SOIL ADDITIVES IMMOBILISING HEAVY METALS IN CONTAMINATED SOILS

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Abstract: Addition of iron oxides, lime, clay minerals and other substances can be used to decrease the plant availability of toxic heavy metals such as Pb, Zn, and Cd. Extractability and consequently plant concentrations may be reduced in some cases by more than 50%. The assessment of remediation processes is supported by biomonitoring methods in the field with *Plantago lanceolata* and in the greenhouse by barley test experiments, in combination with extraction by ammonium nitrate.

Key words: Heavy metals, soil amendments, in situ remediation, biomonitoring methods.

1. Introduction

Heavy metal pollution has received considerable attention as one of the most important environmental problems in industrialized countries. Major sources of heavy metal input to ecosystems are mining, smelting, metallurgical industries, sludge disposal and agricultural practices. Amelioration and rehabilitation of polluted soils can be achieved by in situ treatment, such as phytoremediation or immobilization of metals in soil. The latter technique is subject of research in the Austrian Reaearch Centers and some of the most interesting results are presented in this paper.

Immobilisation of metals in soils is aimed to significant reduction of their bioavailability by liming and addition of adsorptive materials such as iron oxides, clay minerals, zeolites and organic matter. Experiments are conducted mainly with soils from Arnoldstein (Carinthia), contaminated with Pb, Zn, and Cd by smelter emissions. Cu-contaminated soils were taken from Brixlegg (Tyrol, metal processing plant) and from vineyards in South Tyrol.

2. Materials and methods

Batch experiments were carried out with two soils of different pH and contamination levels (Pb, Zn, Cd) for screening 15 soil amendments. In each case, 100 g of soil were mixed with the additives and exposed one month. Afterwards, mobile heavy metal fractions were extracted with 1 M NH_4NO_3 and subsequently analysed.

Plant experiments were conducted in a greenhouse with the two soils in 5 kg-pots and two barley cultivars of different accumulation properties for Zn and Cd. Seven different treatments with combined additives (gravel sludge, iron oxides and lime) were tested for effectiveness to immobilize heavy metals and to reduce their uptake by plants. After a growth period of 99 days barley was harvested and metal analysis was carried out in straw and grains.

Soil amendments were also tested under field conditions in the contaminated area near Arnoldstein where experimental plots were arranged on two sites with barley and a third with pasture vegetation. A detailed description of the experimental methods is given by FRIESL *et al.*, 2006.

A bioavailability test system was designed for monitoring the heavy metal status of soils. Short term growth experiments were carried out in the greenhouse with different soils in plastic pots of quadratic cross section and a volume of 1 litre. *Spring barley* ("Messina") was sown in 4 replications, cut after a growth period of 18 days, oven dried and analyzed for heavy metals.

Analytical methods: Soils were air-dried and the 2 mm fraction was separated by passing a screen. The fine soil was digested by aqua regia for total heavy metal analysis. Mobile metal fractions were extracted with 1 M Ammoniumnitrate (20 g of soil, 50 ml solution) by a shaking procedure of 2 hours. Organic carbon was determined with a Carlo Erba element analyzer and pH was measured in 0.01 M $CaCl_2$. Plant material was digested by a mixture of concentrated nitric and perchloric acid (5 + 1 volume parts). All heavy metal analyses were carried out by ICP-OES or flame-AAS, depending on concentration. Soil extracts with 1 M NH_4NO_3 were measured by ICP-MS.

3. Results and discussion

Some results of the batch experiments are presented in Fig. 1. Soil B, one of the two soils used in this experiment, had a pH of 6.1, a clay content of 12% and total concentrations (aqua regia) of Cd = 4.75 $mg.kg^{-1}$, Zn = 500 $mg.kg^{-1}$, and Pb = 950 $mg.kg^{-1}$. The amount of additives was generally 2% (w/w), 1.28% for TRI, 3.8% for TBS and 0.5% for the dolomite and lime treatments.

Greatest reductions in mobile Cd were achieved with SYZ (70%), FER (55%), and CA (45%). Similar data were obtained for Zn. GS reduced Cd, Pb, and Zn by 19%, 27%, and 31%. Mobile metal concentrations were increased significantly by addition of TRI as a result of decreasing pH. In a second batch experiment dual applications of amendments were tested. A combination of GSO + FER, for example, reduced the extractability of Cd, Zn, and Pb by 39%, 42%, and 55%, respectively. All results of the batch experiments are presented in detail by FRIESL *et al.* (2006).

