



Effects of organic acids on heavy metal release or immobilization in contaminated soil

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Abstract: In order to explicit the environmental activity of heavy metals affected by different organic acids in soil, a batch incubation experiment was explored to investigate the influence of high relative molecular mass organic acid (HMWOA) (humic acid and fulvic acid) and low relative molecular mass organic acid (LMWOA) (threonic acid and oxalic acid) on the release or immobilization of Pb, Cu and Cd in soils. Results showed that LMWOA, especially threonic acid, had a good performance in the release of Pb, Cu and Cd from soils, and decrease in the fractions of HOAc-extractable, reducible and oxidable Pb, Cu and Cd. Conversely, HMWOA, especially humic acid, decreased the release of Pb, Cu and Cd, while it increased the fractions of HOAc-extractable, reducible and oxidable Pb, Cu and Cd, indicating that HMWOA can immobilize heavy metals. The release of Pb, Cu and Cd caused by LMWOA was attributed to the dissociation of soil organic matter and amorphous iron oxides since the total organic carbon and the water-soluble iron increased. The immobilization of Pb, Cu and Cd by HMWOA was attributed to the adsorption onto HMWOA followed by amorphous iron since HMWOA resulted in a significant decrease of zeta potential and an increase of amorphous iron oxide. It can be concluded that LMWOA has a potential application in soil washing remediation, while HMWOA can be used in the immobilization remediation for heavy metals contaminated soils.

Key words: low relative molecular mass organic acid; humic acid; fulvic acid; soil remediation; fractionation transformation of heavy metals

1 Introduction

Organic acids are widely distributed in soil and can affect the bioavailability of heavy metal by forming complex with a large number of functional groups [1–4]. Organic acids can be divided into low molecular weight organic acid (LMWOA) and high molecular weight organic acid (HMWOA) [5]. LMWOA in soil is produced by plants and microorganisms, and primarily comprised fatty and amino acids, such as threonine, glutamic, glycine,

oxalic, malic, and tartaric acids [6,7]. HMWOA in the soil is mainly produced by degradation of plants and animal residues and is principally composed of fulvic acid (FA) and humic acid (HA). Due to its large number of hydrophilic groups, LMWOA is easily soluble in water and is often used as a chelate to enhance heavy metal mobility. Organic ligands in soil enhanced heavy metal mobility by engaging in ligand exchange reactions on the sorption sites of soil [8]. The LMWOA also promoted dissolving of heavy metal by promoting the dissolving of iron oxidation hydrogen [2]. MONTIEL-ROZAS et al [9]

studied the effect of LMWOA on heavy metal adsorption by plants and found that LMWOA increased the concentration of heavy metals in the shoot and root. CHEN et al [10] illustrated that LMWOA increased the quantity of chromium (Cr) release. TAGHIPOUR and JALALI [11] reported that LMWOA, specifically oxalic and citric acids, plays a substantially more critical role in facilitating Cd release from soil. However, HMWOA exists as soil organic material (SOM), promoting the heavy metal ion adsorbed by complex [12,13]. Thus, HMWOA, insoluble in water, is frequently applied to adsorbing and reducing the activity of heavy metals. TAYLOR and THENG [14] found that Cd adsorbed on kaolinite increased in response to increasing the HA concentration; while SHAKER and ALBISHRI [15] reported that Cd and Cr can be effectively adsorbed in soil with HA.

However, in other studies, LMWOA and HMWOA showed opposite roles. LIAO [16] reported that citric, oxalic, and acetic acids increased the adsorption of Cd on clay. JIANG et al [17] also determined that citric, oxalic, and malic acids decreased the release of Cd and Pb from soil, even at low concentration. Concerning the HMWOA, DINH et al [2] found that heavy metals were released by HMWOA due to the competition between HMWOA and heavy metals of the adsorption site in soil. LURLING et al [1] found that HA promoted the release of lanthanum from lake clay by coordinating with calcium and decreasing the clay fraction size. GUNGOR and BEKBOLET [18], and NHOH et al [19] showed that HA and FA increased the release of Zn from soil because of the HMWOAs adsorbed on the soil and occupied the adsorption site. Thus, the influence of organic acids on the release of heavy metals in the environment is a very complicated process, and it could not be explained only by the perspective of complexation. Thus, it is necessary to verify the effects of different molecular organic acids on the dissolution and complexation of heavy

metal in soil. The objective of this study was to investigate the effect of LMWOA and HMWOA on heavy metal release or immobilization in soil, examine the fraction change of heavy metal in soil, and identify the mechanism of LMWOA and HMWOA contribution to heavy metal behavior in soil. In this study, the fractionation transformation of heavy metals was explained by the change of iron oxides and soil surface electronegativity. The outcomes can help to provide the understanding of application potential to the remediation of heavy metal- contaminated soil for different organic acids.

2 Experimental

2.1 Materials

The threonic acid (TA) and oxalic acid (OA), referring to LMWOA, were purchased from Shanghai Macklin Biochemical Co., Ltd. Humic acid (HA) and fulvic acid (FA), representing HMWOA, were extracted from peat using the method promoted by the International Humic Substances Society (IHSS).

An alkaline soil from Kaifeng City (KF) in northern China and an acidic soil from Hengyang City (HY) in southern China were chosen in this study. Both of soils were contaminated by copper (Cu), cadmium (Cd) and lead (Pb). The moisture soil was collected from 10 to 30 cm in depth, air dried, ground through an 18-mesh sieve, and individually mixed, prior to use. The basic properties of soils are present in Table 1.

