J. Plant Nutr. Soil Sci. 2006, *169,* 205–212 **DOI:** 10.1002/jpln.200421685

Remediation of a soil contaminated with heavy metals by immobilizing compounds

Abdul R. A. Usman[1]**, Yakov Kuzyakov**[1]**, Klaus Lorenz**[1]**,** and **Karl Stahr**[1]*****

[1] Institute of Soil Science and Land Evaluation, University of Hohenheim, Emil-Wolff-Str. 27, D-70593 Stuttgart, Germany

Accepted December 1, 2005 PNSS P168/5B

Summary

The labile fraction of heavy metals (HM) in soils is the most important for toxicity for plants and microorganisms. Thus, it is crucial to reduce this fraction in contaminated soils to decrease the negative effect of HM. In a greenhouse experiment, the effects of several additives on the labile fractions of Zn, Cd, Cu, Ni, and Pb were investigated in a soil contaminated during long-term sewage-sludge application. The accumulation of HM was studied in the aboveground biomass of wheat (*Triticum aestivum* L.). The additives used were the clay minerals Na-bentonite, Ca-bentonite, and zeolite; the Fe oxides hematite and goethite; the phosphate fertilizers superphosphate and Novaphos. Wheat was planted three times during 5 months, allowed to grow for 7 w, and harvested. Dry matter and HM content of shoots were determined after each harvest. Soil samples were taken after the first and third harvest, and the NH_4NO_3-extractable HM contents were determined.

After the addition of 2% Na-bentonite as well as 2% Ca-bentonite, a strong reduction of the labile HM soil fraction and shoot HM concentration was observed. At the end of the experiment, the labile fraction was reduced due to the addition of Na-bentonite and Ca-bentonite by 24% and 31% for Zn, by 37% and 36% for Cd, by 41% and 43% for Cu, by 54% and 61% for Ni, and by 48% and 41% for Pb, respectively. Furthermore, the shoot HM concentrations with the exception of Zn were reduced below the phytotoxicity range. Accordingly, the shoot dry-matter production was significantly increased.

The addition of phosphate fertilizers (notably Novaphos) strongly reduced the bioavailability of Pb for wheat plants. By addition of 0.05% Novaphos, the labile fraction and the shoot concentration of Pb were lowered by 39% and 64%, respectively. However, the addition of Fe oxides and zeolite resulted only in a small reduction in HM bioavailability to wheat plants. Among the studied additives, Na-bentonite and Ca-bentonite have the most promising potential to reduce the bioavailability for the studied HM.

Key words: soil remediation / immobilizing compounds / heavy metals / *Triticum aestivum* / clay minerals / Fe oxides / phosphate fertilizers

1 Introduction

The utilization of sewage sludge for soil improvement is limited by their frequently increased heavy-metal contents (*McGrath* et al., 2000). The bioavailability of heavy metals (HM) in soil depends on their concentration in the soil solution and on the release of HM ions from the solid soil phase (*Krishnamurti*, 1999). Depending on sewage-sludge characteristics and HM content, application of sewage sludge may increase or decrease the soluble HM fraction in soil and may affect the HM transfer into the food chain (*Moreno* et al., 1997). Reducing the HM solubility and bioavailability without removing them from contaminated soils is one measure that could weaken detrimental HM impacts on the environment (*Ma* and *Rao*, 1997). Several strategies promote the immobilization of HM in soils: Immobilization can be achieved by adding natural and synthetic additives such as alkaline materials, phosphate minerals, Fe and Mn oxides, aluminosilicates, and coal fly ash (*Mench* et al., 1998). Due to their very large specific surface area, clay minerals are the most promising materials interacting with many contaminants (*Prost* and *Yaron*, 2001). The adsorption of Ni, Cd, Zn, and Pb by montmorillonite was reported by *Schulthess* and *Huang* (1990). Beringite, a modified aluminosilicate can bind Zn and Cd and strongly reduced or eliminated phytotoxicity for beans (*Mench* et al., 1998). Immobilization of HM by natural zeolite (clinoptilolite) and six synthetic zeolites was studied by *Oste* et al. (2002). They observed that the synthetic zeolites immobilized Cd and Zn, but the amount of HM bound to clinoptilolite was negligible. *Gworek* et al. (1991) investigated the possibility to reduce HM availability in sewage sludge by synthetic zeolites and observed that the synthetic zeolites X and 4A caused a reduction in the availability by 70% for Pb, 57% for Cu, 53.5% for Ni, 67.5% for Zn, and 61% for Cd. *Gworek* (1992) reported that zeolites (*i.e.*, 4A, 13X) also reduced the Pb contents in the tissues of several plant species.

