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Effect of Immobilizing Substances and Salinity on Heavy Metals Availability to Wheat Grown on Sewage Sludge-Contaminated Soil

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*The objective of the investigation was to evaluate the effect of immobilizing substances and NaCl salinity on the availability of heavy metals: Zn, Cd, Cu, Ni, and Pb to wheat (*Triticum aestivum *L.). In greenhouse pot experiment, a sewage sludge amended soil was treated with the following immobilizing substances: three clay minerals (Na-bentonite, Ca-bentonite and zeolite), iron oxides (goethite and hematite), and phosphate fertilizers (superphosphate and Novaphos). The pots were planted with wheat and were irrigated either with deionized or saline water containing 1600 mg L^{-1} NaCl. Wheat was harvested two times for shoot metal concentrations and biomass measurements. Metal species in soil solution were estimated using the software MINEQL+.*

The addition of metal immobilizing substances to the soil significantly decreased metal availability to wheat. The largest reduction in metal bioavailability was found for bentonites. The irrigation with saline water (1600 mg L^{-1} NaCl) resulted in a significant increase in metal chloride species (MCl^+ and MCl_2^0). The highest metal complexation with Cl occurred for Cd, which was about 53% of its total soil solution concentration. The total concentration of Cd (Cd_T) in soil solution increased by 1.6–2.8-fold due to saline water. The NaCl salinity caused a significant increase in uptake and shoot concentration of Cd for two harvests and small but significant increase in shoot Pb concentration for the second harvest. It was concluded that the use of bentonites is the most promising for the reduction of heavy metal availability to plants. Saline water containing 1600 mg L^{-1} NaCl increased the availability of Cd and Pb to wheat and decreased the efficiency of bentonites to immobilize soluble Cd.

Keywords Heavy metal species, clay minerals (Na-bentonite, Ca-bentonite, and zeolite), iron oxides, phosphate fertilizers, NaCl salinity, heavy metals uptake.

Introduction

Application of sewage sludge is a common practice in many countries for utilization of the increasing amounts of municipal waste produced by urban populations. Sewage sludge contains significant quantities of organic matter and nutrients such as nitrogen, and phosphorus, and therefore increases organic carbon (OC) level in soil and provides readily available nutrients for plants (Weggler-Beaton *et al.*, 2000; Sommers *et al.*, 1976). However, sewage

sludge also contains heavy metals (HM) such as cadmium (Cd), zinc (Zn), copper (Cu), nickle (Ni), and lead (Pb), which can be taken up by plants in excess amount, with potential implications for food quality. The total contents of metals in soils, however, may not reflect their bioavailability (Silveira *et al.*, 2003). The soluble and exchangeable metal fractions are the most important pools regarding their bioavailability and toxicity. Thus, it is very important to reduce HM solubility and bioavailability in contaminated soils. In situ immobilization of HM in contaminated soil is one of the common practices reducing the negative impacts on the environment and improving the soil and food quality (Oste *et al.*, 2002). Many additives have been screened for their potential to immobilize HM in soil (Oste *et al.*, 2002; Mench *et al.*, 1998; Ma, 1996). The additives must obviously possess a high binding capacity, but they should not impair soil structure, fertility, and nutrient availability. Immobilization of HM could be carried out by adding additives such as clay minerals, lime, phosphate minerals, and iron and manganese oxides. Before this technology can be field-applied, however, many factors affecting HM immobilization by these additives must be understood. One of the many factors affecting the solubility and immobilization of heavy metals is complex formation with inorganic ligands in soil solution (Temminghoff *et al.*, 1995; Hirsch *et al.*, 1989; Mattigod and Sposito, 1977; Garcia-Miragaya and Page, 1976). The presence of complexing ligands may increase metal retention or greatly increase metal mobility (McLean and Bledsoe, 1992). The common inorganic ligands, complexed with heavy metals, are SO_4^{2-}, Cl^-, OH^-, PO_4^{3-}, NO_3^-, and CO_3^{-2} (Scheffer and Schachtschabel, 2002). Among these ligands, chlorides are highly mobile and therefore, under certain conditions, they could be an important factor in the distribution of heavy metals between binding fractions. Therefore, in many arid regions, saline irrigation water containing high level of Cl^- might aggravate heavy metal pollution problems and any technology to immobilize heavy metals may not be effective, as a result of the formation of HM-Chloride complexes. Chloro-complexes are particularly strong with some heavy metals such as Cd, Hg, Pb, and Zn (Hahne and Kroontje, 1973). Doner (1978) reported that Cl^- increased the mobility of Ni, Cu, and Cd in soil and attributed this phenomenon to the formation of HM-chloride complexes. Maas *et al.* (1972) studied the effects of NaCl salinity on the uptake of Fe, Mn, and Zn by plants grown in nutrient solution cultures. They observed increased leaf concentration of these metals, but not an actual increase in total uptake. Chloro-complexation raises total Cd concentrations in soil solution (Smolders *et al.*, 1998) and could lead to enhanced Cd uptake by crops through either faster diffusion of Cd to roots through soil, or larger uptake of Cd if chloro-complexes are transported across the root membrane. Several authors have found enhanced Cd uptake by plants when grown in Cl^--affected soils (Bingham *et al.*, 1984; McLaughlin *et al.*, 1994). Weggler-Beaton *et al.* (2000) demonstrated that cadmium concentrations in soil solution and shoots of wheat and Swiss chard plants increased linearly with increasing Cl concentration in solution from the biosolids-amended soil.

The aim of this work, therefore, was to study the effect of different immobilizing substances (clay minerals; Fe-oxides; phosphate fertilizers) and complexing HM with Cl on concentration of heavy metals (Zn, Cd, Cu, Ni, and Pb) in soil solution and their availability to a common crop (wheat).

