Effects of rice straw on the speciation of cadmium (Cd) and copper (Cu) in soils

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ABSTRACT

Four soils were collected from different sites of China in Lechang (LC, Guangdong province), Changsha (CS, Hunan province), Jiaxing (JX, Zhejiang province) and Hangzhou (HZ, Zhejiang province), and were spiked with Cu (50 mg kg⁻¹) and Cd (5 mg kg⁻¹). The effects of rice straw addition (6%) on the chemical distribution of both metal ions were studied by measuring the soluble metal ion concentrations and the free metal ion concentrations (using the Donnan membrane technique) after 1-, 3- and 6-month incubation. Results show that the addition of rice straw increased soil pH by about 0.4 pH unit on average, and increased DOC significantly in soil LC, CS and JX, but not in soil HZ. With the addition of rice straw, total soluble Cu concentration increased from 0.82 μmol l⁻¹ (0.26–2.4 μmol l⁻¹) to 1.22 μmol l⁻¹ (0.70–3.60 μmol l⁻¹), whereas total soluble Cd concentration decreased from 20 nmol l⁻¹ (2–70 nmol l⁻¹) to 15 nmol l⁻¹ (2–56 nmol l⁻¹). When rice straw was added, both free Cu²⁺ and Cd²⁺ concentrations decreased, for free Cu²⁺ concentration from 217 nmol l⁻¹ (31 to 369 nmol l⁻¹) to 124 nmol l⁻¹ (22 to 263 nmol l⁻¹) and for free Cd²⁺ concentration from 16 nmol l⁻¹ (1–55 nmol l⁻¹) to 12 nmol l⁻¹ (1–43 nmol l⁻¹). With the increase of incubation time, free Cu²⁺ concentration tended to increase but free Cd²⁺ concentration decreased. Speciation model calculations show that compared to the binding capacity of soil organic matter, the capacity of rice straw is much less important. The decrease of free metal ion concentration upon rice straw addition can be attributed mainly to the increased pH. The higher DOC content in the rice straw treatment could be the reason for higher soluble Cu concentration when rice straw was added. Adsorption to DOC is much less important for Cd than for Cu. Calculation also shows that adsorption to clay minerals plays a more important role for Cd than for Cu, which may explain the stronger ageing effects on Cd distribution.

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1. Introduction

Heavy metal pollution in agricultural area can lead to toxic metal level in crops. Cadmium (Cd) and copper (Cu) are two of the most common heavy metals in the environment. Cd is not an essential element in metabolic processes in almost all plants and animals, including human, and it can accumulate to levels that are toxic or lethal to organisms. Cu is an essential micronutrient for plants and animals, but it can also accumulate to toxic concentrations in the environment (Oliver, 1997). Therefore, it is important to predict the risk of soil Cd and Cu to human and ecological receptors. In this process, bioavailability is increasingly being used as a key indicator of potential risks that Cd and Cu pose to both environmental and human health (Adriano et al., 2004; Basta et al., 2005).

Agricultural wastes or by-products have been investigated of their uses as sorbent materials for heavy metals due to the tendency of heavy metals to form stable complexes with organic ligands (Marshall and Champagne, 1995; Almas et al., 2000; Ho, 2003; Shen and

Duvnjak, 2005). In fact, plant materials are annually applied to soil in order to improve soil chemical and physical properties. Contradictory results were found about the effect of organic matter on bioavailability and mobility of heavy metals in soils. Almas et al. (1999) found that Cd in the mobile fractions decreased significantly in the soil treated with organic matter. Strobel et al. (2005) found that dissolved organic carbon (DOC) had no effect on the amount of soluble Cu and Cd in soil with DOC addition. Sauvé et al. (1998) applied leaf compost to a Pb-contaminated soil and found that the solubility of Pb decreased linearly from pH 3 to 6.5 and was independent of soil organic matter in this pH range. From pH 6.5 to 8, increasing pH promoted the formation and dissolution of organo-Pb complexes that increased Pb solubility. On one hand, added organic matter can immobilize the metals by forming solid organo-metal complexes (McBride et al., 1998). This process could reduce the solubility of some metals in soil. On the other hand, an increase in dissolved organic matter (DOM), can contribute to the enhancement of metal concentration in soil solution (Weng et al., 2001b; Strobel et al., 2005). Several investigations have revealed that the soluble organics are able to raise the trace metal carrying capacity of soil solution (McBride et al., 1998; Naidu and Harter, 1998; Sauvé et al., 1998).