Phosphate minerals have the potential to immobilize Pb in contaminated soils (*Basta* et al., 2001; *Ma* et al., 1995; *Ma*, 1996). The formation of insoluble Pb orthophosphate minerals depends on soil conditions like pH and concentrations of various anions and cations (*Ma* et al., 1993, 1995). Both, phosphate rock and hydroxyapatite effectively immobilized Pb from aqueous solutions and soils (*Ma* and *Rao*, 1997; *Ma* et al., 1994). *Mench* et al. (1994) found that alkaline Thomas phosphate lowered Pb bioavailability and subsequently resulted in the reduction of the Pb content in plants. The addition of K_2HPO_4 to a contaminated soil lowered the bioavailability of Zn and reduced soybean-tissue Zn concentration (*Pierzynski* and *Schwab*, 1993). However, phosphates may also increase, decrease, or have no effects on Zn retention and solubility (*Barrow*, 1987). In several contaminated soils, availability of Cd and Zn for maize was reduced after the amendment of apatite (*Mench* et al., 1998). *Williams* and *David* (1977) reported that the effects of phosphate applica-

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* Correspondence: Prof. Dr. K. Stahr;
e-mail: kstahr@uni-hohenheim.de

tion on the Cd content of plants varied depending on the studied soil. In P-deficient soils, increasing additions of phosphate generally led to decreases in the plant Cd contents. In contrast, in a soil high in P, the addition of phosphate increased Cd content in the plant.

Other additives, such as hydroxides of Fe, Al, and Mn, are also known to enhance HM immobility in soils (*Mckenzie*, 1980; *Fu* et al., 1991; *Mench* et al., 1994). *Brümmer* et al. (1986) described the importance of Fe hydroxides, especially at neutral to slightly alkaline pH, in lowering the HM content in the soil solution. The soluble and exchangeable fractions of Cd, Ni, and Zn in two contaminated soils were decreased by the application of hydrous Fe oxide. However, this did not result in reduced shoot metal uptake by ryegrass and tobacco (*Mench* et al., 1998). *Liang* and *Goen* (1997) reported that the addition of red mud prior to sludge composting reduced HM leaching. Accordingly, the HM release from sludge compost through adsorption and complexation by inorganic components was also reduced.

We studied the effects of varying immobilizing substances on HM lability in a highly contaminated soil. Furthermore, the HM bioavailability for a common crop (wheat) was investigated. Easily available immobilizing substances were selected for this experiment including three clay minerals (Na-bentonite, Ca-bentonite, and zeolite), two phosphate fertilizers (superphosphate and Novaphos), and two Fe oxides (goethite and hematite).

2 Materials and methods

2.1 Soil sampling and analyses

Soil samples were collected from a site located 15 km NE of Stuttgart, SW Germany, where sewage sludge was deposited 50 y ago. According to *FAO-UNESCO* (1997), the soil type is an Urbic Anthrosol ("Reduktosol" according to the German classification for urban soils, *Lehmann* et al., 2000). Soil samples were taken at 15–35 cm depth, corresponding to the Ah2 horizon. The air-dried soil was ground to pass a 2 mm sieve prior to the physico-chemical analysis (Tab. 1). Soil pH was measured with a glass-membrane electrode using a ratio of soil to 0.01 M $CaCl_2$ of 1:2.5 (v/v). Total soil C and N were measured using a LECO 2000 CN analyzer. The inorganic C was determined by a Scheibler apparatus (*Schlichting* et al., 1995). Soil organic carbon (C_{org}) was calculated as the difference between total C and inorganic C. The soil texture was measured by the pipette method (*Schlichting* et al., 1995). The plant-available P was extracted by calcium-acetate-lactate and determined colorimetrically (*Hoffmann*, 1991).

The total concentrations of Zn, Cd, Cu, Ni, and Pb were determined in the soil samples after extraction by the *aqua regia*–microwave digestion method. Microwave digestion was performed using 10 mL of *aqua regia* (HCl : HNO_3 3:1, v/v) with a 9-stage program; the microwave power ranged from 0 to 750 W, the temperature from 70°C to 105°C, and the digestion time was 30 min. Heavy-metal concentrations in the extracts were determined by atomic-absorption spectrometry (AAS Perkin Elmer 3100). For the determination of the soil clay minerals, X-ray–diffraction analysis was performed using a Siemens Instrument (D-500) with Cu-Kα radiation (*Zarei* et al., 2001). In the clay fraction, poorly crystalline clay minerals of kaolinite, illite, and vermiculite/smectite were detected.

