



Effect of moisture regime on the redistribution of heavy metals in paddy soil

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Abstract

Sequential extraction procedure was applied to assess the dynamics of solid-phase transformation of added Cu, Pb, Cd, and Hg in a typical Chinese paddy soil incubated under three moisture regimes (75% field capacity, wetting-drying cycle, and flooding). The heavy metals spiked in the soil were time-dependently transferred from the easily extractable fraction (the exchangeable fraction) into less labile fractions (Fe-Mn oxide- and organic matter-bound fractions), and thus reduced lability of the metals. No significant changes were found for the carbonate-bound and residual fractions of the heavy metals in the soil during the whole incubation. Change rate of the mobility factor (MF), a proportion of weakly bound fractions (exchangeable and carbonate-bound) in the total metal of soil, reflected the transformation rate of metal speciation from the labile fractions toward stable fractions. It was found that soil moisture regime did not change the direction and pathways of transformation of metal speciation, but it significantly affected the transformation rate. In general, the paddy soil under flooding regime had higher metal reactivity compared with 75% field capacity and wetting-drying cycle regimes, resulting in the more complete movement of metals toward stable fractions. This might be related to the increased pH, precipitation of the metals with sulfides and higher concentration of amorphous Fe oxides under submerged condition.

Key words: heavy metal; speciation; moisture regime; redistribution; paddy soil

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Introduction

It is now widely recognized that the toxicity and mobility of heavy metals mainly depend on their specific chemical forms and binding states (Ma and Rao, 1997; Kabala and Singh, 2001). In the soil-water environment, the chemical form of a metal determines the biological availability and chemical reactivity, such as sorption/desorption and precipitation/dissolution and so on, towards other components of the system. The binding form in the solid phase is relative to the kinetic and equilibrium of metal release to the liquid phase and hence the possibility of remobilization and bioavailability (Tack and Verloo, 1995). Sequential selective dissolution procedures have often been used to provide more information on the forms, availability, mobility, and transformation of heavy metals in the solid phase components of soils and sediments (Tack and Verloo, 1995). Many studies show that, when added to soils, various forms of heavy metals slowly redistribute among their solid-phase components. This long-term process was influenced by many factors,

including metal species, pH, temperature, redox potential (Eh), organic matter, leaching, ion exchange and microbial activity (McGrath and Cegarra, 1992; Han and Banin, 1999; Han et al., 2001; Kashem and Singh, 2004; Kabra et al., 2007).

Soil moisture regime is one of the most important factors for the control of the physical, chemical, and biological properties of soil. It can affect pH, Eh, organic matter and CaCO₃ contents of soil (Van den Berg and Loch, 2000), and accordingly, may indirectly influence the transformation and repartition of heavy metals in soil, further altering their availabilities to plants. Generally, under saturated conditions, the pH tends to converge to neutral, whether the initial one was acidic or alkaline (McBride, 1994). In addition, the Eh decreases by microbial respiration and, as a result, Fe and Mn oxides are reduced under anaerobic conditions, making heavy metals released and redistributed among the solid-phase components (Iu et al., 1981). Consequently, there would be two contrary processes, the mobilization of the native metals on account of the mild chemical reduction after saturation (Phillips, 1999; Davranche et al., 2003) and the immobilization of the added heavy metals, owing to their transform from

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more labile fractions into stable ones on the other side (Han and Banin, 1997; Kashem and Singh, 2004; Sun et al., 2007). Simultaneously, many efforts have been devoted to the study of processes in unsaturated soils under controlled conditions, reporting that added metals were transformed gradually from soluble fractions to more stable ones, depending upon the type of soil, soil pH and rate of application (Han and Banin, 1999).

Paddy soil in China has been recognized as an anthropogenic soil type formed due to long-time and hydro-agric managements under seasonally submergence for rice growth. The metal speciation in paddy soil is likely to undergo changes among different moisture regimes, e.g., (1) moist, oxic conditions at a certain field capacity; (2) waterlogged conditions; (3) a short period of saturation (the establishment of temporary low oxygen conditions), followed by drying the surface soil (oxidizing conditions). These situations frequently occur in the rice fields, which are related to the transformation of metal fractions, and hence affect the mobility and bioavailability of heavy metals. Limited information, however, is available regarding the effect of varying moisture regimes on the speciation changes of harmful metals, especially Hg, in paddy soil. Therefore, this study was designed to assess solid-phase transformation of added Cu, Pb, Cd and Hg during 150-day period of incubation under three moisture regimes in a typical Chinese paddy soil, and to evaluate the extent of moisture regime influence on the redistribution of heavy metal speciation. This work should offer a significant insight into the redistribution of freshly spiked metals among soil components regarding moisture regimes.

1 Materials and methods

1.1 Soil samples

The paddy soil (topsoil, a depth of 0–20 cm) was collected from Taoyuan Agroecological Station of Chinese Academy of Sciences in Hunan Province, China. It is a reddish clayey paddy soil (Inceptisol, USDA soil taxonomy) with slightly acidic reaction, which developed on the Quaternary red earth and is widely distributed over South China.