2.2 Experiments

Five treatments of organic acids including distilled water control (CK), TA, OA, HA, and FA were performed. Serials concentrations of each organic acid (100, 200, 400, 600, 800, and 1000 mg/L) were used and the pH of organic acid solution was initially adjusted to 7. Each treatment had three replicates. The experiment was conducted by respectively mixing 5 g HY and KF soil with a

Table 1 Basic properties of soil samples

Soil	Organic matter proportion/%	Clay proportion (<0.002 mm)/%	Sand proportion (2–0.02 mm)/%	Silt proportion (0.02–0.002 mm)/%	pH	CEC/ (cmol·kg ⁻¹)	Cd content/ (mg·kg ⁻¹)	Cu content/ (mg·kg ⁻¹)	Pb content/ (mg·kg ⁻¹)
KF soil	1.5	17.37	71.51	11.12	7.3	17.48	1.45	80.7	1627.3
HY soil	4.88	16.92	68.32	14.76	6.7	21.41	3.42	147.9	7153.6

*CEC: Cation exchange capacity

serially increasing organic acid concentration at soil/solution ratio of 1:10 g/mL. The mixture of soil and organic solutions was shaken at 200 r/min for 48 h, while being kept at 25 °C. Thereafter, the zeta potential was determined. The supernatant and soil were separated by centrifuging at 5000 r/min for 10 min. The supernatant was used to analyze the concentrations of Cd, Pb, Cu, water-soluble iron, and total organic carbon (TOC). The separated soil was employed for fractionation of Cd, Pb and Cu, and amorphous iron concentration.

2.3 Analytical methods

2.3.1 Concentrations of heavy metal and water-soluble iron

The concentration of Cd, Pb, Fe and Cu in supernatant was analyzed with an ICP-OES (Agilent 5100). The total organic carbon (TOC) was measured with a visible range spectrophotometer (Shimadzu TOC-4200).

2.3.2 Fractionation of heavy metals in soil

The fractionation of Cd, Pb and Cu in soil was determined with the sequential extraction method promoted by the Community Bureau of Reference (BCR). The heavy metals were divided into four categories, consisting of HOAc-extractable, reducible, oxidizable, and residual fraction metals, which were extracted with four extractants: (1) 0.11 mol/L acetic acid (AcOH) was added into soil to extract the exchangeable species and the weak acid soluble fraction (HOAc-extractable fraction); (2) 0.5 mol/L hydroxylamine hydrochloride was adjusted to pH 2 with HNO₃ to extract the reducible metal species bound to Fe–Mn oxyhydroxides (reducible fraction); (3) 8.8 mol/L hydrogen peroxide and 1 mol/L ammonium acetate (AcONH₄) was employed to extract oxidizable metal species bound to organics and sulphides (oxidizable fraction); (4) aqua regia was used to obtain the residual fraction. The concentrations of Cd, Pb and Cu in extractants were analyzed with an ICP-OES (Agilent 5100).

2.3.3 Zeta potential

The zeta potential of soils treated with different concentrations of LMWOA and HMWOA was determined by a zeta-meter with the value change less than 2 mV.

2.3.4 Amorphous iron

For amorphous iron measurement, a dithionite-citrate-bicarbonate (DCB) was prepared by mixing

77.4 g sodium citrate, 84 g sodium hydrogen carbonate and 0.5 g sodium dithionite in 1 L distilled water. The soil was washed with distilled water to remove the soluble iron. A 40 mL DCB solution was added into the washed soil shaken at 200 r/min for 16 h. Subsequently, the supernatant was collected and stored. The soil was then extracted again with 40 mL of 0.05 mol/L magnesium sulfate for 24 h and centrifuged. These two supernatants were mixed and the concentration of amorphous Fe was determined by ICP-OES (Agilent 5100).

3 Result

3.1 Release or immobilization of Cu, Cd and Pb by organic acids

As depicted in Fig. 1, the effects of LMWOA (TA and OA), and HMWOA (HA and FA) on heavy metal release or immobilization were studied in the concentration range from 100 to 1000 mg/L. Without organic addition (control treatment), Cu released from soil was undetected since there were no changes of Cu concentration in solution (Fig. 1). As expected, an overall increasing trend of Cu release was attained with respect to the increase of LMWOA concentration both in HY and KF soils. For instance, the highest Cu concentrations in soil solution were 21.59 and 15.44 mg/L for the treatment with 1000 mg/L TA on HY and KF soil, respectively, which were 100 times higher than that in control group. For an OA concentration of 1000 mg/L, the Cu concentrations in solution were 7.58 and 13.82 mg/L in HY and KF soil, respectively, which were higher than that in original soil. In the range of 300 to 1000 mg/L LMWOA, an overall increase trend of Cd concentration was obtained with respect to increasing LMWOA concentrations in HY soil. The highest Cd concentrations in soil solution are 121.66 and 118.74 µg/L at 1000 mg/L OA and 1000 mg/L TA respectively. Similarly increase trend was also found for Pb. The results implied that LMWOA promoted the release of Cu, Pb and Cd from the soil.

In contrast, HMWOA slightly declined the concentrations of Cu, Pb and Cd in soil solution as compared with control treatment (without organic acid addition) (Fig. 1). The lowest Cd concentration in soil solution was 35.11 and 4.87 µg/L in HY soil