Materials and Methods

Soil Characteristics

Soil samples were collected from a site located 15 km northeast of Stuttgart, southwest of Germany, where sewage sludge was deposited 50 years ago. According to FAO-UNESCO

(1997), the soil type is an Urbic Anthrosol. The German name for this soil type is Reduktosol (Lehmann *et al.*, 2000). The soil samples were taken from the 15- to 35-cm layer, corresponding to Ah2 horizon. The particle size distribution was 18% clay, 40% silt, and 42% sand. The soil pH measured in 1:2.5 soil to water suspension was 6.9. This soil had 13.3% organic carbon, 8.9% $CaCO_3$. The contents of heavy metals in the soil were: 4500 mg $Zn\,kg^{-1}$; 77 mg $Cd\,kg^{-1}$; 2000 mg $Cu\,kg^{-1}$; 1650 mg $Pb\,kg^{-1}$; 442 mg $Ni\,kg^{-1}$. X-ray diffraction analysis to determine the soil clay minerals 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 type were detected.

Additives

Na-bentonite and Ca-bentonite used in this study are composed of clay minerals of the smectite group. The most common smectites are montmorillonites (62–70%). Ca-bentonite with smectites that are predominantly occupied with Ca^{2+} ions originated from Bavarian mines. Na-bentonite was produced by exchange of earth-alkaline cations from smectite by Na^{2+} ions in a technical process (alkali-activation). Clinoptilolite (zeolite) is the most abundant naturally occurring zeolite consisting of hydrated aluminosilicate with alkali and earth alkali cations in a three-dimentional crystal structure. Zeolite was another additive, which is composed of clay minerals of clinoptilolite (80%), montmorillonite (10%), and feldspar (5%). The synthetic Fe-oxides used in this study were goethite (Bayferrox 920) and Hematite (Bayferrox 110). The Fe-oxides are composed of (85–87%) and (94–96%) of Fe_2O_3 for goethite and hematite, respectively. As P additives, superphosphate and Novaphos were used. The superphosphate is a compound [Ca $(H_2PO_4)_2$] produced by a treating rock phosphate with a strong sulfuric acid or phosphoric acid, or both and it contains about 36% P_2O_5. The Novaphos is a compound [Ca $(H_2PO_4)_2$ + apatite] produced by treating rock phosphate with a small amount of sulfuric acid and it contains about 23% P_2O_5.

Pot Experiment

The soil samples were air-dried and sieved through a 15-mm diameter stainless steel screen. Afterwards, the soil samples were mixed with the following immobilizing substances: three clay minerals of either Na-bentonite, Ca-bentonite or zeolite at 2% (w/w); Fe-oxides of either goethite or hematite at 1% (w/w); phosphate fertilizers of either superphosphate or Novaphos at 0.05% P (w/w). Soil samples (1.5 kg) of untreated soil and soil treated with immobilizing agents were placed in pots in 3 replicates for each treatment. The soil samples, without plants, were then incubated at 70% moisture content of the water holding capacity for one year in a greenhouse.

   After one year of incubation, the samples of each pot were then air-dried, divided into two 0.75 kg portions, and each portion was filled into a plastic pot. A greenhouse pot experiment was conducted with summer wheat (*Triticum aestivum* L.) in six replicates for control soil and soil treated with immobilizing substances. For each treatment, three replicates were irrigated with deionized water while the remaining three replicates were irrigated with saline water (1600 mg L^{-1}). Wheat was planted two times in the pots (10 seeds per pot). For each time, the wheat shoots were harvested after 30 days of growth. Cultivation began on May 5, 2003, and ended in July 6, 2003. All pots were adjusted daily

to water content of 70% water holding capacity using TDR (*Time Domain Reflectrometry*) with deionized water or saline water containing 1600 mg L^{-1} NaCl.

Analyses

Wheat shoots were cut at the soil surface and washed. Wheat shoots were then oven-dried at 80°C for 48 h, weighed for dry matter yield, and ground using a ball mill. Shoot concentrations of HM were determined after digesting in 10 mL hot (130°C) HNO_3 for 2 h. The digested samples were diluted with 25 mL 0.5 M HNO_3 before filtering through Whatman no. 540 filter paper (Pichtel and Salt, 1998). The digestates were analyzed for Zn, Cd, Cu, Ni, and Pb by atomic absorption spectrometry (AAS Perkin Elmer 3100).

At the end of the experiment, soil samples from the pots were collected, air-dried, crushed to pass through a 2 mm sieve, and stored for further chemical analysis. The soil solution from these samples was extracted using 1:2.5 soil to water. Electrical conductivity (EC), pH and concentrations of Ca, Mg, Na, K, SO_4, CO_3, HCO_3, PO_4, NO_3, Cl, as well as Cd, Zn, Cu, Ni, and Pb were measured in the soil solution. The pH of the solutions was measured with a glass electrode. The concentrations of Na and K were determined using a flame photometer. The concentrations of Ca, Mg, Cl, CO_3, and HCO_3 were determined using titrimetry (Page *et al.*, 1982). Sulfate (SO_4) was determined using the turbidimetric method and the resulting turbidity is measured by a spectrometer (Page *et al.*, 1982). Phosphorus in the soil solution was determined colorimetrically (Hoffmann, 1991). The concentration of NO_3 was determined using an autoanalyser (Fa. Scalar). The total concentration of HM $[M_T]$ in the soil solutions was analyzed by AAS.

The MINEQL+ PC software was used to estimate activity of chemical species of heavy metals in soil solution (Schecher and McAvoy, 2001). Concentration of major cations, anions, HM, and pH were used as input parameters to calculate the concentration of free hydrated HM (M^{2+}) and ligand species with MINEQL+. In our speciation calculations, the organic HM complexes were ignored.

