

Critical Assessment of Chelant-Enhanced Metal Phytoextraction

BERND NOWACK,* RAINER SCHULIN, AND
BRETT H. ROBINSON

*Institute of Terrestrial Ecosystems, ETH Zurich Universitaetstrasse 16,
8092 Zürich, Switzerland*

Chelant-enhanced phytoextraction has received a lot of attention in the past decade. In theory, this technique could cleanse metal polluted soils by solubilizing contaminating metals, allowing them to be taken up by plants that would subsequently be removed from the site. We review the processes of metal solubilization, uptake by plants, and leaching during chelant-enhanced phytoextraction. A large excess of chelant is required to solubilize the target metal due to the co-solubilization of Ca and Fe. Chelated metals are taken up via the apoplastic pathway. Disruption of the Casparian Band is required to achieve the high shoot concentrations needed for phytoextraction. Therefore, adding chelants to a soil increases not only the total dissolved metal concentration but also changes the primary route of plant metal-uptake from the symplastic to the apoplastic pathway. Depending on metal, plant species, and chelant concentration, significant increases in metal uptake are likely. Soil solution chelate concentrations of at least several mM are required to induce appreciable shoot concentrations. A simple calculation reveals that at such soil solution concentrations plants will remove only a small fraction of the solubilized metals. Leaching, exacerbated by preferential flow processes, is unavoidable. Chelant-enhanced phytoextraction is therefore limited to areas where the connection with groundwater has been broken, or where leaching is unimportant. Chelant-enhanced phytoextraction may nonetheless have a role in enhancing the uptake of essential trace metals. Such a role warrants further investigations into the use of biodegradable chelants such as ethylenediaminedisuccinic acid (EDDS).

Introduction

In the past decade, chelant-enhanced phytoextraction has received much attention from the scientific community. This technique aims to cleanse metal-polluted soils by inducing plants to accumulate the contaminating metal in the harvestable parts by adding chelating agents to the soil. The metal-rich biomass could then be removed from the site, and stored in an area where it does not pose a risk to the environment, such as a sealed landfill, or burned (1). However, adding chelating agents to soil may be harmful. The environmental fate of aminopolycarboxylate chelating agents has been discussed extensively (2–4) because they perturb

the natural speciation of metals and influence metal bioavailability (5). Many chelating agents (e.g., EDTA) are not readily degraded under natural conditions and thus persist in the environment (6). The addition of large amounts of chelating agents to soils therefore warrants a thorough evaluation.

Research into the interaction of plants with chelating agents started in the 1950s with a view to alleviating deficiencies in the essential nutrient metals Fe, Mn, Cu, and Zn (5). Initial results also showed that chelants such as EDTA enhanced plant uptake of Pb and Hg (7). Jorgensen in 1993 (8) and Huang and Cunningham in 1996 (9) showed that addition of chelating agents to soils increased Pb accumulation by crop plants to such an extent that they might be used for cleanup of Pb-contaminated soils. A subsequent flurry of research showed that the addition of chelating agents could increase Pb accumulation in shoots of various plants by factors as high as 265 (9–12). Enhanced uptake was not only observed in nutrient solution and pot experiments but also in the field (13–15).

Publications about chelant-enhanced phytoextraction have increased steadily to about 15–20 per year in the last few years, indicating that this is a growing and active research field. Although some reviews and compilations of the available literature have been published (16, 17), there is only limited discussion of the key mechanisms of chelant-induced phytoextraction. Two groups of mechanisms dominate chelant-enhanced phytoextraction. Soil processes determine the mobilization and transport of metals, while plant processes control the uptake and translocation of the solubilized metals. We aim to provide a critical evaluation of the underpinning processes of chelant-enhanced phytoextraction with a view to elucidating the feasibility of this technology and reveal fertile areas for future research.

Terminology

The term “chelate-enhanced phytoextraction” has been frequently used in the literature. However, this term is misleading because it suggests that chelates are applied to the soil. The term “chelate” denotes a complex between a metal and a chelating agent and not the chelating agent itself (18, 19). A shorter word for chelating agent is “chelant” or “chelator”. We therefore suggest using the term “chelant-enhanced phytoextraction”. Other terms such as “chelant-induced” and “chelant-assisted” phytoextraction can be used as synonyms to chelant-enhanced phytoextraction. “Chelate” should be used whenever a metal–chelating agent complex is meant, e.g., when talking about a specific complex.

Soil Factors

The addition of chelants to soil usually increases the concentration of total dissolved metals. Under normal soil

* Corresponding author present address: EMPA – Materials Science & Technology, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland. Phone: +41 (0)71 274 7692; Fax: +44 (0)71 274 7862; E-mail: nowack@empa.ch.