Table 1: Physico-chemical properties of the soil contaminated with sewage sludge.

Properties	
Particle size fraction	
Sand	42%
Silt	40%
Clay	18%
pH	7.0
$CaCO_3$	8.9%
Organic C	13.3%
Total N	1.7%
Available P, mg kg^{-1}	440
Total heavy-metal content, mg kg^{-1}	
Zn	4500
Cd	77
Cu	2000
Pb	1650
Ni	442

2.2 Additives

Three clay minerals (Na-bentonite, Ca-bentonite, and zeolite by IKO Minerals GmbH, 45772 Marl, Germany) were used as soil additives. Na-bentonite and Ca-bentonite were composed of clay minerals of the smectite group, mainly montmorillonite (62%–70%). Ca-bentonite with smectites that are predominantly occupied with Ca^{2+} ions originated from mines in Bavaria. Na-bentonite was produced by the exchange of the original earth-alkaline cations of smectites by Na^+ ions in a technical process (alkali-activation). Clinoptilolite (zeolite) is the most abundant naturally occurring zeolite consisting of hydrated alumino-silicate with alkaline-earth cations in a three-dimensional crystalline structure. The studied zeolite was composed of the clay minerals clinoptilolite (80%), montmorillonite (10%), and feldspar (5%). The specific surface area of clay minerals amounted to 88.6, 44.1, and 24.6 m^2 g^{-1} for Ca-bentonite, Na-bentonite, and zeolite, respectively (information from IKO Minerals GmbH).

The synthetic Fe oxides used in this study were goethite (Bayferrox 920) and hematite (Bayferrox 110). Goethite and hematite were composed of 85%–87% and 94%–96% Fe_2O_3, respectively. The phosphate fertilizers studied for their HM-immobilizing capability were superphosphate and Novaphos. The superphosphate is produced by treating rock phosphate with strong sulfuric acid or phosphoric acid or both, resulting in the formation of $Ca(H_2PO_4)_2$ containing 36% P_2O_5. Novaphos is produced by treating rock phosphate with a small amount of sulfuric acid, resulting in $Ca(H_2PO_4)_2$ + apatite, consisting of 23% P_2O_5.

2.3 Pot experiments and analyses

Pot experiments were conducted with wheat plants growing for 7 w in a greenhouse. The air-dried soil samples were sieved through a stainless steel screen (mesh size 15 mm). Afterwards, the soil samples were mixed with the following additives: Na-bentonite, Ca-bentonite, zeolite at 1%, 2% (w/w); goethite and hematite at 1% (w/w); superphosphate, Novaphos at 0.01%, 0.05% P (w/w). Soil-additive mixtures (1.5 kg) were filled in Mitscherlich pots. Each treatment was replicated three times and compared with three nonamended control pots. After 10 d equilibration time in the greenhouse, summer wheat (*Triticum aestivum* L.) was planted. For the first cultivation and harvest, 20 seeds of wheat were planted in each pot and allowed to grow from May 1 until June 19. For the second harvest, 30 seeds were planted in the remixed soil that included all roots and allowed to grow from June 20 until August 8 and from August 10 until September 28 for the third harvest. Soil moisture content was regularly adjusted by adding distilled water in all pots to a water content of 70% water-holding capacity determined using TDR.

For harvesting, the plant shoots were cut directly above the soil surface, washed with deionized water, oven-dried at 80°C for 48 h, weighed for dry-matter yield, and finely ground in a ball mill (Fa Retsch). The shoot concentrations of HM were determined after digestion in 10 mL hot (130°C) HNO_3 for 2 h, dilution of the digestate with 25 mL 0.5 M HNO_3, and filtering through Whatman 540 filter paper (*Pichtel* and *Salt*, 1998). After the first and the third harvest, soil samples were taken from each pot by stainless-steel augers, air-dried, sieved (<2 mm), and stored. The labile fractions of Zn, Cd, Cu, Ni, and Pb were measured after extraction of 2 g soil with 50 mL of 1 M NH_4NO_3 and shaking for 2 h (*Schlichting* et al., 1995). Concentrations of HM in the extracts were measured by AAS.

The bioavailability indices (Bi) were calculated by the equation (*Moreno* et al., 1997):

$$Bi = \text{mg HM (kg shoot)}^{-1} \times 100 \,/\, \text{total content HM (mg (kg soil)}^{-1})\text{.}$$

Results presented are the mean of three replicates, passed the tests for normality, and were statistically analyzed by ANOVA and subsequent *post-hoc* comparisons of means (LSD test, $p = 0.05$).

