leumann et al., 1995). Phytoremediation, the use of plants to clean soils, can be a cost-effective in situ alternative for low- or medium-contamination soils and does not adversely affect soil fertility (Cunningham and Ow, 1996; Schnoor, 1997; Salt et al., 1998). Two main phytoremediation strategies are available for reducing the plant-available metal concentration in soils:

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**Abbreviations:**
CDTA, 1,2-cyclohexylenedinitrilotetraacetic acid; DTPA, diethylenetriaminopentaacetic acid; EDTA, ethylenediaminetetraacetic acid; HEDTA, hydroxyethylethylene diaminetriacetic acid; NTA, nitrilotriacetic acid.
site stabilization (phytostabilization) and phytoextraction. The aim of site stabilization is to rapidly reduce heavy metal availability to crops; this can be achieved by adding various agents to the soil to reduce heavy metal mobility. Nonetheless, the heavy metal concentration in the soil remains unchanged. The state of the art of phytostabilization is outlined by Vangronsveld and Cunningham (1998) and, therefore, not discussed in further detail here.

Phytoextraction involves the uptake of heavy metals and their accumulation in harvestable portions of plants to promote long-term soil cleaning. Experimental studies conducted over the last two decades show that several plant species extract high amounts of metals from contaminated soils. Hyperaccumulating plants can have very high concentrations of heavy metals in their tissue, but have comparably low biomass production (Baker, 1981; Baker and Brooks, 1989). The authors define hyperaccumulating plants as those in which the concentrations of Cd, Cu, Pb, and Zn in the dry matter of leaves exceed the thresholds of 100, 1000, 1000, and 10 000 mg kg$^{-1}$, respectively. This class of plants is often found at metalliferous sites; metal accumulation may help to protect against herbivorous insects or bacterial or fungal diseases (Baker and Brooks, 1989). These wild plant species are low yielding and currently have no relevance for agricultural use. In contrast, several metal-tolerant plants have lower heavy metal concentrations in their tissues, yet contribute to metal extraction by high biomass yields.

To achieve high heavy metal removal rates, however, the concentrations of soluble heavy metals in the soil must be enhanced in most cases. The purpose of this review is to describe the state of the art of increasing the metal accumulation of plants. It will be shown that this can be achieved by adding certain organic and inorganic agents to the soil. Also, the relationship between enhancing metal solubility in soils and plants, and applying strategies to minimize the risk of heavy metal leaching, will be discussed. Finally, the topics of plant choice and field application of phytoextraction will be presented.

**USING ORGANIC AGENTS TO ENHANCE PHYTOEXTRACTION**

Several organic agents can effectively increase the solubility of metallic contaminants in soils and subsequently enhance their uptake by several crops. Because many studies focused on the effect of adding EDTA and related substances on heavy metal accumulation, these substances receive prominent treatment in this chapter. Other artificial and naturally occurring agents efficiently promote heavy metal accumulation.

**Mechanisms of Solubilization**

The choice of appropriate agents for extracting certain heavy metals from a contaminated soil is the first issue that must be raised. Here, the solubilization of heavy metals must be enhanced to increase extraction efficiency. This solubilization is mainly based on the capacity of organic chelating agents to form water-soluble metal–organic complexes (Martell and Calvin, 1958). By complexation, metals are extracted or desorbed from different soil components or from the surfaces of these components. The extent of heavy metal solubilization by chelation with organic complexing agents follows the order of their stability constants, which were determined in aqueous solutions using the ratio of metal to chelating agent (as their protonated forms) of 1:1 (Martell and Calvin, 1958). In soils, complexation of heavy metals with various complexing agents typically follows the order EDTA and related synthetic chelates > nitritotri-acetic acid (NTA) > citric acid > oxalic acid > acetic acid, as was shown by several comparative experiments (Hong and Pintauro, 1996b; Krishnamurti et al., 1998; Wenger et al., 1998). However, according to Hong and Pintauro (1996a) and Wu et al. (1999), in uncontaminated soils the complexation of EDTA with Cd and Pb is more effective than for other heavy metals. EGTA (Ethylene glycol-[aminoethyl ether]-N,N,N′,N′-tetraacetic acid) is reported to selectively increase Cd mobility over a wide pH range; NTA was more selective on Cu and Cd than for Pb (Hong and Pintauro, 1996b). When concentrations of these artificial chelating agents in the soil increased, however, the metal selectivity decreased (Hong and Pintauro, 1996b).

Because acid functional groups are deprotonated with increasing pH, the solubility of organic substances increases, as does the stability of metal–organic complexes (Harter and Naidu, 1995; Scheffer and Schachtschabel, 1998). Thus, especially at higher pH, organic substances can contribute to heavy metal mobilization and accumulation.

Most of the experiments designed to test the effect of applying organic agents on the accumulation of heavy metals by plants focused on lead and were conducted with chelating agents of high metal binding capacity (like EDTA, hydroxyethylendiaminetriacetic acid [HEDTA], 1,2-cyclohexylenedinitriotetraacetic acid [CDTA], and diethylenetriaminpentaaetic acid [DTPA]). These chelating agents have a chelate binding constant (log $K$) with Pb of more than 15 (Martell and Calvin, 1958).

**Enhancing Lead Accumulation by Applying EDTA and Related Substances**

In the pot experiments described in the literature, the concentrations of total Pb in soils ranged between 110 and 14 350 mg kg$^{-1}$, and the amounts of chelating agents applied varied between 0.44 and 5.8 g kg$^{-1}$. Although not every study reports the soluble Pb concentration after agent application, the fraction of dissolved Pb ranged between 3 and 78% of total Pb in the soils ($n = 25$ paired samples from various pot experiments). This fraction is not related to the amount of chelate added, but to specific soil characteristics.

**Shoot Lead Concentration and Pot Experiments**

When conducting studies with a particular soil, many authors reported that the Pb concentration in the shoots
of various test plants was directly proportional to the amount of EDTA or related agents added to the soil. Because the fraction of Pb being desorbed by chelating agents varies considerably between soils, when comparing different studies it is assumed that the concentration of soluble Pb should correlate better with the concentration of Pb in plants grown on these soils. In the six studies that provided enough data, a positive relationship apparently existed between the Pb concentrations in the soil solution and in the plant tissues (Fig. 1; see references in Table 1).

The highest Pb transfers from the soil solution to shoots were found in Indian mustard and pea (*Pisum sativum* L.), followed by corn and sunflower. However, because for most crops the database was too small, no statistical calculations on the dependencies of the two parameters were conducted. The most data were available for corn (n = 13 paired samples from three studies conducted with different soils and Pb contamination levels; for references, see Table 1). Here, $R^2$ was 0.77 ($R^2 = 0.97$ after the removal of one outlier). According to a linear relationship, the Pb concentration in the tissue of corn plants is 8.9 times higher than in the soil solution. Once the database is enlarged to include other crops and agents, plant Pb concentrations can probably be predicted based on the concentration of soluble Pb in soils, if measured.

Many studies found extremely high Pb concentrations in the biomass of several crops (Table 1). Especially in such studies, which were conducted with highly Pb contaminated soils, the addition of EDTA, CDTA, or HEDTA at high concentrations increased Pb concentrations tremendously to as much as 24 g Pb kg$^{-1}$ dry matter.

Several studies showed that once chelates are assimilated, they are transferred nearly entirely from roots to shoots (Barber and Lee, 1974; Hamon et al., 1995; Vassil et al., 1998). Labeling the carbon fraction of EDTA revealed that plants can take up metal–EDTA complexes, which are subsequently transported in the xylem sap (Vassil et al., 1998).

Based on the few available studies, it appears possible to quantify some methodological peculiarities, such as the effect of plant growth conditions and of the frequency of agent application on heavy metal accumulation.

Wu et al. (1999) found that the Pb concentrations in corn plants differed if the seedlings were transplanted to or directly germinated in the contaminated soil. Lead concentrations of 4500 mg kg$^{-1}$ (which is 45-fold the control concentration) could be achieved when corn plants were transplanted 10 d after germination, whereas only sixfold the control concentration was measured when plants germinated in the contaminated soil. Thus, compared with plants that germinated on the contaminated soil, the metal translocation efficiency, expressed as shoot-to-root ratio of Pb concentration, increased from 0.23 to 1.57. In the transplanted seedlings, the Pb accumulation would probably have been smaller if they had been germinated on contaminated soil. Because transplantation is not a viable option for field remediation work, this finding implies that those pot experiments which may lead to later field work should not be conducted with transplants.

Grcman et al. (2001) studied the effect of agent application frequency on Pb accumulation efficiency. They

### Table 1. Maximum Pb concentration in plants after the addition of different chelating agents with a log $K^+$ of $>15$.  

