Effects of low-molecular-weight organic acids and residence time on desorption of Cu, Cd, and Pb from soils

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Abstract

Effects of low-molecular-weight organic acids (LMWOAs) and residence time on desorption of Cu, Cd, and Pb from two typical Chinese soils were studied. Citric, malic, and acetic acids were chosen as representatives of LMWOAs commonly present in soils. CaCl_2 and NaNO_3 were used in desorption as they were main soil background electrolytes for comparison. Desorption of Cu, Cd, and Pb from both soils followed the descending order: citric acid > malic acid > acetic acid > CaCl_2 > NaNO_3 , which was consistent with the order of stability of Cu^- , Cd^- , and Pb-LMWOAs complexes from large to small and ion exchange ability of Ca^{2+} and Na^+ . Desorption of metals by inorganic salts decreased with increasing desorption solution pH. Whereas desorption of metals by LMWOAs showed different trend in response to pH change due to their different complexing abilities. Malic and acetic acids released less metals at low pH 3.1 compared with citric acid at pH 7, indicating that pH was not the dominant factor governing the release of metals. In addition, all LMWOAs desorbed more metals than inorganic salts, CaCl_2 and NaNO_3 . Therefore, organic ligands played a dominant role in desorption of heavy metals. More metals were released from Jiangxi soil than from Heilongjiang soil due to lower soil pH, CEC, organic matter content and manganese oxide of Jiangxi soil. Generally, desorption of metals decreased with increasing residence time of metals in soils.

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1. Introduction

Heavy metals in the environment are posing significant threats to human health and the environment. Soils are an important sink for these metals due to soils' high metal retention capacities. Therefore, the behavior of heavy metals in soils is of increasing scientific concern. Many studies have demonstrated that adsorption–desorption is the most important process affecting the behavior of heavy metals in soils, hence their bioavail-

ability and potential toxicity (Backes et al., 1995). The toxicity and bioavailability of metals also depend on their speciation (Kasawneh, 1971). A variety of factors such as organic acids in soils can affect the metal release from soil and speciation in soil solution (Mench and Martin, 1991; Rieuwerts et al., 1998). Low-molecular-weight organic acids (LMWOAs) are originated from decomposition of soil organic matter (SOM) in the upper soil horizons, plant root exudates, and microbial metabolites (Jones, 1998; Strobel, 2001). High amounts of LMWOAs are concentrated in rhizosphere zones with intense biological activity. The characteristics of rhizosphere microenvironment are often different from bulk soil (Cieslinski et al., 1998; Jones, 1998). Increasing evidences have suggested that the anions of LMWOAs

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may play an important role in the fate of metals (Naidu and Harter, 1998; Glover et al., 2002; Collins et al., 2003; Onyatta and Huang, 2003). LMWOAs can form soluble complexes with metal cations (Robert and Berthelin, 1994; Stevenson and Fitch, 1994), thus modify the fixation of metals by soil organic matter, oxides, clays, and enhance their release (Krishnamurti et al., 1997; Chen et al., 2003). Such properties can be used in phytoremediation to increase metal bioavailability and hence the bioaccumulation of metals into plants (Wu et al., 2003), minimizing the environmental risk. There were several reports on the effect of LMWOAs on adsorption of metals (Haas and Horowitz, 1986; Chairdchai and Ritchie, 1990; Wu et al., 2003), however, there was very little information about the effect of LMWOAs on desorption of metals. Naidu and Harter (1998) studied Cd desorption from soils in the presence of different organic ligands and demonstrated that pH was the dominant factor controlling metal desorption. Xu and Ji (2003) reported different results on Al adsorption on and desorption from kaolinite, in which oxalate, malonate, malate, and lactate were used as desorption reagents. Despite these studies, the influence of LMWOAs on metal desorption is poorly understood.