Statistical Analysis

An analysis of variance (ANOVA) was carried out to estimate significant differences depending on the concentration of HM (M_T) and ligand species (M^{2+}, MCl^+, and MCl_2) in soil solution, as well as the shoot weight and shoot heavy metal concentrations (LSD, test, at $P = 0.05$). In addition, forward stepwise multiple regression was used to establish the relation between the independent variables (concentration of HM $[M_T]$, $[M^{2+}]$, and $[MCl^+]$) in the soil solution, and the dependent variables (either the HM uptake or the HM shoot concentration) for harvest 2.

Results and Discussion

Effect of Immobilizing Substances on Heavy Metal Concentrations in Soil Solution

The addition of immobilizing substances (clay minerals, Fe-oxides, and phosphate fertilizers) decreased significantly metal concentrations in soil solution (Tables 1a and 1b),

Table 1a

Effect of immobilizing substances and salinity on concentrations and speciation of Zn, Cd, and Ni (M_T, M^{2+}, MCl^+, and MCl_2) in solution of sewage sludge soil

Treatments	Zn_T	Zn^{2+}	$ZnCl^+$	$ZnCl_2^0$	Cd_T	cd^{2+}	$CdCl^+$	$CdCl_2^0$	Ni_T	Ni^{2+}	$NiCl^+$	$NiCl_2^0$
					μM L^{-1} Irrigation with deionized water							
Control	44.6	41.4	0.074	0.0	0.41	0.36	0.025	0.0	10.9	10.2	0.019	0.00
Na-bentonite	21.6	20.1	0.037	0.0	0.23	0.20	0.014	0.0	2.10	1.97	0.004	0.00
Ca-bentonite	27.3	25.6	0.044	0.0	0.21	0.18	0.012	0.0	3.07	2.89	0.005	0.00
Zeolite	38.8	35.9	0.068	0.0	0.28	0.24	0.017	0.0	4.71	4.40	0.008	0.00
Goethite	35.2	32.4	0.062	0.0	0.33	0.29	0.021	0.0	7.50	6.96	0.014	0.00
Hematite	43.1	39.9	0.073	0.0	0.36	0.31	0.022	0.0	10.1	9.40	0.017	0.00
Superphosphate	38.4	35.4	0.062	0.0	0.42	0.36	0.025	0.0	10.1	9.39	0.017	0.00
Novaphos	42.2	39.0	0.078	0.0	0.40	0.33	0.031	0.0	9.71	9.02	0.018	0.00
LSD 1 ($P = 0.05$)	3.48	3.22	0.011	3.8E-05	0.09	0.08	0.01	6E-05	1.85	1.73	0.004	3.0E-08
					Irrigation with saline water containing 1600 mg L^{-1} NaCl							
Control	47.9	43.6	1.57	0.053	0.71	0.28	0.38	0.034	12.7	11.70	0.43	0.0
Na-bentonite	25.2	23.1	0.81	0.027	0.52	0.21	0.28	0.024	2.72	2.51	0.09	0.0
Ca-bentonite	28.4	26.2	0.90	0.029	0.58	0.24	0.31	0.027	3.86	3.57	0.13	0.0
Zeolite	41.0	37.4	1.33	0.045	0.67	0.26	0.36	0.032	5.34	4.88	0.18	0.0
Goethite	38.0	34.5	1.26	0.043	0.63	0.25	0.34	0.031	9.03	8.26	0.31	0.0
Hematite	45.4	41.4	1.49	0.050	0.67	0.26	0.36	0.032	11.2	10.30	0.38	0.0
Superphosphate	41.3	37.5	1.33	0.045	0.69	0.27	0.37	0.032	11.5	10.50	0.38	0.0
Novaphos	42.6	38.6	1.39	0.047	0.72	0.28	0.39	0.034	11.8	10.7	0.39	0.0
LSD 1 ($P = 0.05$)	4.40	4.03	0.15	0.006	0.10	0.04	0.05	0,005	1.68	1.51	0.06	7E-06
LSD 2 ($P = 0.05$)	NS	NS	0.11	0.004	0.05	NS	0.018	0.002	NS	NS	0.05	6E-06

0.0 The concentration of the species ranged from 10^{-4} to 10^{-6}; 0.00 The concentration of the species ranged from 10^{-7} to 10^{-8}; LSD 1: Significant differences between treatments of immobilizing substances; LSD 2: Significant differences between saline and non-saline treatments; NS: Not significant.

Table 1b

Effect of immobilizing substances and salinity on concentrations and speciation of Cu and Pb (M_T, M^{2+}, MCl^+, and MCl_2) in solution of sewage sludge soil