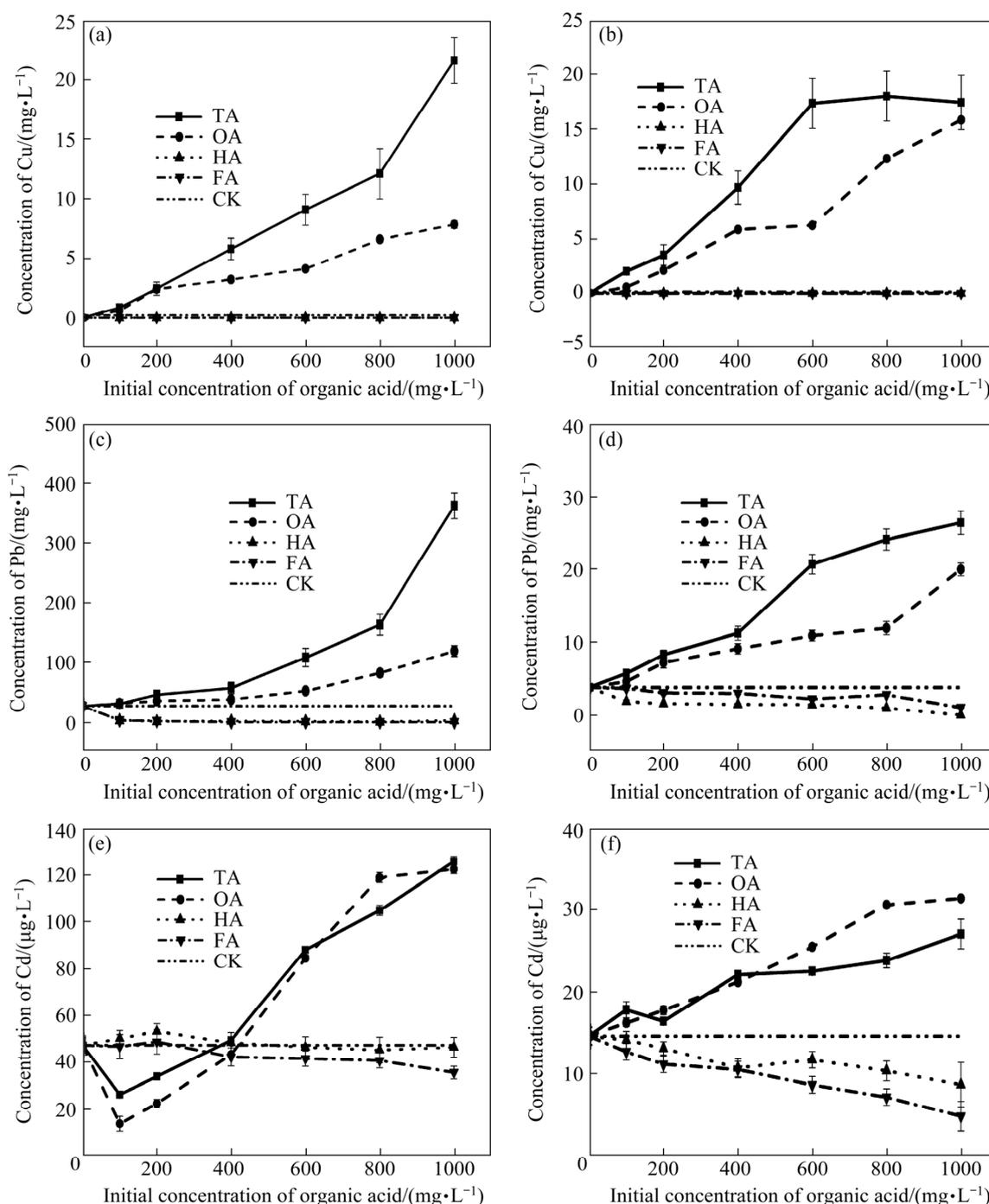


Fig. 1 Release of Cu (a, b), Pb (c, d), and Cd (e, f) from HY soil (a, c, e), and KF (b, d, f) soil in response to organic acid

and KF soil, respectively, at 1000 mg/L FA. Meanwhile, at the identical concentration (1000 mg/L), HA addition resulted in more decrease in Cd concentration in soil than FA, by 5.20 and 3.48 $\mu\text{g/L}$ for HY and KF soils, respectively. Similar trend was also obtained for Pb, and ever Pb was found to be undetected in soil solution at 100 mg/L HA and FA in HY soil.

3.2 Fractionation transformation of heavy metals in soil

The heavy metals were divided into four categories, consisting of HOAc-extractable, reducible, oxidizable, and residual fraction metals. The HOAc-extractable fraction metals, which are regarded as the most active metals, are further divided into exchangeable and carbonate metals.

Exchangeable metals are adsorbed on a soil component and easily released into the environment. Carbonate metals are bound up with carbonate, which is sensitive to pH of soil. In soil, the reducible metals are regarded as more stable than HOAc-extractable fraction metals and are bound to oxidation minerals through formation of an exosome on a mineral with free anions. The oxidizable metals, which are regarded as relatively stable metal species, are bound to soil organic matter by chelating with organic acid functional groups. Finally, the residual metals mainly exist in the crystals and are difficult to disassociate.

As shown in Tables 2 and 3, Pb, Cu and Cd in

HOAc-extractable, reducible, oxidable and residual fractions decreased both in HY and KF soils, in the presence of LMWOA. Here, HY soil was chosen for illustrating the effects of LMWOA on fractions of Pb, Cu and Cd. Cd mainly existed in reducible fraction. TA and OA decreased the reducible fraction of Cd from 1148.24 to 910.36 and 953.61 $\mu\text{g}/\text{kg}$, respectively. The oxidable fraction of Cd decreased from 951.31 to 705.84 and 750.17 $\mu\text{g}/\text{kg}$ by TA and OA, respectively. The HOAc-extractable fraction of Cd decreased from 432.1 to 351.96 and 310.29 $\mu\text{g}/\text{kg}$ by TA and OA, respectively. The residual fraction of Cd was slightly decreased from 614.56 to 601.65 and

Table 2 Contents of Cd, Cu and Pb in fraction of HY soil in the presence of 1000 mg/L organic acid

Content	Fraction	CK	TA	OA	FA	HA
Cd/($\mu\text{g}\cdot\text{kg}^{-1}$)	HOAc-extractable	432.1	351.96	310.29	859.24	869.43
	Reducible	1148.24	910.36	953.61	1370.36	1451.02
	Oxidable	951.31	705.84	750.17	1469.52	1641.51
	Residual	614.56	601.65	584.88	651.86	686.91
Cu/($\text{mg}\cdot\text{kg}^{-1}$)	HOAc-extractable	22.35	5.12	3.08	52.32	51.84
	Reducible	21.01	14.28	15.39	21.67	19.34
	Oxidable	59.12	35.74	29.59	88.78	85.96
	Residual	20.76	18.74	15.98	32.78	29.42
Pb/($\text{mg}\cdot\text{kg}^{-1}$)	HOAc-extractable	316.25	261.09	218.56	805.74	1046.57
	Reducible	845.32	314.69	140.15	895.46	954.38
	Oxidable	1194.1	551.42	392.4	2204.31	2622.09
	Residual	4642.6	4271.17	4390.92	5024.43	5392.6