Recent studies have suggested that increasing residence time reduced desorption of metals from soils and potential bioavailability (McLaren et al., 1998; Ford et al., 1999). Therefore, examining the influence of residence time on desorption of heavy metals is essential to understand the possible environmental behaviors of heavy metals and accurately predict their potential bioavailability in soils. Soil solution is a pool of inorganic and organic solutes that can compete with metals for adsorption sites on solids. However, the majority of such studies about residence time effect on desorption have been done only in the presence of inorganic cations. The information on the residence time effect in the presence of organic matter is scarce.

In this study, we investigated the effects of LMWOAs and residence time on desorption of Cu, Cd, and Pb from two typical Chinese soils at different soil pH. Cu, Cd, and Pb were chosen, which are among priority pollutants of the USEPA's list and are also major pollutants among various toxic metals in China. Acetic, malic, and citric acids were chosen as the representative of LMWOAs commonly existed in the soils because they are the main components present in the rhizosphere microenvironment and plant exudates.

2. Materials and methods

2.1. Soil characteristics

Two soil samples were collected from the surface layer (0–20 cm) of cultivated soils in Jiangxi and Hei-

longjiang Province. The soil samples were air dried, and mildly grounded to pass through a 20-mesh sieve, homogenized, and stored for subsequent analysis.

Soils were classified according to the American Classification System. Soil pH value was measured in de-ionized water at a soil to solution ratio of 1:1 (w:v). Cation exchange capacity (CEC) was determined by the method described by Rhoades (1982). Organic matter content was determined by the Walkley–Black's procedure (Nelson and Sommers, 1982). Amorphous iron (Fe) and aluminum (Al) oxides were determined by ammonium oxalate extraction (McKeague and Day, 1966). Crystalline Fe and Al oxides were determined by the oxalate-ascorbic acid extraction method of Shuman (1982). Manganese oxide content was determined by extraction with 0.1 mol l⁻¹ of hydroxyl-ammonium hydrochloride (Shuman, 1982). Specific surface areas were obtained via Brunauer–Emmett–Teller (BET)-N₂ adsorption method (Brunauer et al., 1938). After soils were shaken end-over-end for 24 h at a soil to solution ratio of 1:30, centrifuged at 4000g for 30 min, and filtered through a 0.45 µm of cellulose nitrate membrane, the filtrates were measured by an autoanalyzer (Shimadzu TOC 5000) to determine dissolved organic carbon (DOC). The background concentrations of Cu, Cd, and Pb of both soils were determined by inductively coupled plasma mass spectrometry (ICP-MS, PQ3, Fisons Instruments, UK) after digestion of 0.100 g soils in 3 ml of HNO₃/HClO₄/HF (1+1+1) mixture in PTFE vessel under high-pressure conditions (Zhang and Shan, 1997). These selected properties of soils are listed in Table 1.

2.2. Extraction reagents

Acetic, malic, and citric acids have different pK_{as}, ligand forms, and numbers of functional groups (Table 2). The stability constants of LMWOA–metal complexes were different from one another. NaNO₃ and CaCl₂ were often used as soil background electrolytes in desorption study. In this study they were chosen as contrastive extractants.

2.3. Adsorption isotherms

Batch adsorption experiments were conducted at an ionic strength of 0.01 mol l⁻¹ NaNO₃. Twenty milliliters of varying concentrations of Cu(NO₃)₂, Cd(NO₃)₂, or Pb(NO₃)₂ were added to 0.500 g of either Heilongjiang or Jiangxi soil. The samples were shaken end-over-end in polypropylene centrifuge tubes at 25 °C for 24 h, then centrifuged at 4000g for 30 min, and filtered through a 0.45 µm membrane. The concentrations of Cu, Cd, and Pb in the filtrates were determined by ICP-MS. The amounts of adsorbed metals were calculated by the difference between the amount added initially and that remained in the solution after the adsorption. All the