Soil samples were air-dried, ground and sieved through a 2-mm sieve. Some basic physicochemical properties of the soil are given in Table 1. Soil pH was measured in a 1:2.5 (W/V) ratio of soil to water by a glass electrode (Lu, 2000). Soil organic matter was determined by oxidation with $K_2Cr_2O_7 \cdot H_2SO_4$ (Lu, 2000). Particle size distribution was analyzed using the micro-pipette method (Miller and Miller, 1987). Cation exchangeable capacity (CEC) was measured as described by Chapman (1965). Amorphous

and free (amorphous-plus-crystalline) Fe oxides of the soil were respectively determined by with ammonium oxalate and dithionite-carbonate-bicarbonate (DCB) extractants (Mehra and Jackson, 1960).

1.2 Incubation experiment

The incubation experiment was performed with 0.5 kg (oven-dry weight) soil in plastic beaker. Nitrate salts of heavy metals Cu, Pb, Cd and Hg in aqueous solution were added and then mixed with soil samples thoroughly. The amounts of metals spiked were 100 mg/kg for Cu and Pb, 2 mg/kg for Cd and Hg (metal/soil), respectively, which represented the medium contaminated level according to the classifications defined by Samsøe-Petersen et al. (2002). Then the soil samples were stored at 25°C for equilibration. After 14 days, the soil samples were subjected to treatments of three different moisture regimes: (1) 75% field capacity (75% FC): incubated in a moisture regime of 75% field capacity, the soil samples were weighted every day, and deionized water was added to keep the soil humidity constant; (2) wetting-drying cycle (WDC): the soil samples were incubated under a moisture regime entailing periodic wetting-drying cycles. Each cycle lasted for 30 days, including five days of wetting (field capacity) and a subsequent 25 days of air-drying; (3) flooding (FD): deionized water was added to the soil samples to form a 5-cm layer of water over the soils.

During the incubation process, the plastic beakers were covered with the porous plastic membrane and placed in an incubator under the constant temperature (25°C) and air humidity (75%). Each treatment was replicated in three beakers. After 5, 30, 60, 90 and 150 days of incubation, subsamples were taken from each beaker for measuring concentrations of total and various forms of heavy metals, as well as pH and iron oxides. Prior to sampling, each soil sample was mixed completely to ensure homogeneity and representativeness. In addition, a part of the subsample from each beaker was used to determine the moisture content to present the data on an oven-dry weight basis.

1.3 Sequential extraction procedure

The sequential extraction proposed by Tessier et al. (1979) was employed in this study, but water was not used as an extractant because the concentration of water soluble fraction in the soils was very low in most cases. The chemical fractions of heavy metals are operationally defined in Table 2.

Extractions were conducted in 100 mL polypropylene centrifuge tubes. Between each successive extraction, the supernatant was centrifuged at 4000 r/min for 30 min, and then filtered.

Table 1 Physical and chemical properties of the tested paddy soil

pH	CEC (cmol/kg)	Free Fe oxides (g/kg)	Amorphous Fe oxides (g/kg)	Total sulfur (mg/kg)	Organic matter (g/kg)	Particle-size distribution (g/kg)			Metal concentration (mg/kg)			
						Clay	Silt	Sand	Cu	Pb	Cd	Hg
5.020	8.094	37.71	2.868	371.4	32.12	367.9	512.1	120.0	22.89	34.14	0.2301	0.1792

CEC: cation exchangeable capacity.

Table 2 Sequential extraction procedure and the corresponding fractions

Step	Fraction	Extraction procedure
1	Exchangeable (EXC)	2 g soil sample (oven-dry weight), 16 mL of 1.0 mol/L MgCl ₂ , pH 7, shake 1 hr, 20°C
2	Carbonate-bound (CAR)	16 mL of pH 5, 1.0 mol/L sodium acetate, shake 5 hr at 20°C
3	Fe-Mn oxide bound (OX)	40 mL of 0.04 mol/L NH ₄ OH-HCl in 25% (V/V) acetic acid at pH 3 for 5 hr at 96°C with occasional agitation
4	Organic matter bound (OM)	6 mL of 0.02 mol/L HNO ₃ and 10 mL of 30% H ₂ O ₂ (pH adjusted to 2 with HNO ₃), water bath, 85°C for 5 hr with occasional agitation. 10 mL of 3.2 mol/L NH ₄ OAc in 20% (V/V) HNO ₃ , shake 30 min
5	Residual (RES)	Dried in a force-air oven at 40°C, 24 hr. Subsamples after sieving with 0.15 mm openings were used for determining Cu, Pb, Cd and Hg contents

1.4 Metal determination and quality control

The total metal concentrations and the metal concentrations of residual fractions of Cu, Pb and Cd in soil were determined by digesting 0.5 g soil samples (oven-dry weight) with HNO₃·HF·HClO₄ mixture followed by elemental analysis, while these of Hg were measured after digestion with H₂SO₄·HNO₃·KMnO₄ mixture. The concentrations of Cu, Pb and Cd in all solutions were analyzed by an atomic absorption spectrophotometer (AA800, PerkinElmer, USA), while Hg was detected by an atomic fluorescence spectrometry (AFS9130, Titan, China) equipped with a mercury hollow-cathode lamp.

All the reagents used for analysis were of analytical grade or better. The standard substances (geochemical standard reference sample soil in China, GSS-1) were used to examine the precision and accuracy of determination. As a check for the reliability of sequential extraction procedure, the relative errors between the sum of the metal concentration in individual fractions and the measured total metal concentration in soil samples were calculated and ranged from -13.6% to 10.1%, and the sums of extracted metal fractions over the experimental period were fairly constant (coefficients of variation, CV < 13%). Therefore, it is more convenient to use fractional distribution patterns to study the redistribution of metals with time, and the percentages of metals in different fractions were used to reflect the metal redistribution in the incubated soil samples in the study.