The amendments giving the most promising results were used afterwards in the plant experiments. In Fig. 2, as an example of the pot experiments, the Cd-concentration in barley is presented. Besides some of the amendments, shown in Fig. 1, red mud (RM), a by-product of bauxite processing was used. It consists of about 15 – 17 % Al_2O_3, 12 – 14 % SiO_2, 39 – 43 % Fe_2O_3, and 8 – 10 % Na_2O. RM was successfully tested in previous experiments (FRIESL *et al.*, 2003; 2004). The pot experiments were conducted with the two Barley cultivars "HELLANA" and "BODEGA", which were found to differ significantly in foliar accumulation of Cd. In Fig.1, the first block represents the control treatment of HELLANA (CO-H). The results show the difference between the two cultivars and a significant reduction of the Cd accumulation in the cultivar "B", mainly in the treatments with iron oxides. The most effective treatment was that with combined addition of Ferrihydrite + gravel sludge, decreasing the Cd-content in grain from 0.38 mg.kg^{-1} to 0.14 mg.kg^{-1}. Zn accumulation in barley was not influenced by the treatments while for Pb a reduction between 20 and 33% could be observed.

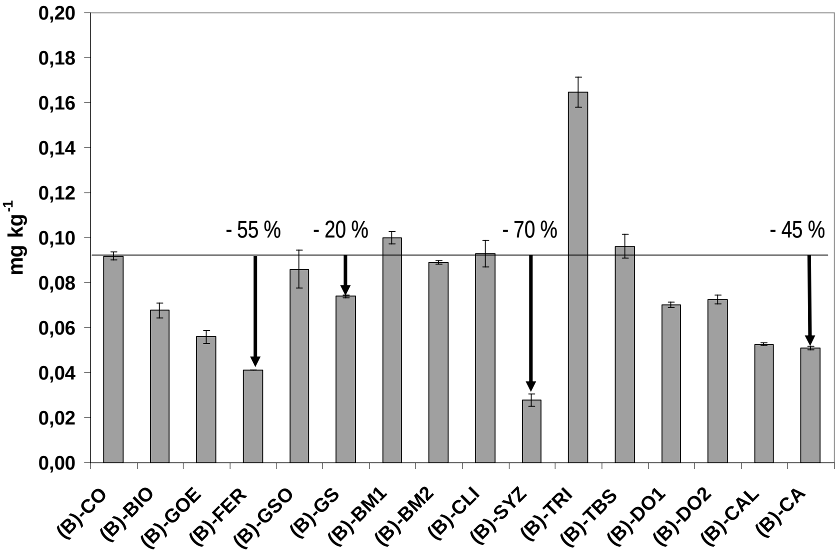

Fig. 1. Results of a batch experiment with soil from the experimental site B. Cd-concentrations extractable by 1M Ammoniumnitrate versus soil treatment. *Treatments: CO (control), BIO (compost), GOE (Goethite), FER (Ferrihydrite), GSO, GS (gravel sludge), BM, BM2 brick meal), CLI (Clinoptilolite), SYZ (synthetic zeolite), TRI (Triplesuperphosphate), TBS (Thomasphosphate) DO1, DO2 (Dolomite), CAL (calcite), CA (lime fertilize)*

