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ORIGINAL PAPER

Transformation of metal speciation in purple soil as affected by waterlogging

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Abstract This study was conducted to investigate the effect of waterlogging on copper, lead and cadmium fractionation in Chinese purple soil. Heavy metals were added to purple soil at 80 % field capacity and waterlogging regimes as nitrate salts of 500 mg kg^{-1} of copper and lead, and 5 mg kg^{-1} of cadmium. Metals in the incubated soil samples were fractionated termly from 1 to 35 days by the sequential extraction procedure. Under both treatments, the heavy metals spiked in the soil were transformed slowly from the exchangeable fractions into more stable fractions, whereas their residual fractions barely changed. The transformation process of exchangeable fraction in soil was estimated by Elovich kinetic equation for the above incubation periods, and the constant B in Elovich equation was applied to reflect the transformation rates of metal speciation. It was found that waterlogging incubation could immobilize heavy metals, resulting in decreased lability and availability of the metals in purple soil. The effect of waterlogging on the redistribution of heavy metals in purple soil might be mainly related to the changes of pH, potential redox and hydrous oxides in varying soil-water systems.

Keywords Cadmium · Chemical speciation · Copper · Lead · Waterlogged purple soil

Introduction

Soils often act as a sink for heavy metals derived from various anthropogenic sources. The reactivity of trace metals in soils, in direct relation with their physico-chemical form and localization in different soil components, is the main parameter ruling their bioavailability and mobility (Tack and Verloo 1995). The determination of the total concentration of metal ions in soils does not give sufficient information about mobility and bioavailability of trace metals. Sequential extraction, although operationally defined, can give information about the association of heavy metals with geochemical phases of soil, and hence helps to reveal the distribution of heavy metals infractions and to assess the mobility and toxicity of metals in soils (Amanda Jo and David 2010). Among numerous sequential extraction methods, the method proposed by Tessier et al. (1979) was most widely used. According to this protocol, metals in soil were fractionated into exchangeable, carbonate-, Fe-Mn oxide-, organic matter-bound and residue fractions. Generally, the exchangeable fractions are considered readily mobile and bioavailable, whereas other metal fractions, especially a residual fraction, are considered immobile and tightly bound and may not be expected to be released under natural conditions. Field studies prove that heavy metals added to soils are transferred with time from the soluble and exchangeable fractions into less labile fractions (Han and Banin 1999). A term that is used to indicate the increased retention of metals with aging time is fixation.

Fixation of metals takes place by the slow diffusion of metals into Fe oxides, hydrous oxides of Al and Mn, clay minerals and by diffusion or precipitation in carbonates (Alexander 2000). Soil moisture regime is one of the most important factors for control of the physical, chemical, and

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biological properties of soil. It can affect pH, potential redox (Eh), organic matter and $CaCO_3$ 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.

Purple soil is the representative soil type in Sichuan province, which is the biggest province in western China with a population of over 88 million. Due to the soil background and human activities, the soil has been contaminated by heavy metals in many areas, resulting in potential risk to local human health and environment. Rice cultivation in purple soil has generally experienced rotation of waterlogged and non-waterlogged conditions to meet the need of growth, 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 waterlogging on the speciation changes of harmful metals in purple soil. Therefore, this study was designed to assess solid-phase transformation of added copper (Cu), lead (Pb), and cadmium (Cd) during 35-day period of incubation under two moisture regimes of 80 % field capacity and waterlogging in a typical Chinese purple soil, and to evaluate the extent of influence of waterlogging 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 waterlogged situation. The whole experiment and analysis were conducted in Key Laboratory of Production Environment and Agro-product Safety, Ministry of Agriculture, Tianjin, China, from October 2010 to March 2011.