Table 3 Contents of Cd, Cu and Pb in fraction of KF soil in the presence of 1000 mg/L organic acid

Content	Fraction	CK	TA	OA	FA	HA
Cd/($\mu\text{g}\cdot\text{kg}^{-1}$)	HOAc-extractable	252.12	185.21	208.33	648.87	671.65
	Reducible	593.21	341.98	356.87	726.98	631.54
	Oxidable	312.36	243.74	215.32	481.91	497.44
	Residual	254.56	234.56	241.2	311.47	312.99
Cu/($\text{mg}\cdot\text{kg}^{-1}$)	HOAc-extractable	12.32	3.67	2.31	13.02	16.04
	Reducible	10.21	5.01	6.89	11.82	12.05
	Oxidable	23.46	18.61	19.32	24.56	25.41
	Residual	16.74	17.04	15.78	22.78	21.42
Pb/($\text{mg}\cdot\text{kg}^{-1}$)	HOAc-extractable	107.05	48.87	56.91	291.54	287.04
	Reducible	205.32	107.54	106.15	213.12	221.02
	Oxidable	311.6	175.64	198.21	514.79	498.32
	Residual	481.6	441.33	403.12	652.64	601.39

584.88 $\mu\text{g}/\text{kg}$. It was obvious that the HOAc-extractable, reducible and oxidable fractions of Cd were dissolved by LMWOA. Cu mainly existed in oxidable fraction. In the presence of LMWOA, the oxidable fraction of Cu decreased from 59.12 to 35.74 and 29.59 mg/kg by TA and OA, respectively. The HOAc-extractable and reducible fraction also decreased by LMWOA. However, there was no obvious change of the Cu residual fraction under the effect of TA and OA. Pb mainly existed in residual fraction, and the residual fraction of Pb decreased from 4642.6 to 4271.17 and 4390.92 mg/kg by TA and OA, respectively. The oxidable fraction of Pb decreased from 1194.1 to 951.42 and 992.4 mg/kg by TA and OA, respectively. The reducible fraction of Pb decreased from 845.32 to 314.69 and 140.15 mg/kg by TA and OA, respectively. The HOAc-extractable fraction of Pb decreased from 316.25 to 261.09 and 218.56 mg/kg by TA and OA for HY soil, respectively.

Conversely, in the presence of HMWOA, Pb, Cu and Cd in HOAc-extractable, reducible, oxidable and residual fractions increased both in HY and KF soil. At 1000 mg/L HA and FA, the HOAc-extractable fraction of Cd, Cu and Pb in HY soil increased from the initial value of 432.1 $\mu\text{g}/\text{kg}$, 22.35 mg/kg and 316.25 mg/kg to 829.24–869.43 $\mu\text{g}/\text{kg}$, 48.32–51.84 mg/kg and 850.74–1046.57 mg/kg , respectively. The oxidable fraction of Cd, Cu and Pb in HY soil increased dramatically from the initial value of 951.31 $\mu\text{g}/\text{kg}$, 59.12 mg/kg and 1194.1 mg/kg to 1469.52–1641.51 $\mu\text{g}/\text{kg}$, 88.78–85.96 mg/kg and 2204.31–2622.09 mg/kg , respectively. The residual fraction of Pb, Cd and Cu in HY soil slightly increased from the initial value of 614.56 $\mu\text{g}/\text{kg}$, 20.76 mg/kg and 4642.6 mg/kg to 751.91–761.86 $\mu\text{g}/\text{kg}$, 29.78–32.78 mg/kg and 5024.43–5392.6 mg/kg , respectively. The result in KF soil was similar to that in HY soil. The reducible fractions of Cd, Cu and Pb in KF soil in presence of 1000 mg/L HA and FA increased from 593.21 $\mu\text{g}/\text{kg}$, 10.21 mg/kg and 205.32 mg/kg to 631.54–726.98 $\mu\text{g}/\text{kg}$, 11.82–12.05 mg/kg and 213.12–221.02 mg/kg . The reducible fraction of Cd, Cu and Pb also increased in HY soil from 1148.24 $\mu\text{g}/\text{kg}$, 21.01 mg/kg and 845.32 mg/kg to 1370.36–1451.02 $\mu\text{g}/\text{kg}$, 19.34–21.67 mg/kg and 895.46–954.38 mg/kg . From the results, it could be inferred that most of Cd, Pb and Cu adsorbed from

solution to soil existed in oxidable and reduction fractions.

3.3 Changes of soil surface electronegativity

The soil surface charge, which is assessed by using the zeta potential, is an important index, as it influences the adsorption of heavy metal in the soil. As shown in Fig. 2, the zeta potentials of the HY and KF soils at pH 7.0 were -45.85 and -6.5 mV, respectively. After organic acid addition, the zeta potential significantly decreased in the presence of organic acid, implying an increase in the soil surface's negative charge. At 200 mg/L LMWOA, the zeta potential of HY soil decreased to -50.14 mV by OA and -59.32 mV by TA; while at 200 mg/L HMWOA, its zeta potential was sharply decreased to -78.47 mV by FA and -92.4 mV by HA. Higher concentrations of LMWOA and HMWOA resulted in higher decline of zeta potential. Moreover, more decrease in zeta potential was obtained in HMWOA compared to LMWOA. As demonstrated by PLAZA et al [20], there were coordinative interactions between positive surface sites and HMWOA, which results in a surface zeta potential decrease and introduces cation adsorption on the surface.