Table 1
Selected properties of studied soils

Item	Soil	Soil
Sample site	Jiangxi	Heilongjiang
Order	Ultisol	Mollisol
Sand (%)	19.5	9.80
Silt (%)	18.7	62.8
Clay (%)	42.4	27.4
pH	4.56	7.35
CEC (cmol kg ⁻¹)	14.2	26.0
Organic matter (%)	1.53	6.86
Fe (%)		
Crystal.	3.52	1.50
Amorp.	0.720	0.400
Al (%)		
Crystal.	1.39	1.60
Amorp.	0.280	0.340
Mn (mg kg ⁻¹)	27.6	326
DOC (μg g ⁻¹)	15.0	25.0
DOC of treated soil (μg g ⁻¹)	11.9	18.5
BET surface area (m ² g ⁻¹)	26.5	4.64
Background concentration (mg kg ⁻¹)		
Pb	26.7	39.8
Cu	20.5	33.8
Cd	2.17	3.06

measurements were made in triplicate and only the means were reported afterwards.

To investigate the influence of DOM on Cu, Cd, and Pb adsorption by soils, the soils were treated with a mild method detailed as following to partly remove DOM from the soils. Soils (20 g) and water (600 ml) were added in a 1000 ml conical flask and shaken end-over-end for 24 h, then centrifuged at 4000g for 30 min. After the supernatants were decanted, the treated soils were air dried and mildly grounded to pass through a 20-mesh sieve, homogenized. Then adsorption isotherms were done following the procedures detailed above.

2.4. Adsorption of Cu, Cd, and Pb as a function of pH

A portion of 0.500 g of soil and 20 ml of 0.01 mol l⁻¹ NaNO₃ were mixed in a 50 ml polypropylene centrifuge tube. Suspension pH values of approximately 2–7 were attained by adjustment with either HNO₃ or NaOH. After the suspensions were shaken at 25 °C for 24 h, the

pH values were measured and readjusted if necessary. 50 μl of Cu, Cd, or Pb as nitrate salts was then added to get the final metal concentration of 1 mmol l⁻¹. After metal addition, the solutions were shaken for 24 h at 25 °C. Suspension pH values were measured and the samples were centrifuged and filtered to determine the concentrations of Cu, Cd, and Pb in the filtrates by ICP-MS.

In order to investigate the effect of LMWOAs on pH-dependent adsorption citric acid and Pb were chosen as an example as citric acid has the highest complex stability (Martell and Smith, 1977). Twenty milliliters of 0.01 mol l⁻¹ citric acid (0.01 mol l⁻¹ NaNO₃ as background electrolyte) was added to 0.500 g soil. After pH adjustment with either HNO₃ or NaOH to approximately 2–7 and 24 h end-over-end shaking at 25 °C, the pH values of the suspension were measured and readjusted if necessary. Pb (50 μl) as nitrate salt was then added to get the final metal concentration of 1 mmol l⁻¹ and followed another 24 h of shaking. The pH and Pb in the equilibrium solution were determined.

2.5. Effect of residence time on desorption of Cu, Cd, and Pb

Portions of 50 g soils were mixed with 500 ml solutions containing 100 mg l⁻¹ of Cu, Cd, and Pb (pH 6) and shaken continuously for 24 h. Subsequently the mixtures were incubated for 2–70 days, during this process they were periodically weighed and any weight loss was made up with regular addition of distilled, de-ionized water. Then supernatant was removed and the concentrations of heavy metals remained in the supernatant were determined. After that the incubated soils were rinsed several times with 95% ethanol to remove Cu, Cd, and Pb in the entrapped solutions until none of them was detected. The washed soils were air dried, grounded to pass through a 20-mesh sieve, homogenized and stored in polyethylene bags for subsequent study.

To investigate the effect of residence time on desorption of metals, a portion of 0.500 g of each soil was placed in a 50 ml polypropylene centrifuge tube. Twenty milliliters of 0.01 mol l⁻¹ LMWOAs with 0.01 mol l⁻¹ NaNO₃ as background electrolyte was added. The samples were shaken end-over-end for 24 h, then centrifuged at 4000g for 30 min, and filtered through a 0.45 μm membrane. The concentrations of Cu, Cd, and

Table 2
Low-molecular-weight organic acids (LMWOAs) used in this study

Organic acid	Formula	Ligand form	pK _a ^a
Acetic acid	CH ₃ CO ₂ H	HL	4.76
Malic acid	HO ₂ CCH ₂ CH(OH)CO ₂ H	H ₂ L	3.46, 5.10
Citric acid	HO ₂ CCH=C(CO ₂ H)CH ₂ CO ₂ H	H ₃ L	3.13, 4.78, 6.43

^a pK_a values were adopted from Serjeant and Dempsey (1979).