Materials and methods

Description of soil samples

The purple soil used in the study was collected from a vegetable field of Pongzhou city in Sichuan Province, China, in October 2010. It was classified as a Regosol in the Food and Agriculture Organization of the United Nations (FAO) taxonomy, which was derived from Trias-Cretaceous system and widely distributed in Sichuan basin located in southwestern China with an area of 165,000 km^2 and an elevation varying from 200 to 500 m above sea level (He and Huang 1993). The climate of studied area is subtropical humid monsoon with an average annual precipitation of 1,000–1,200 mm and the average annual temperature is 14–19 °C (Yang 1982). More than 10 topsoil (0–20 cm) samples were randomly collected in the vegetable field, composited by mixing together and air-dried, ground and sieved through a 2-mm sieve. Selected soil characteristics determined by standard methods (Lu 2000) were 6.27 for pH, 0.64 g kg^{-1} for $CaCO_3$, 26.51 g kg^{-1} for organic matter, 20.81 g kg^{-1} for CEC, 23.71 g kg^{-1} for free Fe oxides, 2.41 g kg^{-1} for amorphous Fe oxides, 265.41 g kg^{-1} for clay (<0.002 mm), 43.92 mg kg^{-1} for total lead, 51.84 mg kg^{-1} for total copper, and 0.356 mg kg^{-1} for total cadmium. Metal speciation of native soil was also determined (detailed information shown in "Results and discussion").

Experimental design

The incubation experiment was performed with 1.5 kg (oven-dry weight, 105 °C) soil sample in plastic beaker. Nitrate salts of heavy metals Cu, Pb and Cd in aqueous solution were added in a single soil sample and then mixed thoroughly. The amounts of metals spiked were 500 mg kg^{-1} for Cu and Pb, 2 mg kg^{-1} for Cd (metal/soil), respectively, which represented the medium contaminated level according to the classifications defined by Samsoee-Petersen et al. (2002) and Chinese Environmental Protection Agency (1995).

The metal-spiked soil samples were then subjected to two treatments of moisture regimes:

1. Non-waterlogging (80 % field capacity (FC)): incubated in a moisture regime of 80 % field capacity, the soil samples were weighted every day, and deionized water was added to keep the soil moisture constant.
2. Waterlogging: deionized water was added to the soil samples to form a 5-cm layer of water over the soil samples.

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 humidity (80 %). Each treatment was replicated in triplicate. At different incubation times, 1, 3, 7, 14 and 35 days, subsamples were taken from each beaker for the measurement of total content and speciation of heavy metals, pH, Eh, free Fe oxides and amorphous Fe oxides. Prior to sampling, each soil sample was mixed completely to ensure homogeneity and representativeness. Besides, a part of the subsample from each beaker was used to determine the moisture content in order to present the data on an oven-dry weight basis.

Sequential extraction procedure

The sequential extraction proposed by Tessier et al. (1979) was employed in the current study. Chemical reagents, extraction conditions and corresponding fractions are defined as follows:

1. Exchangeable fraction (EXC): 2 g of soil sample (oven-dry weight, 105 °C), 16 mL 1.0 mol L^{-1} $MgCl_2$, pH 7, shake 1 h, 20 °C.
2. Carbonate-bound fraction (CAR): 16 mL of pH 5, 1.0 mol L^{-1} sodium acetate, shake 5 h at 20 °C.
3. Fe-Mn oxide-bound fraction (OX): 40 mL of 0.04 mol L^{-1} $NH_4OH \cdot HCl$ in 25 % (v/v) acetic acid at pH 3 for 5 h at 96 °C with occasional agitation.
4. Organic matter-bound fraction (OM): 6 mL of 0.02 mol L^{-1} HNO_3 and 10 mL of 30 % H_2O_2 (pH adjusted to 2 with HNO_3), water bath, 85 °C for 5 h with occasional agitation. 10 mL of 3.2 mol L^{-1} NH_4OAc in 20 % (v/v) HNO_3, shake 30 min.
5. Residual fraction (RES): Dried in a forced-air oven at 40 °C, 24 h. Subsamples after sieving with 0.149 mm openings were used for determining Cu, Pb, Cd contents.