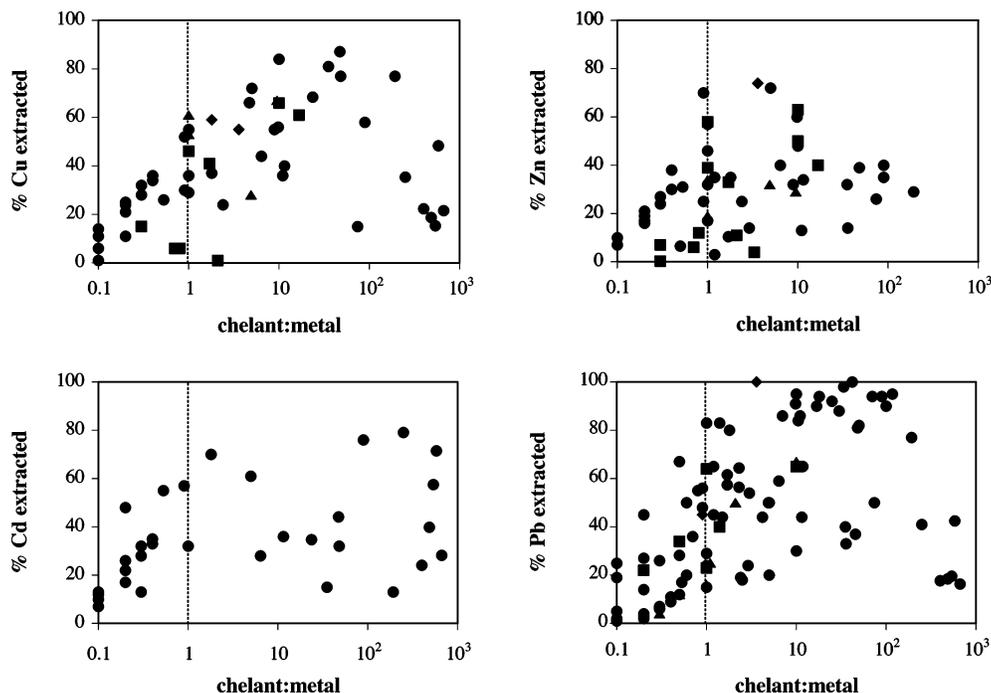


FIGURE 1. Extraction of Cu, Zn, Cd, and Pb from soils polluted naturally in the field with chelating agents (●EDTA, ■NTA, ▲EDDS, or ◆DTPA) as a function of the ratio chelant to total heavy metals. Data are from 28 publications, see Supporting Information for complete bibliography.

conditions, one mole of an aminopolycarboxylate chelating agent complexes one mole of metal. The ratio of chelants to metals in the soil is of overriding importance. As the ratio increases, more chelant is present in soil solution, and metal solubilization is faster and more complete (20). However, this ratio is seldom used to guide the design of experiments. The application rates of chelants are normally 0.5–5 g chelant kg^{-1} soil (9, 11, 21–24), or 1–20 mmol kg^{-1} (10, 25–28), which corresponds to 0.3–6 g EDTA kg^{-1} . Unfortunately, the knowledge of the applied amount is not sufficient to calculate the concentrations of solubilized metals.

To evaluate the metal extraction potential of chelating agents, we compiled data from 28 publications. We selected articles that used soils contaminated under field conditions and where the extractions were carried out over about 24 h at an approximately neutral pH. Figure 1 shows the percentage of extracted metals as a function of the ratio of chelant to total metals in the soil for Cu, Zn, Cd, and Pb. A chelant-to-metal ratio of at least 1 is needed to solubilize all the target metal. However, except for Pb, complete solubilization did not occur, even at a chelant-to-metal ratio of greater than 10. The data show a large variation between soils for a given chelant-to-metal ratio. In particular, the extraction of Zn varied between <5% and 70% at equimolar ratio. This indicates that other factors had a strong influence on the amount of target metal extracted at a given rate of chelant addition.

Modeling Metal Extraction. *Effect of Ca.* Clearly, not all chelant added to soil binds the target metals and other ions also interact with the chelant. In most soils, Ca and Fe are likely to compete with the target metal, due to their high concentrations and the relatively high stability of their complexes (29). The effect of Ca on Pb extraction from a model soil in the presence and absence of EDTA and EDDS (ethylenediaminedisuccinic acid) in the extracting solution is used to discuss the importance of co-dissolved Ca.

First, we modeled the effect of Ca on the extraction of Pb. Calculations were done for different concentrations and sources of Ca in the extraction solution. The description of the used model for Pb binding and solubilization from a soil

(contaminated by sewage sludge applications in the field) is given in the Supporting Information. Three cases are considered: (1) no Ca is present, (2) the solution is in equilibrium with exchangeable Ca, and (3) the solution is in equilibrium with 10% calcite.