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The solid–solution distribution of heavy metals determines the soluble metal ion concentration in soil solution, which is an important factor that controls the transport and mobility of heavy metals. For bioavailability and toxicity, free metal ion concentration is the key species. There are several approaches that have been widely used to determine the free metal ion concentration, such as ion selective electrode (ISE), anodic stripping voltammetry (ASV), competitive chelation method and cation exchange resin method (Winistorfer, 1995; Nordstrom, 1996; McBride et al., 1997; Weng et al., 2001a). Each method has its advantages and limitations. In recent years, Donnan membrane technique (DMT), based on the theory of Donnan membrane equilibrium, has been proposed by Salam and Helmke (1998), and further studied and improved by Temminghoff et al. (2000) and Weng et al. (2001a). DMT can measure free metal ion concentration at a wide range of concentrations without perturbing the substrate solution equilibrium, and different cations in each sample can be measured simultaneously.

The objective of this study was to examine the effect of addition of rice straw on the solid–solution distribution and free Cu^{2+} and Cd^{2+} concentrations in four soils collected from different parts of China spiked with Cu and Cd and incubated for a period up to 6 months.

2. Materials and methods

2.1. Soil preparation

The top 20 cm of four uncontaminated soils were collected from sites throughout China in Lechang (LC, Guangdong province), Changsha (CS, Hunan province), Jiaxing (JX, Zhejiang province) and Hangzhou (HZ, Zhejiang province). The soils were air-dried, ground, and passed through a 2-mm mesh sieve. Five mg kg^{-1} Cd (as $\text{Cd}(\text{NO}_3)_2$) and 50 mg kg^{-1} Cu (as $\text{Cu}(\text{NO}_3)_2$) were added in each soil sample (4800 g) respectively. The soil samples were mixed thoroughly, air-dried and homogenized. Each soil sample was then divided into two parts. Into one part (2400 g), 144 g rice straw (<2 mm) was added to artificially increase the organic matter by about 6% and the samples were mixed thoroughly. These treatments are referred as LC6, CS6, JX6 and HZ6. Another part of the soil samples was set as controls (LC0, CS0, JX0, and HZ0). All the samples were air-dried and homogenized again by sieving. Subsamples of 200 g were weighed into plastic cups. Double distilled water was added to the cups to adjust the soil moisture to 15% (w/w) every week. All soils were stored in the dark at 25 °C. At different time intervals (1, 3, and 6 months after the addition of Cd, Cu and rice straw), the soil samples were collected, air-dried, ground and passed through a 2-mm mesh sieve. There were 24 treatments all together in this experiment, and four replicates for each treatment. Two replicates were selected to do soil column experiment (Donnan membrane method).

2.2. Characterization of soils

Particle size composition of the <0.25-mm soil fraction was analyzed with a laser particle size analyzer (Mastersizer 2000,

Malvern Co., UK). Soil pH was measured at a 1:2.5 ratio of soil to 0.01 M CaCl_2 after 1 h of end-to-end shaking. The content of soil organic matter was determined using the acid dichromate oxidation method described by Bao (2000). Cation exchange capacity (CEC) of soil was determined by NH_4^+ retention after percolation with a solution of 1 M NH_4OAc (pH 7.0) (Bao, 2000). The background concentrations of Cd and Cu in soil were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Optima-2000, Perkin-Elmer Co. Lt., USA) or inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500i USA) after being digested with aqua regia (HNO_3 : HCl =1:3 in volume) and HClO_4 (1:1 in volume). Some basic characteristics of the soils including the background Cd and Cu concentrations are shown in Table 1.