Pb in the filtrates were determined by ICP-MS. Desorption experiments were also performed by using NaNO_3 and CaCl_2 as desorption solution. All desorption experiments were in triplicate.

2.6. Effects of LMWOAs and initial pH on desorption of Cu, Cd, and Pb

It remained unknown whether LMWOAs were present as free acids or alkali metal salts (Jones, 1998). The nature of LMWOAs differed dramatically at different pH value due to their different pK_{a} s, so combined effect of pH and LMWOA ligands should be studied. Samples incubated for five weeks were desorbed with 0.01 mol l^{-1} of various LMWOAs (with 0.01 mol l^{-1} NaNO_3 as background electrolyte), and two inorganic salts (NaNO_3 and CaCl_2) with concentration of 0.01 mol l^{-1} at the pH range of 3.1–7.0. Desorption followed the procedures detailed in the above section.

3. Results and discussion

3.1. Adsorption isotherm

Langmuir model is widely used to describe adsorption behaviors of heavy metals because of its simplicity and ability to describe experimental results in wide ranges of concentrations. The general form is $x/m = \frac{k_1 k_2}{(1+k_1 C)}$, where x/m is the adsorption amount of heavy metals by soils (mmol kg^{-1}); C is the heavy metal concentration remained in the equilibrium solution (mmol kg^{-1}); k_1 (l kg^{-1}) is a constant relating to the binding energy of metal to soils; k_2 is the maximum desorption capacity (mmol kg^{-1}), which seems useful for comparing potential adsorption capacity of different soils and different metals.

Cu, Cd, and Pb adsorption onto both Heilongjiang soil and Jiangxi soil were well described by Langmuir model ($\gamma^2 > 0.95$, $P < 0.05$, Table 3). As can be seen from Fig. 1, adsorption capacities of metals were higher

for Heilongjiang soil than for Jiangxi soil, and the adsorption capacity for different metals onto the same soil differed from one another. The preference in adsorption capacity exhibited by Heilongjiang soil over Jiangxi soil due mainly to higher pH, CEC, organic matter content, manganese oxide of Heilongjiang soil (Table 1). This observation was supported by a report of Andersen et al. (2002) that total Cd concentration correlated with the effective cation-exchange capacity, clay content, and organic matter content. The preferential adsorption order of $\text{Pb} > \text{Cu} > \text{Cd}$ within a soil type may attribute to the different adsorption affinities of metals for soil surface according to their different properties. The properties generally related to adsorption affinity were metal hydrolysis (negative log of first hydrolysis constant: pK_{H} and hydrated radius), electronegativity, and softness (Appel and Ma, 2002; Saha et al., 2002).

The discrepancy in metal adsorption onto Heilongjiang and Jiangxi soils showed that soil property had an important influence on adsorption. Agbenin and Olojo (2003) investigated the effects of removal of OM and hydrous oxides of soils by H_2O_2 (60%) and oxalate solution (buffered at pH 3.0), respectively, on Cu and Zn adsorption. The methods they used may destroy the structure and other properties of soils. We pretreated soils with water at a ratio of 1:30 (w:v) to remove DOM partly from soils, thus help to investigate the influence of DOM in adsorption of heavy metals. The agent (water) was mild, and destruction of soil structure could be avoided. After treatment, DOC of Heilongjiang soil and Jiangxi soil decreased from 25.0 and 15.1 to 18.5 and $11.9 \mu\text{g g}^{-1}$, respectively, indicating that part of dissolved organic matter (DOM) was removed from these soils since DOM concentration can be calculated from DOC in solution by assuming that DOM contains 60% of DOC on a mass basis (Ben-Hur et al., 2003). DOM has an important influence on metal adsorption since, in most situations, a majority of the dissolved metal is found in metal–organic complex. For example, more than 98% of dissolved Cu is bounded to DOM in non-