Without any Ca present (case 1, Figure 2a), EDTA would be able to extract most of the Pb up to pH 8. When exchangeable Ca is present (case 2, Figure 2a), the extraction of Pb is greatly reduced above pH 6 due to the co-extraction of Ca and competition between Ca and Pb for EDTA. If the soil contains calcite, the Pb extractability is reduced over an even wider pH range. The large excess of co-extracted Ca effectively prevents the mobilization of Pb. Although CaEDTA has a much lower log K value than PbEDTA (10.65 compared to 18.0, all log K values are from ref 30), the high concentration and high solubility of Ca^{2+} makes this ion a powerful competitor for metals around neutral pH values.

Figure 2b shows the analogous calculations for EDDS, which is a weaker chelating agent for both Pb (log K PbEDDS 12.7 compared to 18.0 for PbEDTA) and Ca (log K CaEDDS 4.6 compared to 10.65 for CaEDTA). Pb extraction by EDDS is lower than by EDTA at pH <8. Due to the relatively weak CaEDDS complex, the presence of Ca does not result in a large reduction in the extraction efficiency of Pb (case 2). The presence of calcite (case 3) shifts the Pb-mobilization edge from pH 6 to 7, thereby further decreasing the already weak extraction of Pb by EDDS. However, it should be noted that at pH 8 EDTA and EDDS have a similar extraction efficiency for Pb. Weak extraction of Pb by EDDS has been reported several times (20, 31, 32).

These calculations show that Ca, which is always present in soils at high concentrations, will greatly reduce the mobilization of target metals. Even at chelant-to-metal ratios >1 where enough chelant is present to complex all target metals, a large fraction of the chelating agent may actually be complexed by Ca.

Effect of Iron. Fe(III) is another important competitor for chelating agents. In contrast to Ca, Fe(III) complexes are many orders of magnitude more stable than most metal complexes (30). To illustrate the importance of Fe for chelant

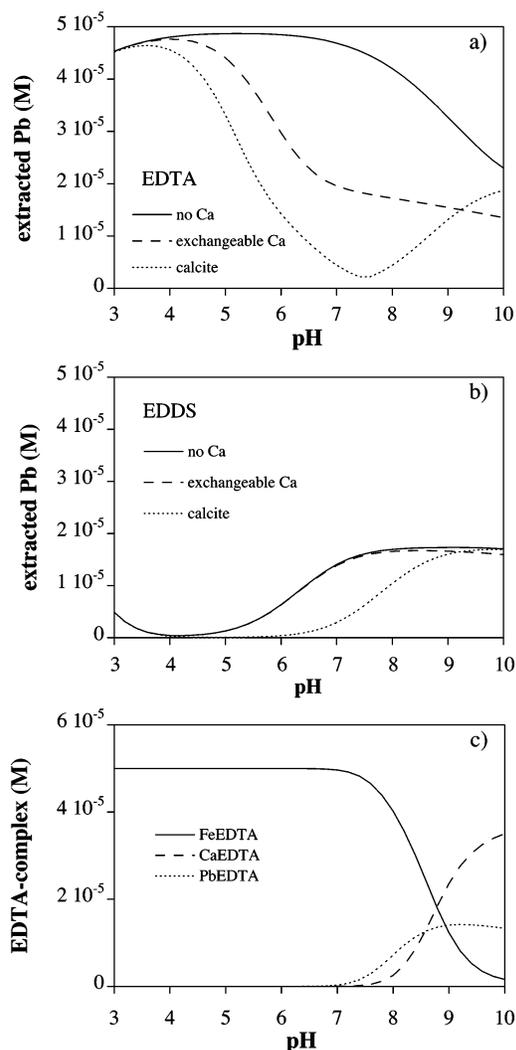


FIGURE 2. Influence of Ca on Pb extraction by (a) EDTA and (b) EDDS and (c) of Fe(III) by EDTA. Chelant to Pb ratio = 1. Model calculations have been performed with the constants shown in Tables 1S and 2S (Supporting Information) for a system without any Ca (case 1), with Ca in equilibrium with soil Ca from ion exchange sites (case 2), in equilibrium with calcite (case 3), and with Fe(III) in equilibrium with amorphous iron hydroxide (case 4).

speciation in soil solution, we performed another model calculation (case 4). The model described above was adapted to assume that amorphous Fe hydroxide controls the solubility of Fe (Table 2S, Supporting Information). Figure 2c shows that, under these conditions, Fe(III) would complex almost 100% of the EDTA up to a pH of 7. PbEDTA only starts to appear above pH 7.5 together with CaEDTA. At equilibrium, most of the chelating agents added to a soil will be bound to Fe below neutral pH because of the much higher stability of Fe(III) complexes compared to Ca or metal complexes. Above neutral pH Ca becomes the main competitor of Pb because of the low solubility of Fe at alkaline pH.