Treatments	Cu_T	Cu^{2+}	$CuCl^+$	$CuCl_2^0$	Pb_T	Pb^{2+}	$PbCl^+$	$PbCl_2^0$
	μM L^{-1} Irrigation with deionized water							
Control	26.3	24.0	0.027	0.0	1.25	1.01	0.025	0.0
Na-bentonite	12.7	11.7	0.013	0.0	0.38	0.31	0.008	0.0
Ca-bentonite	10.6	9.79	0.011	0.0	0.55	0.45	0.011	0.0
Zeolite	17.4	15.9	0.019	0.0	0.76	0.61	0.016	0.0
Goethite	10.7	9.7	0.012	0.0	0.60	0.47	0.013	0.0
Hematite	16.7	15.2	0.018	0.0	0.77	0.62	0.016	0.0
Superphosphate	17.1	15.5	0.017	0.0	0.80	0.64	0.016	0.0
Novaphos	15.0	13.3	0.022	0.0	0.43	0.33	0.012	0.0
LSD 1 ($P = 0.05$)	2.48	2.00	0.008	4.0E-06	0.15	0.12	.005	4E-05
	Irrigation with saline water containing 1600 mg L^{-1} NaCl							
Control	25.5	23.2	0.53	0.004	1.22	0.71	0.36	0.034
Na-bentonite	12.4	11.4	0.25	0.002	0.40	0.23	0.13	0.012
Ca-bentonite	12.8	11.8	0.25	0.002	0.52	0.31	0.15	0.014
Zeolite	16.6	15.2	0.34	0.003	0.82	0.47	0.24	0.023
Goethite	11.7	10.7	0.25	0.002	0.64	0.37	0.19	0.018
Hematite	17.5	16.0	0.36	0.003	0.84	0.48	0.25	0.024
Superphosphate	18.3	16.7	0.38	0.003	0.72	0.42	0.21	0.020
Novaphos	17.2	15.7	0.37	0.003	0.47	0.27	0.14	0.013
LSD 1 ($P = 0.05$)	2.73	2.49	0.06	4.6E-04	0.13	0.08	0.04	0.004
LSD 2 ($P = 0.05$)	NS	NS	0.04	3.0E-04	NS	0.1	0.03	0.003

0.0 The concentration of the species ranged from 10^{-4} to 10^{-6}; LSD 1: Significant differences between treatments of immobilizing substances; LSD 2: Significant differences between saline and non-saline treatments; NS: Not significant.

ranging from 12% to 81% compared with untreated soil. The highest decrease in concentrations of HM in soil solution was found for bentonites. Bentonites are known as good adsorbents for HM ions (Tiller *et al.*, 1984; Stockmeyer and Kruse, 1991). The Na- and Ca-bentonites used in this study reduced soil solution metal concentration by 52% and 39% for Zn, 44% and 50% for Cd, 52% and 60% for Cu, 81% and 72% for Ni, and 70% and 56% for Pb, respectively, compared to the control. The addition of zeolite caused a significant reduction in soil solution metal concentrations, ranging from 13% to 57%. The zeolite addition decreased Ni concentration in soil solution by 57% as compared to the control. The results suggest that Na-bentonite and Ca-bentonite have a stronger impact on reducing the concentrations of HM in soil solution than the zeolite. This could be explained by the high contents of montmorillonite in the bentonites. The Na- and Ca-bentonite have a higher proportion of montmorillonite (62–70%) than the zeolite (10%). Clay minerals such as montmorillonite are suitable as binding additives because they have large specific surface areas and large cation exchange capacity (Lothenbach *et al.*, 1995, 1998). The adsorption of HM cations on montmorillonite is mainly by ion exchange, and so they can be readily exchanged for other cations such as calcium and magnesium (Van Bladel *et al.*, 1993). The binding of Ni, Cd, Zn, and Pb onto montmorillonite was reported by Schulthess and Huang (1990).

The results suggest that all tested clay minerals have a high effect on reducing Ni in the soil solution. This is because of the fact that Ni^{2+} has the highest crystal field stabilization energy of the common divalent metals and thus has a high potential to be enriched in clay minerals (Iskandar and Kirkham, 2001). While addition of clay minerals reduces soluble metal concentration by exchange reactions, one needs to consider the release of adsorbed HM into soil solution due to mass action by other more common cations such as H^+, Al^{3+}, Ca^{2+}, Mg^{2+}, and Na^+. Many studies demonstrated that the presence of Ca^{2+} or Al^{3+} ions reduced the efficiency of heavy metals adsorption by clay minerals (Garcia-Miragaya and Page, 1977; Bittel and Miller, 1974), suggesting Ca^{2+} or Al^{3+} competition for adsorption sites. Cavallaro and McBride (1978) reported that low soil pH has the effect of increasing the fraction of functional groups in soil organic matter that is associated with H^+ or Al^{3+}, thereby reducing the ability of either Cu^{2+} or Cd^{2+} to be adsorbed. Therefore, the changes in the soil environment over time, such as the turnover of the organic matter and changes in pH, or soil solution composition, may enhance metal mobility and reduce the efficiency of clay minerals to immobilize HM.

The addition of superphosphate and Novaphos reduced significantly Cu and Pb concentrations in the soil solution (Table 1b). Moreover, only the addition of superphosphate reduced significantly the concentration of Zn (Table 1a). The added phosphate fertilizers, however, had no significant effect on the reduction of Cd and Ni concentrations. The highest reduction of HM concentration in soil solution was found for Pb by using Novaphos. The addition of Novaphos decreased concentration of Pb by 65% compared to the control soil. The literature on the use of phosphate minerals for remediation of contaminated soils deals mainly with Pb (Ma and Rao, 1997; Ma *et al.*, 1993, 1995). The primary mechanism of Pb immobilization appears to be through phosphate-mineral dissolution and subsequent precipitation of pyromorphite-like minerals, through mechanisms such as cation substitution, adsorption and precipitation as other Pb minerals are also possible (Ma, 1996). Several insoluble Pb orthophosphate minerals are formed after P reaction with Pb-contaminated soils depending on the reaction condition, such as pH and presence of other anions and cations (Ma *et al.*, 1993, 1994a, 1994b, 1995).

The addition of goethite reduced significantly the concentration of Zn by 21%, Cu by 59%, Ni by 32%, and Pb by 53% compared to control (Tables 1a and 1b). But, the addition of hematite reduced significantly the concentration of Cu by 35% and Pb by 39%. Fe-oxides are known to enhance metal immobility in soils (Müller and Pluquet, 1997; Mench *et al.*, 1994; McKenzie, 1980). By using both goethite and hematite, the large reduction of these heavy metals in soil solution was found for Cu and Pb. This finding concurs with that of Schwertmann and Taylor (1989) who reported that both goethite and hematite had selectivity for adsorption of Cu and Pb higher than for Zn, Cd, and Ni.

