Leaching and phytoavailability of zinc and cadmium in a contaminated soil treated with zero-valent iron

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Abstract

Immobilization of heavy metals by stabilization amendments is a promising method to restore contaminated soils. In our study, we investigated the efficiency of zero-valent iron (Fe^0) added to the soil in the form of iron grit to reduce leaching and uptake of Zn and Cd by *Lupinus albus* L. Results of column leaching experiments show that metal leaching decreased proportionally to the rate of amendment application (1%, 2% or 5%: w/w) and that the reduction reached up to 98% and 83% for Zn and Cd respectively. An increase in pH and in the number of sorption sites which bind ionic free metals and organometal complexes are possible mechanisms for this attenuation. Moreover, a rhizobox experiment has demonstrated that phytoavailability of Zn and Cd was reduced by 63% and 45% respectively when soil was treated with 5% (w/w) iron grit, and that *L. albus* did not develop strategies to reduce Zn and Cd uptake in untreated soil. We conclude that covering contaminated soil with *L. albus* could be used in association with immobilization techniques for soil remediation. However, it is crucial that the amendment and the soil be thoroughly homogenized in order to ensure the maximum reduction of metal uptake.

Key Words

Heavy metals, metal immobilization, stabilization amendments, mobility; *Lupinus albus*, iron grit.

Introduction

In Belgium, the non-ferrous metallurgical industry has caused severe contamination of soils by heavy metals. Since the beginning of the Industrial Revolution, metal refining plants using pyrometallurgical processes were responsible for significant atmospheric emissions of metals such as Zn and Cd, which have affected soils in widespread areas. Due to the large size of the contaminated areas, classical remediation techniques (*e.g.* excavation) are not appropriate because of the prohibitive cost. It is thus crucial to find cheaper alternatives. Among these technologies, *in situ* stabilization, having low environmental impact and thus better accepted by the public, is one of the most promising (Guo *et al.* 2006). This technique consists in reducing the risks of groundwater contamination, plant uptake, and exposure of other living organisms by immobilizing metals (Boisson *et al.* 1999). This objective can be reached by the application of contaminant immobilizing additives to the soil (Kumpiene *et al.* 2008). Due to its oxidation by corrosion (Dries *et al.* 2005) which slightly modifies the pH and offers new surfaces for sorption of both cations and anions (Cornell and Schwertmann 2003), zero-valent iron (Fe^0) could be an effective stabilizating amendment. Compared with other Fe containing compounds, Fe^0 also offers the advantage of being available in large quantities (Kumpiene *et al.* 2007) as industrial by-products.

In addition to the immobilization of heavy metals, covering soil with suitable plants has proven helpful in preventing the dispersion of the contaminant through erosion (Ruttens *et al.* 2006). *Lupinus albus* L. (white lupin), a nitrogen-fixing (i.e. fertility-improving) plant, adaptable to poor acid soils and tolerant to nitrate and lime excess, high salinity and high heavy metal contents in soils, appears to be an excellent candidate combined with heavy metal immobilization by amendments (*cfr* authors cited by Castaldi *et al.* 2005).

This study aims at assessing the efficiency of Fe^0 in reducing mobility and phytoavailability of Zn and Cd in soil contaminated by heavy atmospheric metal fallouts. Emphasis will be put on the physico-chemical processes responsible for the immobilization of heavy metals and on the feasibility of using white lupin in order to cover metal stabilized soils.

Materials and methods

Soil sampling and soil treatment

Organic horizon of a shale soil (pH=4.8; CEC=38.0 $cmol_c$/kg; organic carbon=38.5%) contaminated by atmospheric metal fallouts was collected in Prayon (Belgium). Zn and Cd total contents were 7400 mg/kg and 150 mg/kg respectively. The sample was air-dried, passed through a 2 mm nylon sieve and then stored at 4°C before analysis. The Fe^0 source, referred to here as iron grit, was in the form of iron filings produced by machining tools in a machine shop. Sub-samples of soil were treated with iron grit as follows (%w/w): untreated polluted soil (UNT); iron grit 1% (IG1); iron grit 2% (IG2); iron grit 5% (IG5). Mixtures were prepared by 2 hours of thorough agitation just before use.

Leaching column design

Leaching column experiments were carried out to investigate the effect of the zero-valent iron amendment in soil on the mobility of Zn and Cd. Each PVC column (8 cm diameter, 10 cm height) was filled with 50.0 g of UNT, IG1, IG2 or IG5. The complete design is shown in Figure 1a. Control experiments, consisting of columns containing only sand, were also conducted. All the experiments were carried out in triplicate. Deionized water input, based on the average annual rainfall recorded for Prayon (731 mm), was 10 ml four times a week during 12 weeks. The water input began one week after equilibrating the substrates at 80% of the water holding capacity (WHC). Sampling was performed every 14 days, which was the time required to reach a sufficient volume to allow for pH analysis, conductivity, anions, cations and DOC. Aqueous speciation using the Stockholm Humic Model (SHM) was performed using Visual MINTEQ (version 2.61).