2.3. Soil column experiment

Free metal ion concentrations were measured with the Donnan membrane method coupled with soil columns. Temminghoff et al. (2000) and Weng et al. (2001a) have described the Donnan membrane method. A little modification of the method was used in this experiment. Fifty-gram air-dried soil sample was used to prepare the soil column. Two hundred ml of 0.002 M $\text{Ca}(\text{NO}_3)_2$ solution was used as the salt solution that was circulated through the soil column (donor solution) and 18 ml 0.002 M $\text{Ca}(\text{NO}_3)_2$ was circulated in the other side of the Donnan membrane cell (acceptor solution). The column percolation speed was 2 ml per minute. After 48 h, the donor and acceptor solutions were sampled. pH was measured with a pH meter in all the samples. The donor solution was filtered over a 0.45- μm nitrate-cellulose membrane filter. The concentrations of Cd and Cu in donor and acceptor solutions were determined by ICP-OES or ICP-MS. The concentrations of Ca, Mg, K and Na in donor and acceptor solutions were determined by ICP-OES. DOC was measured with TOC Analyzer (Phoenix 8000, Tekmar-Dohrmann USA). Total Cu and Cd concentration measured in the donor solution represents the soluble metal concentration.

2.4. Modeling metal speciation

Speciation of Cu and Cd was calculated with adsorption models for the soil solution and for the whole soil. The solution speciation of Cu and Cd is calculated by considering solution inorganic complexes and ion adsorption to dissolved organic matter (DOM), in which the metal ion adsorption to DOM is simulated with the NICA-Donnan model (Kinniburgh et al., 1999) using the generic model parameters published (Milne et al., 2001, 2003). The DOM concentration was calculated as two times of that of dissolved organic carbon (DOC), because humic and fulvic acids contain on average about 50% carbon. The model calculation was carried out with the assumption that 30% of DOM has the same properties in terms of ion adsorption as generic fulvic acids, and the rest 70% DOM is inert. The measured data of pH, DOC, total soluble concentrations of Cu and Cd were used as the input data.

The speciation of Cu and Cd in the whole soil was calculated by considering Cu and Cd adsorption to the soil organic matter (SOM), a

Table 1
Basic characteristics of the soils

Soil		LC	HZ	CS	JX
		Alluvic primosols	Udic cambosols	Udic ferrosols	Udic cambosols
pH		7.44	5.96	5.38	5.90
OM (g kg^{-1})		25.06	16.13	15.51	28.73
CEC (cmol kg^{-1})		12.41	14.54	10.79	7.45
Particle size composition (%)	Clay	14.34	15.26	21.52	22.86
	Silt	67.15	61.87	73.14	63.07
	Sand	18.51	22.87	5.34	14.07
Total Cd (mg kg^{-1})		0.26	0.39	0.19	0.22
Total Cu (mg kg^{-1})		16.05	36.98	19.81	29.84

Table 2
Soil pH (donor) changes over time with or without the addition of rice straw

Soil	1-month	3-month	6-month
LC0	7.09±0.01a	7.21±0.03a	6.81±0.04b
LC6	7.42±0.05b	7.64±0.02a	7.48±0.02ab
HZ0	5.93±0.15a	4.62±0.05b	5.09±0.17ab
HZ6	5.88±0.17a	4.85±0.05b	5.19±0.09ab
CS0	6.10±0.07a	5.65±0.01a	6.00±0.01a
CS6	6.60±0.01a	6.51±0.14a	6.61±0.11a
JX0	5.35±0.06b	5.86±0.12ab	5.93±0.06a
JX6	6.09±0.09a	6.15±0.00a	6.30±0.14a

Data were presented as mean±standard error.

