

IMPACT OF DIFFERENT SOIL AMENDMENTS ON THE MOBILIZATION AND PHYTOAVAILABILITY OF TOXIC METALS IN A CONTAMINATED FLOODPLAIN SOIL

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Introduction

Soil contamination by potentially toxic metals (PTMs) is a serious environmental concern. Many floodplain soils are highly contaminated with PTMs (e.g., Rinklebe and Shaheen, 2014). Thus, the development of suitable remediation approaches of metal contaminated soils should be a challenge for the near future. The *in situ* immobilization is considered as one of the most effective ways to remediate the PTMs contaminated soils (Shaheen and Rinklebe, 2015). The study objectives were i) to study the impact of the emerging amendments such as BI, CH, HA, and OC as well as some low cost alternative soil amendments (e.g., AC, BE, CBD, FA, LS, SBFL, and Z) on the (im)mobilization and on the geochemical fractions of Cd, Cu, Ni, Pb, and Zn, and ii) to assess the effectiveness of these amendments on the phytoavailability and the uptake of Cd, Cu, Ni, Pb, and Zn by rapeseed plants. The novelty of this study is that we examined some emerging amendments [i.e., nano-hydroxyapatite (HA), biochar (BI), chitosan (CH), and organo-clay (OC)] and a variety of low cost amendments and byproducts (i.e., activated carbon (AC), bentonite (BE), cement bypass kiln dust (CBD), fly ash (FA), lime stone (LS), sugar beet factory lime (SBFL), and zeolite (Z)) that were not tested as immobilizing agents for PTMs in a highly contaminated and weakly acidic floodplain soil.

Materials and methods

A greenhouse pot experiment was conducted using the contaminated floodplain soil. The studied soil was collected from the lower course of the Wupper River, near Leverkusen, about 20 km north of Cologne, Germany. The studied soil texture was dominated by silt (92%). The soil was weakly acidic (pH = 6.7), contained high organic carbon (7.05%). The studied soil has elevated concentrations (mg kg⁻¹) of Cd (8.1), Cu (3041.0), Ni (80.0), Pb (412), and Zn (1324.0). In a portion of 3 kg of each air-dried sample we added 30 g of each of the ten amendments (AC, BE, BI, CBD, CH, FA, LS, OC, SBFL, and Z) and 6 g of HA which were placed into 20-cm-diameter and 25-cm-height pots. The soil and each amendment was mixed thoroughly and placed in the pots. One week after the amendment applications, rapeseed (*Barassica napus*) was planted and harvested sixty five days after seeding. The aboveground biomass was removed from the pots, prepared, and dry-ashed in a muffle furnace at 450°C according to Jones et al., 1991. The geochemical fractions of Cd, Cu, Ni, Pb, and Zn were extracted using a sequential extraction technique based on the work of Tessier et al. (1979) and proposed by Shaheen et al. (2015). This method discriminates the metals into soluble + exchangeable (F1), sorbed and bound to carbonate (F2), occluded and bounded to Fe–Mn oxides (F3), and organically bound (F4). The Cd, Cu, Ni, Pb, and Zn concentrations in the digested soil samples and the concentrations of different metal fractions after extractions of the soil were measured by ICP-OES (Ultima 2, Horiba Jobin Yvon, Unterhaching, Germany). Statistical analyses were performed using the analysis of variance (ANOVA) and Duncan's multiple range tests to compare the means of the treatments at a level of significance of $p < 0.05$ using the SPSS 22 package.

Results

The amendments (except organo-clay) improved the plant growth and decreased soluble + exchangeable Cd (4-60%) compared to the control. Although the CBD, SBFL, and LS showed the highest decreasing rate of soluble + exchangeable Cd, they increased Cd in plants. The Z, B, AC, BI, and CH decreased Cd in plants (22-36%) (Table 1).

Table 1 Impact of soil amendments on the changes (%) of metal mobility (F1) and the plant tissues concentrations of metals in the treated soil compared to the control.

Treatment	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb	Zn
	soluble + exchangeable fraction (F1)					Plant tissues concentrations				
AC	10.9	23.4	28.13	28.7	25.27	31.2	-142.2	5.37	70.1	-3.78
BE	12.7	12.5	34.38	28.7	26.17	32.1	-199.6	39.40	58.7	9.24
BI	10.9	7.3	25.00	12.0	16.76	22.9	-158.2	30.75	62.7	16.83
CBD	58.2	11.8	75.00	86.7	72.69	-243.1	-150.7	65.97	78.1	40.41
CH	3.6	8.5	12.50	8.3	12.59	26.6	-120.9	22.99	34.6	14.75
FA	3.6	5.0	12.50	14.7	10.87	-47.7	-178.7	-59.70	66.1	-21.22
HA	3.6	3.1	12.50	6.0	9.65	-41.3	-173.9	7.16	99.1	1.12
LS	49.1	23.8	71.88	86.7	65.41	-18.3	-167.2	56.42	62.9	45.34
OC	-21.8	-9.8	-25.00	-8.3	-17.66	-329.4	3.4	-17.61	-13.8	-45.38
SBFL	60.0	6.4	78.13	86.7	72.20	-1.8	-142.2	68.66	80.6	49.31
Z	-5.5	-0.9	-3.13	-6.3	-0.57	35.8	-215.3	8.66	-0.9	-19.49

Increasing/decreasing percentage = control-treatment/control*100; (-): increasing; (+): decreasing

The amendments (except organo-clay and zeolite) decreased soluble + exchangeable Pb by 6-87% and decreased Pb in the plant by 35- 99% compared to the control. The SBFL, CBD, and LS showed the highest decreasing rate of soluble Pb. The HA showed the highest decreasing rate of Pb uptake which highlights the high potential of these amendments for Pb immobilization in the soil and reduce Pb accumulation by plants. Application changed distribution of Cu among geochemical fractions: alkaline materials lead to increased carbonate bounded fraction and the acid rhizosphere zone might cause release of this Cu. Thus, mobilization of Cu and uptake of Cu by rapeseed were increased compared to the control (except for organo-clay) under the prevailing conditions. This indicates that these amendments are able to increase phytoremediation efficiency of heavily Cu-contaminated soils. The SBFL, CBD, LS, BE, AC, and BI were most effective in decreasing the mobile Ni and Zn. The addition of SBFL, CBD, and LS leads to the highest decreasing rate of concentrations of Ni in plants (56 to 68%) and Zn (40 to 49 %). The results demonstrate the high potential of CBD, SBFL, LS, BE, AC, and BI for the immobilization of Ni and Zn in contaminated floodplain soils.

References

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