3 Results and discussion

3.1 Changes in the labile HM fraction in soil during the wheat growing

The initial percentages of HM extractable by NH_4NO_3 were 1.10%, 2.13%, 3.12%, 4.39%, and 0.17% of the *aqua regia*–extractable content of Zn, Cd, Cu, Ni, and Pb, respectively (Fig. 1). Accordingly, the order of HM lability at the beginning of the experiment was Ni > Cu > Zn > Cd > Pb. The high lability of Ni and Cu can be attributed to their high complexation with soluble fractions of soil organic matter (SOM). This is in agreement with *Amrhein* et al. (1992) who found an increased mobility of Cu and Ni in the presence of dissolved organic matter (DOM). In contrast, *Tyler* and *McBride* (1982) reported that Cu and Ni had a greater tendency to form stronger covalent bonds to organic ligands compared to Zn and Cd. Therefore, Cu and Ni should be difficult to extract from SOM. Lead has a strong affinity to organic ligands, and the formation of such complexes can significantly increase the soil Pb lability. Our results indicated that Pb had the lowest lability. Lead may form insoluble, highly stable complexes with the sludge organic matter (*Scheffer* and *Schachtschabel*, 2002).

At the end of the experiment, the labile fractions of Cu, Ni, Zn, and Pb were significantly lower compared to the beginning. This implies that the labile forms of HM were redistribu-

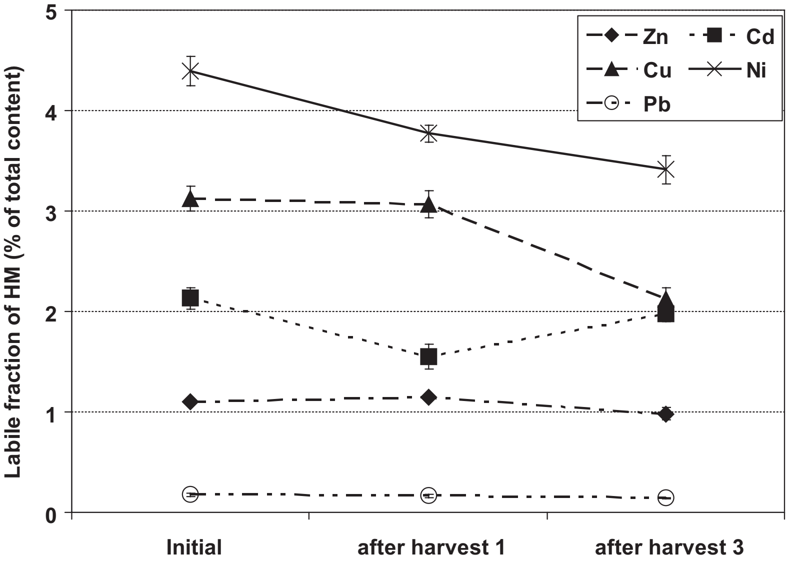

Figure 1: Lability of heavy metal (% of total content) in the control soil during the sampling dates (Mean ± SD).

ted in the course of the experiment. *McBride* et al. (2000) found a strong retention of HM in a sewage-sludge soil high in OM and lime. Recently, it was suggested that sludge-applied HM are mainly associated with sludge organic matter in the soil (*McBride*, 1995). *Ong* and *Bisque* (1968) explained the HM reduction by the fact that humic substances behave as negatively charged colloids, which may be coagulated by electrolytes (*i.e.*, HM). Another observation is that after the release of HM from the sewage sludge, they react with the soil resulting in a decline of HM toxicity with time (*Lewin* and *Beckett*, 1980).

Our results indicated that the initially labile Cd was reduced significantly from 2.13% to 1.55% of total content (at the first sampling date). At the end of the experiment, however, the labile Cd did not change significantly as compared to the beginning. This result may be explained by the formation of soluble organic Cd complexes. *Lamy* et al. (1993) reported that soluble OM from sludge diminished soil Cd retention at pH values between 5 and 7. As OM is stabilized and DOC decreased, however, subsequent Cd precipitation resulted in decreased Cd bioavailability (*Sloan* et al., 1997; *Holm* et al., 1996). Our results showed that the highest reduction of HM lability was found for Cu at the end of the experiment. Organic matter is most important compared to other components in sludge and soil in determining the chemical distribution of Cu with a high affinity for various organic compounds (*Luo* and *Christie*, 1998). Using sequential extractions of sludge-amended soils, Cu was found predominantly in the organic fraction (*Sposito* et al., 1982).