Values followed by the same letter indicate no difference in rows.

clay type ion exchanger, rice straw (for rice straw treatment) and DOM. Adsorption to DOM was simulated in the same way as discussed above. Adsorption to SOM was calculated using also the NICA-Donnan model (Kinniburgh et al., 1999) with the generic model parameters published (Milne et al., 2001, 2003) with the assumption that 50% of SOM has the same properties in terms of ion adsorption as generic humic acids, and the rest 50% SOM is inert. Ion adsorption to clay mineral was calculated by including an ion exchange solid phase with no preferences for different cations. The CEC of the exchanger is calculated by subtracting the charge of SOM (calculated with the NICA-Donnan model) from the measured CEC (Table 1), which results in a site density of 0.61, 0.82, 0.42 and 0.17 mol kg⁻¹ clay for samples from respectively LC, HZ, CS and JX. Adsorption of Cu to rice straw was considered in the calculation using Langmuir model. The model parameters were taken from the study of Marshall et al. (1993). The maximum binding capacity is 0.19 mol Cu/kg rice straw and the affinity constant is 5.85×10⁴ l mol⁻¹. We didn't find similar parameters for Cd. As will be discussed below, the calculation shows that binding capacity of rice straw is much lower than that of SOM. Therefore we expect no big influence on the Cd speciation calculated by omitting binding to rice straw. The measured data of pH, SOM, DOC,

CEC were used as the input data. Total Cu and Cd content were calculated as the sum of the original metal content (Table 1) and metal spiked.

Calculations for both the soil solution and whole soil were carried out using the speciation program ECOSAT (Keizer and Van Riemsdijk, 1994). The electrolyte background is 0.002 M Ca(NO₃)₂, as used in the soil column experiment. Activity of Al³⁺ and Fe³⁺ was controlled by the solubility of gibbsite (logK_{so}=−34.0) and amorphous iron oxides (logK_{so}=−38.5). The competition of Ca, Al and Fe for adsorption to SOM, DOM and ion exchanger (clay) was taken into account.

2.5. Statistical analysis

Statistical analysis was carried out using SPSS11.5 for Windows. All data were subjected to ANOVA and subsequently to Duncan's multiple range tests.

3. Results

3.1. pH and DOC

Soil pH as measured in the donor solution ranged from 4.6 (soil HZ) to 7.6 (soil LC) (Table 2). The addition of rice straw increased soil pH by about 0.4 pH unit on average. But in soil HZ, the increase of pH on rice straw addition is smaller than in the other soils. No regular change of pH over 1-, 3- and 6-month incubation time was observed. The addition of rice straw led to higher dissolved organic carbon content in soil solution. The DOC increase is statistically significant in soil LC, CS and JX (*p*<0.01), but not in soil HZ. The soil DOC did not change significantly with the incubation time (Fig. 1).

3.2. Free Cu²⁺ and Cd²⁺ concentrations

When no rice straw was added, the free Cu²⁺ concentration ranged from 31 to 369 nmol l⁻¹ (Table 3) and the free Cd²⁺ concentration

Fig. 1. Soil DOC concentration change overtime with or without the addition of rice straw. A, LC; B, HZ; C, CS; D, JX. (Filled symbols: with rice straw. Empty symbols: no rice straw.)

Table 3Free Cu²⁺ concentration in soils over time with or without the addition of rice straw ($\mu\text{mol l}^{-1}$)

Soil	1-month	3-month	6-month
LC0*	0.050±0.009b	0.236±0.047ab	0.275±0.062a
LC6**	0.030±0.001b	0.127±0.064a	0.250±0.067a
HZ0	0.312±0.077a	0.336±0.036a	0.369±0.059a
HZ6	0.189±0.067a	0.262±0.001a	0.263±0.013a
CS0	0.179±0.048a	0.233±0.081a	0.179±0.069a
CS6	0.048±0.011a	0.055±0.045a	0.069±0.050a
JX0	0.031±0.012b	0.150±0.040b	0.252±0.086a
JX6	0.022±0.008b	0.137±0.016a	0.040±0.015b

Data were presented as mean±standard error.