Table 3

Adjustable parameters and correlation coefficients of Langmuir equation for Cu, Cd, and Pb adsorption by Heilongjiang and Jiangxi soils before and after partial removal of soil organic matter

Soil	Metal	γ^2		K_2 (mmol kg^{-1})	
		Non-removal of DOM	Partial removal of DOM	Non-removal of DOM	Partial removal of DOM
Heilongjiang soil	Pb	0.982	0.973	133	119
	Cu	0.976	0.960	125	110
	Cd	0.966	0.984	120	103
Jiangxi soil	Pb	0.975	0.980	16.0	12.7
	Cu	0.985	0.988	10.6	9.78
	Cd	0.998	0.999	9.89	8.44

Fig. 1. Adsorption isotherms for Cu, Cd, and Pb onto (▲) no removal and (△) partial removal of DOM from: (a) Heilongjiang soil and (b) Jiangxi soil. Soil background electrolyte of 0.01 M NaNO_3 was used at the soil:solution ratio of 1:40 (0.500 g soil and 20 ml solution).

acidic soil solutions (Sauvé et al., 1997). Adsorption of metals on the pretreated soils at low metal concentrations did not show any significant difference between the pretreated and non-treated soils. However, adsorption decreased by about 20% was observed at high metal concentrations (Fig. 1, significantly different, at $P < 0.05$). When equilibrium concentrations of Cu, Cd, and Pb were lower than 0.3 mmol l^{-1} (Pb $< 0.05 \text{ mmol l}^{-1}$ in Heilongjiang soil), adsorption sites on surface of both pretreated and non-treated soils were sufficient for metals in solution, thus the partly removal of DOM showed little effect on metal adsorption. These sites tend

to be saturated at high metal concentrations. The relatively higher DOM of non-treated soils favored the adsorption of metals due to the formation of more sorbable metal-complexes than metal alone. Therefore, this study indicated that DOM contributed to the adsorption of heavy metals in soils.

3.2. Adsorption of Cu, Cd, and Pb as a function of pH

Adsorption of Cu, Cd, and Pb in both soils increased with increasing pH value (Fig. 2), which can be ascribed to increasing metal adsorption sites of soils. The pH

Fig. 2. Cu, Cd, and Pb adsorption as a function of pH: (a) Heilongjiang soil and (b) Jiangxi soil. (■) Cu; (●) Cd; (▲) Pb and (△) Pb in presence of 0.01 M citric acid.

value, at which 50% of the initial heavy metal ions were adsorbed, was termed herein pH_{50} (Wang and Xing, 2004). The pH_{50} is a measure of the relative affinity of metal cations for adsorbent surface. The smaller the pH_{50} value is, the higher the affinity of metal for adsorbent surface. The pH_{50} values of the three metals were higher in Jiangxi soil than in Heilongjiang soil. Within a soil type, the pH_{50} values followed the trend: $\text{Cd} > \text{Cu} > \text{Pb}$. These results reflected that the affinity of metals for Heilongjiang soil was higher than for Jiangxi soil, and the affinity followed the decreasing order: $\text{Pb} > \text{Cu} > \text{Cd}$ within a soil type. Therefore, the metals adsorbed onto Jiangxi soil were more easily to be desorbed than those adsorbed onto Heilongjiang soil. Cd was the most easily to be desorbed among three metals due to its low affinity for soils.

Pb adsorption onto both Heilongjiang and Jiangxi soils in the presence of citric acid did not produce the typical pH-dependent adsorption patterns. Pb adsorption on both soils in the presence of citric acid decreased obviously, which was consistent with the previous results by Zhou et al. (2003). Such decrease

was more remarkable with increasing pH. Haas and Horowitz (1986) attributed this suppression effect to the formation of non-adsorbable complexes. In the absence of citric acid, only electrostatic attraction and repulsion existed in the system. While in the presence of citric acid, there is a competitive effect for Pb between soil adsorption sites and aqueous organic ligands. The affinity of organic ligands that caused the decrement of Pb adsorption increased with increasing pH. Therefore, more Pb was stabilized in the solution, and less Pb was adsorbed onto the soils with the increase in pH.