Effect of NaCl Salinity on Speciation of Heavy Metals in Soil Solution

The soil solution characteristics, such as pH, Ca, Mg, PO_4, NO_3, SO_4, and HCO_3, remained mainly unaffected after irrigation with saline water (1600 mg L^{-1}) compared with the irrigation with deionized water. But the irrigation with saline water caused a significant increase of Na and Cl in soil solution (data not shown). Moreover, the irrigation with saline water caused small but significant increase of K.

In soil solution, metals can be present either as free-ions or complexes with inorganic and organic ligands. The resulting association has a lower positive charge than the free metal ions, and may be uncharged or carry a net negative charge, thereby higher mobility (McLean and Bledsoe, 1992). In our investigation, the speciation calculations for the soil
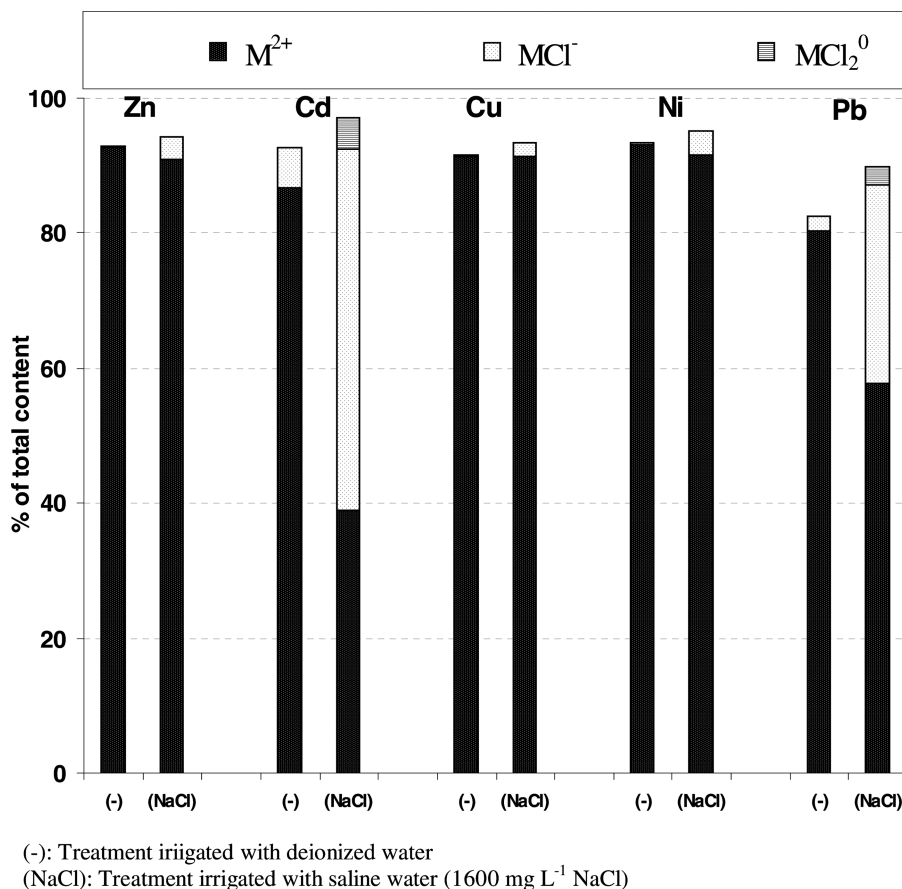
(-): Treatment iriigated with deionized water
(NaCl): Treatment irrigated with saline water (1600 mg L^{-1} NaCl)

Figure 1. Effect of NaCl salinity on major chemical species of heavy metals (Zn, Cd, Cu, Ni, and Pb) in soil solution, as percentages of total concentration. The residue to 100% consists from MSO_4^0, $M(NO_3)_2^0$, MNO_3^+, and $M(OH)_2^0$, and MOH^+.

solution predicted that the studied metals (Cd, Zn, Cu, Ni, and Pb) were mainly present as the free metal (M^{2+}) ion in soil solution (Figure 1). The free ion (M^{2+}) of HM amounted to 76–90% of total concentration. A shortcoming in our speciation calculation is that the organic heavy metal complexes are ignored. If organic ligands are taken into account in our speciation calculation, a significant proportion of some heavy metals might be complexed with organic ligands. Among studied HM, Cu is known to have a high complexing nature with soluble organic matter (McLean and Bledsoe, 1992; Inskeep and Baham, 1983). In many studies, the speciation calculation for soil solution predicted that the high proportion of Cd, Zn and Pb in soil solution presents as free Cd^{2+} (80–90%), Zn^{2+} (78–97%), and Pb^{2+} (43–75%) (Holm *et al.*, 1995; Percival *et al.*, 1999). In soil solution Ni can also present mainly as free Ni^{2+} (Scheffer and Schachtschabel, 2002). It was observed that the small percentage of studied HM was found as MSO_4^0, MCl^+, $M(NO3)_2^0$, MNO_3^+, $M(OH)_2^0$, and MOH^+ in soil solution, ranging from less than 1% to 12% of total concentration.