<table>
<thead>
<tr>
<th>Plant</th>
<th>Chelate added‡</th>
<th>Concentration in the plant tissue</th>
<th>Total Pb</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Without chelate</td>
<td>After chelate addition</td>
<td>mg kg$^{-1}$ dry matter</td>
</tr>
<tr>
<td><strong>Perennial French ryegrass</strong></td>
<td>4 g EDTA kg$^{-1}$</td>
<td>96</td>
<td>24 000</td>
<td>6 750</td>
</tr>
<tr>
<td>Pea</td>
<td>2 g HEDTA kg$^{-1}$</td>
<td>90</td>
<td>10 600</td>
<td>2 450</td>
</tr>
<tr>
<td>Corn</td>
<td>2 g HEDTA kg$^{-1}$</td>
<td>60</td>
<td>10 200</td>
<td>2 450</td>
</tr>
<tr>
<td>Cabbage</td>
<td>0.9 g EDTA kg$^{-1}$</td>
<td>125</td>
<td>5 010</td>
<td>10 600</td>
</tr>
<tr>
<td>Sunflower</td>
<td>5.8 g CDTA kg$^{-1}$</td>
<td>67</td>
<td>5 200</td>
<td>10 600</td>
</tr>
<tr>
<td><em>Indian mustard</em></td>
<td>2.9 g EDTA kg$^{-1}$</td>
<td>313</td>
<td>5 000</td>
<td>3 000</td>
</tr>
<tr>
<td>Redtop</td>
<td>5.8 g CDTA kg$^{-1}$</td>
<td>25</td>
<td>3 000</td>
<td>2 500</td>
</tr>
<tr>
<td>Corn</td>
<td>5.8 g CDTA kg$^{-1}$</td>
<td>36</td>
<td>2 600</td>
<td>1 100</td>
</tr>
<tr>
<td>Corn</td>
<td>0.44 g EDTA kg$^{-1}$</td>
<td>90</td>
<td>500</td>
<td>2 500</td>
</tr>
<tr>
<td><em>Perennial ryegrass</em></td>
<td>3 g EDTA kg$^{-1}$</td>
<td>50</td>
<td>300</td>
<td>700</td>
</tr>
<tr>
<td>Cabbage</td>
<td>2.9 g EDTA kg$^{-1}$</td>
<td>3</td>
<td>90</td>
<td>1 100</td>
</tr>
</tbody>
</table>

‡ Chelate binding constant.

§ CDTA, 1,2-cyclohexylenedinitrilotetraacetic acid; EDTA, ethylenediaminetetraacetic acid; HEDTA, hydroxyethylendiaminetriacetic acid.
found that a single dose of 2.9 g EDTA kg\(^{-1}\) enhanced Pb accumulation of cabbage (Brassica oleracea L.) grown in a greenhouse 105-fold, as compared with a 44-fold increase if the same amount of EDTA was split and added in four dosages. The effects on Pb solubilization or leaching were not compared, however.

In contrast, in the study of Puschenreiter et al. (2001), the Pb concentration in corn grown on a soil with 5600 mg total Pb kg\(^{-1}\) increased eightfold to 49 mg kg\(^{-1}\) after adding 1 g EDTA kg\(^{-1}\) 3 wk before harvesting; this value increased to 18-fold when the EDTA application was split into three dosages over a period of 3 wk. Also Cd, Ni, Zn, and Cu concentrations in the plants increased after splitting the EDTA.

The heavy rainfall simulated in the first study may have removed Pb chelates from the soil before they could be accumulated by the crop. The authors reported high Pb losses during the experiment.

**Growth Response of Plants to Chelate Addition in Pot Experiments**

As mentioned above, nearly all studies were conducted over short time periods and the plants were harvested in early growth stages. Some studies present biomass data, whereas in others it can be assumed that plants stopped growing after the agent application or after transplantation to the contaminated soil. This hinders the assessment of the effect of chelate application on plant growth and survival.

With increased additions of EDTA, plant biomass of rape (Brassica napus L. var. napus) and Indian mustard decreased when the soluble Pb concentrations exceeded values of 70 and 150 mg Pb kg\(^{-1}\), respectively (Grcean et al., 2001; Blaylock et al., 1997). After adding 1 g EDTA kg\(^{-1}\) to a soil containing 110 mg Pb kg\(^{-1}\), perennial ryegrass plants stopped growing and died (Albasel and Cottenie, 1985). After adding 0.5 g HEDTA kg\(^{-1}\) the soluble Pb concentration exceeded approximately 200 mg Pb kg\(^{-1}\) and corn and pea plants died and were harvested 1 wk after the application of HEDTA (Huang et al., 1997a). Cooper et al. (1999) applied the chelate in seven waterings, not at once as in other studies. Growth of the test plants was probably hampered by P deficiency in this study, due to the low concentration of available P in the soil. Further growth depressions of corn and redtop (Agrostis gigantea Roth) related to CDTA addition were observed when the soluble Pb concentration exceeded approximately 160 mg kg\(^{-1}\) during 6 wk, while growth of pea was already hampered at a value exceeding 80 mg kg\(^{-1}\). Sunflower plants showed relatively low dry matter accumulation but the highest Pb concentration, with more than 5 g Pb kg\(^{-1}\) dry matter. Accordingly, under optimized agricultural practice (foliar-applied P fertilization to prevent the formation of Pb phosphates in the soil solution), sunflower is a metal-tolerant and high-yielding crop that provides good perspectives for phytoextraction purposes.

**Field Experiments**

The discussion of field experiments is presented separately from the discussion of pot experiments because the effects of enhanced phytoextraction on heavy metal accumulation of plants differ in the two approaches. Kayser et al. (2000), for example, showed that in pots filled with the same soil as later used for a field study, three times more Cd was found in tobacco (Nicotiana tabacum L.) and sunflower and even seven times more in Indian mustard than in the field. On average, in the field heavy metal removal was only 20% of what was originally expected from the pot results.

In pot experiments, heavy metal concentrations in plant dry matter increased more than in field experiments. Several explanations have been presented: (i) more pot experiments have been conducted than field experiments, and in some pot experiments, the soil was artificially enriched with heavy metal salts, hence increasing the variability of results and the probability of achieving extraordinary high heavy metal concentrations; (ii) the soluble heavy metal concentrations of the soils were lower in the field versus pot experiments; (iii) the efficiency of soil amendments is higher in pot experiments because plant roots explore potted soil very intensely and are always in contact with the soil amendments; and (iv) pot experiments have been conducted over short time periods, because plants were harvested in an early growth stage or their growth was curtailed. Restricted plant growth was reported in most experiments, probably due to toxic levels of plant-available heavy metals in the soil solution. As a consequence, the reported concentrations were comparatively high, but due to low biomass accumulation, the total removal remained low. For the development of new phytoremediation strategies, therefore, pot or column studies are valuable tools. This low-cost approach can test different soils and crops in combination with different agents, and test appropriate concentration levels and different applications of these agents. It also simplifies measurements of all relevant parameters needed for element balances, including the measurement of leached metals. Moreover, such initial tests using pots or columns can help improve the design of field experiments.

Salt et al. (1998) described that as much as 28% of all Pb of a contaminated soil (up to 1600 mg Pb kg\(^{-1}\)) was removed by Indian mustard over one cropping season after an unspecified amount of EDTA was applied. Some other results from the same experimental site were published by Blaylock et al. (1999): in the target area, the soil Pb concentration decreased by an average of 13% after three harvests of Indian mustard and several additions of a total of 57 g EDTA m\(^{-2}\) through the irrigation water. However, no information was given about the Pb concentrations in the crop, and about the fraction of Pb that was mobilized and subsequently washed out from the sampled soil layer in both studies.

Blaylock et al. (1997) demonstrated that the efficiency of organic agents on metal accumulation by plants can be enhanced by lowering the soil pH. In their field study, applying 1.4 g EDTA kg\(^{-1}\) increased Pb accumulation of Indian mustard shoots 28-fold to 785 mg Pb kg\(^{-1}\); however, when 5 mmol acetic acid was additionally applied, the concentration increased to 1471 mg kg\(^{-1}\). The
authors explained this by lower cell wall retention of the Pb as lead carbonate at lower rhizosphere pH. After EDTA addition, plant growth stopped and the yield fell to only 50% of the nontreated plants. For future experiments, it is suggested that plants be allowed to grow to full size before adding mobilizing agents.

The Effect of EDTA Application on the Phytoextraction of Other Heavy Metals

Artificial chelating agents enhance the concentrations of heavy metals other than Pb in the soil solution and in the biomass of several plants, but to smaller extents. The Cu and Zn concentrations of perennial ryegrass (*Lolium perenne* L.) were doubled (60 mg kg⁻¹) and increased 2.6-fold (2.3 g kg⁻¹), respectively, after 60 d of growth in a pot experiment with moderately Cu-contaminated (40 mg kg⁻¹) and limed soil and after the application of 1 g EDTA kg⁻¹ (Albasel and Cottenie, 1985); the Ni concentration, however, decreased 25-fold (from 13 to 0.5 mg kg⁻¹). The Ni concentration in the soil was not reported, but appears to be relatively low, and its uptake was obviously hampered in favor of the other cations by competition during the plant uptake. Luo et al. (2001) showed that applying 0.9 g EDTA kg⁻¹ to a Cu-polluted paddy soil (158 mg Cu kg⁻¹) increased Cu concentrations in the leaf tissue of Indian mustard from 18 to 54 mg kg⁻¹.

