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Effects of Flooding on Changes in Eh, pH and Speciation of Cadmium and Lead in Contaminated Soil

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Abstract Artificially contaminated soils (A, B) and naturally contaminated soil (S2) in China were used as the tested soils, and the effect of continuous flooding on the changes of Eh, pH and the speciation of cadmium, lead in contaminated soils was studied in the paper. The results indicated that soil Eh decreased with flooding time, and that soil pH increased with flooding time. The changes of soil pH ceased after 60 days of submergence. The exchangeable Cd and Pb decreased obviously during the flooding process from the results of five-step sequential extraction. The calculations of mobility factor (MF) showed that Cd mobility significantly decreased in artificially contaminated soils (A, B) after the flood. But the change of Pb mobility was not significant after the flood, although a decrease of Pb concentration in the exchangeable fraction (SE) was observed.

Keywords Cadmium · Lead · Flooding · Speciation

Heavy metals in soils can originate from two main sources: (1) heavy metals from weathering bedrocks, and (2) heavy metals from anthropogenic sources, e.g. industrial emissions, use of fossil fuels, fertilizers and sewage irrigation. Sewage irrigation in farmland as a technique for wastewater disposal and agricultural reuse was widely applied in many districts in the world (Sun et al. 2001). Now the heavy metal contamination of soils derived from sewage irrigation and the consequent ecological security problems have become a focus of worldwide attention. The Shenyang Zhangshi Irrigation Area (SZIA), China, is a representative area of heavy metal contamination of soils resulting from sewage irrigation. The irrigation area occupied 2.8×10^4 hm^2 and has been used for sewage irrigation for 30 years since 1954 (Chen et al. 1980). Many studies on heavy metal contamination in SZIA were carried out after 1970, because the high cadmium (Cd) concentration was detected in rice grain. The land was partly rezoned from crop planting to industry use in 1992. However, currently there are some parts in the area still used for planting vegetables and crops.

Rice cultivation in SZIA is generally experienced rotation of flooded and non-flooded conditions to meet the need of growth. The mobility of heavy metals in soils is influenced by many factors: pH, temperature, oxidation–reduction potential, organic matter, leaching, ion exchange and microbial activity. Besides the soil properties and the total load of metals, sources of heavy metal entering to soils, whether added artificially or presented naturally, may also affect the solubility and availability of metals. Among these factors, oxidation–reduction status (Eh) and pH are important for the solubility of heavy metals in flooded soils, and for their availability to plants. When oxidized soils are submerged they become anaerobic and reduced, and the pH tends to converge to neutrality irrespective of initial pH, whether acidic or alkaline (McBride 1994). Submergence of soils is reported to decrease the

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availability of heavy metals in soils attributed to the increase adsorption of metals on hydrous Mn and Fe oxides and also formation of insoluble compounds with sulfide (Van et al. 1998). However, available information on the solubility changes of harmful metals, such as Cd and Pb under flooding conditions in artificially contaminated and naturally metal-rich soil is rather limited. The aim of this work is to study the effect of continuous flooding on the changes of Eh, pH values and the speciation of Cd, Pb in meadow brown soil, one of the main typical soils in northeast of China. The speciation of Cd, Pb in contaminated soils during different flooding times was compared using a five-step sequential extraction technique. This work should show the influence of flooding on speciation of heavy metals in soils and is helpful to the assessment of their potential environmental risks.

Materials and Methods

Two surface (0–20 cm) meadow brown soils from Shenyang, China, were used in the study. One was S1 which was clean soil collected from Shenyang Ecological Station; the other was S2 which was collected from Shenyang Zhangshi Irrigation Area and was polluted slightly by heavy metals Cd, Pb. Some basic physical and chemical properties of the soils were listed in Table 1. Soil pH (soil/water = 1:2.5) and organic matter of soils were determined according to the methods which were recommended and depicted by NAU (1996). Particle size was determined by a pipette method (Elenon 1971). The concentrations of Cd and Pb in soils were analyzed with an atomic absorption spectrophotometer (SpectrAA-220, Australia) with background correction after a wet digestion of the air-dried sample with the mixture of HNO_3 and $HClO_4$ (Guo et al. 2006).