1.5 Calculation of transformation rate of metal speciation

The weakly bound fractions (EXC and CAR) of heavy metals are considered easily to mobilize and thus represent a potential risk for the environment. Thereby, the mobility factor (MF) had been proposed by Kabala and Singh (2001) and applied by several authors (Ettler et al., 2005; Sun et al., 2007) to describe heavy metal behavior in soils

and sediments:

$$MF = ((EXC + CAR)/(EXC + CAR + OX + OM + RES)) \times 100\% \quad (1)$$

where, EXC, CAR, OX, OM and RES represent the proportion of corresponding fraction.

The change of metal mobility factor during the incubation can reflect the transformation of metal speciation from labile fractions towards more stable fractions. Therefore, in this study, the change rate of metal mobility factor was used as an index of transformation rate of metal speciation.

1.6 Statistical analysis

Statistical analysis and data regression were performed using the software of SPSS 17.0 for windows.

2 Results

2.1 Fraction distribution of heavy metals in the native soil

The distribution of background metals in the native soil without any treatment is presented in Fig. 1. The background Cu, Pb and Cd in each fraction were generally in the order of RES > OX > OM > CAR > EXC, while the order for Hg followed RES > OM > OX > CAR > EXC. Heavy metals in the native soil were mostly presented in the RES fraction which accounted for over 45%. The OX fractions of Cu, Pb and Cd occupied the second important proportions (> 15%) in solid-phase components. The proportion of Pb in the OX fraction in the soils was approximately 40%. The proportions of CAR and OM fractions for all of heavy metals varied from 4 % to 12% and 8% to 12%, respectively. The EXC fractions of the metals in the soil, however, took up only < 4% for Cu, Pb and Hg, and 9.23% for Cd.

2.2 Long-term transformation of spiked metals in the soil

Chemical fractions of added Cu, Pb, Cd and Hg in the paddy soil varied with incubation time (Fig. 2). There were some distinct differences between the distributions of indigenous and spiked metals in the paddy soil. In the case of indigenous metals, the proportions present as the EXC fraction were very low in the soil, with the overwhelming majority of the metals distributed among

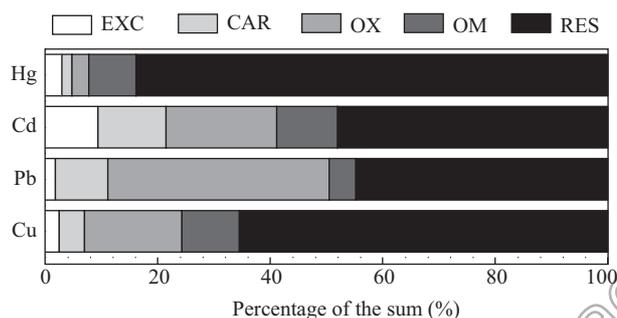


Fig. 1 Fraction distribution of background heavy metals in the native soil.