3.4 TOC in soil solution

As shown in Fig. 3, the TOC concentrations in solution of original KF and HY soil were 25.34 and 30.82 mg/L , respectively. In the presence of LMWOA, the TOC significantly elevated with increasing LMWOA concentration. At 1000 mg/L OA (Fig. 3(a)), the TOC concentrations were 638.64 and 550.33 mg/L in HY soil and KF soil, respectively, which were higher than original TOC of OA solution by 374.43 and 286.15 mg/L . Similarly, at 1000 mg/L TA, the TOC concentrations were 973.46 and 823.39 mg/L in HY soil and KF soil, respectively, which were higher than the original ones of TA solution by 582.23 and 432.16 mg/L . This result indicated that the LMWOA mainly existed in solution. The higher TOC content in HY soil might attribute to the higher organic matter content than that in KF soil.

The effect of HMWOA on TOC in soil solution was less than LMWOA (Fig. 3). At 1000 mg/L FA (Fig. 3(c)), the TOC was 39.41 and 28.73 mg/L in KF and HY soil, respectively. At 1000 mg/L HA (Fig. 3(d)), the TOC was 50.26 and

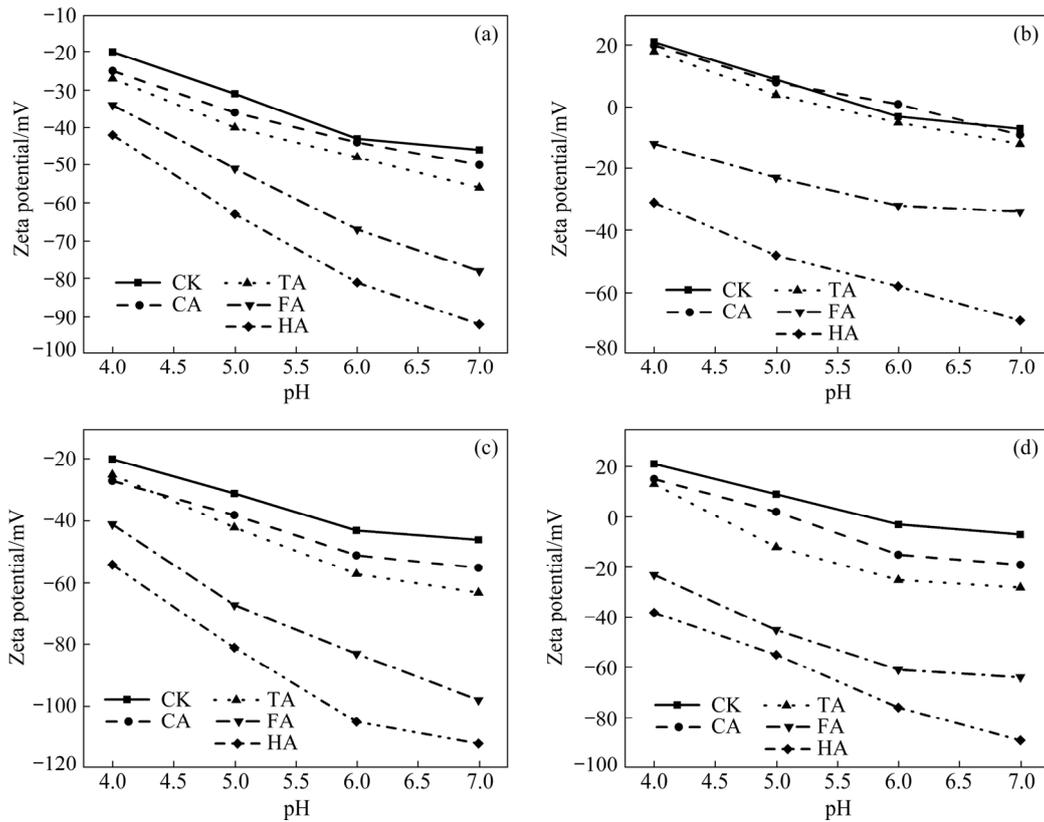


Fig. 2 Zeta potential of HY with 200 mg/L organic acid (a), KF soil with 200 mg/L organic acid (b), HY with 1000 mg/L organic acid (c), and KF soil with 1000 mg/L organic acid (d)