Two artificially contaminated soils were made of S1 and the load quantities of Cd ($CdCl_2 \cdot 2.5H_2O$) and Pb ($Pb(NO_3)_2$) were as followed: Cd + Pb = 5 + 500, 25 + 1,000 mg kg^{-1}, marked by A and B. Soils A and B were aged for 6 months under natural condition prior to experiments. Artificially contaminated soils A, B and naturally contaminated soil S2 were respectively weighted 1.00 g, which was contained in a centrifuge tube (polypropylene, 100 mL), and 25 mL deioned water was infused into each centrifuge tube. During the continuous flooding process, these tubes were placed under room temperature. At different flooding times, 5, 10, 20, 30 and 60 days, the centrifuge tubes were brought out and centrifuged for 30 min, then the supernatant was used for pH, Eh measurement (pH/oxi 340i multi-parameter instrument, made in German) and the soil remained in tube was used for metal speciation measurement. The total number of tubes for each soil was 15 including triplicates.

Table 1 The basic physical and chemical properties of the tested soils

Soil	PH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)	Cd (mg kg^{-1})	Pb (mg kg^{-1})
S1	6.50	1.55	21.4	46.5	32.1	0.12	18.35
S2	6.72	1.07	34.2	31.9	33.9	0.96	60.50

The metal speciation of soil samples were sequentially extracted using defined sequential fraction procedure (Tessier et al. 1979). The extraction was carried out progressively on an initial weight of 1.00 g test soil, which was contained in a centrifuge tube (polypropylene, 100 mL) and shaking with variable speed on a reciprocal shaker at 220 strokes min^{-1}. The extractant and operationally defined chemical fractions were shown in Table 2. After each successive extraction, separation was done after centrifuging for 30 min. The supernatant was filtered and placed in a tube for measurement.

All chemicals used in the experiments were of analytical grade. Analysis of heavy metals in supernatants was carried out using a SpectrAA-220 atomic absorption spectrophotometer. The limits of detection for Cd and Pb are 0.0015 and 0.014 μg mL^{-1} respectively. Certified reference material (GBW07404) was used for quality control of instrument performance. The recovery and precision were found to be within 100 ± 10%. The results were presented as the average of three replicates. Statistic analysis was performed using the software of SPSS 11.0 for windows.

Results and Discussion

Fraction changes of Cd in soils during the flooding process were summarized in Fig. 1. In artificially contaminated soils A and B, most of Cd was in fractions of SE (36.6–63.6%), WSA (17.6–29.9%) and OX (15.6–25.4%), followed by RES (2.4–6.9%) and OM (0.8–2.4%). While in naturally contaminated soil S2, Cd was mainly in fractions of SE (23.9–33.7%) and RES (23.0–26.3%), next WSA (16.3–20.7%), OX (15.8–18.3%), and OM (11.2–14.8%). For A, B and S2 soils, the exchangeable Cd (SE) decreased obviously during the flooding process, which was associated with increases of Cd concentrations in WSA, OX, OM and RES.

In soils A and B, Pb was mainly in fractions of OX (50.4–52.8%) and WSA (15.2–25.7%), next RES (10.4–14.9%) and OM (7.7–12.6%), while SE (4.1–6.0%) was very little (Fig. 2). In soil S2, Pb in OX and RES were account for 69.3–70.6%, next WSA (16.3–17.6%), OM (9.9–10.7%), and SE (2.7–4.3%). Previous studies have also proved that anthropogenic Pb in freshwater sediments