Extractions were conducted in 100 mL polypropylene centrifuge tubes. Between each successive extraction, the supernatant was centrifuged at 4,000 rpm for 30 min and then filtered.

Metal determination and quality control

Total and residual fraction of Cu, Pb and Cd in soil were determined by digesting 0.5 g soil samples (oven-dry weight, 105 °C) with $HNO_3 \cdot HF \cdot HClO_4$ mixture followed by elemental analysis. The concentrations of Cu, Pb and Cd in all solutions were analyzed by an atomic absorption spectrophotometer (AA220Z, Varian, USA). Nitrates of heavy metals were analytical grade. Digestion acids were guaranteed reagent. Ultrapure water was obtained from a Milli-Q system (Quantum EX, Millipore, USA). All containers were soaked in 10 % HCl, rinsed thoroughly in deionised water and dried out before use. 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 (REs) between the sum of the metal concentration in individual fractions and the measured total metal concentration in soil samples were calculated and ranged from −12.1 to 9.4 %, and the sums of extracted metal fractions over the experimental period were fairly constant (coefficients of variation, CV < 12.5 %). 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.

Statistical analysis

One-way analysis of variance (ANOVA) were performed at 5 % level to determine whether there were significant differences in changes of metal fractions and soil properties during incubation time between 80 % field capacity and waterlogging. Statistical analysis and model fit were performed using the software of SPSS 17.0 for windows.

Results and discussion

Distribution of background heavy metals in native soil

The fraction of each background metal in native purple soil is presented in Fig. 1. In the native soil, the dominating chemical form for Cu was the RES (68.57 % on an average, the same follows). Its association in the non-residual fraction was in the order: OM (14.63 %) > OX (8.17 %), > CAR (5.98 %) > EXC (2.65 %). Pb in native purple soil showed the order of association: RES (75.62 %) > OX (11.65 %) > OM (5.62 %) and CAR (5.57 %) > EXC (1.54 %). The Cd association with different fractions in native purple soil followed the order: RES (59.35 %) > OX (13.62 %) > CAR (10.68 %) > OM (7.76 %) > EXC (8.59 %). The high percentage of heavy metals in the residual fraction in unpolluted soils has been observed by many studies (Kashem et al. 2007; Jalali and Khanlari 2008). Exchangeable fractions accounted for a very low percentage of Cu and Pb which were in agreement with the previous studies of Ma and Rao (1997) and Ramos et al. (1994). In the non-residual fractions the relative high percentage of Cd was associated with the exchangeable fraction, which is in agreement with the findings (Kim and Owens 2009; Tang et al. 2006) that Cd usually was present more labile in soils.

Transformation of spiked metals in purple soil

Figure 2 shows the time-dependent fraction transformations of Cu, Pb, and Cd in purple soil incubated from 1 to 35 days. There were some clear and major differences between the distributions of indigenous and spiked metals in purple soil. In the case of indigenous metals, the proportions present as EXC fractions were very low for all