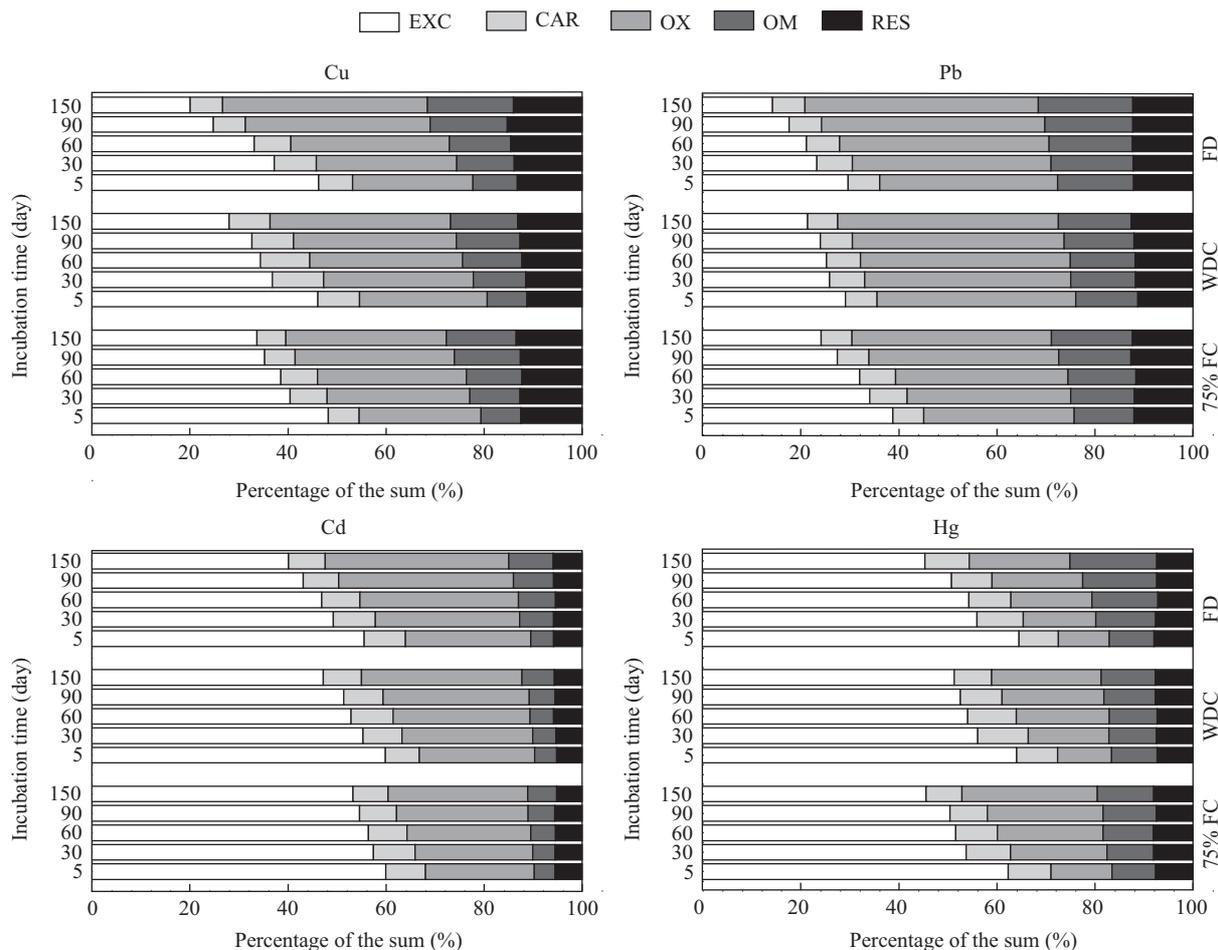


Fig. 2 Chemical fractions of Cu, Pb, Cd and Hg in the soil as a function of incubation time. 75% FC: 75% field capacity; WDC: wetting-drying cycle; FD: flooding.

the RES, OX, CAR and OM fractions. In contrast, the greatest proportions of newly spiked metals appeared in the EXC fraction during the first 5-day incubation in the paddy soil. After 5-day incubation, the proportions of exchangeable form (EXC) of heavy metals in all soils treated with different moisture regimes still kept at a high level. The proportions were 46%–49% for Cu, 35%–40% for Pb, >60% for Cd and Hg. As the incubation time was prolonged, the EXC fractions of the metals decreased significantly and consistently ($P < 0.05$). From 5 to 150 days of incubation, the proportions of exchangeable Cu and Pb in the paddy soil decreased by more than 15%, while those of Cd and Hg decreased by more than 7% and 12%, respectively. The decreases of exchangeable metals were particularly noticeable for flooding treatment ($P < 0.05$). After 150-day incubation, exchangeable fractions of heavy metals in the soils decreased to lower levels. The proportions were 20%–34% for Cu and Pb, 40%–54% for Cd and Hg.

Metals in the carbonate-bound fraction (CAR) in the treated soils accounted for 6%–10%, which were close to the proportions of the indigenous metals in this fraction in the native paddy soil. The proportions of carbonate-bound fractions barely changed with time ($P < 0.05$) in the soil treated with different moisture regimes (Fig. 2).

Oxide bound fractions (OX) of the heavy metals were

the second largest fraction in the treated paddy soils at the 5-day of incubation. They occupied 24%–27% of the spiked Cu, 30%–48% of the spiked Pb, 22%–26% of the spiked Cd and 10%–13% of the spiked Hg. Oxide bound fractions of the heavy metals in the soils increased significantly with increasing incubation time, particularly for flooding treatment. Up to 150 days of incubation, the proportions of oxide bound fractions of Cu, Pb, Cd and Hg in the all treated soils ranged from 32%–42%, 40%–48%, 28%–38% and 20%–28%, respectively. Compare to the native soil, the spiked-soils treated with different moisture regimes had the larger proportions of heavy metals in the OX fractions.

The change patterns of the organic matter bound fractions (OM) of the heavy metals were similar to those of the oxide bound fractions in all treated soils. The proportions of organic matter-bound fraction of the metals increased with increasing incubation time, particularly for flooding treatment. After 150 days of incubation, the proportions of organic matter-bound fractions of spiked metals were 8%–19% for Cu, Pb and Hg, 5%–10% for Cd, which were close to those of indigenous metals in the native paddy soil.

Statistical analyses confirmed that the concentration of the residual fraction of each metal in spiked-soil was consistent with that in the native soil, and remained almost unchanged during the whole incubation period ($P < 0.05$).

The proportions of residual fractions of spiked metals in the paddy soil accounted for on an average 12.87%, 12.41%, 5.45% and 7.78% for Cu, Pb, Cd and Hg, respectively, which were much lower than those of indigenous metals in the native paddy soil.

In summary, there were clear changes in the proportional distribution of the spiked Cu, Pb, Cd and Hg in the paddy soil treated with different moisture regimes during the 150 days of incubation. The proportions of spiked metals associated with the most weakly bound fractions (EXC) tended to decrease, with corresponding increases in the other more strongly binding fractions (OX and OM), whereas the proportions of Cu, Pb, Cd and Hg associated with the carbonate and residual fractions kept steady in the paddy soil during the whole incubation period. There were differences in the rates at which redistribution took place with the changes occurring generally faster in the flooded soil compared to the other soils treated with 75% field capacity and wetting-drying cycle regimes.

2.3 Effect of moisture regime on the redistribution of spiked metals in paddy soil

2.3.1 Transformation rates of metal speciation among different moisture regimes

The change rate of metal mobility factor (MF) reflected the transformation rate of metal speciation from the labile fractions toward stable fractions. It was clear that the metal MFs decreased consistently with incubation time.