Outstanding results were obtained with perennial French ryegrass (*Arrhenatherum elatius* (L.) P. Beauv. ex J. Presl & C. Presl subsp. elatius) grown in a pot experiment conducted by Deram et al. (2000). With 0.5 g EDTA kg⁻¹ added to a soil that contained high amounts of Cu and especially Ni (187 and 6300 mg kg⁻¹, respectively), the Cu and Ni concentrations in increased 38- and 160-fold, respectively, to 7.5 g Cu kg⁻¹ and 1.3 g Ni kg⁻¹. Further research on other Cu-contaminated sites is needed to prove the ability of this promising crop, however.

After the addition of 2.5 g EDTA kg⁻¹ to a highly Zn-contaminated soil (3100 mg kg⁻¹), the soluble Zn concentration in the soil increased 450-fold to 90 mg kg⁻¹, and the Zn concentration in Indian mustard was doubled (to 500 mg kg⁻¹, Ebbs and Kochian 1998), but did not increase in oat (*Avena sativa* L.; 200 mg kg⁻¹) and barley (*Hordeum vulgare* L.; 620 mg kg⁻¹). After spiking soils with high amounts of heavy metal salts followed by 0.73 g kg⁻¹ EDTA, Indian mustard shoot concentrations of Zn and Cu were at or above 1000 mg kg⁻¹ and Cd and Ni concentrations were 480 and 200 mg kg⁻¹, respectively (Blaylock et al., 1997).

In a soil column experiment, Grcman et al. (2001) found that Cd and Zn concentrations in cabbage did not change after adding 2.85 g EDTA kg⁻¹ to an industrially contaminated soil with a total Cd and Zn concentration of 5.5 and 800 mg kg⁻¹, respectively. The authors measured a high leaching rate of the heavy metals, however.

Heavy Metal Accumulation after Combined EDTA and Glyphosate Treatments

In several experiments it was found that the application of glyphosate enhanced Pb accumulation of crops. The mechanism of enhanced metal accumulation after glyphosate application was explained by a disruption of plant metabolism, leading to enhanced transport of heavy metals from root to shoot (Ensley et al., 1999). Glyphosate is the active substance of the broad-spectrum herbicide RoundUp, which is produced by Monsanto Agricultural Products, St. Louis, MO.

In a field experiment, when 0.6 g kg⁻¹ EDTA were applied to a highly contaminated calcareous soil (total and soluble Pb: 8000 and 1.9 mg kg⁻¹, respectively), the Pb concentration in the soil solution increased 100-fold and in the tissue of Indian mustard fivefold to 600 mg kg⁻¹ (Kayser et al., 1999a). Combining EDTA and glyphosate increased the Pb concentration in the tissue of this crop even 15-fold, when glyphosate was added shortly before harvest. None of the measures undertaken by Kayser et al. (1999a) hampered the growth of Indian mustard. With approximately 20 Mg ha⁻¹ of harvestable dry matter, it was calculated that 12 or 33 kg of Pb could be removed from 1 ha without and with glyphosate addition, respectively.

In a pot experiment with the same soil as used by Kayser et al. (1999a), 1 wk after EDTA application (0.17 g kg⁻¹) Indian mustard was sprayed with glyphosate and the plants died 3 d later (Mathis and Kayser, 2001). Applying EDTA doubled the Pb concentration to 90 mg kg⁻¹, whereas after glyphosate application this concentration was enhanced to 680 mg kg⁻¹. Both in the field and pot experiments of this working group, a combination of EDTA and glyphosate yielded higher Pb accumulations of Indian mustard than these agents alone.

Maxted et al. (2001) found smaller Cd concentrations as compared with the control in corn plants after glyphosate application of 1 L ha⁻¹. In a pot experiment with the same soil as used by Kayser et al. (1999a), 1 wk after EDTA application (0.17 g kg⁻¹) Indian mustard was sprayed with glyphosate and the plants died 3 d later (Mathis and Kayser, 2001). The application of EDTA had no significant effect on Cu concentrations, but after glyphosate application, the Cu concentration increased 10 times to 400 mg kg⁻¹.

The reported differences in the efficiency of glyphosate for metal accumulation by different plants might be due to observed different absorption and translocation rates (Green et al., 1992) and also to the rate of glyphosate applied.

The Effect of NTA on Heavy Metal Phytoextraction

Compared with EDTA addition, a lower, but still significant phytoextraction enhancement has been observed by several authors after adding NTA to the soil. In a pot experiment with a calcareous, mainly Cu-contaminated soil (530 mg kg⁻¹), even low dosages of 0.5 g NTA kg⁻¹ (split into two applications) increased the concentrations of Cd, Zn, and Cu 1.4- to 1.9-fold in lettuce (*Lactuca sativa* L.) and perennial ryegrass (*Kulli* et al., 1999). After adding 1.8 g NTA kg⁻¹, the Cd and Zn concentrations of perennial ryegrass doubled compared
with the control plants with average Cd and Zn concentrations of 2.7 and 505 mg kg\(^{-1}\), respectively. Chlorotic leaves and restricted root growth were observed. Copper accumulation was only slightly enhanced from 820 to 1000 \(\mu g\) kg\(^{-1}\) dry matter. A higher NTA application rate of 5 g kg\(^{-1}\) did stop the growth of ryegrass. The plants showed necrosis and impaired root length growth, which are both metal toxicity symptoms (Lepp, 1981; Bergmann, 1983).

A field experiment to test the effect of increased rates of NTA on heavy metal accumulation was conducted by Kayser et al. (2000) on the same soil as previously used by Kulli et al. (1999) for their pot study. Here, the NTA application was also split into small dosages. The experimental setup differed further from other studies because NTA was injected into the rooting zone of the plants. Nine injections of NTA led to a total of 4.6 and 9.2 g NTA m\(^{-2}\), which significantly increased heavy metal accumulation by several plants. At 9.2 g NTA m\(^{-2}\), the Cd, Zn, and Cu concentrations in most crops were doubled: in tobacco to 5, 200, and 45; in corn to 1, 190, and 18; in willow to 5, 400, and 30; in sunflower to 2, 200, and 43; and in Indian mustard to 2, 190, and 26 mg kg\(^{-1}\), respectively. Dry matter yields of the crops did not change significantly after NTA treatment. Highest Cd removal was achieved by tobacco (48 g ha\(^{-1}\)), the highest Zn removal by sunflower and corn (3600 and 3000 g ha\(^{-1}\)), and the most Cu was accumulated by sunflower (850 g ha\(^{-1}\)). Although no metal toxicity symptoms were visually observed in any of the aerial parts of the crops tested, root growth of willow and Indian mustard plants tended to be smaller. Heavy metal leaching in the soil was not examined, but the measurements of soluble heavy metals shortly after one NTA application showed that, compared with the control, Cd, Zn, and Cu concentrations increased 75-, 45-, and 10-fold, respectively, to 20, 4000, and 9000 \(\mu g\) kg\(^{-1}\).

In that study, biomass crops were compared with the hyperaccumulating crops yellow-tuft (Alyssum murale Waldst. & Kît.) and Thlaspi caerulescens J. Presl & C. Presl. With the exception of Indian mustard, even without NTA application, Cd, Zn, and Cu accumulation was higher or at least on the same level as that of the hyperaccumulating crops; especially tobacco showed considerably higher Cd accumulation than the hyperaccumulators. The authors explained the rather low heavy metal removal of the latter by the low dry matter production, which was between 0.5 and 1 Mg ha\(^{-1}\). Methodical problems can be excluded because plot size was 2.5 \(\times\) 2.5 m with four replicates, enabling reliable yield extrapolation.

In a field experiment with Pb-contaminated soil (8000 g Pb kg\(^{-1}\)), Kayser et al. (1999a) showed that, in combination with the addition of NTA, glyphosate increased the Pb concentration in Indian mustard more effectively than NTA application alone. The combination resulted in a 2.5-fold increase to 280 mg Pb kg\(^{-1}\) (NTA alone, 1.2-fold). This increase was somewhat lower than when glyphosate was combined to the application of EDTA (Kayser et al., 1999a).

On a site contaminated with Pb (total and dissolved Pb: 660 and 1.2 mg kg\(^{-1}\)) and Zn (total and dissolved: 500 and 10 mg kg\(^{-1}\)), 22 g of sodium NTA were injected into the rooting zone of corn plants, split into four applications (Schmidt and Kaupenjohann, unpublished data, 2002). Slight increases of Pb (23–35 mg kg\(^{-1}\)) and Zn (150–180 mg kg\(^{-1}\)) concentrations in corn were observed. Glyphosate application had no effect on heavy metal removal.