Values followed by the same letter indicate no difference in rows.

ranged from 1 to 55 nmol l^{-1} (Table 4). The highest free Cu²⁺ and Cd²⁺ concentration was observed in the soil sample collected from HZ, which has the lowest pH value among soils studied (Table 2). When rice straw was added, the concentration of free Cu²⁺ ranged from 22 to 263 nmol l^{-1} (Table 3) and the concentration of free Cd²⁺ ranged from 1 to 43 nmol l^{-1} (Table 4). The free Cu²⁺ concentration was decreased by rice straw and the reduction is maximum 5 times. The concentration of free Cd²⁺ was also reduced by rice straw addition, except in soil LC. With the incubation time, free Cu²⁺ concentration showed an increasing trend and free Cd²⁺ a decreasing one (Tables 3 and 4). But the change with time for both metals is not always consistent.

3.3. Soluble Cu and Cd concentrations

When no rice straw was added, the concentration of soluble Cu ranged from 0.26 to 2.4 $\mu\text{mol l}^{-1}$ (Table 5) and the concentration of soluble Cd ranged from 2 to 70 nmol l^{-1} (Table 6). Generally speaking, the level of soluble Cu and Cd in the four soils follows the order of HZ>JX>CS>LC, which is in accordance with the order of soil pH (Table 2). At lower pH, soluble Cu and Cd concentration is higher, due to probably less adsorption to soil components.

When rice straw was added, the concentration of soluble Cu ranged from 0.70 to 3.60 $\mu\text{mol l}^{-1}$ (Table 5) and the concentration of soluble Cd ranged from 2 to 56 nmol l^{-1} (Table 6). The incorporation of rice straw led to up to 3 times increase of soluble Cu concentration. In contrast, concentration of soluble Cd decreased upon rice straw addition in all soils except soil LC, which is characterized by a neutral pH whereas the pH in other soils is in acidic range (Table 2).

4. Discussion

4.1. Soil pH

The cause of increasing pH in the rice straw treatment is not clear. Possible explanation can be attributed to the denitrification or/and

Table 4Free Cd²⁺ concentration in soils over time with or without the addition of rice straw ($\mu\text{mol l}^{-1}$)

Soil	1-month	3-month	6-month
LC0	0.003±0.001a	0.001±0.000b	0.001±0.000b
LC6	0.004±0.001a	0.001±0.000b	0.002±0.001b
HZ0	0.055±0.019a	0.049±0.001a	0.038±0.003a
HZ6	0.043±0.008a	0.038±0.001a	0.027±0.003b
CS0	0.004±0.001a	0.002±0.000b	0.001±0.000b
CS6	0.002±0.001a	0.001±0.000a	0.001±0.000a
JX0	0.011±0.000b	0.016±0.001a	0.013±0.001ab
JX6	0.011±0.000a	0.007±0.000b	0.006±0.001b

Data were presented as mean±standard error.

Values followed by the same letter indicate no difference in rows.

Table 5Dissolved Cu concentration in soils over time with or without the addition of rice straw ($\mu\text{mol l}^{-1}$)

Soil	1-month	3-month	6-month
LC0	0.378±0.006b	0.500±0.028a	0.541±0.019a
LC6	0.696±0.050c	0.874±0.006b	1.080±0.014a
HZ0	1.109±0.088a	1.111±0.028a	1.210±0.101a
HZ6	1.394±0.019a	1.154±0.017a	1.211±0.110a
CS0	0.645±0.037a	0.315±0.021b	0.264±0.010b
CS6	0.995±0.054a	0.731±0.012b	0.953±0.027a
JX0	2.372±0.026a	0.620±0.016c	0.785±0.049b
JX6	3.570±0.033a	0.962±0.045b	1.045±0.031b

Data were presented as mean±standard error.

Values followed by the same letter indicate no difference in rows.

dissolution of iron hydroxides as a result of reduction that is coupled with oxidation of rice straw. Both organic matter degradation and increased pH can lead to higher DOC concentrations in the rice straw treatments. Major component of rice straw is (semi)cellulose. Degradation of rice cellulose releases various organic acids (Motellier and Charles, 1998; Motellier et al., 1998). Increase of pH promotes the dissolution and desorption of organic matter and therefore results in higher DOC concentration (Weng et al., 2002a,b; Dijkstra et al., 2004; DeWit et al., 2007).