However, the dissolution of Fe oxides is a slow process (33). The time to reach equilibrium depends on the type (amorphous or crystalline) and amount of Fe oxides in the soil. This explains why in most cases the measured Fe-chelate concentration was lower than the value calculated using stability constants. Despite the importance of Fe for the speciation of chelants, Fe has rarely been measured. In column studies Fe was found at very high concentrations in the leachate (23, 29, 34–38). We used the few available studies providing data from which the fraction of Fe complex could

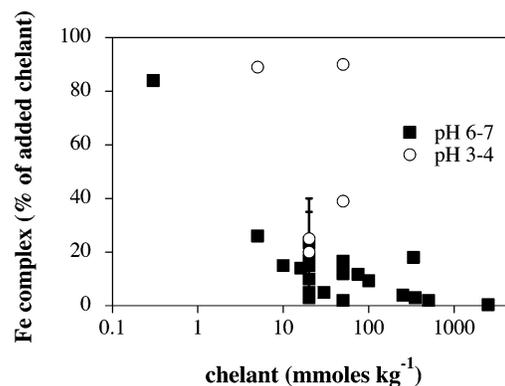


FIGURE 3. Fraction of added chelant present as Fe complex in soil solution as a function of the applied chelant dose for two pH ranges (6–7 and 3–4). Data are from refs 20, 38, 61, 83–86.

be calculated to construct Figure 3. The percentage of the Fe complex is shown as a function of the added amount of chelant. For most soils, in the range of 5–20 mmol kg⁻¹ chelating agent, about 5–30% of total chelant can be expected to be complexed with Fe after 2 days or less. The Fe-bound chelant is no longer available to extract the target metals. At lower pH values or where less chelant is added the amount of Fe complex will be relatively higher.

Knowledge of the speciation of the applied chelating agent in soil solution is critical when assessing phytoextraction. With a few notable exceptions (e.g., 35, 39–41), this information is absent in most studies concerning chelant-enhanced phytoextraction. Information on the target metal in soil solution is more useful if accompanied by measurements of Ca, Mg, and Fe, which are also solubilized by the chelants. Because under most conditions the chelant in solution is present in excess of the metals, it is reasonable to assume that all dissolved metals are present complexed to the chelant. For weaker complexes (e.g., Ca or Mg) speciation calculations could give information about their presence (42).

When biodegradable chelants such as EDDS are used, the total chelant concentration in soil solution should also be reported. Simple HPLC methods for the analysis of these compounds are available (43–45). The use of dissolved organic carbon (DOC) as a surrogate measurement for dissolved chelants may give misleading results because chelants are also effective in extracting organic matter from the soil (46). Therefore, the total DOC overestimates the chelant concentration. DOC may also be a competitor for metal complexation but calculations have shown that this only becomes important at very low chelant concentrations (47).

Transport Limitations. Metal transport from the bulk soil to plant roots can occur by diffusion as well as by convection with the transpiration water stream. There is only limited information about the relative importance of the two mechanisms. Diffusion appears to be the dominant mechanism of Zn transport to the roots of the hyperaccumulator *Thlaspi caerulescens* (48, 49). Formation of complexes can considerably enhance diffusive fluxes toward roots by increasing the dissolved metal concentration and increase uptake, even if the complexes themselves are excluded from uptake. Theoretically it is sufficient that the time scale of complex dissociation is small in comparison to the time scale of the diffusion process (50–52). By increasing the total metal concentration in solution, the formation of chelates will also increase any convective transport.

Plant Factors

Uptake of Chelants and Chelates. There are two parallel transport pathways for water through the root cortex toward

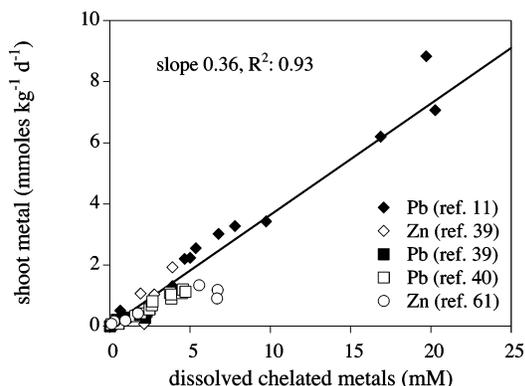


FIGURE 4. Metal uptake by plants (in $\text{mmol kg}^{-1} \text{d}^{-1}$) in the presence of chelating agents as a function of the solubilized metal concentration in soil solution. Data are from refs 11, 39, 40, 61.