The Effect of Other Organic Acids on Heavy Metal Phytoextraction

Ebbs et al. (1998b) and Huang et al. (1998) reported that the addition of citric acid and its salts selectively increase uranium mobility in soil and subsequently also plant uptake. The authors suggest that the strong mobilization of U by citric acid is due to the formation of citrate–uranyl complexes rather than to the decreased pH. Huang et al. (1998) found a close correlation between the U and the Fe and Al concentrations in the soil solution after the addition of citric acid, which they explained by the dissolution of Fe and Al sesquioxides and hence release of U from soil material to the soil solution. In a carbonate solution, U can form carbonate or hydroxide complexes, which are highly soluble (Grabovnikov and Samsonova, 1968). Elless and Lee (1998) state that for U solubility in soils, U-bearing minerals are more important than sorption–desorption processes.

Adding 10.5 mg citric acid kg\(^{-1}\) to a potted soil that contained 310 mg U kg\(^{-1}\) enhanced uranium solubility 73-fold to 110 mg U kg\(^{-1}\), whereas adding HEDTA at the concentration of 5 g kg\(^{-1}\) had no significant effect (Ebbs et al., 1998a). The authors chose the different concentrations of these agents from positive results of other studies, which were made with Pb. In the same study, 10.5 mg citric acid kg\(^{-1}\) increased the U concentration in the dry matter of Swiss chard (Beta vulgaris L. subsp. vulgaris) 14-fold from 15 to 200 mg kg\(^{-1}\), whereas no effect was observed after the HEDTA application. Ebbs et al. (1998b) observed optimum U solubilization with citrate over the pH range from 4 to 5, with soluble U concentrations considerably higher than those at pH 6 or 6.8. In this study, at pH 5, adding 0.61 g kg\(^{-1}\) of potassium citrate increased the soluble U concentration 93-fold.

In a pot study (with a soil U concentration of 280 mg kg\(^{-1}\)), the addition of 0.95 g kg\(^{-1}\) of citric acid enhanced the soluble U concentration in the soil 35-fold, whereas the addition of several artificial chelating agents (EDTA, HEDTA, DTPA) at the same molar concentrations (5 mmol kg\(^{-1}\)) had negligible effects (Huang et al., 1998). When 20 mmol kg\(^{-1}\) were added, the increase was 200-fold and several times stronger than after applying malic acid or mineral acids, which reduced the soil pH by a similar magnitude from 7.3 by 0.5 to 1 units. In this study with more highly contaminated soil (750 mg U kg\(^{-1}\)), the U concentration in the tissue of 4-wk-old Indian mustard increased 1000-fold from <5 mg U kg\(^{-1}\) up to 5200 mg U kg\(^{-1}\) within 3 d after adding citric acid. When other organic acids (malic and acetic acid) were added in the same concentrations, the U concentrations...
were 2100 and 1700 mg U kg\(^{-1}\), respectively. No information is available on the concentration of U in the soil solution after the addition of the acids in this soil. Citric acid increased the U concentrations in all plant species tested. Among the best species, that is, those with shoot concentrations of more than 3500 mg U kg\(^{-1}\), Indian mustard showed higher U concentrations and U contents per pot than Chinese cabbage \([Brassica rapa L.\) subsp. pekinensis (L.) Hanelt\], Chinese mustard \([Brassica rapa L.\) subsp. chinensis (L.) Hanelt\], and amaranth \((Amaranthus spp.)\). The U concentration of pea was 1000 mg kg\(^{-1}\), but was below 500 mg kg\(^{-1}\) in sunflower, cowpea \([Vigna unguiculata (L.) Walp.]\), wheat \((Triticum aestivum L.)\), and corn. Despite those differences, note that citric acid generally had an enormous effect because the control plants had all U concentrations of \(<5\) mg kg\(^{-1}\). The authors showed that the choice of cultivars also had a significant effect on the U yields realized per pot; they observed variations of a factor of 2.

Little information is available about heavy metal accumulation following the application of other natural organic acids to contaminated soils. Nigam et al. (2001) found that the Cd accumulation by corn after applying the carboxylic acids citric and malic acid to a Cd-spiked soil \((3.5\ \mu M kg^{-1}\) or 0.39 mg kg\(^{-1}\)) was enhanced; it was also higher than with the amino acid aspartic acid or glycine. The organic acids were applied in the same molar concentrations as Cd to the soil, and the Cd concentrations in corn shoots were more than doubled with citric acid \((to\ 19\ mg\ kg^{-1})\) and also significantly increased with malic acid \((to\ 15\ mg\ kg^{-1})\). A dominant pH effect can be excluded here because, in all treatments, pH was adjusted to 5.5 with 0.1 M HCl. This study therefore showed that organic acids, which are commonly exuded by the roots of corn plants, also effectively enhance phytoextraction when added to the soil.

Blay et al. (1997) explain the heavy metal mobilization of natural organic acids by several mechanisms including surface complexation with subsequent complex dissociation, soil acidification, cation exchange (through ammonium) and reductive solution of soil metal (hydr)oxides. In a column experiment without growing plants, Fischer et al. (1998) found that grass silage effluents, mainly consisting of malate and lactate, reduced the total Zn, Cd, Pb, and Cu concentrations of highly contaminated soils by 56, 75, 5, and 54%, respectively. A fraction of 62% of the total Cu was extracted from soil by percolating a blood meal hydrolysate (consisting of a range of several amino acids) through soil columns (Blay et al., 1997).

The Application of Complex Organic Matter

The addition of peat and manure increased Cu, Zn, and Ni accumulation by wheat in the study of Narwal and Singh (1998), but in other studies reduced the uptake of Pb, Cu, and Cd by corn \((Gorlach and Gambus, 1992)\) and of Cd by ryegrass \((Erikkson, 1988;\) He and Singh, 1993). No positive or negative effect on Cd and Zn accumulation by adding peat to perennial ryegrass was found by Juste and Solda (1988). Peat and manure are quite heterogeneous substances that can concurrently exert mobilizing and stabilizing effects. Small structural and chemical differences can favor one or the other effect. On the one hand, acid peat reduces soil pH, which increases the concentration of soluble metals in soils. On the other hand, it increases the cation exchange capacity (CEC) of soils, providing sorption sites and reducing metal mobility, having a higher binding affinity but fewer binding sites for Cu than for Pb \((Logan et al., 1997)\). Besides these chemical processes, which directly affect the solubility of heavy metals in soils, peat and manure can facilitate plant growth in poor soils, providing a higher nutrient and water supply to the crops. Possibly, the higher reported heavy metal extractions are a side effect of higher biomass accumulation.

The effect of peat or manure for either phytostabilization or for phytoextraction purposes cannot be predicted because of poorly quantifiable heterogeneous effects.

USING INORGANIC AGENTS TO ENHANCE PHYTOEXTRACTION

Enhanced phytoextraction through inorganic amendments can be clearly separated from organic amendments because the mechanisms of solubilization differ considerably. This chapter cites several studies to show that these mechanisms were utilized for enhanced phytoextraction. As was the case for organic agents, inorganic agents were also mainly tested in pot experiments. The agents were added after the crops were germinated or transplanted from uncontaminated culture substrates.

Mechanisms of Solubilization

In contrast to complexation processes, the solubilization of heavy metals through inorganic agents relies mainly on desorption \((Brümmer et al., 1986)\). Heavy metal solubility in soils is mainly controlled by the soil reaction \((pH)\), the amount and kind of sorption sites, and the total amount of heavy metals in the soil \((Brümmer et al., 1986;\) Hornburg and Brümmer, 1993; Gray et al., 1999). Soluble metals are potentially bioavailable and can either be taken up by plants, leached into the ground water, or desorbed again by the exchange sites of the soil.

The proportions of the soluble content of Cd and Zn increased strongly as pH decreased below 6.5 and 5.3, respectively \((Hornburg and Brümmer, 1993)\). The Cu and Pb solubilities increased strongly as pH decreases below 4.5 and 3.5, respectively; above these values, solubilities are mainly controlled by organic and inorganic metal complexes. According to Hornburg and Brümmer \((1993)\) and McKenzie \((1980)\), mobilization decreases in the order Cd $>$ Ni $>$ Zn $>$ Cu $>$ Pb. The mobility of As, however, decreases with decreasing pH \((Irgolic, 1994)\). Most inorganic agents used for phytoextraction reduce the soil pH. Soil pH can be lowered by adding reduced sulfur with subsequent oxidation by soil microbes, or by physiological acidification of the rhizo-
sphere soil after ammonium fertilization, due to a surplus of cation uptake relative to anion uptake (Marschner, 1986). However, the growth of most crops is hampered if the soil pH is <4 (Marschner, 1986) because of the toxicity of soluble aluminum and/or calcium and magnesium deficiency.