4.2. Speciation in soil solution

Metal ions in the solution phase can be in the form of free ion, complex with inorganic ligands (Cl^- , OH^- , CO_3^{2-}) and organic ligands (dissolved organic matter). The free Cu²⁺ and Cd²⁺ accounts for 0.6–74% and 26%–100% of total soluble Cu and Cd in the soil solution, respectively (Fig. 2). The percentages of free Cd²⁺ and Cu²⁺ concentrations in soil solution were estimated in some other studies. Free Cd²⁺ concentration ranged from 0% to 60% with an average of about 20%, and free Cu²⁺ concentration ranged from 0% to 29% (Sauvé and Novell, 2000; Ma et al., 2006). In Fig. 2, the fractions of free metal ions to that of the total soluble concentration are plotted against the soil solution pH. Both for Cu and for Cd, the fraction of free metal ion in the soil solution decreases with increasing pH. However, the pH shows a much clear effect on the Cd speciation in soil solution than on Cu speciation. The figure shows that, at the same pH, the free Cu fraction is in general lower in the treatment with rice straw than in those without rice straw. This could be due to the increasing DOC in the treatment with rice straw, which increased the amount of Cu adsorbed to DOM. This figure illustrates the bigger importance of DOM complexation for Cu speciation in soil solution than for Cd.

By assuming 30% of DOM has the same binding properties of fulvic acids, the speciation of Cu and Cd in the soil solution was calculated. In Fig. 3, the model calculated fractions of free metal ions in soil solution are compared to those measured. For Cu, no good agreement is found between the prediction and measurement, whereas the agreement is

Table 6Dissolved Cd concentration in soils over time with or without the addition of rice straw ($\mu\text{mol l}^{-1}$)

Soil	1-month	3-month	6-month
LC0	0.008±0.001a	0.002±0.000b	0.003±0.000b
LC6	0.008±0.004a	0.002±0.000a	0.004±0.000a
HZ0	0.070±0.005a	0.049±0.001b	0.045±0.000b
HZ6	0.056±0.005a	0.033±0.001b	0.039±0.002b
CS0	0.006±0.001a	0.003±0.000b	0.004±0.001ab
CS6	0.004±0.001a	0.002±0.000a	0.002±0.001a
JX0	0.017±0.000a	0.017±0.000a	0.016±0.001a
JX6	0.012±0.000a	0.009±0.000a	0.012±0.003a

Data were presented as mean±standard error.

Values followed by the same letter indicate no difference in rows.

Fig. 2. Percentage of free metal ion to the total soluble metal concentration in soil solution. (Filled symbols: with rice straw. Empty symbols: no rice straw.)

better for Cd. It has been found that most of DOM in soil solution is humic substance and the fraction of humic and fulvic acids in DOM varies in soil samples. However, from this modeling exercise, it shows that in these samples the reactivity of the DOM for ion binding is relatively low. By assuming a higher percentage of fulvic acids in the DOM leads to overestimation of ion complexation to DOM (results not shown). This 30% fraction of fulvic acids is relatively lower than found in other studies. For example, Weng et al. (2002b) have assumed that 60% of DOM is humics.

The soil solution speciation calculations suggests that most of the complexed Cu and Cd in the soil solution is organic complex with DOM. Inorganic Cu and Cd complexes in soil solution take up a very small fraction. Cu and Pb have higher affinity for DOM and therefore a very small fraction of these metals exists as free hydrated metal ions in soil solution (Aualiitia and Pickering, 1986; Sauvé et al., 1998; Weng et al., 2001b). On the other hand, metals such as Cd, Ni and Zn are less prone to form such stable metal–organic complexes (Aualiitia and Pickering, 1986; Pinheiro et al., 1994; Holm et al., 1995). Thus, a larger fraction of these metals is recovered as free hydrated metal ions. Nevertheless, the association of Cd, Ni and Zn with DOM in soil solution is not insignificant and should not be overlooked (Neal and Sposito, 1986; del Castillo et al., 1993; Naidu and Harter, 1998; Weng et al., 2001b).