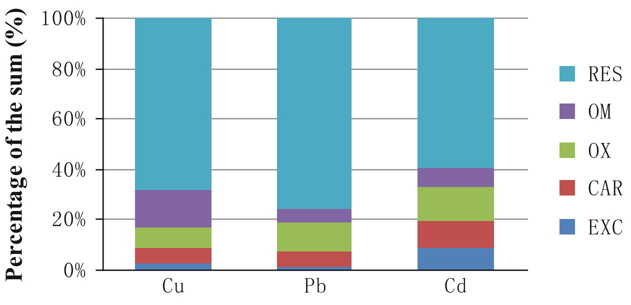


Fig. 1 Fractionation of background heavy metals in native purple soil

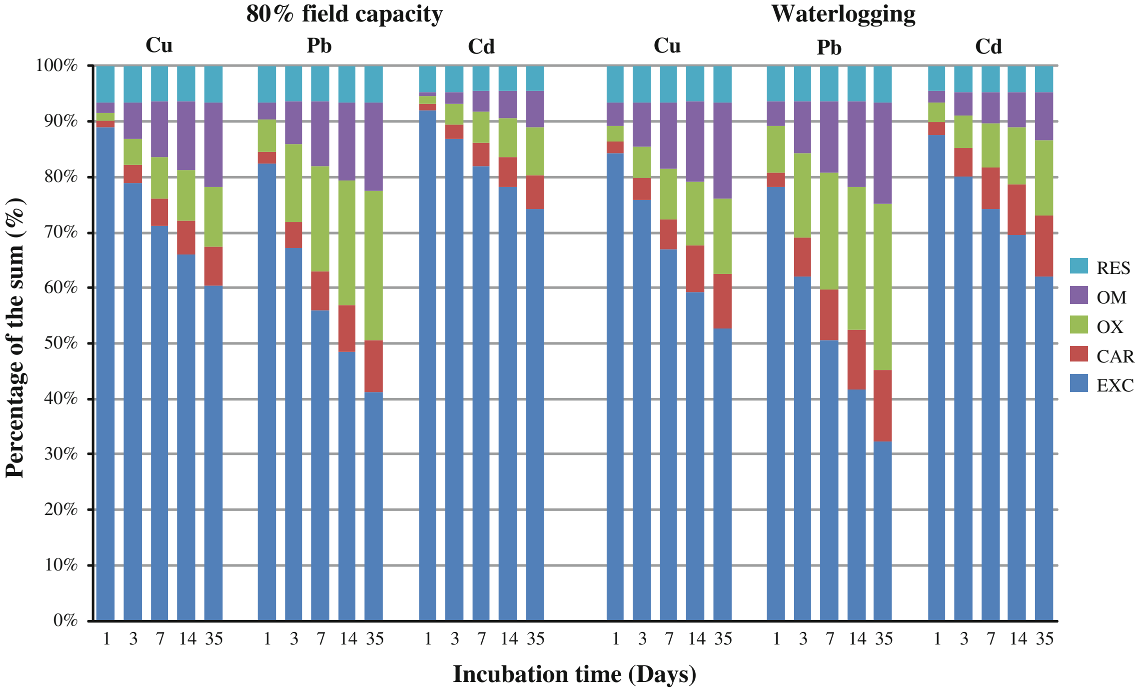


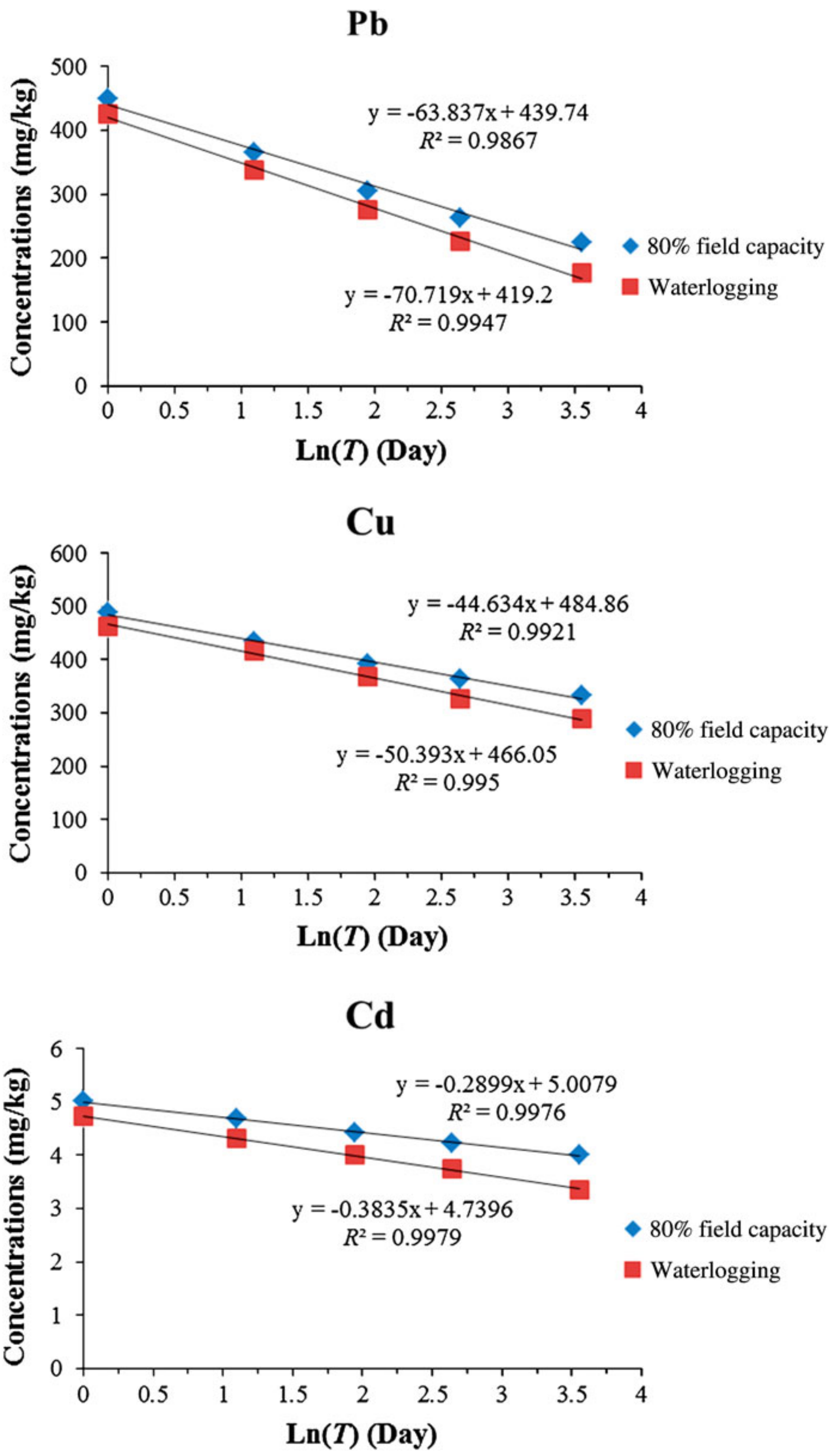
Fig. 2 Fractionation of spiked metals in purple soil as a function of incubation time

moisture regimes in purple soil, with the bulk of the metals distributed between RES, OX, CAR and OM fractions. As for spiked metals, it was supposed that at the time zero of the incubation period, almost all the newly added heavy metals existed either in the soil solution or in the surface of soil particles (e.g. EXC fraction). When the incubation time was prolonged, the EXC fractions of heavy metals decreased significantly and consistently in purple soil under all treatments. By the time of first sampling (1st day), the proportions of the EXC fractions at 80 % field capacity regime were 89.03 % for Cu, 82.37 % for Pb and 92.02 % for Cd, while those at waterlogging regime were 84.28 % for Cu, 78.09 % for Pb and 87.48 % for Cd. From 1 to 35 days of incubation, the proportions of exchangeable Cu, Pb and Cd at 80 % field capacity regime in purple soil decreased by more than 27, 40 and 17 %, respectively, while those at waterlogging regime decreased by more than 32, 46 and 26 %, respectively. The decreases of exchangeable heavy metals were particularly noticeable in waterlogged purple soil ($p < 0.05$). After 35-day incubation, the exchangeable fractions of heavy metals in purple soil decreased to the relatively lower degrees, where were 60.48 % for Cu, 41.31 % for Pb and 74.11 % for Cd at 80 % field capacity regime, and 52.70 % for Cu, 32.39 % for Pb and 61.94 % for Cd at waterlogging regime.