Once heavy metals are transferred from their sorption sites into the soil solution and eventually removed from the soil, further proton attack will dissolve several soil minerals (Tessier et al., 1979; Zeien and Brümmer, 1989). The extent of this process is dependent on the capacity of a soil to buffer protons, as determined by the nature of the soil minerals. During continuous proton attack, the solubilization rate decreases with time, and in aerated soils, solubilization can mostly be described by first-order kinetics for several metals (Aringhieri and Pardini, 1985); this was shown by a pHstat technique in which the soil was kept at pH 3 for several hours (Schwarz et al., 1999). The authors showed that the extent of resupply varied considerably between soils due to the soil-specific mineralogy. The technique allows the classification of soils into groups describing their metal-specific buffer capacities. By providing this classification, the method could potentially be used to characterize the susceptibility of a certain soil for enhanced phytoextraction, and also for heavy metal leaching, by decreasing pH.

When salts are added to soils, they dissociate in the soil solution to positively charged metal ions and negatively charged anions. Depending on their concentration and type, these cationic components can exchange heavy metals from (unspecfic) sorption sites in the soil. As an additional effect, soluble metal-chloride salts, especially the relatively stable Cd-chlorides, followed by Pb-chlorides, can be formed (Doner, 1978; Zeien and Brümmer, 1989).

**Sulfur Application**

The addition of different amounts of S in a series of pot experiments lowered the soil pH from 5.7 to values below 4 (Tichy et al., 1997). The highest increase of Cd removal by common mustard (*Sinapis alba* L.) from an artificially highly polluted soil was 1.3-fold at a pH of 5; the Cd concentration was 100 mg kg\(^{-1}\) in the shoot and about 1 mg Cd could be removed from 1 kg of soil, which was previously spiked with a Cd salt to achieve a Cd concentration of 25 mg kg\(^{-1}\). At lower pH values, Cd concentrations in the plants increased (doubled at pH 3.5), but crop yields greatly decreased. In the same study, the authors found that microbially produced elemental sulfur, which was produced by *H. S* oxidation, oxidized without lag period after its addition to the soil. In contrast, commercially available orthomurbic sulfur flour showed a considerable delay before oxidation and a lower oxidation rate.

In field and pot studies with several plant species (Kayser et al., 1999b, 2000), enhancing phytoextraction through sulfur application on calcareous soils was studied. In a pot experiment with contaminated calcareous soil (calcium carbonate content 6.4%), adding 12.8 g of sulfur kg\(^{-1}\) lowered the pH from 7.2 to 3.6 and enhanced Cd mobility 10-fold (Kayser et al., 1999b). The Cd concentrations in the plant tissue of Indian mustard increased 27-fold to 84 mg kg\(^{-1}\). In the same experiment, the Cd concentration in tobacco increased 14-fold to 700 mg Cd kg\(^{-1}\). No change was observed in another soil that contained 14% CaCO\(_3\).

In a field experiment conducted with the latter soil, however, relatively high amounts of sulfur had significant effects (Kayser et al., 2000). When 1.15 kg sulfur m\(^{-2}\) were mixed into the rooting zone of tobacco, sunflower, corn, and willow, the Cd and Zn concentrations in the crops increased 1.4- to 2.2-fold, but the Cu concentrations did not change. Between germination or transplanting and harvesting, the soil pH dropped from 7.2 to 6.9 on average. Since the carbonate content was high and by far sufficient to buffer H\(^+\) input through S oxidation, this indicates that buffering is limited kinetically. During this field experiment, no biomass reduction was observed; the most Cu (510 g ha\(^{-1}\)) and Zn (3.4 kg ha\(^{-1}\)) were accumulated by sunflower and the most Cd (41 g ha\(^{-1}\)) was accumulated by tobacco. The Cd concentration of tobacco was approximately six times the soluble Cd concentration of the soil, and sunflower accumulated 13 times the soluble Zn, but only a quarter of the soluble Cu. This indicates that during the 120 d of plant growth in the contaminated soil amended with sulfur, considerable amounts of Cd and Zn were released from the soil sorption places into the soil solution and were consequently taken up by the plants.

Probably less sulfur will be necessary when the soils that have to be remediated have lower buffer capacities than those used by Kayser and coworkers. Before phytoextraction is implemented, the soil buffer characteristics should be determined to estimate the proper amount of agents to be used for phytoextraction.

**Ammonium Sulfate Application**

The effect of ammonium sulfate fertilization on phytoextraction was especially tested for enhanced Cd and Zn accumulation because these heavy metals can easily be solubilized at those pH values that are predominant in agricultural soils, whereas the solubilization of Pb and Cu occurs at lower pH values, as already mentioned above.

After the application of ammonium sulfate (equal to 500 kg N ha\(^{-1}\)) to a soil contaminated with 20 mg Cd kg\(^{-1}\) and planted with perennial ryegrass, the soil pH decreased from 5.5 to 4.9 (Juste and Solda, 1988). No soluble Cd concentrations in the soil were measured, but the Cd concentrations of the crop increased 1.5-fold to 27 mg kg\(^{-1}\) as compared with ammonium nitrate fertilization. Even though the Zn and Ni concentrations of this soil were rather low (38 and 56 mg kg\(^{-1}\)), their crop concentrations were doubled to 204 and 100 mg kg\(^{-1}\), respectively, and plant yield was not affected.

In a pot experiment the effect of ammonium sulfate fertilization on the accumulation of Cd and Zn by willow was tested (Schremmer et al., 1999). Noncalcareous moderately contaminated soils (1.9–2.4 mg Cd kg\(^{-1}\))...
were fertilized with ammonium sulfate (equal to 100 mg N kg$^{-1}$) and the plants grew for 120 d. The Cd and Zn concentrations in willow increased up to 2.2-fold (up to 45 and 400 mg kg$^{-1}$, respectively), compared with potassium nitrate fertilization. The Cd and Zn concentrations in the rhizosphere soil solution increased up to 2- and 2.5-fold, respectively, but in the bulk soil (defined as the soil material more than 2 mm away from the root surface) the increase was significantly smaller. No effect on the growth of willow was observed from the different fertilizers.

Because N fertilization is a common agricultural measure, the use of ammonium sulfate can be considered as a low-cost strategy, but one which only minimally enhances phytoextraction.

**Salt Application**

Because Cl$^{-}$ ions are known to form stable inorganic Cd complexes, most experiments that examined the effect of salt addition to contaminated soils used Cl salts, mostly NaCl. Unfortunately, some studies failed to provide the application rates of salts, complicating comparisons between the different investigations.

**Chloride Salts**

In a field study conducted on a Cd-contaminated field with a range of pH (6–8) and salinity (expressed as Cl concentration with 2–1700 mg Cl kg$^{-1}$), Norvell et al. (2000) found that 66% of the variability of Cd in durum wheat grain (Triticum turgidum subsp. durum) could be explained by both the chloride concentration in the soil and the DTPA-extractable (roughly plant-available) Cd pool. Interestingly, the Cd concentration in grain was not closely related to soil pH.

In a pot experiment with very high soluble Cd concentrations in the soil (5 mg kg$^{-1}$), increasing additions of NaCl increased the Cd concentration in the soil solution and in the leaf tissue of Swiss chard (Bingham et al., 1983). Biomass yields decreased, but not proportionally, resulting in a net enhancement of Cd removal. The maximum Cd accumulation with a 1.9-fold net increase (to a maximum of 95 mg Cd kg$^{-1}$) compared with the control treatment was achieved at a NaCl concentration in the saturation extract of 6 mM. In another study, the Cd concentration of Swiss chard leaves was doubled to 3.3 mg Cd kg$^{-1}$ in a soil of pH 4.6 with a concentration of 0.2 mg EDTA-extractable Cd kg$^{-1}$, when the NaCl concentration in the saturation extract was 60 mM (Smolders et al., 1998). The plant biomass grown on this soil was generally low and remained low after the salt addition, but the Cd concentration in the plant tissue doubled. Adding NaNO$_3$ in the same molar concentration did not affect Cd concentration in either soil or plant. The authors found that with another soil of pH 5.4, the yield potential was higher, but Cd removal per pot remained unchanged after NaCl application; this is because the biomass yield decreased and the Cd concentration in the plant tissue increased proportionally. Thus, enhanced heavy metal accumulation after NaCl application is not a general rule. The authors found that the solution concentration of free metal Cd$^{2+}$ was not significantly affected by NaCl and concluded that the enhancing effect of NaCl on Cd concentration in the crop is due to chloride complexation of Cd.

Maxted et al. (2001) field-tested the application of KCl to a corn stand on a highly Cd-polluted soil (15.9 mg soluble Cd kg$^{-1}$). Here, 3 g KCl kg$^{-1}$ enhanced Cd concentration in the plants from 5 to 7.5 mg kg$^{-1}$, giving the same result as a 0.6-g EDTA treatment. The authors stated that, for phytoextraction, the use of KCl is preferred over EDTA due to lower costs and shorter persistence of soluble Cd complexes in the soil solution.