4.3. Speciation in whole soil

The solid–solution distribution of Cu and Cd was calculated using speciation models considering adsorption to the soil solid particles: SOM, clay and rice straw (for Cu only) and adsorption to suspended particles: DOM. Because the calculation uses default model para-

meters, it is a pure prediction. In Fig. 4, the model predicted Cu and Cd concentration in the soil solution was compared to that measured. The magnitude of Cu concentration in soil solution is predicted reasonably. The deviation between the prediction and measurements is mostly within 0.5 log unit. However, the model predicted Cd concentration in soil solution is on average about 1.5 log unit higher than measured. It is not clear to us what has caused this big discrepancy for Cd. Formation of Cd sulfide precipitation seems unlikely because sulfide is formed under very strong reduced conditions. From the 15% (w/w) water content in the soil samples it can be estimated that less than 50% of soil pores is filled with water, which means that the soil is not water saturated. In addition, if higher concentration of sulfide would be present, Cu concentration in the soil solution would be much lower, because the solubility of Cu sulfides is lower than Cd sulfides. Another possible explanation of the model overestimation of Cd concentration can be due to a stronger binding capacity of the SOM or clay mineral in the soil samples than the model predicted.

The model calculations can also estimate the relative importance of various soil particles in the adsorption of Cu and Cd. Fig. 5 shows the distribution of Cu and Cd over various solid phases considered in the model. The results in this figure are based on the speciation model calculations and are the average of all measurements for each soil without or with rice straw addition respectively. The calculation shows that soil organic matter is far more important in the adsorption of both Cu and Cd than clay minerals. The importance of soil organic matter in the adsorption of heavy metals has been realized by many researchers (Yin et al., 2002; Wong et al., 2007). Based on the calculation, Cu and Cd adsorbed to SOM account respectively for 91–100% and 57–97% of total metal adsorbed in the solid phase. Less than 1% Cu is adsorbed to the clay minerals. Adsorption to clay is more

Fig. 3. Comparison between model predicted and measured fraction of free metal ion in soil solution. (Filled symbols: with rice straw. Empty symbols: no rice straw. The line is 1:1 line.)

Fig. 4. Comparison between model predicted and measured Cu and Cd in soil solution. (Filled symbols: with rice straw. Empty symbols: no rice straw. The line is 1:1 line.)

important for Cd than for Cu. Up to 43% of Cd is predicted to be associated with clay minerals. The most significant Cd adsorption to clay is predicted for soil HZ, which has a relatively low pH and low SOM content (Tables 1 and 2). Because the model ignores the specific adsorption to clay and only considers ion exchange, it is possible that adsorption of Cu and Cd to clay is underestimated to a certain extent by the model. Compared to SOM, the binding capacity of rice straw for Cu is much weaker. Model calculations show that only in soil HZ, a substantial amount (8%) of Cu is adsorbed to rice straw. In the other soils, rice straw adsorbed Cu accounts for less than 1% of Cu adsorption. The capacity of metal ion adsorption of fresh organic matter is in general less than the humified soil organic matter. In addition, it has been shown that rice straw has lower adsorption capacity than some other plant materials (Marshall and Champagne, 1995).