3.2 Effect of additives on the labile HM soil fraction

All additives caused a reduction in the HM lability, ranging from 6% to 61% compared to the control. The highest reduction occurred after addition of Na-bentonite and Ca-bentonite at an application rate of 2% (w/w) (Fig. 2). Bentonites are well known as good adsorbents for HM (*Tiller* et al., 1984; *Stockmeyer* and *Kruse*, 1991). Compared to the control, the addition of bentonites significantly decreased HM lability by 25%–54% for Na-bentonite and by 25%–61% for Ca-bentonite at both sampling dates. By adding the bentonites, the contents of immobilized HM followed the order of Ni > Pb > Cu > Cd > Zn at the end of the experiment (data not shown for Zn). By the addition of zeolite at 1% (w/w), the labile Pb and Cd fractions were significantly reduced only until the first harvest. But the addition of zeolite at 2% (w/w) led to a significant reduction of labile fraction of all HM in a range of 9%–23% at both sampling dates. Among the tested clay minerals, additions of Na-bentonite and Ca-bentonite had stronger reducing effects on the lability of HM than zeolite. This is because Ca-bentonite and Na-bentonite have a higher percentage of montmorillonite (62%–70%) compared to zeolite (10%). This mainly explains the high amount of HM immobilized after addition of Ca-bentonite and Na-bentonite. In a previous study, we found that Na-bentonite and Ca-bentonite had a strong reducing effect on water-extractable forms of Zn, Cd, Cu, and Ni in a sewage sludge–amended soil compared to zeolite (*Usman* et al., 2004).

The addition of superphosphate and Novaphos reduced the labile fractions of Zn, Cu, and Pb at an application rate of 0.05% (w/w) (data not shown for Zn). However, this had no significant effect on the reduction of Cd and Ni lability. Compared to the control, addition of Novaphos significantly reduced labile Zn by 9% and Cu by 14% at the first harvest. At the end of the experiment, however, no significant reductions of both elements were observed. By using superphosphate at 0.05% (w/w), the lability of Zn, Cu, and Pb decreased significantly at both sampling dates. The lability of Pb was strongly reduced using Novaphos by 34% and 39% in the soil samples taken at the first and the third harvest, respectively. The phosphate minerals have the potential to immobilize Pb and to reduce Pb solubility in contaminated soils (*Ma* and *Rao*, 1997; *Ma* et al., 1993, 1994, 1995; *Ruby* et al., 1994). Obviously, P amendments were less effective for immobilization of Zn and Cu compared to Pb (*Ma* et al., 1994). In experiments with several metals, minerals with lower solubility emerge first (*Cao* et al., 2003). Solubility products of Zn and Cu phosphate are much higher compared to Pb phosphate (*Lindsay*, 1979). Therefore, Pb phosphate was formed prior to phosphates of Cu and Zn (*Cao* et al., 2003).

The addition of Fe oxides caused a significant reduction in HM lability. This reduction, however, was small ranging from 9% to 27% for goethite and from 6% to 21% for hematite at both sampling dates. At the end of the experiment, the addition of goethite significantly reduced labile fractions of Cd by 16%, Zn by 14%, Cu by 22%, Ni by 14%, and Pb by 12% compared to the control. However, the addition of hematite caused a significant decrease in labile fractions of Zn (13%), Cu (17%), and Ni (12%). Iron oxides are well known to enhance HM immobility in soils (*Müller* and *Pluquet*, 1997; *Mench* et al., 1994; *Mckenzie*, 1980).

3.3 Effects of additives on HM concentration in wheat shoot and the bioavailability index

Correlations between wheat-shoot HM concentrations and NH_4NO_3-extractable HM indicated significant relationships for Zn ($r = 0.77$ and 0.75), Cd ($r = 0.60$ and 0.59), Cu ($r = 0.89$ and 0.93), Ni ($r = 0.74$ and 0.89), and Pb ($r = 0.60$ and 0.84) in the first and last harvest, respectively. This implies that the HM extracted by NH_4NO_3 are good indicators for their bioavailability to wheat plants, especially for Cu and Ni in the last harvest.