3.3. Effect of residence time on extractability of Cu, Cd, and Pb from soils

The effect of residence time on desorption is displayed in Fig. 3. It was clear that the desorption amount of metals decreased with increasing residence time for all the extractants of citric, malic, and acetic acids, CaCl_2 , and NaNO_3 . If we took the amount of Cu, Cd, and Pb desorbed from soils incubated for two days as 100%, the desorption amounts of metals from soils incubated for 10 weeks were 51.7–87.6% by acetic, malic, or citric acids, while the desorption amounts of metals were 28.9–65.2% by NaNO_3 or CaCl_2 (Table 4). Lim et al. (2002) reported that the sorbed phases of metals changed from the loosely bounded phases to strongly bounded phases with increasing residence time. In other words, transformation of Cu, Cd, and Pb took place from loosely bound phases to more persistent phases with increasing residence time. Despite the redistribution of metals from loosely bounded phases to strongly bounded phases with increased residence time, LMWOAs can still desorb part of strongly bounded metals from soils for their complexing abilities.

Among the three metals studied, Cd desorption amount decreased the least. As for the two soils, the desorption amount of metals from Jiangxi soil decreased less than that from Heilongjiang soil (Table 4). Recently, Lu et al. (2004) studied the residence time effect (3 h to 8 weeks) on fractionation and transformation of heavy metals in soils. Metals in soils were fractionated into water soluble, carbonate, Fe–Mn oxide, organic matter and sulfide bound fractions by a sequential extraction method (Tessier et al., 1979). The results demonstrated that very little redistribution of Cd among each fraction was observed with increasing residence time, while residence time affected the fraction distribution of Cu and Pb significantly. Their data supported our results that residence time exerted little influence in Cd desorption. The data also showed that more Cu and Pb transformed from exchangeable fraction into other fractions such as carbonate and Fe–Mn oxide bound fractions in Heilongjiang soil than in Jiangxi soil. Such redistribution of

Fig. 3. Residence time effect on desorption of Cu, Cd, and Pb from (a) Heilongjiang soil and (b) Jiangxi soil. (■) Citric acid; (□) malic acid; (▲) acetic acid; (◇) CaCl_2 and (◆) NaNO_3 . Error bars represent standard deviation of triplicate measurements.

Cu and Pb among different geochemical phases of soils led to more significant decrease of Cu and Pb desorption from Heilongjiang soil. Therefore, the discrepancy in redistribution of metals among different geochemical phases may be responsible for the different effect of residence time on desorption of Cu, Pb, and Cd from different soils.

3.4. Effects of LMWOAs and initial pH on desorption of Cu, Cd, and Pb from soils

Desorption of metals can be significantly influenced by soil properties and characteristics of extractants. Such effects are shown in Fig. 4. For all the extractants, desorption amounts of metals from Jiangxi soil were

Table 4

Residence time effect (10 weeks) on desorption of metals from Heilongjiang and Jiangxi soils based on normalization of metal desorbed from soils incubated for two days as 100%

Soil	Metal	NaNO ₃ (%)	CaCl ₂ (%)	Acetic acid (%)	Malic acid (%)	Citric acid (%)
Heilongjiang soil	Pb	30.1	37.7	57.3	53.5	73.6
	Cu	48.2	49.6	62.2	51.7	60.3
	Cd	55.0	62.8	79.6	80.5	84.3
Jiangxi soil	Pb	28.9	42.5	78.7	76.9	75.0
	Cu	43.2	53.1	81.5	75.0	76.7
	Cd	62.7	65.2	82.5	86.1	87.6