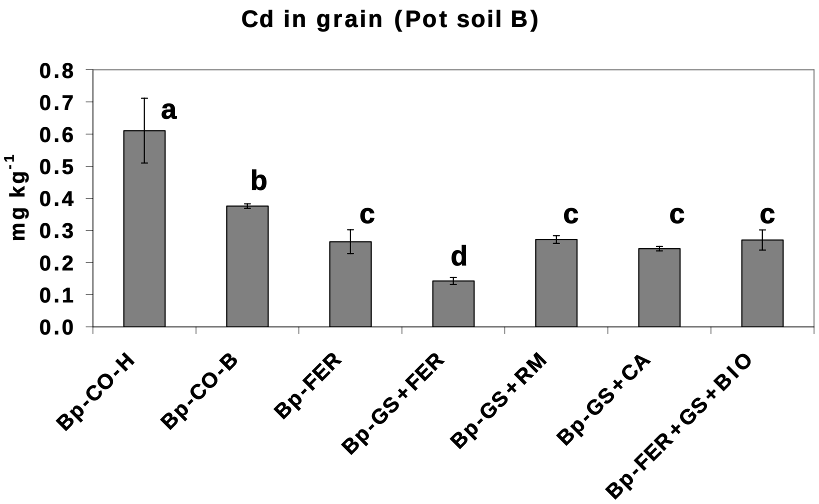

Fig. 2. Results of a pot experiment with soil from the experimental site II (soil B). Cd-concentrations in barley grains versus soil treatment. RM = Red mud.

The assessment of heavy metal bioavailability is very important in connection with the decision for soil remediation on the one hand and monitoring of the progress of remediation on the other hand. On pasture sites *Plantago lanceolata* may be used as an indicator plant for available metals. For all elements the concentration in the tissue of the plant shows a relationship with soil pH, which is the main parameter influencing the solubility of the metals (HORAK *et al.*, 2006 a). Table 1 gives an example of monitoring Pb-concentrations on different sites in Arnoldstein, compared to an uncontaminated site in Vienna. Pb is generally not accumulating to high concentrations in aboveground plant parts (low BF). In plants growing on highly polluted soil of experimental site A (further soil data are shown in Table 2) the limit for animal feed (EU Guideline 1999/29 EG) will be exceeded.

Table 1. Lead in Plantago lanceolata and corresponding soils (mg.kg^{-1} DM), pH-values and bioconcentration-factor

Soil, indication	pH	Soil (mg.kg^{-1})	Plant (mg.kg^{-1})	BF
Exp. plot B, control	5.15	970	4.6	0.005
Exp. plot B, limed	6.69	914	2.0	0.002
Orchard, Stossau	6.47	739	3.6	0.005
Pasture, Stossau	5.25	503	12.0	0.023
Close to Exp. plot A	6.81	5177	49.0	0.010
Vienna, garden	6.80	35	0.3	0.008

Table 2. Data from the barley test experiment. Total and mobile (NH_4NO_3 extractable) heavy metal concentrations in soils, compared with corresponding barley concentrations.

Soil	Element	Total mg.kg^{-1}	Mobile mg.kg^{-1}	Plant mg.kg^{-1}
Arnoldstein A	Zn	973	1.11	483
	Pb	2983	1.083	98
	Cd	15.1	0.196	8.4
Arnoldstein B	Zn	524	0.38	127
	Pb	912	0.185	2.48
	Cd	5.5	0.054	1.93
Arnoldstein 3 Treatment Red mud *)	Zn	1573	0.88	190
	Pb	3553	0.236	2.4
	Cd	10.1	0.034	0.59
Stossau 1 D	Zn	2133	35.0	1064
	Pb	1383	1.20	24
	Cd	14.7	0.54	8.8
Seibersdorf uncontaminated soil	Zn	76	0.03	46
	Pb	16.8	<0.01	0.35
	Cd	0.30	0.008	0.04

*) Red mud (iron oxide) was added in spring 1999

Table 2 shows data from the barley test experiments. There is a relationship between the mobile metal fraction and the concentration in the barley plants. The long term effect of treatment with iron oxides can be observed in soil Arnoldstein 3. This soil was taken from a container experiment conducted under outdoor conditions since 1987 in the experimental field of Austrian Research Centers.

Cu-polluted vineyard soils may be generally problematic for growing other crops as a consequence of the high plant toxicity of this element. In the barley test the Cu concentration in plant tissue was found in a range between 25 and 40 $mg.kg^{-1}$, which is above the plant toxicity level of 20 $mg.kg^{-1}$. Results are given in more detail by HORAK *et al*., 2006 b.

4. Conclusions

Soil amendments with combined addition of iron oxides and lime may be a suitable method to reduce the mobility and hence the plant uptake of toxic heavy metals. The sustainability of this treatment is confirmed by results from the long term container experiments (FRIESL *et al*., 2004). The basic reaction of metal immobilization is the specific adsorption on hydrated surfaces of the iron oxides, which is most effective in the pH-range of >6.5.

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