Table 2 The sequence extraction processes of Cd, Pb in soil

Sequence	Speciation	Extractant
Fraction 1	SE (water soluble plus exchangeable)	1 mol L^{-1} $MgCl_2$ (pH = 7.0), oscillation for 1 h at 25°C
Fraction 2	WSA (bound to carbonate or weakly specifically adsorbed)	1 mol L^{-1} NaOAc (adjusted to pH = 5.0 with HOAc) for 2 h with continuous stirring
Fraction 3	OX (bound to Fe–Mn oxides)	0.04 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25% HOAc (v/v), oscillation for 6 h at 96°C
Fraction 4	OM (bound to organic matter)	3 mL of 0.02 mol L^{-1} HNO_3 and 5 mL of 30% H_2O_2 (adjusted to pH = 2.0 with HNO_3), 85°C for 2 h ; addition of 3 mL of 30% H_2O_2 (pH = 2.0) 85°C for 3 h, cool, 5 mL 3.2 mol L^{-1} NH_4OAc in 20% (v/v) HNO_3, diluted to 20 mL and agitated continuously for 30 min
Fraction 5	RES (residual)	Digested with 9 mL HNO_3 and 3 mL $HClO_4$

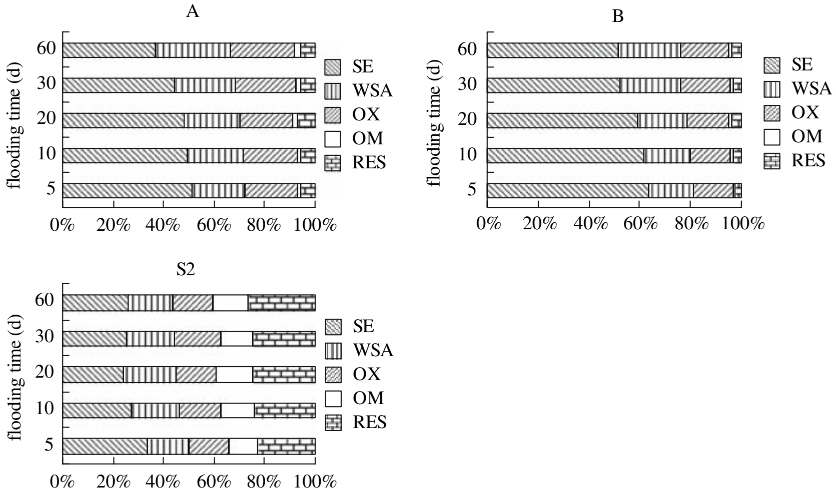

Fig. 1 Cadmium distribution into separate fractions in three soils during flooding process

can be mostly associated with the Fe–Mn oxides fraction (Stead and Ward 2004). The amount of exchangeable Pb (SE) dropped down in A, B and S2 soils during the flooding process, which was caused by a transform of Pb from the most mobile fraction, but no other significant change was observed (Fig. 2).

The mobility of heavy metals can be determined by a comparison of the weakly bound fractions (SE and WSA) with the total metal content. These fractions are considered easily to mobilize and thus represent a potential risk for the environment. Therefore the mobility factor (MF) had been proposed by Kabala and Singh (2001) and used by several authors (Ettler et al. 2005) to describe heavy metal behavior in soils and sediments:

$$\mathrm{MF} = [(\mathrm{SE} + \mathrm{WSA})/(\mathrm{SE} + \mathrm{WSA} + \mathrm{OX} + \mathrm{OM} + \mathrm{RES})] \times 100(\%)$$

where SE is the concentration of metal present in the exchangeable fraction, WSA is the acid extractable fraction, OX is the reducible fraction, OM is the oxidisable fraction and RES is the residual fraction. The mobility factor of Cd decreased in A, B and S2 soils during the flooding process, but only in A and B soils the significant differences ($p < 0.01$ and $p < 0.05$) decrease of Cd in the mobile fraction was observed (Table 3). During the flooding process the changes of Pb mobility factor were not significant. Compared the artificially polluted soils (A and B) with the naturally metal-rich soil (S2), the mobility factors of Cd and Pb in the latter were lower during the submergence period.