By plotting MF of each metal against the incubation time, a logarithmic regression equation can be simulated as follows:

$$MF = A + B \ln(x) \quad (2)$$

where, MF (%) is the metal mobility factor, x (day) is incubation time, A and B are constants related to the properties of soil and heavy metals. As illustrated in Fig. 3, the coefficients of determination ranged from 0.9687 to 0.9955 ($n = 5$, $P < 0.05$). The logarithmic equation used was fitted well to the experimental data.

The constant B in Eq. (2) represents the slope and used as an index of transformation rates. Statistical analyses demonstrated that the transformation rate of Cu, Pb and Cd in the paddy soils for three moisture regimes decreased in the sequence of flooding > wetting-drying cycle > 75% field capacity ($P < 0.05$). There was, however, no significant difference in the rates of Hg of the soil between 75% field capacity and flooding regimes, and the rates of Hg of the soil for both 75% field capacity and flooding regimes were greater than that under wetting-drying cycle regime.

2.3.2 Fraction distribution of spiked metals in paddy soil treated with different moisture regimes after 150-day incubation

Figure 4 shows the speciation of each metal after 150-day incubation. It was clear that metals in the CAR and RES fractions did not differ significantly among the three

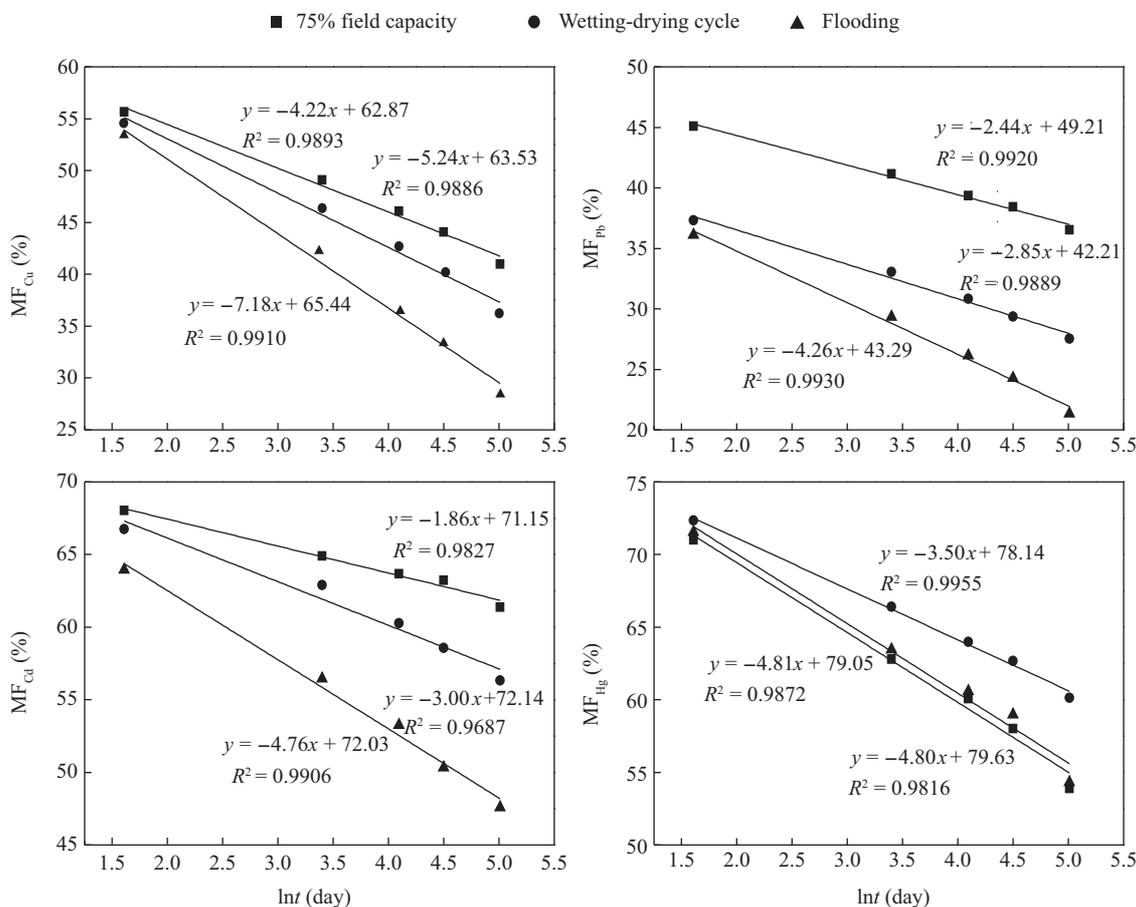


Fig. 3 Metal mobility factor (MF) as a function of the incubation time.