Rhizobox experiments

Rhizobox growth chambers were based on the design of Whiting *et al.* (2000) and constructed from 10 x 10 x 2 cm square Petri dishes. A large opening at the top makes it possible for the plant stem to emerge and facilitates the watering while a 1.5 cm sand layer at the bottom prevents water stagnation in the soil (Figure 1b1). When filling the Petri dishes with soil, a cardboard strip was temporarily inserted into the dish to divide the box into two equal left and right compartments. Homogeneous treatments were obtained by filling both compartments with the same substrate (UNT or IG5) while heterogeneous treatments were obtained by filling one side with UNT and the other side with IG5 (Figure 1b2). The cardboard strip was then removed, the lid was fixed over the base with silicon and each rhizobox was wrapped in a black plastic sheet to avoid exposing the roots to light. Finally, the rhizoboxes were placed at an angle of 50° on an inclined support with the lid on the underside to ensure root growth close to the lid. The substrates in each rhizobox were equilibrated during one week by maintaining the WHC at 80%. A 7-day-old seedling of *Lupinus albus* was then transplanted in each rhizobox taking care that the roots were well positioned on the central line where the cardboard strip had been previously placed. All experiments were conducted in triplicate. The plant growth was carried out in a phytotron (16 h at 20°C with light; 8 h at 15°C without light) during 28 days and the plants were watered regularly. The shoots were then harvested, dried (60°C) and their Zn and Cd contents were determined by ICP-AES after *aqua regia* digestion.

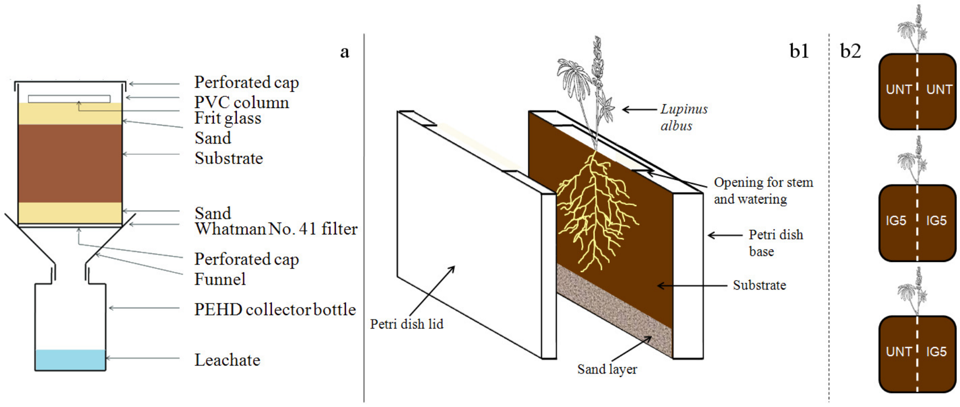

Figure 1. Design of the leaching column (a) and rhizobox (b1) and experimental designs (b2).

Results and discussion

Effects of zero-valent iron amendment on Zn and Cd leaching

Figure 2 shows a clear decrease of Zn and Cd leaching in iron grit amended soils. At the end of the experiment, the total amount of leached Zn (mg) was reduced by up to73%, 87% and 98% in the leachate from IG1, IG2 and IG5 respectively while the total of leached Cd (µg) was reduced by up to 48%, 66% and 83% in the leachate from IG1, IG2 and IG5 respectively. Zn and Cd leaching attenuation by zero-valent iron amendment is thus very effective and is slightly more efficient for Zn. In addition, this decrease in leaching is a function of the proportion of iron grit in soils and occurs immediately, as is it observed even in the first leachate samples. This can be explained by the higher number of sorption sites in the amended soil and the fast sorption of metals to oxide surface (equilibrium time ranging from 24 to 72 h; Smith 1996).

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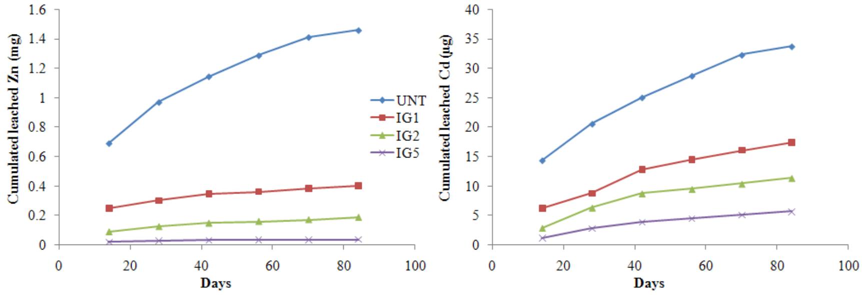

Figure 2. Cumulated quantity of Zn (mg) and Cd (µg) in column leachates.