the stele: a pathway of passive transport by diffusion and convection through the apoplast, namely cell walls and intercellular spaces, and a pathway of active transport from cell to cell in the symplast (selective transport across membranes) (53). The apoplastic pathway is discontinuous, being interrupted by the endodermis, the innermost layer of cells of the cortex. In the radial and transverse walls of the endodermis, hydrophobic incrustations of suberin, i.e., the Casparian band, obstruct the passive transfer of solutes into the stele. However, the endodermis is an imperfect barrier for apoplastic transport (54). In addition to passage cells, there are sites distributed along the root axis where this barrier is "leaky". At the root apex the Casparian strip is not yet fully developed and, thus, allows apoplastic transport to reach the stele.

Cellular active uptake mechanisms are highly selective for essential metals such as Cu and Zn as free metal ions. There is limited cellular uptake of nonessential metals such as Pb through this pathway. There is debate whether some metal complexes are taken up into plants (55), but it is generally assumed that anionic metal–ligand complexes are not bioavailable (56). This is contradicted by the observed increase in metal uptake in the presence of high concentrations of chelants. However, it is widely accepted that uptake of chelants and their metal complexes occurs via the apoplastic pathway (5, 35, 54, 57, 58). Disruption of the endodermis could therefore facilitate plant-metal accumulation by allowing the free passage of chelated metals into the stele. This may be achieved by the addition of herbicides, which, when combined with chelating agents, have been shown to enhance plant-metal accumulation (59, 60). The endodermis may also be damaged when high concentrations of chelants are added to the soil, or if a crop is transplanted into contaminated soil.

If the "leakiness" of the root is not influenced by the added chelant, a linear relationship between the soil solution concentration and the amount taken up is expected. This has been observed for Cu, Zn, and Pb uptake in the presence of chelants (11, 39, 40, 61) (Figure 4). Although a variety of plants and soils have been used, there is a good agreement between the uptake in the different experiments for both Pb and Zn. For Zn the uptake data are corrected for the uptake of Zn into the leaves before addition of the chelant (61). Zn is an essential micronutrient that is usually present in shoots at 100–1000 mg kg^{-1} . Such correction is not necessary for Pb because there is almost no translocation into the shoots in the absence of chelants. The linear relationship may break down at high chelant concentrations when the root cells are damaged and uncontrolled inflow of soil solution may occur into the stele (35).

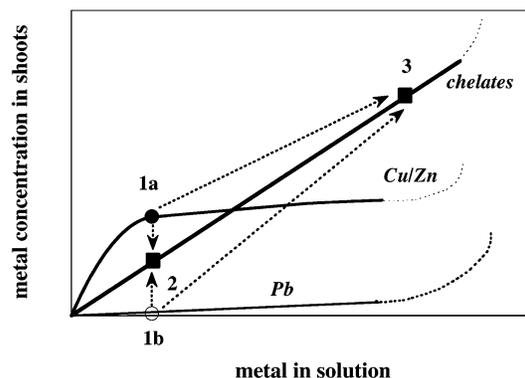


FIGURE 5. Simplified schematic of the accumulation of Cu, Zn, and Pb in shoots in absence (lines labeled "Pb" and "Cu/Zn") and presence of chelating agents (line labeled "chelates"). Circles 1a and 1b represent the uptake of metals in the absence of chelants at low dissolved metal concentration, squares 2 and 3 represent metal uptake in the presence of chelants at low and high concentrations, respectively.

Figure 5 gives a simplified schematic of the accumulation of Cu, Zn, and Pb in shoots or translocation from roots to shoots in the absence and presence of chelating agents based on actual pot and hydroponic experiments (61, 62). In the absence of chelants, Zn and Cu accumulation is governed by uptake of free metal ions in the symplastic pathway, which is efficient at low solution concentrations (Figure 5, line labeled "Cu/Zn"). Only a little Pb is taken up into the shoots (line labeled "Pb"). If the same metal concentrations in solution were chelated, then the uptake would occur through the apoplastic pathways (line labeled "chelates") and Cu and Zn uptake would be reduced while Pb uptake would be strongly increased. From Figure 5 it becomes clear why there is in most cases an increase in Pb uptake in the presence of the chelants. In contrast, the few hydroponic data on Cu and Zn uptake in the presence of chelants mostly show a decrease in metal uptake in the presence of chelants (62–64).

With a high dissolved metal concentration, translocation of all three metals to the shoots would increase in the presence of chelants because the nonselective uptake in the presence of chelants would exceed selective uptake along the symplastic pathway for both essential and nonessential metals. The positions of the lines for the metals in the absence and presence of chelants depends on the plant species and may vary considerably. Adding chelants to a soil therefore increases not only the total dissolved metal concentration but also changes the uptake mechanism and depending on metal, plant species, and chelant concentration, significant increases not only of plant Pb but also of plant Cu and Zn are likely.