Keller et al. (1999) determined that the addition of ammonium chloride did not affect Zn accumulation. When 10 mmol of NH$_4$Cl kg$^{-1}$ (354 mg Cl$^{-}$ kg$^{-1}$) were added to a calcareous soil with a Zn concentration of 700 mg kg$^{-1}$ and planted with eared willow (Salix aurita L.), the Zn concentration in the soil solution increased 1.5-fold, but the concentration in the crop increased only slightly to a maximum value of 900 mg Zn kg$^{-1}$. In this study, the concentration of salts was considerably lower than in that of Maxted et al. (2001) and, clearly, the ammonium cations had an only small cation exchange effect that did not boost phytoextraction. Moreover, the extent of the formation of Zn–Cl complexes is several times lower than for Cd–Cl complexes (Hornburg et al., 1995).

**The Role of Liming in Heavy Metal Accumulation**

Liming is a common method to decrease the heavy metal mobility in soils and their accumulation in plants. However, applying calcium carbonate to contaminated noncalcareous soils has been observed to both reduce (Sims and Kline, 1991; Hooda and Alloway, 1996; Krebs et al., 1998) and increase metal mobility (Sims and Kline, 1991; Maier et al., 1997). In the field, liming reduced Cd and Zn concentrations in field pea (Pisum sativum L. var. arvense (L.) Poir.) (Krebs et al., 1998) to 50 and 60%, respectively, but increased the Cd content of potato (Solanum tuberosum L.) tubers 1.5-fold (Maier et al., 1997). In the long term, liming of acidic soils can decrease metal mobility by increasing soil pH. On the other hand, the calcium cation is a competitive exchanger for cations that are unspecifically bound to sorption sites in the soil. Mainly in slightly acidic soils, the addition of Ca$^{2+}$ may therefore enhance metal availability.

Cunnane et al. (1993) and Elless and Lee (1998) reported that, because of the formation of relatively highly soluble U–carbonate complexes after liming of carbonate-rich, uranium-contaminated soils, the mobility of U in these soils increased and the underlying ground water was polluted. Vangronsveld and Cunningham (1998) summarized that in most cases heavy metals in soils can be effectively stabilized with iron or manganese oxides. Especially at low soil pH, liming is recommended as a supporting measure because heavy metal complexation on the surface of those minerals has its optimum at pH 7 (Mench et al., 1998).

Further studies should be conducted with salts other
Table 2. Relative effects (categorized as high, medium, small, or none) of different agents on heavy metal accumulation across all studies cited regardless of heavy metal leaching effects.

<table>
<thead>
<tr>
<th>Agent†</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Zn</th>
<th>U</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDTA, CDTA</td>
<td>high</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>NTA</td>
<td>medium</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>Organic acids</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>small</td>
<td>none</td>
</tr>
<tr>
<td>Sulfur</td>
<td>none</td>
<td>medium</td>
<td>none</td>
<td>medium</td>
<td>none</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>none</td>
<td>small</td>
<td>none</td>
<td>small</td>
<td>small</td>
</tr>
<tr>
<td>Salts</td>
<td>small</td>
<td>none</td>
<td>small</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

† CDTA, 1,2-cyclohexylenedinitrilotetraacetic acid; EDTA, ethylenediaminetetraacetic acid; NTA, nitrilotriacetic acid.
‡ With Cd-spiked soil.
§ Citric > malic ≥ acetic acid.
¶ NaCl > KCl.

than NaCl because Na damages soil structure more than other salts (Scheffer and Schachtschabel, 1998). Because specific Pb–Cl complexes can also be formed (albeit to a lesser extent than Cd–Cl complexes), experiments on enhanced phytoextraction are encouraged that study the effect of chloride salt applications on Pb-contaminated soils.

As a result of the compilation of the cited literature and to allow a comparison of organic and inorganic agents, the efficiencies of these agents for the accumulation of several heavy metals by crops are classified in Table 2. Note, however, that this table exclusively presents the effects on enhanced phytoextraction and that environmental pollution by enhanced leaching is not assessed.

LEACHING OF HEAVY METALS
Enhanced Leaching through Enhanced Phytoextraction

Only in rare cases was heavy metal leaching after enhanced phytoextraction quantified. Most studies did, however, report that soluble heavy metal concentrations in the soil were affected by enhanced phytoextraction. The common feature across all studies was that heavy metal solubility in soils was more strongly enhanced than accumulation by plants. Moreover, with increased additions of agents, the ratio of soluble versus accumulated heavy metals increased (Fig. 2). Based on data availability, this effect is illustrated using results from experiments on the effect of EDTA addition on Pb accumulation (25 paired samples from various pot experiments).

On average, plants extracted 1% of the soluble Pb after the addition of EDTA or related substances; in the vast majority of all studies, this value was lower than 0.2%. The highest values of the ratio of soluble versus accumulated heavy metals were clearly obtained at low or no chelate additions. Above 1 g EDTA kg⁻¹, plants never extracted more than 1% of the soluble Pb. The conclusion of this relationship is that the risk of Pb leaching definitely increases with increased chelate application. Together with the high persistence of Pb–chelate complexes, the use of these agents in contaminated fields could pose severe environmental problems.

In soil column experiments conducted with several soils of differing calcium carbonate content and concentrations of heavy metals, considerable amounts of heavy metals were leached after the addition of 14 g EDTA kg⁻¹ (Sun et al., 2001). The fractions of the total heavy metal amounts leached after 8 d were: Zn, 9 to 51%; Cd, 12 to 45%; Pb, 3 to 31%; and Cu 3 to 57%. Although this EDTA concentration was higher than those used in the phytoextraction experiments presented here, the results showed that heavy metal leaching differed considerably across the soils. By conducting sequential heavy metal extractions, the authors were able to show that EDTA also extracted Zn and Pb from the residual fraction (which is considered to be the silicate-bound heavy metals) of some of the tested soils.

In a soil column phytoextraction experiment, cabbage was planted on a Pb- and Cd-contaminated soil (1100 and 5.5 mg kg⁻¹, respectively) and 2.9 g EDTA kg⁻¹ were added to each soil (Grcman et al., 2001). Three weeks after the EDTA treatment, 19% of the total Pb was leached from the soil. After calculating a mass balance, the authors found that 315 times more Pb, 200 times more Zn, and 245 times more Cd were leached than taken up by the crop. The authors also showed a correlation between the amount of water added in this column study and the amount of heavy metals accumulated and leached after EDTA application. More metals were leached and less accumulated when the total of 3 L water per column was increased to 4.2 L. The ratio of leached to accumulated Pb, Zn, and Cd increased from 315 to 1000, from 200 to 400, and from 245 to 425, respectively.

Much lower heavy metal leaching was found by Schremmer et al. (1999), who tested the effect of ammonium sulfate vs. calcium nitrate as N fertilizers (equal to 100 kg N ha⁻¹) on heavy metal accumulation of willow. In a noncalcareous soil (pH = 6.4) with 1.9 mg Cd kg⁻¹ and 250 mg Zn kg⁻¹, ammonium sulfate fertilization doubled the Cd concentration in the rhizosphere soil and increased the Zn concentration 2.7-fold. As a consequence, in contrast to nitrate fertilization, the amount of Cd and Zn leached per pot increased from 1.4 to 2.6 µg Cd and from 0.22 to 0.53 mg Zn pot⁻¹.
A mass balance showed that after ammonium sulfate fertilization, 11 and 7 times more Cd and Zn were accumulated than leached, respectively, whereas after nitrate fertilization, this ratio was only 4.7 and 4, respectively.

The prerequisites for heavy metal leaching are that (i) heavy metals can generally only be transported downward in the soil when they are in a water-soluble state (ionic or complexed) and (ii) the soil solution percolates. Heavy rainfalls no doubt wash soluble heavy metals into deeper soil layers as ions or, to a lesser extent, as colloids; in soils that tend to show preferential flow characteristics (in contrast to matrix flow), fast transport is possible. When on the field scale the mobilization is limited to the upper soil layer or to the main rooting zone, it can be assumed that metals will be transported into deeper soil horizons through downward water flow. In soils with predominant preferential flow, metals can be moved to the ground water quickly (Camobredo et al., 1996).

After the vegetation period, evapotranspiration is generally reduced due to reduced irrigation and plant growth. This promotes the downward movement of water in soils and, therefore, promotes leaching. This leaching has to be prevented in contaminated soils when the water balance is positive and/or strong rainfalls can cause percolation. It is, therefore, an important objective of all measures of enhanced phytoextraction that, especially after the vegetation period, the concentrations of heavy metals in the soil solution (which were previously enhanced during plant growth) are now reduced to their initial values if possible. When persistent organic agents are used to enhance phytoextraction, however, and especially as they are applied shortly before harvest, this objective clearly cannot be achieved.