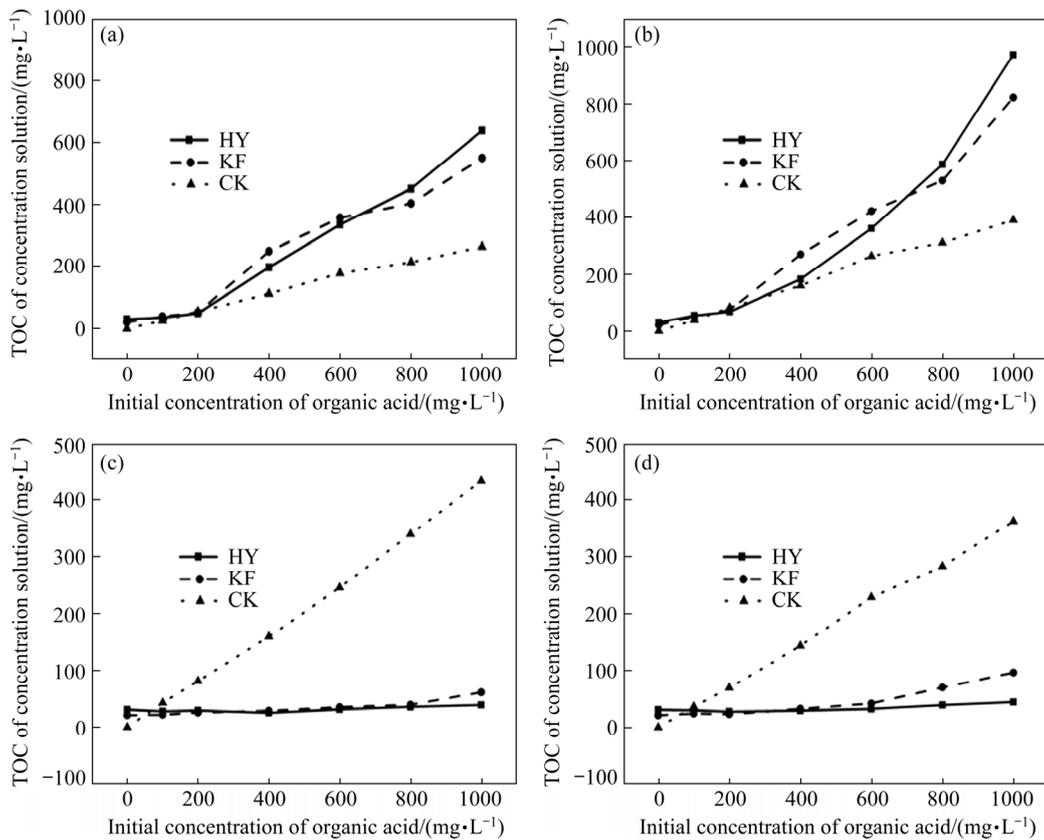


Fig. 3 TOC concentrations of soil solution in the presence of OA (a), TA (b), FA (c), and HA (d)

32.14 mg/L for KF and HY soil, respectively. The TOC concentration was only slightly increased in both FA and HA treated soils. This result might attribute to the adsorption of humic substances by ligand exchange mechanism and/or cation bridge formation onto ferric and aluminum oxides.

3.5 Effects of organic acid on iron dissolution and transformation

Reducible heavy metal was mainly adsorbed on the surface of oxidized iron or co-precipitated on secondary iron minerals. As shown in Fig. 4, the content of water-soluble iron in both HY and KF soils increased with elevating the LMWOA concentration. When the LMWOA concentration increased from 0 to 1000 mg/L, water-soluble iron increased from 15.48 to 19.16 mg/kg by OA and 19.53 mg/kg by TA in HY soil, from 6.52 to 12.29 mg/kg by OA and 12.02 mg/kg by TA in KY soil. These results imply that LMWOA promotes iron dissolution in the soil.

However, HMWOA showed little effect on water-soluble iron. For instance, when HMWOA concentration varied from 0 to 1000 mg/L, water-

soluble iron fluctuated between 6.21 and 6.88 mg/kg by FA in HY soil and between 15.48 mg/kg and 16.02 mg/kg in KF soil. Similar trend was also observed in HA-treated soil. The results indicated that iron dissolution in soil caused by HMWOA was not significant.

As shown in Figs. 4(c) and (d), the influence of LMWOA and HMWOA on amorphous iron was also obtained. LMWOA resulted in a decrease in amorphous iron in both HY and KF soils at high LMWOA. In HY soil, amorphous iron sharply decreased from 120.05 mg/kg (in the absence of organic acids treatment) to 72.54 mg/kg by 1000 mg/L OA and 73.22 mg/kg by 1000 mg/L TA; while that in the KF soil sharply decreased from 78.33 to 54.68 mg/kg by OA and 51.32 mg/kg by TA. This phenomenon might be attributed to the dissolution of iron ions by LMWOA [21].

Under HMWOA treatment, the amorphous iron in the HY soil increased from 120.05 to 158.77 mg/kg by 1000 mg/L FA and 172.41 mg/kg by 1000 mg/L HA. Similar trend was also found in KF soil. As illustrated in previous studies [22,23], organic acids like FA and HA can cause the

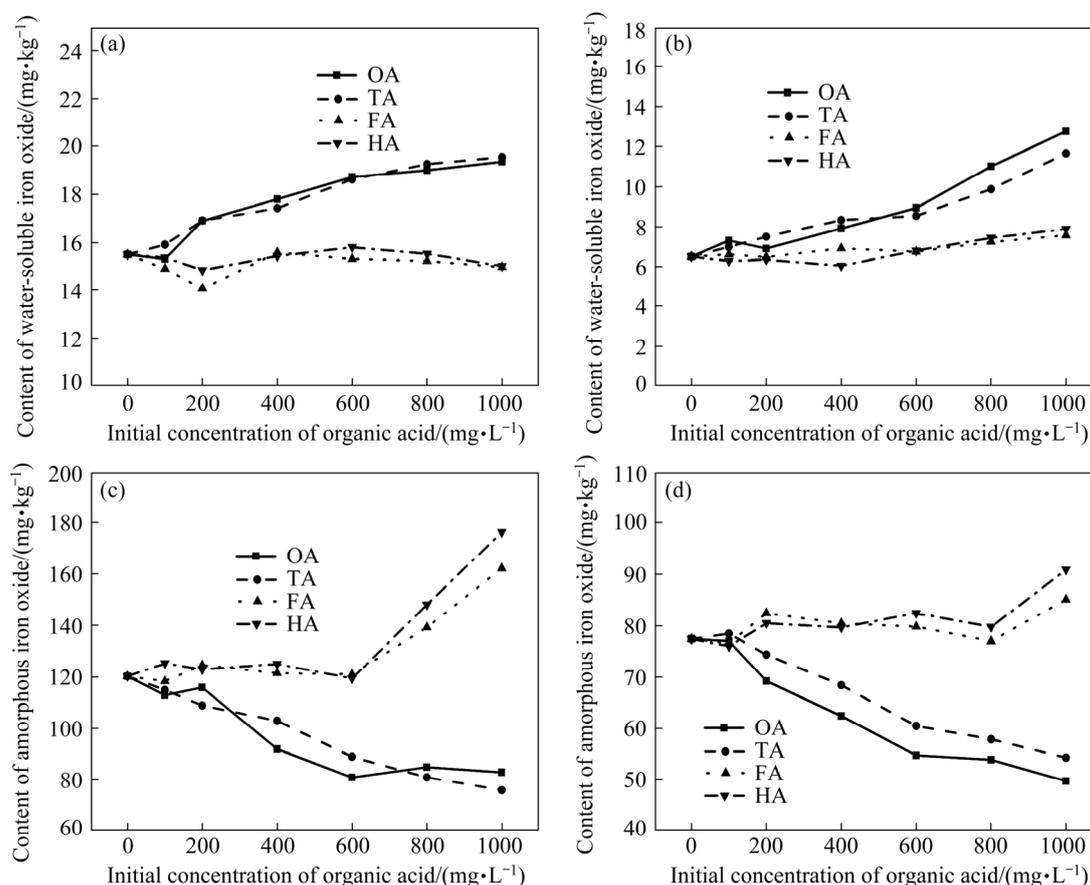


Fig. 4 Content of water-soluble iron (a, b) and amorphous irons (c, d) in HY (a, c) and KF (b, d) soil