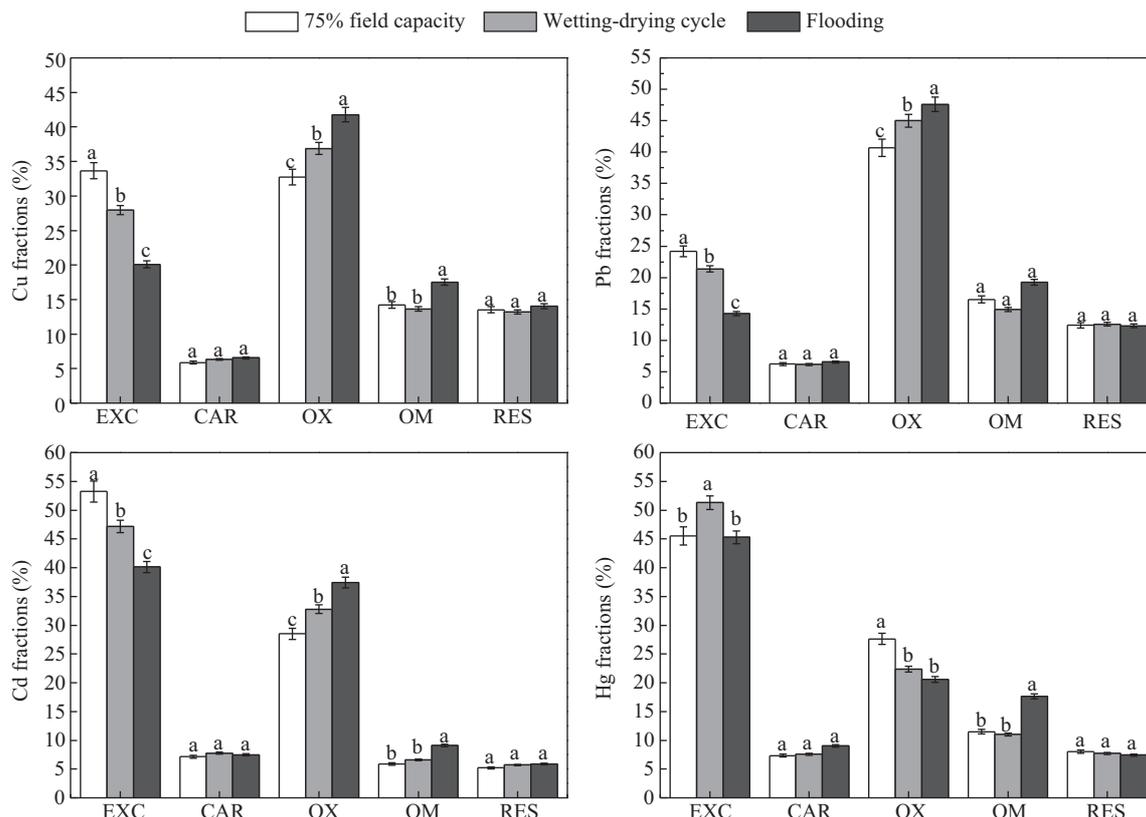


Fig. 4 Effect of soil moisture regime on fraction distribution of Cu, Pb, Cd and Hg after 150-day incubation. Bars within a fraction with the same letter are not significant at 0.05% level. Error bars denote standard deviation ($n = 3$).

moisture regimes. The proportions of Cu, Pb and Cd in the EXC fraction under three moisture regimes were in the order 75% field capacity > wetting-drying cycle > flooding, while those in the OX fraction followed the opposite order. Unlike other three elements, the proportions of Hg in the EXC and OX fraction were relatively higher at wetting-drying cycle and 75% field capacity regimes, respectively. In addition, there were significant increases for metals in the OM fractions under flooding regime.

2.4 Changes of pH and hydrous Fe oxides in the paddy soil treated with different moisture regimes

At the time of first sampling (day 5), the soil pH was 5.06, 5.08 and 5.81 under 75% field capacity, wetting-drying cycle and flooding regimes, respectively. As the incubation time was prolonged, it was found that the soil pH climbed from 5.81 (day 5) to 6.69 (day 150) under flooding regime, with an increment of 0.88 units. The soil pH had barely changed under wetting-drying cycle and 75% field capacity regimes (on an average 5.08 and 5.09, respectively).

Soil moisture also affected the crystallization of Fe oxides in the soils (Fig. 5). Concentrations of amorphous Fe oxides in the soils were higher under wetting-drying cycle and flooded moisture regime than those under 75% field capacity moisture regime. But those of soil free Fe oxides did not differ significantly among three soil moisture regimes after 150-day incubation. As compared with those under 75% field capacity regime, the concentrations of amorphous Fe oxides increased by 1.8 and 3.5 times under wetting-drying cycle and flooding regimes, respectively.

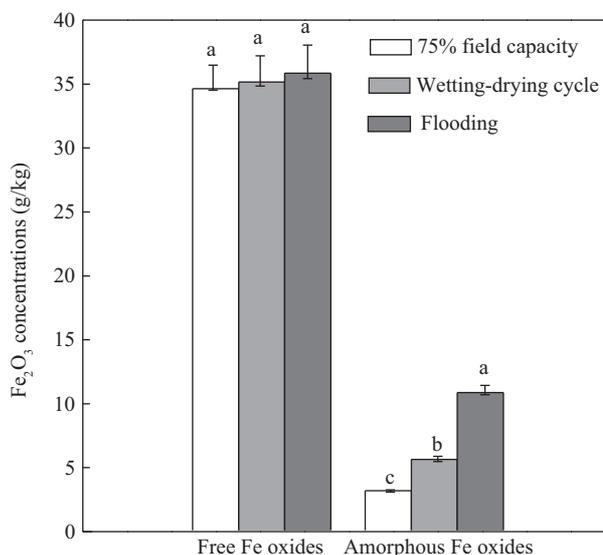


Fig. 5 Free and amorphous iron oxide among different moisture regimes in paddy soil after 150-day incubation. Bars within a fraction with the same letter are not significant at 0.05% level. Error bars denote standard deviation ($n = 3$).