Fig. 4. Effects of organic ligands and initial pH on desorption of Cu, Cd, and Pb from: (a) Heilongjiang soil and (b) Jiangxi soil. (■) Citric acid; (□) malic acid; (▲) acetic acid; (◇) CaCl₂; (◆) NaNO₃. Error bars represent standard deviation of triplicate measurements.

higher than those from Heilongjiang soil. As reported by Jopony and Young (1994), soil pH was positively correlated with cadmium and lead retention, indicating that lower soil pH can release more metals from soils. Soil

organic matter contains many important functional groups, such as –COOH and –OH groups attached to aromatic ring structures. These active components can readily bind metal ions and form complexes that are

difficult to be desorbed. Lower organic matter content of soil also favored desorption of metals from soils. The higher soil CEC generally coexisted with higher content of clay and organic matter, and showed strong ability on the sequestration of metals (Stewart et al., 2003) and vice versa. Another soil property that may be responsible for this effect was manganese oxide, the content of which in Heilongjiang soil was an order of magnitude higher than that of Jiangxi soil. As a very reactive component of soils, manganese oxide can adsorb heavy metals and bind them strongly, then limit desorption of adsorbed metals. The lower pH, CEC, organic matter content, and manganese oxide of Jiangxi soil compared with Heilongjiang soil (Table 1) led to the easier desorption of metals from Jiangxi soil than from Heilongjiang soil. The differences in desorption of metals from both soils were also in accordance with the affinity obtained from the pH_{50} study. It suggests that Heilongjiang soil is capable of receiving and holding more heavy metals compared to Jiangxi soil.

With the increase in pH desorption amount of metals by inorganic salts decreased, whereas those by LMWOAs exhibited different trend. It was well recognized that pH was an important factor affecting metal desorption (Temminghoff et al., 1997). The pH showed the effect from two aspects when there were no organic ligands in the extractants. On one hand, pH changed the affinity of soils for heavy metals, which may be caused by pH-dependent proton competition, surface potential, and surface-charge density on soil colloids (Naidu et al., 1997). This change in affinity led to the decrease of heavy metal desorption with increased pH value. On the other hand, pH changed the ionic forms of metals. With the increase in pH the hydrolysis of metal cations increased. The hydrolyzed forms had lower solvation energies for surface binding than did aquo metal ions (James and Healy, 1972), which in theory would lead to less desorption of heavy metals. Consequently, desorption amounts of metals decreased with increasing pH when the extractants were inorganic salts with no organic ligands in the extractants.

When LMWOAs were introduced to the desorption system, the quantity and species of organic ligands capable of complexing metals increased with increasing pH, which would increase desorption of metals. If the pH effect on metal desorption due to increase in soil negative charge density and metal hydrolysis prevailed over that due to increase in ligand species and quantity, desorption would decrease with increasing pH and vice versa. For acetic acid, the effect on Cu, Cd, and Pb desorption within our experimental pH range was relatively similar because of its weak complexing ability. When pH value increased, desorption amount of metals by acetic acid in both soils decreased. So did malic acid in the case of desorbing Cd and Pb. When it comes to Cu, the complexing ability of Cu with malic acid is

somewhat higher than those of Cd and Pb (Martell and Smith, 1977). When Cu was desorbed by malic acid, the pH effect on desorption due to increase in ligand species and quantity prevailed over that due to increase in soil negative charge and metal hydrolysis. But when pH value was high ($pH > 6$), increased hydrolysis of metal ions caused the latter effect predominant. Thus desorption of Cu by malic acid increased when pH rose from 3.1 to 6, then decreased from 6 to 7. Desorption of metals by citric acid in response to pH followed the same trend with the increase of pH. Citric acid has great chelating ability with Cu, Cd, and Pb. When pH increased, major forms of citric acid changed from H_3L , H_2L^- , and HL^{2-} to L^{3-} . HL^{2-} and L^{3-} always showed greater chelating ability with heavy metals than H_3L and H_2L^- (Martell and Smith, 1977), leading to larger desorption amounts of Cu, Cd, and Pb in the presence of HL^{2-} and L^{3-} than in the presence of H_3L and H_2L^- . The strong tendency of complex formation induced the increase in metal desorption as pH increased from 3.1 to 6. However when $pH > 6$, enhanced hydrolysis of metal ions still induced the decrease of metal desorption. In short, the differences between the complexing ability of LMWOAs with metals may be one possible reason for the different trend of metal desorption by LMWOAs in response to pH change.