The proportions of spiked metals bound to carbonate and Fe-Mn oxides increased consistently with increasing incubation time, especially in waterlogged soil. After 35-day of incubation, the proportions of Cu, Pb and Cd in the CAR fractions accounted for 7.04, 9.26 and 6.08 %, respectively, at 80 % field capacity regime, whereas those were 9.72, 12.82 and 11.23 %, respectively, at waterlogging regime; oxide-bound fractions of the heavy metals occupied 10.71 % of the spiked Cu, 26.90 % of the spiked Pb, 8.72 % of the spiked Cd at 80 % field capacity regime, while those were 13.70 % for Cu, 29.83 % for Pb and 13.44 % for Cd at waterlogging regime. The change patterns of the organic matter-bound fractions of spiked metals were similar to those of the carbonate and oxide-bound fractions in treated purple soil. Up to 35 days of incubation, the proportions of metals bound to organic matter reached 15.20 % for Cu, 15.99 % for Pb and 6.52 % for Cd at 80 % field capacity regime, whereas those were 17.40 % for Cu, 18.40 % for Pb and 8.58 % for Cd at waterlogging regime. The proportions of the metal residual fractions in spiked-soil accounted for on an average 6.56 % for Cu, 6.39 % for Pb and 4.43 % for Cd in treated purple soils. Statistical analyses confirmed that the concentration of the residual fraction of each metal in spiked-soil under all treatments was consistent to that in native soil, and remained almost unchanged during the whole incubation period ($p < 0.05$).

The above results indicated that, through the incubation period, spiked heavy metals transformed slowly from the EXC fraction into the CAR, OX and OM fractions. Accordingly, the metals added in soluble form were gradually transferred from the more labile fractions into the more stable fractions. These metals might be retained by

Fig. 3 Decrease of Cu, Pb, and Cd in EXC fraction as a function of the natural logarithm of incubation time



soil components in the near surface soil horizons or could precipitate and/or co-precipitate as sulfides, carbonates, oxides or hydroxides. No significant differences in the metal concentrations of the RES fraction were observed in soil samples, which meant the added metals hardly entered the crystalline lattice over 35-day incubation. On the other hand, there were clear differences in the rates of the proportional distribution of Cu, Pb, and Cd in purple soil treated with two moisture regimes during the 35 days of incubation with spiked heavy metals, at which

Table 1 Soil properties under two moisture regimes after 35-day incubation (means of triplicate)

Moisture regimes	pH	Eh (mV)	Free Fe oxides (g kg^{-1})	Amorphous Fe oxides (g kg^{-1})
80 % field capacity	6.43 b*	250 a	23.89 a	2.39 b
Waterlogging	6.90 a	−190 b	22.21 a	7.21 a

* Comparison between means was made with the one-way ANOVA test. *Different letters* in a same column indicated a significant difference between moisture regimes at $p < 0.05$

redistribution took place with the changes occurring generally faster in the waterlogged soil as compared to the other soil treated with 80 % field capacity regime.

Transformation rate of spiked metals in purple soil

The exchangeable form is considered readily mobile and easily bioavailable, and thus it deserves a serious concern. As mentioned above, it was clear that the exchangeable metal concentrations decreased consistently with incubation time. By plotting the metal concentration in EXC fraction against the natural logarithm of incubation time, a linear regression equation could be simulated as follows:

$$C_m = A + BLn(T) \quad (1)$$

where C_m is the metal concentration (mg kg^{-1}) in the EXC fraction, A and B are constants relate to the properties of soil and heavy metals, and T is incubation time (Day). As illustrated in Fig. 3, the coefficients of determination (R^2) from 0.9867 to 0.9979 ($n = 5$, $p < 0.05$), which manifested the linear fits were satisfactory.

The Eq. 1 fitted well to experimental data demonstrated that the overall decrease rate of the exchangeable metal can be simulated by the Elovich kinetic model. The constant A reflected the concentration of exchangeable metal fraction in day 1 after exogenous metal spiked in soil. The constant B in Elovich equation reflected the transformation rate of metal speciation from the exchangeable fraction toward stable fractions, which can be used as an index of transformation rates. By judging this parameter for three elements under two moisture regimes, the following order was founded: Pb > Cu > Cd, which coincided with the result by Lu et al. (2005) that the decrease in transformation rate followed the order Pb > Cu > Zn > Cd, indicating Cd's lability in the soil and the lack of strong binding mechanisms for this metal to the solid-phase of soil. Furthermore, it was also clearly that spiked metals under waterlogging regime had relatively higher transformation rates by contrast with 80 % field capacity regime, resulting in the more complete movement of these metals from the exchangeable fraction toward stable fractions (CAR, OX and OM) in waterlogged purple soil.