Among the studied soil additives, bentonites had a strong reducing effect on the bioavailability of HM for wheat (Tab. 2). The addition of bentonites at 1% (w/w) significantly reduced the shoot concentrations of Zn, Ni, and Pb compared to the control in harvest 2 and 3, but for Cu only in harvest 3. However, no significant reduction of Cd concentrations was observed. Furthermore, the results showed that the addition of bentonites at 2% (w/w) led to a significant decrease of HM concentrations in wheat shoots compared to the control for all harvests. By adding Na-bentonite and Ca-bentonite, shoot HM concentrations were significantly reduced in the last harvest by 46% and 42% for Zn, by 36% and 20% for Cd, by

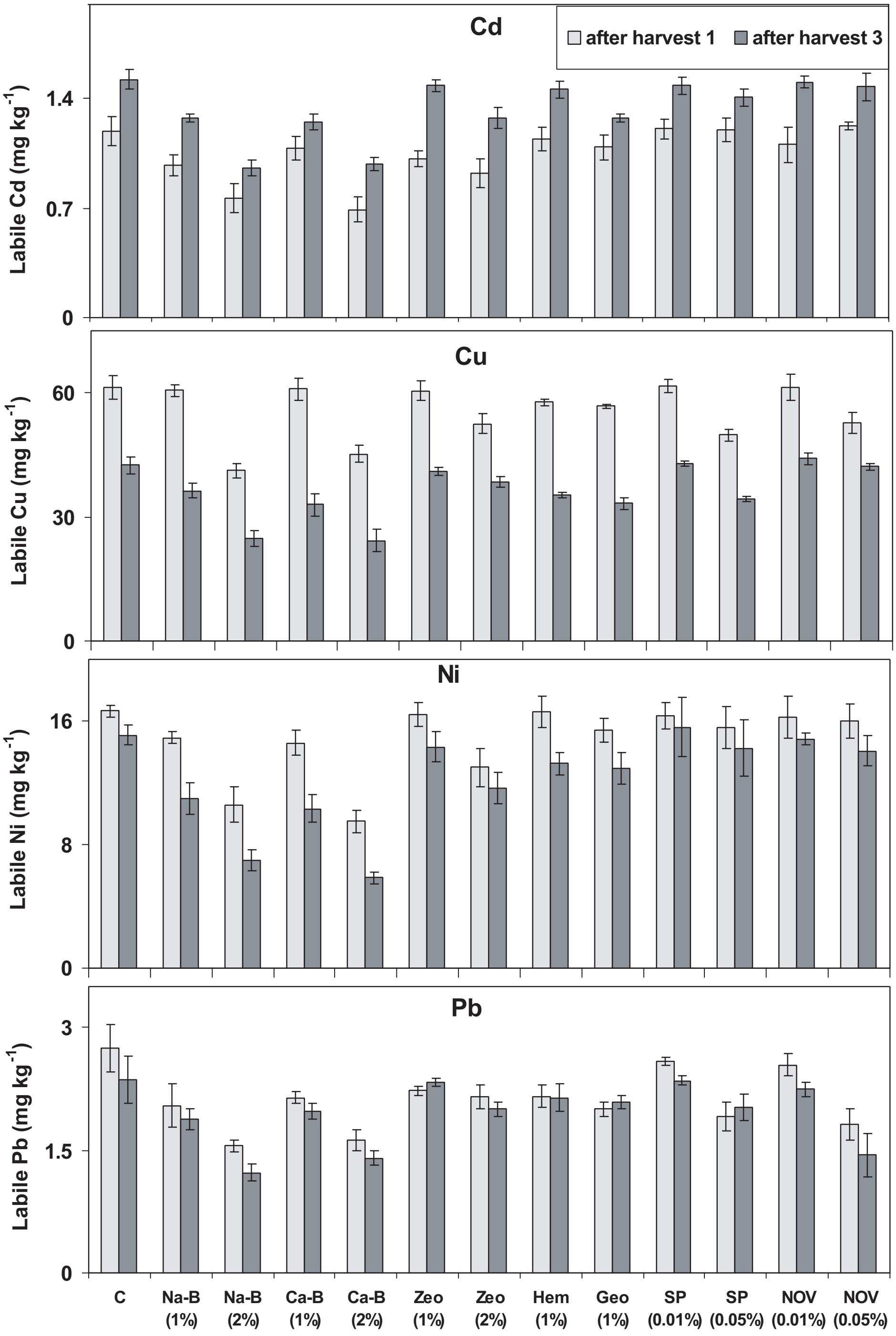

Figure 2: Treatments effect on labile fraction of heavy metals after the first and third harvest (Mean ± SD). (C: control; Na-B (1%): Na-bentonite at 1%; Na-B (2%): Na-bentonite at 2%; Ca-B (1%): Ca-bentonite at 1%; Ca-B (2%): Ca-bentonite at 2%; Zeo (1%): zeolite at 1%; Zeo (2%); zeolite at 2%; Hem (1%): hematite at 1%; Goe (1%): goethite at 1%; SP (0.01%): superphospate at 0.01% P; SP (0.05%): superphosphate at 0.05% P; NOV (0.01%): Novaphos at 0.01% P; NOV (0.05%): Novaphos at 0.05% P*).*