The variability in uptake of chelants by different plant species also needs to be considered. Accumulation of Pb varied considerably from 94 to 1820 mg kg^{-1} for 10 different plant species after addition of EDTA to soils, with an average value of 800 mg kg^{-1} (34). Also, xylem sap concentrations of EDTA were found to vary considerably between plant species at the same solution concentration (35). This indicates that differences in uptake are not only related to the cumulative transpiration, and therefore flow of xylem sap to the leaves, but also the plant-dependent leakiness of the root, and the efficacy of chelate transport in the xylem.

In addition to increasing the concentration of target metal in soil solution, chelants also alter the chemical and physical properties of the soil. Chelant addition increases the ionic strength of the soil solution. The increase in dissolved salts and complexes will reduce the water potential in the root-zone, therefore reducing transpiration (65). As a consequence

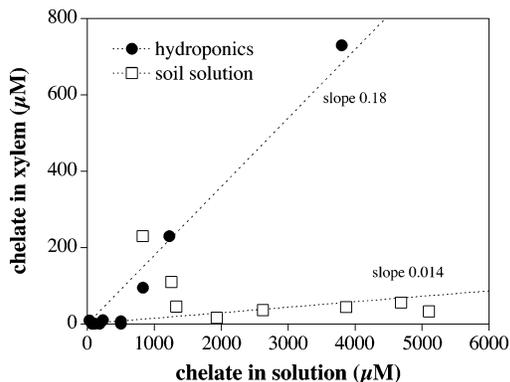


FIGURE 6. Concentrations of chelating agents (EDTA and EDDS) or their metal complexes in xylem sap plotted against their concentration soil solution or hydroponic solution. Data are from refs 11, 35, 40, 62, 87, 88.

of reduced transpiration, the crop will also take up less of the target metal complex (66).

Sodium salts of the chelants are commonly used because of their high solubility and low cost. In addition to reducing the available water, as described above, sodium also alters the soil structure by dispersing clays and bringing organic matter into soil solution. This can increase metal leaching by colloidal transport. Alternatives to sodium salts are more expensive, and do not overcome the problem of increased soil solution strength.

Calculation of Chelant Uptake. The chelants taken up by the root pass through the xylem to the shoots where they are deposited. Information on the xylem concentration of chelants and their metal complexes can therefore provide information about the efficiency of a plant uptake via the unselective apoplastic pathway. Figure 6 shows a summary of the few published data relating the solution chelant concentration with that of the xylem sap concentration. The efficiency of solute transfer into the xylem can be described by a dimensionless root absorption factor, ϕ , (66) as follows:

$$\phi = \frac{[C]_r}{[C]} \quad (1)$$

where C_r is the solute concentration in the root xylem and C is the ambient soil solution concentration. Available values of ϕ range between 0.014 and 0.18. In soils, most measured values are close to the lower limit, while some xylem sap concentrations from hydroponic experiments are higher (Figure 6). A low value of ϕ is expected due to the efficiency of the Casparian band in blocking the inflow of unwanted compounds and the nonexistence of specific transporters for chelated metals. It has been shown that there was no significant difference between the uptake of free chelants and their metal complexes (62). If we therefore know the soil solution concentration of a chelate, we can predict its xylem concentration.

When the xylem concentration of the chelates as a function of the solution concentration is known, we can calculate the amount of chelates that are transferred to the shoots of the plants from the amount of transpired water. The assumption is that once the chelate is in the xylem, it is transported to the leaves with the water stream and is stored there. The accumulation of a metal in the shoots is then given by

$$\Delta M = \int_0^t TC\phi dt \quad (2)$$

where ΔM = change in plant metal content (moles or g), t = time (days), T = water use ($L \text{ day}^{-1}$), C = concentration of metal in soil solution (moles L^{-1} or $g \text{ L}^{-1}$), ϕ = root

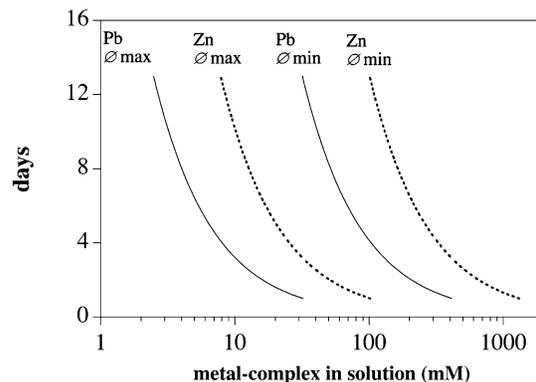


FIGURE 7. Exposure time needed to achieve an increase in shoot metal concentration by 2000 mg/kg Pb or Zn as a function of exposure time. The lines have been calculated using eq 2 for the high and the low root absorption factor ϕ (0.18 and 0.014) with a transpiration rate of 5 mm d^{-1} and a biomass of 30 t ha^{-1} .

absorption factor for the metal. The transpiration of plants in the field can be calculated using environmental variables and a crop coefficient (67).