disassociation of iron oxide crystals and production of amorphous iron oxide, resulting in the heavy metal adsorption onto amorphous iron oxide. Combined with the change of water-soluble iron and heavy metals, we speculate that heavy metals released by LMWOA may be related to the dissolution of iron oxides, while immobilization of heavy metals by HMWOA may be related to transformation of iron from crystalline to amorphous iron in the soil.

4 Discussion

In the present study, Pb, Cu, and Cd contents in soil solution have an overall increase caused by LMWOA addition (Fig. 1). The concentrations of Pb and Cd in the presence of 1000 mg/L TA in HY soil were 13 and 3 times higher than that in control soil (without LMWOA). Conversely, the HOAc-exchangeable fraction of Pb, Cu and Cd, reducible fraction and oxidable fraction sharply decreased by LMWOA (Fig. 2), indicating that the increased Pb, Cu and Cd contents in soil solution mainly come from the release of those relatively stable fractions. The possible mechanism for heavy metal release can be contributed to following aspects. Firstly, as revealed by previous studies, carboxyl groups of LMWOA can complex with metal ions to form soluble organic metal complexes, thereby promoting the dissolution of the metal ions [24,25]. As shown in Fig. 3, the TOC with the treatment of 1000 mg/L OA increased from 264.21 to 638.64 and 550.33 mg/L in HY soil and KF soil, respectively, indicating that the soil organic matters (SOMs) were dissociated by OA. From previous study, the LMWOA was found to dissolve organic matter in the soil due to competition between organic acids, which might influence the release of Pb, Cu and Cd from oxidable fraction [26]. Secondly, the dissociation of iron oxidation is also related to the release of heavy metals. The soluble iron content increased from 15.48 to 18.44 mg/kg by OA and 19.54 mg/kg by TA, while amorphous iron oxidation content decreased from 120.05 to 72.54 mg/kg by OA and 73.22 mg/kg by TA (Fig. 4), indicating dissociation of iron oxidation in the presence of 1000 mg/L LMWOA. The results are consistent with that reported by ABUMAIZAR and

SMITH [27]. LIN et al [28] conducted adsorption experiments by using oxalic and citric acid in conjunction with hematite and found that dissolved iron, pre-adsorbed with oxalic or citric acid, was detected in the hematite suspension, indicating that LMWOA can promote iron oxide dissolution [28]. Thus, it could be inferred that LMWOA promoted Pb, Cu and Cd release mainly through forming soluble complex with these metals from HOAc-exchangeable, reducible, oxidable fractions. The dissociation of SOM and amorphous iron oxides might also contribute to the release of Pb, Cu and Cd from oxidable fraction and reducible fraction, respectively.

HMWOA has a large number of hydrophobic groups and is therefore much less soluble in solution than LMWOA [29,30]. As shown in Fig. 3, the TOC in soil solution treated with HMWOA largely decreased, indicating that most of HMWOA was adsorbed in soil solid. Meanwhile, HMWOA lowered the zeta potential from -45.85 to -92.4 and -78.47 mV by HA and FA in HY soil, respectively. The zeta potential of KF soil also decreased from -6.5 to -89.21 mV by 1000 mg/L HA and from -6.5 to -63.55 mV by 1000 mg/L FA (Fig. 2). The results indicate the increase of negative charge of soil surface and introducing the adsorption of Pb, Cu and Cd. The results can be confirmed by the decline of Pb, Cu and Cd concentration in soil solution by HMWOA (Fig. 1). According to the complexation mechanism, it could be inferred that HMWOA adsorbed in soil solid can promote heavy metals adsorption onto soil solid by complexing. Furthermore, the electrostatic interaction might also facilitate the adsorption of heavy metals to the soil surface [31,32]. As shown in Table 3, these HOAc-exchangeable, reducible and oxidable fractions increased after the addition of 1000 mg/L HMWOA in KF soil. Similar to the result in KF soil, the HOAc-extractable and oxidable fraction of Cu, Pb and Cd increased in HY soil after being treated with 1000 mg/L HMWOA. Previous studies have suggested that reducible heavy metals in the soil are primarily combined with the secondary iron oxide minerals [33]. As stated by LIU et al [34], the adsorption mechanisms of heavy metals on iron oxidation minerals include electrostatic interaction, as well as the formation of anion-bridged ternary

complexes and surface precipitation. QU et al [35] illustrated that the formation of HA bridging complex and $\text{FeOH-HACOO}^-\text{Cd}$ enhanced the adsorption of Cd on the goethite surface. It could be inferred that the HMWOA increased the reducible fraction by electrostatic interaction and forming HA bridging complex with heavy metals. Besides, the HMWOA might also contribute to reduction of iron oxidation in soil and affect the heavy metals in reducible fraction.

YIN et al [36] revealed that the reduction and dissolution of iron oxide crystals contribute the reducible heavy metals decrease in the presence of organic matter [36]. In addition, LUO et al [3] also revealed that the iron spots on plant surface was reduced by organic material, causing increasement of Cd concentration in plant [37]. As stated by LI et al [38], the Fe^{2+} and Fe^{3+} from the reduction of crystalline iron oxidation could be represented and forming amorphous iron oxidation, introducing the adsorption of Cd in reducible fraction. According to previous studies, the amorphous iron oxidation with large surface and amounts of $-\text{OH}$ group, provides a higher absorption capacity for heavy metals [39–41]. As shown in Fig. 4, in the presence of 1000 mg/L HA and FA, the amorphous iron in soils remarkably increased. Thus, it could be inferred that the transforming of amorphous iron introduced increasement of reducible fraction of Cd, Pb and Cu.