For the different extractants, all metals followed the release order: citric acid > malic acid > acetic acid > $CaCl_2$ > $NaNO_3$, which was consistent with the complex stability of organic ligands with metals for LMWOAs from large to small and ion exchange ability of Ca^{2+} and Na^+ . The difference in the effect on metal desorption by LMWOAs was also related to their chemical structures. Among the LMWOAs used, ions of acetic acid can only form monodentate complexes with metals, while ions of malic and citric acids carrying two or three $-COO$ groups can form chelates with 5- or 6-membered ring structure. These chelates are much more stable than monodentate complexes. The greater stability of the citrate- and malate- Me^{2+} complexes led to the greater efficacy of citric and malic acids in desorbing metals from soils than acetic acid. Besides, acetic acid with a smaller acid dissociation constant (pK_a value 4.76) provided fewer anions for complexing with metals than the other two acids (pK_a values 3.13 and 3.46), and thus may show a smaller effect on metal desorption. For example at pH 4.0, about 85%, 96%, and 99% of acetate, malate, and citrate are dissociated into free ions, respectively. The larger amount of free ions and stronger complex ability of citric acid could induce more desorption of metals from soils.

Compared with citric acid at pH of 7, malic and acetic acids did not release more metals at lower pH such as 3.1, indicating that pH was not the dominant factor governing the release of metals. All LMWOAs desorbed more metals than inorganic salts in the studied

pH range, which indicated that the ligands of LMWOAs played a dominant role in desorbing heavy metals. The order of releasing metals from soils with LMWOAs also provides good evidence that complexation processes were controlling the release of metal from soils as it reflects the complex stability of organic ligands with metals. This dominant role of LMWOAs may be interpreted by the following reasons: (a) this complexation would induce a decrease in the concentration of metal ions released by Na^+ ion in solution, leading to a shift in the right direction in the chemical equilibrium: adsorption $\rightleftharpoons$ desorption; (b) the introduction of LMWOAs to the desorption system may cause the change of the surface characteristics of soils, competitive distribution of metal ions between soil surface and organic ligands in the solution, and partly dissolution of minerals in soils, and so on.

Among the studied metals, Pb showed the greatest resistance to desorption followed by Cu and Cd because Pb and Cu tended to be adsorbed more strongly and Cd was usually held rather weakly. In other words, Cd was likely to be more labile and bioavailable than Pb and Cu. This was in line with the results derived from previous adsorption study (isotherm and pH_{50}). Therefore, risks due to metal mobility are higher for Cd than Cu and Pb in the studied soils.

4. Conclusions

We examined the influence of organic acids, pH, and residence time on desorption of Cu, Cd, and Pb from Heilongjiang and Jiangxi soils. The pH was an important factor affecting desorption of heavy metals in soils, as it can change the affinity of sorption sites for heavy metals, the forms of metals and the quantity and species of organic ligands. It seems that LMWOAs also play a dominant role in desorption of heavy metals, as in the presence of LMWOAs metal–LMWOAs complexes disturbed the equilibrium between labile metals on the solid phase and in soil solution, and thus enhanced the release of heavy metals from solid phase to soil solution. The difference in the effectiveness of LMWOAs for desorbing metals was closely relevant to their molecular structure and the stability constant of the metal–LMWOA complexes. Due to their different complexing abilities, desorption of metals by LMWOAs showed different trend in response to soil pH. Soil properties such as pH, CEC, organic matter content, and manganese oxides also had important effects on metal desorption from the soils. Desorption of metals from Jiangxi and Heilongjiang soils reduced with increasing residence time. Data presented here show that LMWOAs are effective chelators of sorbed metals and these ligands may play an important role in the mobilization and phytoavailability of metals in soils.

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