Irrigation with NaCl water resulted in a significant increase in concentrations of MCl^+ and MCl_2^0 species for heavy metals (Tables 1a and 1b). Chloride ions may be regarded as a selective ligand for HM, especially for Cd. The results indicate that the highest

complexation with Cl was found for Cd and Pb. It is known that Cd can readily form stable complexes with chloride ligands even in the presence of organic ligands (Hahne and Kroontje, 1973). Chloride ligands will compete for Cd with other organic and inorganic ligands present in soil solution (Garcia-Miragaya and Page, 1976). Our results showed that NaCl salinity caused a large decrease in the ratios of Cd^{2+}/Cd_T and Pb^{2+}/Pb_T and increase in the ratios of $CdCl^+/Cd_T$ and $PbCl^+/Pb_T$ (Figure 1). As examples, due to NaCl salinity, the estimated percentage of $CdCl^+$ increased from 6% to 53% and that of $PbCl^+$ increased from 2% to 29%, with only a small percentage (2–3%) of chloride complexes with Zn, Cu, 0 and Ni.

Among studied HM, only the total concentration of Cd (Cd_T) in soil solution was increased significantly by chloride salinity (Table 1a), mainly by enhanced solubility of Cd through the formation of chloro-complexes of Cd (Weggler-Beaton *et al.*, 2000; Smolders *et al.*, 1998; Doner, 1978). Sodium may also be implicated in enhancing Cd solubility due to Na in irrigation water displacing Cd from soil exchange sites into solution (McLaughlin *et al.*, 1994). Many studies, however, demonstrated that monovalent cations such as Na are relatively inactive at displacing divalent cations such as Cd, even at relatively high concentration of Na (Norvell *et al.*, 2000; Smolders *et al.*, 1998). The results showed that the concentration of Cd in soil solution increased from 0.21–0.42 μM to 0.52-0.72 μM due to the NaCl salinity. The calculated concentrations of $CdCl^+$ and $CdCl_2^0$ in soil solution increased significantly due to the irrigation with saline water (1600 mg L^{-1} NaCl). The irrigation with saline water increased $CdCl^+$ from 0.012–0.031 μM to 0.28–0.39 μM and $CdCl_2$ from 5.1×10^{-5}–$1.0 \times 10^{-4}\mu$M to 0.024–0.034 μM. These results concur with Bingham *et al.* (1983) who found that NaCl resulted in increases in soluble Cd and $CdCl^+$ activity. In general, the estimated Cd^{2+} activity was unaffected by the NaCl salinity. This is likely due to the strong buffering of Cd^{2+} activity by the soil components. This finding is in agreement with the result of Weggler-Beaton (2000), who reported that NaCl salinity did not affect the activity of Cd^{2+} in soil.

The concentration of Pb (Pb_T) in soil solution was not affected significantly by saline water (Table 1b). The NaCl salinity caused a decrease in the free ionic Pb [Pb^{2+}], $PbNO_3^{+1}$, and $PbSO_4^0$ (data not shown for $PbNO_3^{+1}$ and $PbSO_4^0$). In contrast, the NaCl salinity caused a high increase in concentration of $PbCl^+$. The NaCl salinity resulted in an increase of $PbCl^+$ from 0.008–0.025 μM to 0.13–0.36 μM. Hahne and Kroontje (1973) reported that chloride could form complexes with Pb.

The results showed that the NaCl salinity did not affect the efficiency of immobilizing substances to reduce concentrations of Zn, Cu, Ni, and Pb in soil solution. It was observed that the addition of immobilizing substances to the soil however did not inhibit the increase of soluble Cd due to NaCl salinity. As compared to the soil irrigated with deionized water, the efficiency of clay minerals to immobilize soluble Cd decreased due to the irrigation water salinity (1600 mg L^{-1} NaCl). This observation is explained by the formation of Cd-chloride complexes, which affect the sorptive behavior of Cd, resulting in reducing its sorption by soil or clay surfaces (Garcia-Miragaya and Page, 1976; Temminghoff *et al.*, 1995). The effect of complex formation on HM sorption is dependent on the type and amount of HM present, the type and amount of ligands present, soil surface properties, soil solution composition, pH and redox. In general, the decrease in positive charge on the complexed metal reduces adsorption to negatively charged surfaces (McLean and Bledsoe, 1992). In the presence of inorganic ligands Cl^- and SO_4^{2-}, the adsorption of Cd on soil was inhibited (O'Connor *et al.*, 1984; Hirsch *et al.*, 1989; Egozy, 1980; Benjamin and Leckie, 1982) due to the formation of cadmium complexes that were not strongly adsorbed by the soils.

Table 2

Effect of immobilizing substances and salinity on wheat yield and shoot concentrations of heavy metals

Treatments	Harvest 1						Harvest 2					
	DM	Zn	Cd	Cu	Ni	Pb	DM	Zn	Cd	Cu	Ni	Pb
	g/pot		mg kg^{-1}				g/pot			mg kg^{-1}		
	Irrigation with deionized water											
Control	3.32	363	10.3	32.5	42.5	17.9	2.18	354	8.7	23.0	20.0	16.1
Na-bentonite	3.53	314	7	22.5	32.5	10.9	2.22	301	6.8	13.5	11.2	8.2
Ca-bentonite	3.40	300	7.2	18.3	28.3	14.5	2.18	337	5.6	11.4	12.7	8.7
Zeolite	3.46	363	8.1	24.2	30.0	14.2	2.10	336	7.6	16.6	12.3	14.8
Goethite	3.13	355	8.7	22.4	34.2	15.3	2.17	337	7.8	16.5	17.0	12.2
Hematite	3.22	354	9.4	25.0	36.8	15.6	2.11	346	7.3	17.2	19.4	15.0
Superphosphate	3.64	351	9.0	20.8	37.5	15.0	2.21	348	8.0	16.9	20.3	13.0
Novaphos	3.53	357	9.6	25.0	39.2	13.2	2.13	340	7.7	17.8	19.3	9.6
LSD 1 ($P = 0.05$)	NS	33.8	1.7	4.4	5.69	1.75	NS	30.4	1.60	2.13	2.55	2.30
	Irrigation with saline water containing 1600 mg L^{-1} NaCl											
Control	3.28	357	15.3	33.3	40.0	19.1	1.88	348	16.8	21.5	22.3	19.1
Na-bentonite	3.60	327	11.4	21.4	29.2	12.8	1.93	324	15.4	11.6	9.0	9.7
Ca-bentonite	3.64	331	9.3	20.3	30.0	14.1	1.91	320	12.0	12.7	13.5	12.3
Zeolite	3.31	353	11.2	23.1	31.7	15.3	1.84	328	15.0	16.4	12.6	17.5
Goethite	3.19	358	13.3	24.2	35.0	15.4	1.89	341	15.8	12.7	18.1	16.6
Hematite	3.34	347	13.4	23.3	35.8	16.2	1.76	343	16.1	19.8	18.2	17.9
Superphosphate	3.50	347	13.4	21.3	40.6	16.8	1.83	339	15.1	19.7	18.1	16.1
Novaphos	3.40	340	14.1	28.8	38.0	14.8	1.90	338	15.9	18.3	18.6	9.1
LSD 1 ($P = 0.05$)	NS	28.9	2.16	5.84	4.93	2.35	NS	29.8	1.89	3.71	2.97	2.23
LSD 2 ($P = 0.05$)	NS	NS	1.35	NS	NS	NS	0.05	NS	0.83	NS	NS	2.05