3 Discussion

3.1 Transformation kinetics and rates of spiked metals in paddy soil treated with different moisture regimes

Many research works have indicated that the process of metal redistribution in soil is driven by reactions of the metals with more stable solid-phase components of

the soils, which depends upon elemental characteristics (e.g., atomic size, valence, and chemical affinity) and soil properties (Han and Banin, 1997, 1999; Ma and Dong, 2004; Kim and Owens, 2009). These effects might be further complicated by ligand competition from other cations (Norrström and Jacks, 1998). In recent years, numerous studies have been focused on the fraction transformation of heavy metals in soils at a certain moisture regime (Jalali and Khanlari, 2008; Tang et al., 2008), but few of them analyzed and compared the differences of transformation kinetics and rates among different moisture regimes. In this study, during 150-day incubation under all three moisture regimes, metals in the EXC fraction decreased consistently, which was accompanied with the increase of the metals in the OX and OM fractions. Metals bounded to carbonate occupied a small proportion and changed slightly during the incubation, which probably was attributed to the acidic nature of studied paddy soil. Tang et al. (2008) also reported that carbonate-bound fraction of spiked Pb and Cd accounted for a low proportion in strongly acidic soils which were under the nearly steady state during 120-day incubation. The spiked metal concentrations in the RES fraction kept unchanged with time, implying the added metals hardly entered the crystalline lattice during the 150-day incubation. This was in agreement with the reports of Lu et al. (2005) in which they observed that there were almost no changes for Cu, Zn, Pb and Cd in the residual fractions in three typical Chinese soils incubated for 64 days at 70% field capacity. The same transformation dynamics could be observed in each moisture regime. It seemed that the water regimes did not affect the direction and pathways of the transformations of metal speciation in paddy soil. This result was somewhat different from the findings from previous study (Han and Banin, 1997, 1999; Han et al., 2001). In which the solid-phase redistribution of spiked heavy metals in two arid-zone soils incubated under field capacity, wetting-drying cycle and saturated regimes was investigated respectively, and it was reported that at the field capacity, Cd added to the arid-zone soils was transferred from the EXC into CAR fraction; added Pb was transferred very slowly to the easily reducible oxide (ERO) fraction; added Cu was transferred from the EXC and CAR fractions into the ERO fraction and to some extent OM fractions. During the incubation in the saturated moisture regime, Cd and Pb underwent the same transformation pathways, with slightly different rates. At wetting-drying cycle regime, Cr was transferred from the carbonate fraction into the organic matter fraction; Cu, Ni, and Zn moved from the EXC and CAR fractions into the reducible oxide (RO), OM, easily reducible oxide (ERO), and RES fractions with time. The variations of transformation kinetics of heavy metals in two studies may be attributed not only to the difference in the origin (native or polluted) of heavy metals, pollution source, and soil properties (soil pH, organic matter, clay mineralogy), but also to the difference in adopted sequential extraction procedure.

Generally, the exchangeable form was considered readily mobile and easily bioavailable, while residual form

was considered to incorporate into crystalline lattice of soil minerals and appeared to be the most inactive. The carbonate-, Fe-Mn oxide-, and organic matter-bound fractions can be considered relatively active depending on the actual physical and chemical properties of soil (Tessier et al., 1979). Therefore, it can be concluded that spiked heavy metals transformed slowly and consistently from the more labile fractions to the more stable fractions during the incubation, by means of adsorption, complexation and chemical reactions with oxides, organic matter in paddy soil, and such transformation rate can be significantly affected by moisture regimes (Fig. 3). Hydrous oxides are known as a crucial soil component controlling the retention of trace metals in soils. Oxides that existed in studied paddy soil are relatively abundant (amorphous-plus-crystalline Fe oxides 37.71 g/kg), and the low solubility of metal oxide minerals made metals preferentially combine with oxide phase in the soils. On the other hand, organic matter played an important role in binding heavy metals in the OM fraction owing to the formation of metal-organic complex (Gambrell and Patrick, 1988). Moreover, organic matter could dissociate Fe and Mn from OX fraction, and hence, the enhanced negative sites would likely absorb heavy metals in this fraction (Iu et al., 1981; Kashem and Singh, 2001b).

3.2 Influence mechanism of moisture regime on the transformation of speciation in paddy soil

Paddy soil is intermediate between upland systems and true aquatic systems, and the alternation between anoxic and oxic conditions causes periodically occurring redox reactions. The effects of moisture regime on the redistribution of heavy metals in paddy soil may be mainly related to the difference in pH, Eh and hydrous Fe oxides in varying soil-water systems.

In waterlogged paddy soil, biological and microbiological activities combined with limited oxygen diffusion cause oxygen depletion and thus establish reducing conditions, where an observable change that a decrement of Eh associated with an increase of pH towards neutrality would follow (Narteh and Sahrwat, 1999). Furthermore, the intensity of reduction is higher in the presence of organic matter due to its oxidizability and soil components are reduced by anaerobic microbial respiration (Ponnamperuma, 1972). Under flooding regime, waterlogging contributes to increased pH. This change may result in more negative charges on soil clay colloids and organic matter surfaces, and correspondingly decrease the exchangeable heavy metals by immobilization over these surfaces (Yuan and Lavkulich, 1997). Lim et al. (2002) investigated the changes of speciation of Pb and Cd in soil at various pH values with different time and found that the changes of Pb and Cd in exchangeable fraction were pH-dependent. Generally, the change was small under acidic condition and larger decrease occurred at pH 7. By monitoring the process of heavy metals on iron oxide (α -FeOOH), Martínez and McBride (2001) found that either adsorption or coprecipitation of heavy metals with ferrihydrite were pH-dependent. They also found that the increasing pH

and incubation time resulted in the increase of adsorption and coprecipitation of heavy metals. On the other hand, increased concentrations of OM-bound Cu, Pb, Cd and Hg fraction in the flooded soil, as compared with non-flooded soil, was perhaps due to metal-organic complex formation, which has higher magnitude in the waterlogged soils because lower values of Eh and higher values of pH in this system were propitious to the formation of metal-organic complexes (Gambrell, 1994) and microbial immobilization (Haldar and Mandal, 1979). These pH-dependent mechanisms might have taken place in the flooded soil to immobilize heavy metals in the study.