Metal mobility decreased with flooding is due to the changes of Eh and pH. Both Eh and pH have the effects on decreasing metal solubility under submerged soils. The Eh in A, B and S2 soils decreased after submergence, while the decrease of –33 mV in B soil and –23 mV in S2 soil were observed, which are the highest and lowest value in 60 day (Fig. 3). Soil pH is one of the most important factors controlling metal mobility in soils. Soil pH increased with flooding time and the changes in pH caused by flooding were similar in A, B and S2 soils (Fig. 3). In waterlogged soil once O_2 is consumed out by microbial activity, a observable change that a decrease of Eh associated by an increase of pH towards neutrality would followed. Most reduction reactions consume H^+, resulting in pH rise in soils (Narteh and Sahrawat 1999). In fact, it is

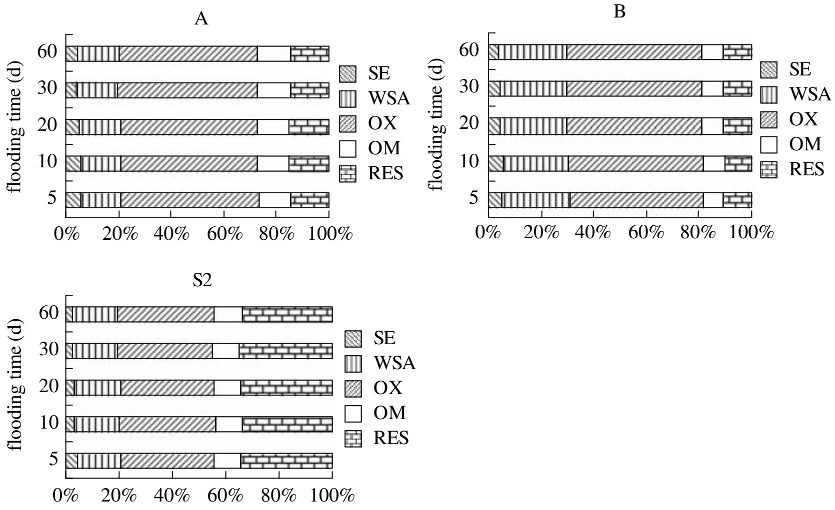

Fig. 2 Lead distribution into separate fractions in three soils during flooding process

Table 3 Mobility factor (MF) of Cd and Pb in soils

Flooding time (d)	$\mathrm{MF_{Cd}}$ (%)			$\mathrm{MF_{Pb}}$ (%)		
	A	B	S2	A	B	S2
5	72.20	81.16	49.97	20.86	30.96	20.62
10	71.39	79.72	46.02	20.93	30.51	19.72
20	70.51	78.53	44.64	20.59	29.65	20.52
30	68.08	76.26	44.13	19.87	29.44	19.50
60	66.46	75.92	43.64	20.17	30.65	19.27

CO_2 in the reduced soil that buffers pH in the range of 6–7 via the H_2CO_3–HCO_3^- reaction (McBride 1994). The intensity of reduction is higher in the presence of organic matter because organic matter is oxidized and soil components are reduced due to anaerobic microbial respiration (Ponnamperuma 1972). This may be a reason for low and negative values of Eh in soils with higher organic matter (A and B) resulting into increase of pH values compared to that in soils with lower organic matter (S2). It seems that more flooding time beyond 60 days was required to attain a stable level of Eh.

Because flooding caused pH increase and Eh decrease, may result in negative charge increase on soil particles, which will allow higher adsorption of metals and consequently decrease the solubility. The affinity of Cd adsorption to soil increased at high pH as Cd tended to form $Cd(OH)^+$ by hydrolysis (Elliott et al. 1986). These pH-dependent mechanisms might have taken place in the flooded soils to immobilize heavy metals in the study. The reduction process (low Eh–high pH) was more obvious in the higher organic matter soil, perhaps due to the formation of metal–organic complexes (Gambrell and Patrick 1988) and microbial immobilization (Halder and Mandal 1979). Under low Eh and high pH conditions, redistribution of metals into different fractions of soils was also observed by Kashem (2000). Flooding seemed to have transformed Cd and Pb from labile fraction to less labile or immobile oxide fraction. A difference in metal solubility was observed between artificially contaminated and naturally metal-rich soils in this study, and it was also reported by Kashem and Singh (2001) that metals added through anthropogenic contamination preferred to remain in the mobile fraction.