The mechanism of organic acid on release or immobilization of heavy metal in contaminated soil was depicted in Fig. 5. In summary, LMWOA mainly exists in the soil in a water-soluble form. Thus, in the presence of LMWOA, heavy metal complexation in the soil increases the release of heavy metal ions into the soil. In addition, dissolution of soil-based organic matter and amorphous iron by LMWOA may further increase the release of heavy metals. HMWOA is primarily confined to the soil (as opposed to the solution) due to its hydrophobic group. Heavy metal complexation with HMWOA brings more heavy metals in the soil. Meanwhile, HMWOA causes the iron oxide transformation forming the crystals to amorphous iron, and the latter has higher absorption capacity for heavy metals. Therefore, HMWOA addition can immobilize heavy metals in soil.

5 Conclusions

(1) The high molecular organic acid (HMWOA) and low molecular organic acid (LMWOA) had inverse effects on the behavior of Cd, Pb and Cu both in acidic and alkaline soils. The LMWOA increased the concentrations of Cd, Pb and Cu, while HMWOA declined the concentrations of Cd, Pb and Cu in soil solution.

(2) The LMWOA significantly promoted the release of heavy metals in the soil, but HMWOA

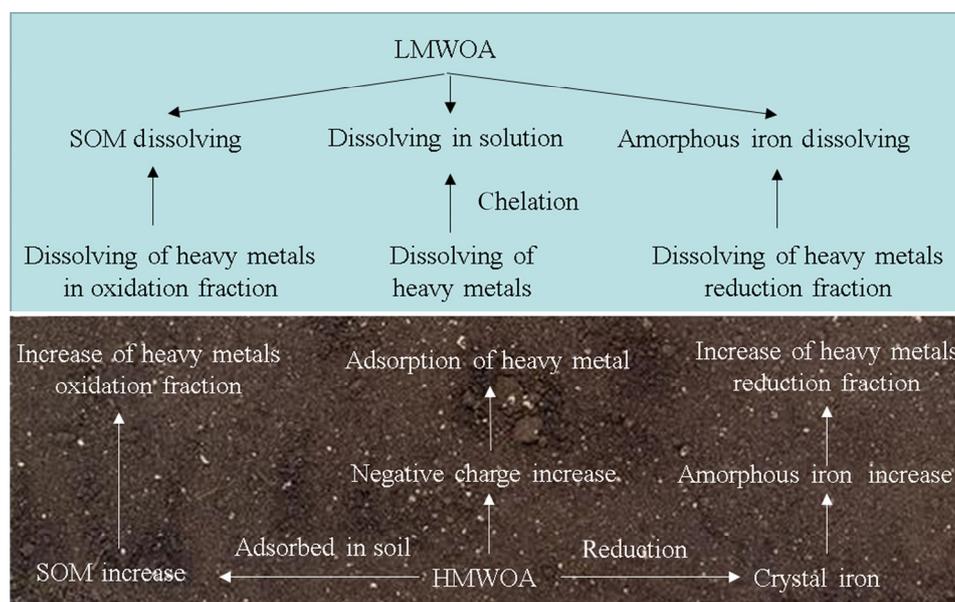


Fig. 5 Mechanism of organic acid on release or immobilization of heavy metal in contaminated soil

enhanced the immobilization of Cd, Pb and Cu in the soil. The fractions of HOAc-extractable, reducible, and oxidable Cd, Pb and Cu reduced after introducing LMWOA, while increased after introducing HMWOA.

(3) The release of Cd, Pb and Cu by LMWOA contributed to the dissociation of heavy metals bound to SOM and amorphous iron oxides. The immobilization of Pb, Cu and Cd by HMWOA attributed to the adsorption onto HMWOA followed immobilization by amorphous iron. The results implied that LMWOA has a potential application in soil washing remediation, while HMWOA can be used in the immobilization remediation of heavy metals contaminated soils.

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有机酸对污染土壤中重金属释放或固定的影响

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摘要: 为了探明土壤中不同有机酸对土壤中重金属环境活性的影响, 通过采用分批次实验分别研究高分子有机酸(HMWOA)(腐殖酸和富里酸)和低分子有机酸(LMWOA)(苏氨酸和草酸)对土壤中 Pb、Cu 和 Cd 释放或固定化效果的影响。结果表明, LMWOA 特别是苏氨酸促进土壤中 Pb、Cu 和 Cd 的释放, 并减少土壤中 HOAc 可提取态、可还原态及可氧化态 Pb、Cu 和 Cd 的含量。相反, HMWOA 特别是腐殖酸降低 Pb、Cu 和 Cd 的释放, 同时增加 HOAc 可提取态、可还原态及氧化态 Pb、Cu 和 Cd 的含量, 这说明 HMWOA 可以对土壤中的重金属进行固定化。通过对溶液中总有机碳(TOC)和水溶性铁含量测定发现, 在 LMWOA 作用下土壤总有机碳(TOC)和水溶性含量增加, 导致土壤中的有机物和氧化铁发生解离, 从而促进土壤中 Pb、Cu 和 Cd 的释放。而在 HMWOA 作用下, 土壤表面的 zeta 电位降低, 非晶型无定型氧化铁含量增加, 有利于 Pb、Cu 和 Cd 的吸附, 从而导致 Pb、Cu 和 Cd 被固定化。因此, LMWOA 在土壤洗涤淋洗修复中具有潜在的应用前景, 而 HMWOA 可用于重金属污染土壤的固定化修复。

关键词: 低分子有机酸; 腐殖酸; 黄腐酸; 土壤修复; 重金属形态转化

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