Moreover, insoluble sulfide forms of metals would generate in reductive conditions driven by flooding, which could be one of the reasons why heavy metals exhibit low mobility in waterlogged soil. Most metal sulfides are highly insoluble (Sposito, 1994), and under the indirect effects of flooding conditions (low Eh), sulfate ions are reduced to the sulfide form, which might form a complex with heavy metals and immobilize them as sulfide salts (Gambrell and Patrick, 1988). Calmano et al. (1993) reported that generally the easily and moderately reducible fractions increase during oxidation while the sulfidic fraction decreases.

In waterlogged soil, reducing conditions would cause the oxides of Fe and Mn in soil solid phases to be reduced and dissolved (Iu et al., 1981; Ma and Dong, 2004). Chuan et al. (1996) pointed that the pH-dependent metal adsorption reaction and the dissolution of Fe-Mn oxyhydroxides under reducing conditions was the mechanism controlling heavy metal mobility in acidic soils. Reduced Fe and Mn via hydrolysis and oxidation precipitate as highly amorphous hydrous oxides that have a strong sorption capacity for trace elements (Shuman, 1976). The X-ray amorphous hydrated oxides and oxides with a low crystallinity showed a larger adsorption capability for heavy metals cations than those with a high crystallinity (Okazaki et al., 1986). As a result, strong sorption reaction decreased concentrations of Cu, Pb and Cd in the EXC fractions, and increased their OX fractions in the flooded paddy soil correspondingly (Fig. 4). This was also observed by Kashem and Singh (2004). In their findings, the breakdown of Fe and Mn oxides caused by water logging provided, on one hand, surfaces with high adsorbing capacity for Cd and Zn, but, on the other hand, increased the concentration of Fe and Mn in the mobile fraction. Kashem and Singh (2001a) suggested that adsorption of trace metals on Fe-Mn oxyhydroxide fractions was the major mechanism of their solubility reduction in submerged conditions. Tack et al. (2006) reported, however, that the moisture regimes did not significantly alter the 0.25 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 0.25 mol/L HCl-extractable (amorphous iron oxides) nor the 0.04 mol/L $\text{NH}_2\text{OH}\cdot\text{HCl}$ + 25% HOAc-extractable (amorphous + crystalline iron oxides) Fe, Mn and Al. But in his study, after being subjected to moisture treatments, soils were re-established and kept at field capacity for 21 days before being subjected to analysis. Therefore, changes of hydrous oxides may well have proceeded significantly, but would then have been reverted during the three subsequent weeks when all soils were again kept at field capacity.

Additionally, amorphous Fe oxides in paddy soil under wetting-drying regime were less than those under flooding regime (Fig. 5), because soil that has been periodically moistened-dried behaves differently from the continuously moist one (Bartlett and James, 1980). Under wetting-drying cycle regime, a subsequent aeration period after flooding would then cause the reprecipitation of fresh hydrous oxides of Fe and Mn, and the hydrous oxides were increasingly dehydrated and converted to a more crystalline state. It is not expected that freshly precipitated oxides would quickly revert to more oxidized, dehydrated, crystalline forms when the moistened soil get dried, where due to favorable moisture conditions for microbial activity, slightly anoxic regions are maintained within the soil (Jenne, 1968); conversely, when the dried soils are moistened, a burst of microbial activity occurs that may cause temporary anaerobiosis, which results in the insufficient reduction and dissolution of oxides (Miao et al., 2006).

The transformation rates of Hg among different moisture regimes, however, were unlike other three elements (Fig. 3), and Hg presented a different distribution in its EXC and OX fractions in flooded paddy soil (Fig. 4) after 150-day incubation. The decreased concentration in the oxide-bound fraction of Hg under flooding regime was probably due to that solubilization of Hg took place from the Fe-Mn oxide fraction with the reductive dissolution of Fe and Mn from the same fraction, and some competition from other cations occurred at the adsorption sites on the oxide surfaces, which would reduce the oxides adsorption capacity for Hg, and hence obstruct its transformation from EXC to OX fraction (Jing et al., 2007).

4 Conclusions

Heavy metals Cu, Pb, Cd and Hg added to paddy soil in soluble form under 75% field capacity, wetting-drying cycle and flooding moisture regimes were transformed slowly and consistently from the exchangeable fraction to more stable fractions (Fe-Mn oxide- and organic matter-bound), leading to the decrease of metal mobility in paddy soil. No significant changes were observed in the carbonate-bound and the residual fractions. It was found that soil moisture regime did not change the direction and pathways of transformation of metal speciation, but affected the transformation rate. In general, the paddy soil under flooding regime had higher metal reactivity compared with 75% field capacity and wetting-drying cycle regimes, resulting in the more complete movement of metals toward stable fractions, which might be related to the increased pH, precipitation of the metals with sulfides and higher concentration of amorphous Fe oxides under submerged condition.

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