LSD 1: Significant differences between treatments of immobilizing substances; LSD 2: Significant differences between saline and non-saline treatments; DM: Dry matter of wheat; NS: Not significant.

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Effect of Immobilizing Substances on Shoot Growth and Heavy Metals Uptake by Wheat

The results showed that the shoot growth of wheat was unaffected by any of the added immobilizing substances (Table 2). The addition of immobilizing substances caused a decrease in the shoot concentrations and the uptake of HM compared to the control (Tables 2 and 3). Among studied HM, the shoot concentration and the uptake of Cu were significantly decreased by all immobilizing substances for both harvests. Most reduction in the shoot concentrations and the uptake of HM was found for Na-bentonite and Ca-bentonite, mainly due to the reduction of availability of HM in the soil. This result suggests that the available forms of HM in such soil were redistributed to non-available forms by bentonites containing a high proportion of montmorillonite. Lothenbach *et al.* (1998, 1995) found that the addition of montmorillonite to the soil reduced the availability of Zn, Cd, and Cu to plants. The reduction in HM shoot concentrations, after addition of Na-bentonite and Ca-bentonite, ranged from 14% to 50% compared to the control soil. Among HM, the uptake and the shoot concentration of Zn showed the lowest decrease by the addition of bentonites, ranging from 14% to 17% compared to the untreated control.

Table 3
Effect of immobilizing substances and salinity on heavy metals uptake by wheat

Treatments	Uptake (Harvest 1)					Uptake (harvest 2)				
	Zn	Cd	Cu	Ni	Pb	Zn	Cd	Cu	Ni	Pb
					g/pot					
				Irrigation with deionized water						
Control	1.21	0.034	0.11	0.14	0.059	0.77	0.019	0.050	0.044	0.035
Na-bentonite	1.11	0.025	0.08	0.11	0.038	0.67	0.015	0.030	0.025	0.018
Ca-bentonite	1.02	0.024	0.06	0.10	0.049	0.73	0.012	0.025	0.028	0.019
Zeolite	1.26	0.028	0.08	0.10	0.049	0.71	0.016	0.035	0.026	0.031
Goethite	1.11	0.027	0.07	0.11	0.048	0.73	0.017	0.036	0.037	0.026
Hematite	1.14	0.030	0.08	0.12	0.050	0.73	0.015	0.036	0.041	0.032
Superphosphate	1.28	0.033	0.08	0.14	0.055	0.77	0.018	0.037	0.045	0.029
Novaphos	1.26	0.034	0.09	0.14	0.047	0.72	0.016	0.038	0.041	0.020
LSD 1 ($P = 0.05$)	0.15	0.007	0.016	0.02	0.009	0.07	0.003	0.005	0.006	0.005
			Irrigation with saline water containing 1600 mg L^{-1} NaCl							
Control	1.17	0.050	0.11	0.13	0.063	0.65	0.032	0.040	0.042	0.036
Na-bentonite	1.18	0.041	0.08	0.11	0.046	0.63	0.030	0.022	0.017	0.019
Ca-bentonite	1.20	0.034	0.07	0.11	0.051	0.61	0.023	0.024	0.026	0.023
Zeolite	1.17	0.037	0.08	0.10	0.051	0.60	0.028	0.030	0.023	0.032
Goethite	1.14	0.042	0.08	0.11	0.049	0.64	0.030	0.024	0.034	0.031
Hematite	1.16	0.045	0.08	0.12	0.054	0.60	0.028	0.035	0.032	0.032
Superphosphate	1.21	0.047	0.07	0.14	0.059	0.62	0.028	0.036	0.033	0.029
Novaphos	1.16	0.048	0.10	0.13	0.050	0.64	0.030	0.035	0.035	0.017
LSD 1 ($P = 0.05$)	0.16	0.008	0.022	0.017	0.01	0.09	0.005	0.008	0.006	0.006
LSD 2 ($P = 0.05$)	NS	0.003	NS	NS	NS	0.03	0.002	0.004	0.005	NS

LSD 1: Significant differences between treatments of immobilizing substances; LSD 2: Significant differences between saline and non-saline treatments; NS: Not significant.