61% and 52% for Cu, by 56% and 65% for Ni, and by 56% and 46% for Pb, respectively. The addition of zeolite at 1% (w/w) did not result in a significant reduction of shoot HM concentrations. But the addition of zeolite at 2% significantly decreased shoot concentrations of Cu by 17% (harvest 1) and of Ni by 20% (harvest 3) compared to the control.

The shoot concentrations of Pb in all treatments were below the phytotoxicity range for plants according to *Scheffer* and *Schachtschabel* (2002) (Tab. 2). By addition of 2% (w/w) Na-bentonite and Ca-bentonite, the shoot concentrations of other HM (except Zn) were reduced below the phytotoxicity range, especially at the end of the experiment. The decrease in shoot HM concentrations after addition of bentonite was reflected by decreased bioavailability indices of HM (Fig. 2), and increased dry-matter yield of wheat. Plant yields can be used as an index of amelioration success and the reduction of HM phytotoxicity (*Mench* et al., 1994).

The addition of superphosphate and Novaphos at 0.05% (w/w) significantly decreased shoot Pb concentrations for all

Table 2: Effect of additives on wheat dry-matter yield (DM) and shoot concentrations of heavy metals in the first and third harvest.

	Harvest 1						**Harvest 3**					
Treatments	DM	Zn	Cd	Cu	Pb	Ni	DM	Zn	Cd	Cu	Pb	Ni
	g pot^{-1}	mg kg^{-1}					g pot^{-1}	mg kg^{-1}				
Control	5.43	283	11.5	40.0	21.1	37.2	7.33	310	6.25	24.3	14.9	13.6
Na-bentonite (1%)	5.67	256	10.9	38.3	19.9	32.5	7.64	232	6.00	20.1	12.7	10.1
Na-bentonite (2%)	6.24	222	7.75	19.6	12.0	21.2	7.97	167	4.00	9.50	6.58	6.00
Ca-bentonite (1%)	5.62	258	10.9	37.5	19.7	33.3	7.58	213	5.83	18.7	12.8	9.58
Ca-bentonite (2%)	6.55	221	9.00	20.0	13.7	23.9	8.06	180	5.00	11.6	8.00	4.83
zeolite (1%)	5.59	279	11.2	37.5	20.6	34.3	7.47	305	6.2	22.4	14.2	13.0
zeolite (2%)	5.29	255	11.1	33.3	19.6	32.5	7.48	293	5.67	22.2	13.5	12.5
hematite (1%)	5.27	260	11.2	37.5	19.1	35.0	7.30	312	5.92	18.6	15.7	12.5
goethite (1%)	5.44	261	11.0	36.7	19.2	36.7	7.51	300	5.67	15.7	14.9	12.3
Superphosphate (0.01% P)	6.14	262	11.3	38.3	17.1	35.0	7.41	296	6.0	24.8	14.5	13.1
Superphosphate (0.05% P)	6.39	229	11.6	31.7	11.7	33.3	7.52	273	5.92	20.3	11.9	12.6
Novaphos (0.01% P)	6.12	271	10.9	39.2	16.3	35.0	7.44	316	6.0	24.9	14.2	13.2
Novaphos (0.05% P)	6.34	252	10.6	34.2	9.42	34.2	7.62	284	5.58	25.1	5.33	13.2
LSD ($p = 0.05$)	0.30	29.7	1.27	3.26	2.09	4.7	0.31	21.9	1.32	2.66	1.45	1.67
*** Phytotoxicity range**	150	220	5–10	14–25	20–35	11–30						

* *Scheffer* and *Schachtschabel* (2002)

harvests as well as significantly increased dry-matter yields (Tab. 2). Among the phosphate fertilizers, the highest decrease in Pb bioavailability was observed by the addition of Novaphos at an application rate of 0.05% (w/w). The efficiency of Novaphos for lowering the bioavailability of Pb to wheat was similar to that of the bentonites. *Laperche* et al. (1997) reported that the addition of apatite to Pb-polluted soil led to a decrease of the Pb concentrations in plant shoots as a result of the formation of pyromorphite in the soil and association of P with Pb in the roots. Although addition of both phosphate fertilizers at 0.01% (w/w) soil had no effect on the reduction of the labile soil HM fraction, it resulted in significantly decreased wheat-shoot concentrations of Pb for the first harvest. Furthermore, dry-matter yield at the first harvest was significantly increased. This reduction in shoot concentration of Pb may be connected with stimulation of plant growth by P and the subsequent dilution of Pb in the plant tissue as well as the inhibition of the translocation of Pb from roots to the shoots.