The degradation rate of metal chelates basically depends on their stability constants, the microbial activity of the soil (which is mainly dependent on the soil water content, soil temperature, and redox potential), and on the concentration of free, ionic metals (Tabatabai and Bremner, 1975; Xun et al., 1996). Organic acids were degraded within 2 wk (Krishnamurti et al., 1998) and the half-lives of several Zn complexes in soils with oxalic, citric, and acetic acid were below 2 d (Wenger et al., 1998). Because the enzymes of microorganisms are not adapted to mineralizing artificial organic matter, their degradation is rather slow (Tiedje, 1977; Bolton et al., 1993; Stumpf, 1996) and metals remain soluble longer. Complexes of several metals (Na, Ca, Mg) with EDTA were degraded aerobically within 4 h, but Fe(II)EDTA remained in the synthetic waste water solution as a relatively inert molecule (Henneken et al., 1998). In soil, only 1% EDTA and 6% DTPA were mineralized within 120 d (Bolton et al., 1993). The latter was found to be entirely complexed with Fe. The heavy metal forms of chelates are usually degraded much slower than other metal chelates (Tiedje and Mason, 1974; Tiedje 1975).

In laboratory experiments, Na,NTA was completely mineralized in several soils after 10 d (Tabatabai and Bremner, 1975), but Wenger et al. (1998) showed that after the addition of 0.95 g NTA kg\(^{-1}\), the decomposition of Zn–NTA complexes did not start until 20 d after formation. When 4.8 g NTA kg\(^{-1}\) were added, no decomposition was observed within 50 d, perhaps due to a toxic effect on soil microbes. Kulli et al. (1999) observed Zn and Cu concentrations near the original level 24 d after applying a considerably lower amount of 0.25 g NTA kg\(^{-1}\).

In contrast, when a soil is acidified by noncomplexing agents, protons can be buffered rather quickly depending on their release rate and the buffer capacity of soils. In several studies, alternative application methods of mobilizing agents were tested to reduce leaching of heavy metals. The main idea is that the metals should be available close to the plant roots and be taken up quickly.

Reducing Metal Leaching

Some studies were designed to test the combination of high metal accumulation of plants and reduced metal leaching. For example, by placing NTA 15 cm deep, the amount needed to enhance heavy metal accumulation was lower than when mixing this agent into the entire soil. In contrast to mixing ammonium sulfate to the soil, the efficiency of phytoextraction was enhanced when it was placed into the rooting zone. This method was adapted from the field of nitrate research.

In laboratory experiments, Na,NTA was completely mineralized in several soils after 10 d (Tabatabai and Bremner, 1975), but Wenger et al. (1998) showed that...
tory and leaching was only partly measured, but not compared between the two measures. Thus, at this point, no definitive assessment can be made of the advantage of dosage splitting via leaching measurements or via calculations of accumulation efficiencies.

Data are lacking concerning heavy metal leaching due to enhanced phytoextraction and on the effect of measures to reduce leaching of heavy metals. More pot and field studies should be made to quantify and assess measures to reduce heavy metal leaching. When designing pot studies to measure leaching, the water content should surpass the soil’s water holding capacity several times to meet realistic conditions. The frequency and amount of these induced leaching events can easily be adapted to the known number of heavy rainfall events. In pot experiments, sampling the leachate produced by excess water supply as well as measuring the amount of leachate and its metal concentration is a simple way to quantify metal leaching from the soil columns. In the field, the following methods can be used: (i) a combination of suction cups with water balance models (but insufficient consideration of preferential flow), (ii) wick-samplers, or (iii) monitoring boxes, which are filled with ion exchange resins and are placed under the rooting zone during the vegetation period (Bischoff et al., 1999).

THE APPLICATION OF PHYTOEXTRACTION

If non-hyperaccumulating plants are used for phyto-remediation of polluted soils, two prerequisites must be fulfilled for the creation of sustainable agronomic systems in which high heavy metal extraction rates are combined with prevention of heavy metal leaching: (i) agronomic and climatic suitability of the particular contaminated site, enabling high dry matter biomass production in the frame of a suitable crop rotation system, and (ii) tolerance for heavy metals. Besides relying on the choice of appropriate crop species and varieties, phytoextraction requires good crop management to optimize growth conditions for given climates and soil and management practices. Various soil amendments are only a supplementary approach to enhancing heavy metal accumulation of plants.

Choice of Suitable Crops

Enhanced Phytoextraction or Hyperaccumulators?

As mentioned earlier, biological soil remediation requires either hyperaccumulating plants or metal-tolerant crops. The main differences between these groups are that the former can have considerably higher heavy metal concentrations in their tissue, and that the latter can boost dry matter biomass production. Because heavy metal removal is the product of both parameters, it is useful to determine which group performs better, especially under consideration of enhanced phytoextraction. Finally, the aim of phytoextraction is its implementation on contaminated fields. Therefore, the processing of the metal-rich biomass after harvest is also an issue.

Field trials demonstrate that the capacity of both plant groups to remove heavy metals is similar, or that those plants which achieve a high biomass accumulation during the growing season (referred to herein as biomass crops) have an even higher rate of metal removal than hyperaccumulators. In pot experiments, Ebbs et al. (1997) found that the dry matter biomass of rape and Indian mustard were 13 times the biomass of *Thlaspi caerulescens*. Cadmium removal was the same for these plants, but four times more Zn was removed by the Brassicaceae. In another pot experiment, Lombi et al. (2001) determined that *T. caerulescens* had the same biomass as corn and extracted 8 to 63 times more Cd and 4 times more Zn than corn due to its higher heavy metal tissue concentrations. On average, the uptake of Pb did not differ in two soils of different contamination levels between *T. caerulescens* and corn. The *T. caerulescens* plants had a maximum dry matter biomass of 12.7 g per pot (1 kg soil) after approximately 30 d of growth time. Earlier, the same working group found a dry matter biomass of only 1 g per pot (600 g soil), probably due to unfavorable growth conditions. After 90 d of growth, Perronnet et al. (2000) measured 3 g dry matter per pot, filled with 500 g of contaminated soil. In field studies, *T. caerulescens* reached dry matter biomasses of 2 Mg ha$^{-1}$ (Kayser et al., 2000) and of 3.7 to 5.7 Mg ha$^{-1}$ (McGrath, 1998). In the former study, it removed roughly the same amounts of Cd and Zn as corn or sunflower (with dry matter biomasses of 19 and 25 Mg ha$^{-1}$, respectively), but when 1.16 kg S m$^{-2}$ or 4.6 g NTA m$^{-2}$ were applied to the non-hyperaccumulating crops, Cd and Zn removals were three to six and two times higher, respectively. More comparative field studies in several climatic zones are needed to assess whether hyperaccumulating plants or metal-tolerant biomass crops have higher Cd and Zn uptake rates.

Metal-tolerant plants clearly show preferences for certain heavy metals (Table 3). They therefore tolerate high concentrations of these metals in the soils, tolerate increased mobility of these metals, and show greater accumulation when availability is increased by soil manipulations. With enhanced phytoextraction, willow has the highest remediation capacity for Cd-contaminated soils. Because too few field experiments on enhanced phytoextraction of Pb have been conducted, it is not possible to recommend a particular crop. Indian mustard, perennial French ryegrass, corn, and sunflower show high Pb concentrations; however, only the combination of heavy metal concentrations, crop dry matter yields, and heavy metal leaching rates will show if these crops can be part of a sustainable phytoextraction management. Willow has a high capacity for Zn phytoextraction, and sunflower is the best choice for the enhanced phytoremediation of Cu-polluted land. Field trials are needed to prove the promising capacity of Indian mustard to extract high amounts of uranium under the conditions of enhanced phytoextraction.