Moreover, Figure 3 shows a strong correlation between Zn and Cd concentrations and pH (R^2=0.82 and R^2=0.75 respectively). As an oxidation phenomenon, iron grit increases the pH. As a consequence, metals are immobilized because of (i) the higher number of negative sites for cation sorption and (ii) the higher proportion of hydrolysed metals species which are preferentially adsorbed compared to the free ionic metals (Cappuyns and Swennen 2008). As shown by Kumpiene *et al.* (2007), pH is thus one of the most significant factors affecting the mobility of heavy metals in Fe^0-stabilized soil.

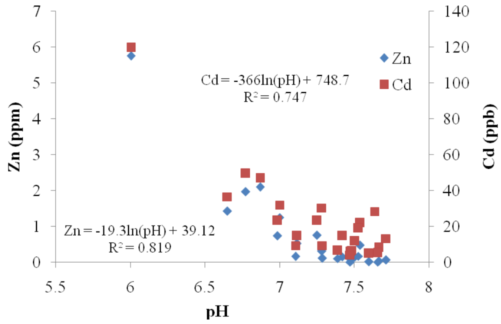

Figure 3. Correlations between Zn or Cd concentrations (ppm and ppb respectively) and pH in leachates.

In addition to increased ionic free metal sorption, the quantity of organometal complexes in soil solution is considerably diminished by the addition of iron grit as shown by the average Zn and Cd speciations (Figure 4). Consequently, as described by Davis and Bhatnagar (1995) and Jones and Brassington (1998), in iron enriched systems, metal immobilization can also be caused by the adsorption of organometal complexes on iron oxides. Since organometal complexes are known to enhance Zn and Cd transport (Schwab *et al.* 2008), their adsorption also contributes in reducing the leaching of these metals.

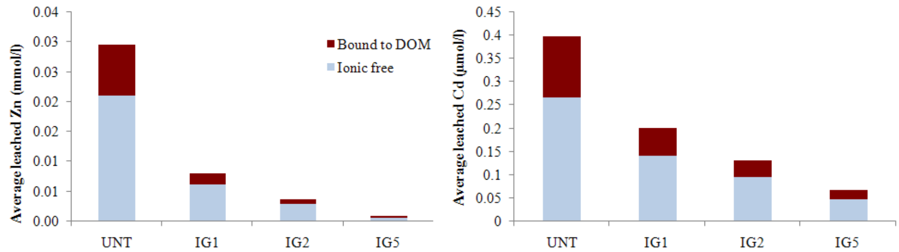

Figure 4. Speciation of average Zn and Cd concentrations (mmol l^{-1} and µmol l^{-1} respectively) in leachates.

Effects of zero-valent iron amendment on Zn and Cd phytoavailability

Table 1 shows (i) a decrease of 33% and 63% in the Zn uptake by *Lupinus albus* in UNT/IG5 and IG5/IG5 respectively and (ii) a decrease of 26% and 45% in the Cd uptake in UNT/IG5 and IG5/IG5 respectively. Similar to what was observed in the column experiments, the reduction of Zn and Cd transfers to plant by amendment of Fe^0 is very effective and proves to be the highest for Zn. Moreover, the Zn and Cd contents in plants grown using the UNT/IG5 treatment indicate that the white lupin has not only taken up Zn and Cd from the amended compartment but also from the untreated side. This suggests that, within the time span of the experiment (28 days), *Lupinus albus* did not develop strategies to avoid metal uptake from the untreated soil. This absence of adaptation is probably due to a tolerance to heavy metals. This indicates that *Lupinus albus*, because of its tolerance to high Zn and Cd concentrations, could be used in combination with heavy metal immobilization techniques. However, the amendment and the soil must be thoroughly homogenized in order to obtain the highest reduction of metal uptake.

Table 1. Zn and Cd contents (mg/kg) in *Lupinus albus* grown in treated and untreated soils.

Rhizobox	Zn content (mg/kg)	Cd content (mg/kg)
UNT/UNT	1223.4 ± 92.8	14.8 ± 1.7
UNT/IG5	818.9 ± 139.5	10.9 ± 1.5
IG5/IG5	460.4 ± 93.8	8.1 ± 1.5

Conclusion

As a by-product of industrial processes, zero-valent iron in the form of iron grit was found to be a promising additive to immobilize heavy metals in soils. This study has shown that the amendment of iron grit in soil was very effective in reducing Zn and Cd leaching (up to 98% and 83% respectively). Likely mechanisms are, among others, a pH increase and the sorption of ionic free metals and organometal complexes. This amendment also reduces the uptake of Zn and Cd (up to 63% and 45% respectively) by *Lupinus albus* plants. However, the iron grit and soil must be perfectly homogenized in order to obtain the most efficient uptake reduction. In order to elucidate with more precision the possible mechanisms responsible for causing the decrease in Zn and Cd transfer, we have planned to analyse treated soil and iron grit with physical techniques (*e.g.* SEM-EDS, EPMA and X-ray diffraction) in the upcoming months.

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