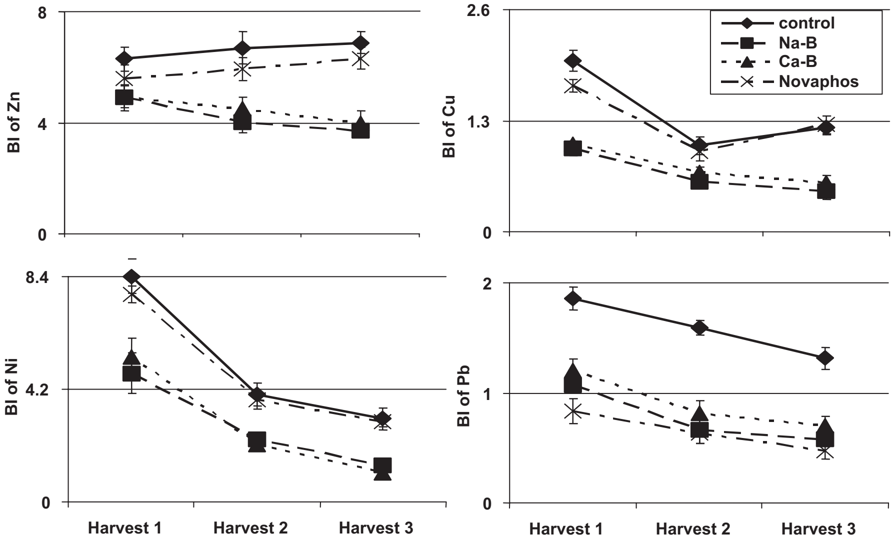

Figure 3: Treatments effect (control; Na-bentonite at 2%; Ca-bentonite at 2%; Novaphos at 0.05% P) on the bioavailability indices (BI) of heavy metals during the experiment (Mean ± SD).

Phosphorus in soils or nutrient solutions can influence plant-tissue Cu and Zn concentrations. Our results showed that bioavailability of Cu for wheat plant was reduced significantly by superphosphate for the three harvests and by Novaphos for the first harvest at the high application rate. Additionally, applying superphosphate significantly reduced the bioavailability of Zn for wheat plants until the first harvest. Applications of P have been reported to cause a decrease in bioavailability of Zn and Cu (*Scheffer* and *Schachtschabel*, 2002; *Mandal* and *Haldar*, 1980). *Pierzynski* and *Schwab* (1993) also reported significant reductions in KNO_3-extractable Zn and plant Zn concentration after P addition, whereas *Singh* et al. (1988) did not find significant changes in water-soluble *plus* exchangeable Zn after adding P.

The addition of both Fe oxides individually had only small effects on the decrease in shoot HM concentrations (Tab. 2). The addition of goethite significantly decreased shoot concentrations of Pb by 17% until the second harvest compared to the control. In contrast, shoot Cu concentrations were reduced significantly by 35% (goethite) and by 23% (hematite) in the last harvest.

4 Conclusions

In a soil developed from sewage sludge, several additives were evaluated in their efficiency to reduce the bioavailability of Zn, Cd, Cu, Ni, and Pb for wheat plant. The additions of 2% (w/w) Na-bentonite and Ca-bentonite were the most effective treatments as indicated by the reductions in lability of HM in the soil, decreases of their content in shoots and increased wheat yields. The addition of phosphate fertilizers, especially Novaphos, at 0.05% (w/w) strongly reduced bioavailability of Pb to wheat plants. The bioavailability of Pb and Cu was reduced by goethite or hematite addition. We conclude that Na-bentonite and Ca-bentonite applied at 2% (w/w) had the highest potential to reduce HM bioavailability for wheat plants.

Acknowledgment

The authors would like to thank Dr. *A. Lehmann* for details provided about the contaminated area. We are very thankful to *IKO Minerals GmbH* for providing their bentonites and zeolite. This work was partly funded by *Egyptian government* within the scope of a fellowship for A. R. A. Usman.

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