When the aim is to increase the efficiency of phyto-remediation by soil manipulations, annual plants seem to be more appropriate than perennial plants. The roots of annual plants grow mainly in the contaminated upper
Table 3. Ranges of dry matter yields, heavy metal concentrations, and heavy metal yields of metal-tolerant crops after enhanced phytoextraction. Heavy metal yields were calculated if dry matter (DM) yields were indicated in the cited literature. No differentiation was made between pot and field experiments. Higher values were mostly measured or calculated from results of pot experiments.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Crop</th>
<th>DM yield</th>
<th>Heavy metal concentration</th>
<th>Heavy metal yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mg ha⁻¹</td>
<td>mg kg⁻¹</td>
<td>g ha⁻¹ yr⁻¹</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>willow</td>
<td>10–16</td>
<td>3–40</td>
<td>80–220</td>
<td>Riddell-Black et al., 1997; Riddell-Black, 1999; Kayser et al., 2000; Schremmer et al., 1999</td>
</tr>
<tr>
<td></td>
<td>tobacco</td>
<td>9–13</td>
<td>9–40 (120)</td>
<td>90–115</td>
<td>Kayser et al., 1999a, 2000</td>
</tr>
<tr>
<td></td>
<td>Indian mustard</td>
<td>4–24</td>
<td>1.5–73</td>
<td>4–60–80</td>
<td>Blaylock et al., 1997; Kayser et al., 1999a, 2000</td>
</tr>
<tr>
<td></td>
<td>corn</td>
<td>10–11</td>
<td>1–9</td>
<td>11–74</td>
<td>Kayser et al., 1999a, 2000</td>
</tr>
<tr>
<td></td>
<td>Swiss chard</td>
<td>33–180 (leaf)</td>
<td>33–180 (leaf)</td>
<td>33–180 (leaf)</td>
<td>Bingham et al., 1983; Smolders et al., 1998</td>
</tr>
<tr>
<td>Pb</td>
<td>perennial ryegrass</td>
<td>5</td>
<td>2.7</td>
<td>13.5</td>
<td>Kulli et al., 1999</td>
</tr>
<tr>
<td></td>
<td>Indian mustard</td>
<td>4</td>
<td>70–280–1670</td>
<td>120–6 680</td>
<td>Blaylock et al., 1997; Kayser et al., 1999a,b</td>
</tr>
<tr>
<td></td>
<td>corn</td>
<td>100–10 600</td>
<td>2.7</td>
<td>13.5</td>
<td>Huang et al., 1997a; Cooper et al., 1999; Wu et al., 1999</td>
</tr>
<tr>
<td></td>
<td>sunflower</td>
<td>5 100</td>
<td>24 000</td>
<td>24 000</td>
<td>Cooper et al., 1999</td>
</tr>
<tr>
<td>Zn</td>
<td>perennial French ryegrass</td>
<td>20</td>
<td>150</td>
<td>3 000</td>
<td>Kulli et al., 1999; Albasel et al., 1985</td>
</tr>
<tr>
<td></td>
<td>sunflower</td>
<td>4</td>
<td>450–700</td>
<td>750</td>
<td>Blaylock et al., 1997; Ebb and Kochian, 1998</td>
</tr>
<tr>
<td></td>
<td>Indian mustard</td>
<td>9–13</td>
<td>200</td>
<td>2 000</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td></td>
<td>tobacco</td>
<td>250–560</td>
<td>450</td>
<td>450</td>
<td>Wilke and Metz, 1992</td>
</tr>
<tr>
<td></td>
<td>perennial French ryegrass</td>
<td>5</td>
<td>505–2 300</td>
<td>2 525</td>
<td>Kulli et al., 1999; Albasel et al., 1985</td>
</tr>
<tr>
<td></td>
<td>willow</td>
<td>10–16 1600</td>
<td>16 000–25 600</td>
<td>16 000–25 600</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td>Cu</td>
<td>sunflower</td>
<td>20</td>
<td>820</td>
<td>16 650–16 400</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td></td>
<td>Indian mustard</td>
<td>4</td>
<td>45</td>
<td>45</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td></td>
<td>tobacco</td>
<td>9–13 45</td>
<td>9–13</td>
<td>45</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td></td>
<td>perennial French ryegrass</td>
<td>7</td>
<td>500</td>
<td>&gt;260</td>
<td>Deram et al., 2000</td>
</tr>
<tr>
<td></td>
<td>perennial ryegrass</td>
<td>5</td>
<td>52–60</td>
<td>52–60</td>
<td>Kulli et al., 1999; Albasel and Cottenie, 1985</td>
</tr>
<tr>
<td></td>
<td>willow</td>
<td>10–16 50</td>
<td>50</td>
<td>50</td>
<td>Kayser et al., 2000</td>
</tr>
<tr>
<td>Ni</td>
<td>perennial French ryegrass</td>
<td>1</td>
<td>300</td>
<td></td>
<td>Deram et al., 2000</td>
</tr>
<tr>
<td>U</td>
<td>red beet (Beta vulgaris L. subsp. vulgaris)</td>
<td>200</td>
<td>500</td>
<td></td>
<td>Ebb and Kochian, 1998</td>
</tr>
<tr>
<td></td>
<td>Indian mustard</td>
<td>1</td>
<td>700–5 200</td>
<td></td>
<td>Huang et al., 1998</td>
</tr>
</tbody>
</table>

soil horizons, whereas the root system of perennials explores deeper horizons and subsoils, which are generally less contaminated (when the metal source was or continues to be anthropogenic). Consequently, during plant growth the shoot metal concentration of perennials tends to decrease with time (Greger et al., 1997). At sites where the soils are contaminated down to deeper horizons, however, perennials might be superior to annual plants. After leaves have fallen to the ground before cutting, a considerable amount of heavy metals cannot be removed from the site, reducing phytoextraction efficiency. When leaves decompose, heavy metals are highly mobile and can easily be leached or taken up by plants, as was shown by Perronnet et al. (2000) for *T. caerulescens*, when one-third of all cadmium in the leaves was water extractable.

Perennial grasses have a high biomass yield but a comparatively low uptake rate of heavy metals under normal field conditions. The perennial grass miscanthus (*Miscanthus sinensis* Andersson) has proven to be a valuable energy crop because it provides a high-energy yield and low concentrations of undesirable contents (ash, chlorides, water) (Lewandowski and Kicherer, 1997). The accumulation of heavy metals, however, is comparably low (Wilke and Metz, 1992; Fernando et al., 1996). Perennial French ryegrass, on the other hand, took up high amounts of Cu, Ni, and Pb when EDTA was added to the soil (Deram et al., 2000). Regarding these results, the possibility of harvesting high amounts of metals with perennial grasses after adding agents to the soil should be studied in more detail.

**Multiple Use**

Phytoextraction, that is, the use of plants for metal accumulation and subsequent physical removal of the contaminated biomass from the site, is not an option on severely polluted soils due to very long remediation times and the risk of plant toxicity. However, to make phytoremediation of low- or moderate-pollution soils economically viable for farmers, additional benefits should be provided. The use of “regrowing resources” is one such multipurpose strategy. On the one hand these crops lower metal concentrations of the polluted soils, while on the other hand their biomass provides potential additional income. It was shown that willow is a crop suitable both for phytoextraction and energy production. This high-yielding crop has proven to be metal-tolerant and to remove high amounts of Cd (Riddell-Black et al., 1997). After combustion, most heavy metals are concentrated in the ash, and a smaller part is retained by activated charcoal filters. A separation between bottom and fly ash fractions during the combustion process concentrated most Cd and Zn into the fly ash (Obernberger et al., 1997).

Perennial trees or grasses are more sustainable for energy production than annual plants, when all relevant factors are considered (Kalschmitt and Reinhardt, 1997; Hartmann and Strehler, 1995). These factors are the energy balance, the emissions of trace gases, the costs, and the combustion quality. At a harvest time that allows maximum biomass accumulation, annual plants have a higher nutrient and metal concentration in the shoots than perennial plants because the elements are not relocated to the root system. Moreover, their interannual water concentration is more variable. As a consequence, the concentration of undesired contents (water, ash) lowers the heating value, which reduces the energy efficiency of annuals versus perennials.

First results show that raw materials containing low
heavy metal contents (like fibers or oil) can also be extracted from plants grown on heavy metal–polluted soils (Grant and Bailey, 1997; Griga et al., 2002).

**Plant Breeding**

Once a suitable plant species for phytoremediation is found for a certain site, cultivars of this species often exhibit high variability of metal accumulation (Kurz et al., 1997; Kloke, 1994). Huang et al. (1997b) reported that three mutants were selected from a vast number of chemically mutagenized *Arabidopsis* plants; these mutants exhibited two- to threefold higher shoot Pb concentrations than their wild-type. Schulman et al. (1999) found a mutant of Indian mustard that exhibited a higher Pb concentration in the tissue due to increased thickness of the cell walls. By agrobacterium-mediated transformation of Indian mustard hypocotyls, Zhu et al. (1999) modified the plant’s metabolism, which was expressed in enhanced levels of glutathione and phytochelatins. These transgensics showed significantly higher shoot levels of Fe, Mn, and Zn compared with wild-type plants due to higher translocation from root to shoot. It is expected that further breeding research with classical or molecular genetic methods will produce a range of crops that can be used for the phytorevetation of several heavy metals. Possibly, these crops can enhance phytorevetation due to their enhanced root to shoot translocation of heavy metals.

**CONCLUSIONS**

For most inorganic contaminants, suitable agents at their proper dosage combined with suitable crops can be chosen for certain sites and contaminants. Enhanced phytorevetation can be the key element to improve the implementation of phytoremediation, because increasing accumulation rates of crops will maximize contaminant removal. It is, however, important to minimize the ecological risks that are connected with enhanced phytorevetation, as reduced plant growth rates or heavy metal leaching. To optimize the ecologic and economic efficiencies, there are still several research needs. Field experiments must be conducted to prove that the measures of enhanced phytorevetation are practicable. Tests should be conducted to combine organic amendments with lowering soil pH or with glyphosate application, split target amounts of agents into several doses, apply agents at late growth stages, and place them into the root zone of crops.

To improve the economic implementation, the measures for enhancing phytorevetation should be tested with crops that have been optimized for phytoremediation by conventional or novel breeding methods. More research is needed to improve combustion techniques of contaminated biofuels, and the production of marketable products from contaminated biomass for industrial use (mainly oils and fibers) should be tested.

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