The effect of natural zeolites on the availability of HM was investigated by Oste *et al.* (2002) and Chlopecka and Adriano (1996, 1997). They found that the addition of natural zeolites to soil shows little or no effect on the availability of HM. In our investigation, however, the addition of a natural zeolite (clinoptilolite) decreased significantly the uptake and the shoot concentration of Cu, Ni, and Pb, and the shoot concentration of Cd for harvest 1. For harvest 2, it caused a significant decrease only in the uptake and shoot concentration of Cu and Ni compared to the control. The results suggest that the effect of zeolite on reducing Ni bioavailability was similar to bentonites.

Among other immobilizing substances, the addition of Novaphos caused a high reduction in the shoot concentration and the uptake of Pb, especially for harvest 2. The results suggest that Novaphos had a similar effect as bentonites in reducing Pb bioavailability. Novaphos reduced the Pb shoot concentration by 40% for harvest 2, as compared to the control. Such a result could be explained by the large decrease in Pb mobile species in soil due to the addition of Novaphos (Table 1b). Cao *et al.* (2003) found that P amendments reduced significantly shoot Pb by 41–66% compared to the control. They hypothesized that association of P with Pb in the plant root appears to be responsible for reduction of shoot Pb.

Iron oxides can markedly affect HM retention, mobility, and bioavailability (Silveira *et al.*, 2003). Our result showed that the addition of Fe-oxides significantly reduced the availability of Cu, Ni, and Pb to wheat. Among these heavy metals, the highest reduction of their bioavailability was found for Cu using goethite or hematite for both harvests, ranging from 23% to 31% as compared to control. Although the addition of Fe-oxides decreased significantly the availability of Cu, Ni, and Pb to wheat, their efficiency was lower than that of bentonites.

Effect of NaCl Salinity on Shoot Growth and Heavy Metals Uptake by Wheat

The irrigation with saline water had no effect on the shoot growth for harvest 1. A significant decrease in the shoot growth, however, was seen for harvest 2 (Table 2). The NaCl salinity had no effect on the shoot concentrations of Zn, Cu, and Ni for both harvests (Table 2), and on their uptake for harvest 1 (Table 3). However, for harvest 2, there was a general decline in the uptake of these metals due to irrigation with saline water. Among these metals, the decline in Zn uptake was significant for all treatments. In contrast, the salinity caused a significant increase in the uptake and the shoot concentration of Cd for both harvests. The results showed that the shoot concentration of Cd was almost doubled at harvest 2 due to the salinity. The stimulatory effect of Cl on Cd uptake by plants has been found in a number of glasshouse experiments using soil as the growth medium (Giordano *et al.*, 1983; Bingham *et al.*, 1983, 1984). The high increase in shoot concentration of Cd is due either to greater diffusion of Cd to roots through soil or to greater uptake of Cd if chloro-complexes are transported across the root membrane (McLaughlin *et al.*, 1997, 1994; Smolders and McLaughlin, 1996). For harvest 2, a stepwise (forward) multiple regression analysis showed that the uptake and the shoot concentration of Cd were positively related to $[CdCl^+]$ (Table 4). However, they were not significantly related to free ionic Cd $[Cd^{2+}]$ and total concentration of Cd $[Cd_T]$ in soil solution. Several investigations have demonstrated that shoot Cd concentrations or Cd uptake by plants correlated best with the activity of $CdCl^+$ species, but unrelated or only weakly correlated to the activities of free Cd^{2+} ion in solution (Weggler-Beaton *et al.*, 2000; Smolders *et al.*, 1998).

The NaCl salinity did not affect Pb shoot concentration for harvest 1 and its uptake for both harvests. However, the salinity increased significantly the shoot concentration of

Table 4

Shoot concentration and uptake of Cd and Pb in relation to their total soluble concentration and species (M_T, M^{2+}, and MCl^+) in soil solution for harvest 2 (Stepwise multiple regression)

	Shoot heavy metal concentration	R^2	Heavy metal uptake	R^2
Cd	$7.03 + 23.50$ ($CdCl^+$)	0.88	$0.013 + 0.038$ ($CdCl^+$)	0.83
Pb	$6.21 + 8.35$ (Pb_T) $+ 12.84$ ($PbCl^+$)	0.66	$0.013 + 0.02$ (Pb_T)	0.61

Pb for harvest 2. It was observed that chloride salinity did not affect significantly shoot concentration of Pb for the soil treated with Na-bentonite or Novaphos. The concentration of total Pb in soil solution was not significantly affected by NaCl salinity, whereas a marked increase in Pb-Cl complexes was found in soil solution. Thus, it can be concluded that a significant increase in shoot concentration of Pb due to NaCl salinity was due to the formation of Pb-chloride complexes. A stepwise (forward) multiple regression analysis showed that the shoot Pb concentration was positively related to $[PbCl^+]$ and $[Pb_T]$ (Table 4). Lead uptake, however, was not significantly related to $[PbCl^+]$.

Conclusion

The addition of immobilizing substances to sewage sludge soil caused a significant decrease of HM availability to wheat. Among immobilizing substances, the addition of bentonites caused highest reduction in HM availability to wheat, mainly due to the redistribution of HM from available forms to non-available forms in the soil. The results also suggest that zeolite had a similar effect to bentonites in reducing Ni bioavailability. The addition of Novaphos caused a large reduction in Pb availability to wheat, as Pb is known to make stable minerals with phosphorus. The NaCl salinity had no effect on the uptake and the shoot concentrations of Zn, Cu, and Ni. The NaCl salinity, however, increased the availability of Cd and Pb to wheat as a result of the increase in total concentration of Cd in soil solution and a high complexation of Cd and Pb with Cl^-. The NaCl salinity caused a decrease in the efficiency of clay minerals to immobilize soluble Cd. The use of bentonites is most promising for the reduction of HM availability to plants. However, the field application of bentonites in large quantities may be limited by their high cost. The chloride concentration of soil and irrigation water should be taken into account while assessing the risk of metal uptake by food plants.

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