Effect of waterlogging on metal speciation

The effect of waterlogging on the redistribution of heavy metals in purple soil might be mainly related to the changes of pH, Eh and hydrous oxides in varying soil-water systems.

When oxidized purple soil samples were submerged, biological and microbiological activities combined with limited oxygen diffusion, which caused oxygen depletion and established reducing conditions, where an observable change, namely, a decrease of Eh associated with an increase of pH towards neutrality would follow (Chuan et al. 1996) (Table 1).

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; Zhang et al. 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. By monitoring the process of heavy metals on iron oxide (α-FeOOH), Martínez and Mcbride (2001) found that either adsorption or co-precipitation of heavy metals with ferrihydrite was pH-dependent. They also found that the increasing pH and incubation time resulted in the increase of adsorption and co-precipitation of heavy metals. On the other hand, increased concentrations of OM-bound Cu, Pb, and Cd fractions in the waterlogged 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). Particularly, metal bound to carbonate in soil is more susceptible to pH increase (Martínez and Motto 2000), which could explain the metal concentrations of CAR fractions increased under waterlogging treatment. These pH-dependent mechanisms might have taken place in the waterlogged soil to immobilize heavy metals in the study.

Waterlogging also affected the crystallization of Fe oxides in the soils (Table 1). After 35-day incubation, concentration of amorphous Fe oxides in waterlogged soil increased by three times than that at 80 % field capacity moisture regime, while the concentrations of free Fe oxides did not differ significantly between two soil moisture regimes. In waterlogged soil, reducing conditions would cause the oxides of Fe and Mn in soil solid phases to be reduced and dissolved. Reduced Fe and Mn via hydrolysis and oxidation precipitate as highly as amorphous hydrous oxides that have a strong sorption capacity for trace elements. The X-ray amorphous hydrated oxides and oxides with a low crystallinity showed a larger adsorption capability for heavy metal cations than those with a high crystallinity (Okazaki et al. 1986). As a result, this process decreased concentrations of Cu, Pb and Cd in the EXC fractions, and increased their OX fractions in the waterlogged soil correspondingly (Fig. 2). 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. They (Kashem and Singh 2001) suggested that adsorption of trace metals on Fe-Mn oxyhydroxide fractions was the major mechanism of their solubility reduction in submerged conditions. Furthermore, microbial immobilizations and antagonistic and/or competitive effects of increased concentrations of Fe, Mn and P have also been suggested as possible reasons for the decreased exchangeable metals in waterlogged soils (Haldar and Mandal 1979; Nwuche and Ugoji 2008).

The OM fractions of Cu, Pb and Cd in waterlogged soil increased significantly (Fig. 2), perhaps due to the metal-organic complex formation. As known, metals are more tightly bound by organics under anoxic conditions, compared with oxic conditions where degraded sediment material has a tendency to decrease and the humic materials may become structurally less complex (Gambrell 1994).

In addition, 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, 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 (Van den Berg et al. 1998).

Conclusion

Heavy metals Cu, Pb, and Cd added to a Chinese purple soil in soluble form at 80 % field capacity and waterlogging regimes were transformed slowly from the exchangeable fractions into more stable fractions, whereas their residual fractions barely changed. Metals in exchangeable fraction decreased with time and such decreases could be simulated by an Elovich kinetic equation. Besides, the transformations of Cu, Pb and Cd from the EXC fraction into other fractions during the incubation period was relatively easier in the waterlogged purple soil as compared with 80 % field capacity regime, resulting in the more complete movement of these metals toward stable fractions.

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