We will now present some calculations based on eq 2 using the soil and plant parameters summarized in Table 3S (Supporting Information). We calculated the metal concentration in soil solution that is needed to achieve a metal concentration in the plant tissue after a given time. We calculated this for a targeted concentration of 2000 $mg \text{ kg}^{-1}$ Pb or Zn in the dry shoots, using a soil with 1000 $mg \text{ kg}^{-1}$ metal, a transpiration rate of 5 $mm \text{ d}^{-1}$, and a biomass of 30 t ha^{-1} . Figure 7 shows the concentrations of Pb and Zn that need to be present in soil solution to achieve this target after different times. To reach 2000 $mg \text{ kg}^{-1}$ Pb in the shoots, a soil solution concentration of 6 mM (1200 $mg \text{ L}^{-1}$) has to be sustained for one week for the highest ϕ and around 60 mM (12 400 $mg \text{ L}^{-1}$) for the low ϕ . To reach 2000 $mg \text{ kg}^{-1}$ Zn, concentrations of more than 15 mM (980 $mg \text{ L}^{-1}$) are needed for the high ϕ and 190 mM (12 400 $mg \text{ L}^{-1}$) are needed for the low ϕ . These conditions are difficult, if not impossible, to obtain in the field situation.

Given that high concentrations of chelating agents reduce transpiration and may kill the plant, the time available for the plant uptake of solution will be shorter at higher solution concentration. Uncomplexed chelants are more toxic to plants than metal chelates (58), and may further reduce plant growth and transpiration. As discussed above, only a fraction of the chelant is complexed to the target metal and the total concentration of the chelant in solution has to be much higher to achieve the desired concentration of metal complex. Figure 7 also shows that reducing the chelant concentration will not be feasible because the increase in uptake will be too small.

Calculation of the Time Needed to Cleanse a Moderately Contaminated Soil. The critical ratio for phytoextraction is the amount of metal extracted per hectare compared to that left in the soil. Here we examine the time needed to halve the Pb concentration in the moderately contaminated model soil under optimal conditions with the values given in Table 3S. If all Pb were solubilized then the initial rate of uptake would be 30 $kg \text{ ha}^{-1} \text{ d}^{-1}$ for the highest ϕ and 2.3 $kg \text{ ha}^{-1} \text{ d}^{-1}$ for the lowest ϕ . If we assume that the water content of the soil is maintained, which is necessary to achieve 5 mm of transpiration, then the soil solution Pb concentration must decrease in proportion to plant Pb uptake. Maintaining a constant soil moisture content, the time needed to achieve a concentration below 200 $mg \text{ kg}^{-1}$ (the investigation threshold in Switzerland) of Pb would be between 128 and >1200 high transpiration days. However, this could not be achieved in a single cropping, as the plants rapidly die after

the application of the chelant. If we optimistically assume that plants continued to transpire for 10 days after chelant application, then between 8 and 100 crops would be needed to reduce the soil Pb concentration to 200 mg kg⁻¹. More chelant would have to be added after each cropping, as the Pb-chelate is unstable with respect to Fe-chelate, there is downward leaching, and, depending on the used chelant, biodegradation. These calculations assume that the plant takes up all of the chelated Pb. However, mass balance calculations in greenhouse experiments show that, at the most, just 10% of the soil metal is taken up by the plant (41, 68). The remainder is either reprecipitated in the soil, or leaches into receiving waters. We now discuss the environmental implications of such massive additions of chelants to soils.

Environmental Concerns

EDTA as a Persistent Contaminant. The use of EDTA in phytoextraction has received considerable attention due to its low cost and high efficacy of metal solubilization. EDTA offers the best cost/performance ratio of all chelants. However, EDTA has also received a lot of attention due to its persistence in the environment. While biodegradation of EDTA has been reported in pure cultures under controlled conditions, negligible degradation has been observed under natural conditions in soil and water (6). Due to this persistence, EDTA is found in almost all natural waters (19). EDTA has therefore been selected by the European authorities as part of the priority substances for extensive evaluation. According to the completed risk assessment report, EDTA has a low toxicity profile for humans and environmental risks are limited to some localized cases of high emissions to surface waters (69). The report concludes that risk reduction measures should be considered at concentrations above 2.2 mg L⁻¹ (about 10 μM), a value hardly ever reached in natural waters. When applied to soil during phytoextraction, EDTA concentrations in soil solution are typically 1–100 mM, some 100–10 000 times higher than the 10 μM threshold above which risk reduction measures should be considered.