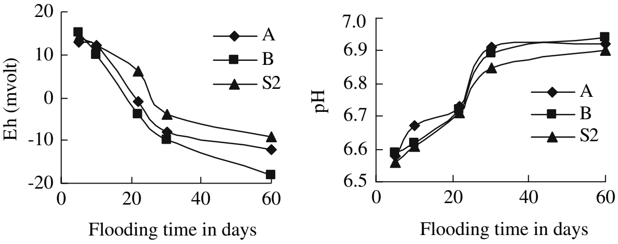

Fig. 3 Changes of Eh and pH with flooding time in three soils

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References

Chen T, Wu YY, Zhang XX (1980) The mend of Cd soils and prevention and cure of Cd contamination in ripe in Zhangshi irrigation area (in Chinese). Environ Sci Sin 1(5):7–11

Elenon P (1971) Particle size analysis of soil. Acta Agric Fenn 122: 1–122

Elliott HA, Liberati MR, Huang CP (1986) Competitive adsorption of heavy metals by soil. J Environ Qual 15:214–219

Ettler V, Vanek A, Mihaljevic M, Bezdicka P (2005) Contrasting lead speciation in forest and tilled soils heavily polluted by lead metallurgy. Chemosphere 58:1449–1459

Gambrell RP, Patrick JWH (1988) The influence of redox potential on the environmental chemistry of contaminants in soils and sediments. In: Hook D (ed) The ecology and management of wetlands, Timber Press, pp 319–333

Guo GL, Zhou QX, Koval PV (2006) Speciation distribution of Cd, Pb, Cu and Zn in contaminated phaiozem in north-east China using single and sequential extraction procedures. Aust J Soil Res 44(2):135–142

Halder A, Mandal LN (1979) Influence of soil moisture regimes and organic matter application on the extractable Zn and Cu content in rice soils. Plant Soil 53:203–213

Kabala C, Singh BR (2001) Fractionation and mobility of copper, lead and zinc in soil profiles in the vicinity of a copper smelter. J Environ Qual 30:485–492

Kashem MA (2000) Mobility, chemical fractionation and plant uptake of Cd, Ni and Zn in contaminated soils, Ph.D. dissertation, Agricultural University of Norway, Norway

Kashem MA, Singh BR (2001) Metal availability in contaminated soils: I. Effects of flooding and organic matter on changes in Eh, pH and solubility of Cd, Ni and Zn. Nutr Cycl Agroecosys 61:247–255

McBride MB (1994) Environmental chemistry of soils. Oxford University Press, New York

Narteh LT, Sahrawat KL (1999) Influence of flooding on electrochemical and chemical properties of West African soils. Geoderma 87:179–207

NAU (Nanjing Agricultural University) (1996) Soil and agrochemical analyses (in Chinese). China Agricultural Press, Bejing

Ponnamperuma FN (1972) The chemistry of submerged soils. Adv Agron 24:29–96

Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51(7):844–851

Stead DK, Ward NI (2004) Mobility of heavy metals within freshwater sediments affected by motorway stormwater. Sci Total Environ 334:271–277

Sun B, Zhao FJ, Lombi E (2001) Leaching of heavy metals from contaminated soils using EDTA. Environ Pollut 113:111–120

Van D, Loch JPG, Winkels HJ (1998) Effect of fluctuating hydrological conditions on the mobility of heavy metals in soils of a freshwater estuary in the Netherlands. Water Air Soil Pollut 102:377–388