Using eq 2, we can also calculate the fraction of the chelant that is taken up by the plants. We used again our model soil for this calculation and assumed uptake during 10 days. The chelant uptake during that time is between 0.14 and 0.011 mol m⁻² using the highest and the lowest ϕ value. This is 12 and 1% of the total amount of chelant in the topsoil. At least 90% of the chelant stays in solution and can be leached down to groundwater. To reach the concentration of 10 μM which was found to be safe by the European risk assessment report on EDTA (69), the plants would need to take up 99.95% of the added EDTA. The deliberate “pollution” of groundwater by EDTA or another chelant in the course of a phytoextraction procedure is therefore unavoidable when using an environmentally persistent chelant such as EDTA except under climatic conditions that completely prevent any leaching of solutes out of the rooted zone.

Metal Contamination of Receiving Waters. Even if a chelating agent is found that is effective, low-cost, and biodegradable, metal leaching into receiving waters is still an environmental concern. Free chelants only weakly interact with mineral surfaces at pH values in the plant-growth range, while strong adsorption occurs under acidic conditions (2). The adsorption of metal complexes generally differs from that of the free ligand (70). The relatively weak adsorption of chelates around neutral pH therefore results in excessive leaching. This has been observed in column experiments and in lysimeters (36, 38, 42, 71, 72). Leaching in the presence of the biodegradable chelant EDDS, however, was found to be significantly less than that for EDTA in small soil column (25).

The action level for Pb in water in the United States is 0.015 mg L⁻¹, equivalent to 0.07 μM. To reduce the 16 mM Pb in our example in the topsoil to this level, the plants would need to take up 99.99999% of the solubilized Pb. One liter of topsoil solution with 16 mM Pb would raise the Pb concentration of 220 000 L of water above the action level without plant uptake. Even if the plants would take up 99% of the mobilized Pb from the example used above, the remaining 1% leached from 1 m² of soil surface would raise 50 million L of water above the action level for Pb.

Solute transport through soils occurs via percolation through the soil matrix and preferential flow through macropores and other structures of rapid transport. Preferential flow, occurring in virtually all soils (73), permits the rapid passage of solutes through the soil with minimal interaction with soil particles and plant roots (74) and may result in solute transport up to 2 orders of magnitude faster than matrix flow (75). Even with noncomplexed metals, these transport pathways have been shown to exacerbate groundwater contamination by reducing the contact time of the soil solution with organic and clay material that could otherwise retard the movement of dissolved metals (76). Therefore, some leaching of chelant and chelated metals is unavoidable.

Implications for Phytoremediation. In the best case scenario, where chelant-induced phytoextraction is used to remediate a modestly contaminated soil under optimal conditions, this technology requires large masses of chelant to be applied to soil over the course of several years. Leaching is unavoidable during this time. Preferential flow processes will result in a significant proportion of the chelant and solubilized metal descending below the root zone, possibly into receiving waters.

Chelant-induced phytoextraction may therefore be limited to applications where the connection to receiving waters has been broken, or where leaching is unimportant. In the former case, phytoextraction could be conducted *ex situ*. Here, the contaminated material would be placed on a liner whereby any leachate could be collected and recycled. Such systems are already used for soil washing and the recovery of gold from low-grade ore bodies. Plants would aid in metal recovery by concentrating the metal in their biomass. The economic feasibility of induced gold phytoextraction has been demonstrated (77).

Alternatively, if groundwater contamination is not an issue, chelants may be used as chemical ploughs, reducing soil metal contamination by leaching below the root zone and precipitating the metal where it is unavailable for plant uptake.

Some research has also been carried out with biodegradable chelating agents. A promising chelant is EDDS, which has received attention in the last years as potential replacement for EDTA in soil washing and chelant-enhanced phytoextraction (20, 25, 31, 42, 61, 78, 79). Metal–EDDS complexes have been shown to be easily biodegradable in soils (42, 47, 80). An approach combining the application of a biodegradable chelant (EDDS), phytoextraction by plants, and a reactive permeable barrier for complete biodegradation of the leached chelant has been proposed (26). An additional factor that should also receive more attention is a possible adverse effects of high chelant doses on soil microbial and fungal activity (25, 81, 82).

Supporting Information Available

A description of modeling the extraction of Pb and Ca in the presence of chelants; a description of the conditions used to calculate the extraction of Pb in the presence of Ca and Fe(III) by EDTA and EDDS; the list of references used to draw Figure 1; a table summarizing the conditions to calculate uptake of Pb into the shoots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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