In this study, it is found that the addition of rice straw decreased the concentrations of free Cu^{2+} and Cd^{2+} (Table 3). This can be attributed to the adsorption capacity of rice straw added and the pH increase in treatments with the rice straw. The very small contribution of rice straw to Cu adsorption predicted by the model suggests that the pH increase (Table 2) is probably the main reason for the decreased free Cu^{2+} and Cd^{2+} concentration in the treatment with rice straw. Amendment of soils with organic matter and subsequent decomposition of organic matter may change the soil pH and thereby indirectly affect the distribution and bioavailability of metals. Studies have shown that addition of peat to pig manure increased soluble metal concentration due to decrease in soil pH (Yuan and Lavkulich, 1997; Arnesen and Singh, 1998; Almas et al., 2000). On the contrary, alkaline organic amendments may reduce the concentration of metal ions in soil solution by raising soil pH, thereby allowing formation of insoluble metal precipitates, complexes, and secondary minerals (Knox et al., 2001; Basta et al., 2005).

As a general trend, the addition of rice straw led to an increase in total soluble Cu concentration, but a slight decrease in total soluble Cd concentration (Tables 5 and 6). The result is contradictory to the finding that Cd was increased significantly in the mobile fractions in the soil with the addition of organic matter (Almas et al., 1999). The total soluble concentration of metal ions in soil solutions depends on the free metal ion concentration, the presence of inorganic and organic ligands and pH. Because of the higher affinity of organic matter to Cu, the changes in DOC will influence Cu concentration in solution more strongly than total soluble concentration of Cd. The increase in the solubility of Cu can be attributed to the increase in DOC upon rice straw addition (Fig. 1). The increased amount of Cu adsorbed to DOC in the rice straw treatments exceeded the effects of decreased free Cu^{2+} concentration. However for Cd, the addition of rice straw led to decrease in free Cd^{2+} concentration. Because the less strong binding of Cd to DOC, the decrease in free Cd^{2+} concentration due to rice straw addition could not be counter balanced by the increased adsorption to DOC, which resulted in a net decrease of total soluble Cd.

4.4. Effects of incubation time on free and soluble metal ion concentration

During the incubation, transformation/decomposition may happen to both the initially present SOM and amended rice straw. In the mean time, the “ageing effects” of ion adsorption to clay minerals will also take place, which has generally been attributed to micropore diffusion, cavity entrapment, occlusion in solid phases by co-precipitation and co-flocculation, and surface precipitation/crystal growth (Alexander, 2000; Seuntjens et al., 2001; Ma et al., 2006). With ageing, metal is generally subject to transformation or incorporation into a more stable solid phase that can lead to a decrease in metal bioavailability. CaCl_2 -extractable Cu in some artificial soils, soluble and exchangeable Cu fractions in sandy soil and sandy loam were found to decrease over time (Han et al., 2001; Tom-Petersen et al., 2004;

Fig. 5. Distribution of Cu and Cd in the solid phase calculated with models.

Daoust et al., 2006). In sequential chemical extraction experiment, Cd concentration decreased in the three mobile fractions with time (Almas et al., 1999). In this study, the effect of incubation time on free Cu^{2+} and Cd^{2+} concentrations showed different patterns for the four soils. As a general trend, free Cu^{2+} concentration was not affected by the incubation time, except that in soil LC, free Cu^{2+} concentration increased with time. This is similar to the results reported by Ma et al. (2006). They found that the free Cu^{2+} activity in soil pore water decreased with incubation time in some soils but was not significantly affected in soils with low pH (<5.5) and high organic matter. For Cu, adsorption to organic matter is expected to be the dominant mechanism in controlling free Cu^{2+} concentration/activity (Weng et al., 2001b). The time effects on Cu speciation would be mainly related to the variation in organic matter in soil, not the “ageing effects” in relation to adsorption to clay. This can explain that the free Cu^{2+} concentration did not decrease with time in general in the present experiment. In contrast to Cu, the concentration of free Cd^{2+} decreased mostly with the incubation time. As mentioned above, Cd binds less strongly to organic matter than Cu. Considering the relatively large amount of clay mineral present in these soils (14–23%, Table 1), adsorption to clay can be an important mechanism that controls free Cd^{2+} concentration. This assumption is supported by the speciation calculations (Fig. 5). The observed decrease of free Cd^{2+} concentration with time can be attributed to the “ageing effects” of metal ion adsorption to clay.

The changes in total soluble concentrations of Cu and Cd should be dependent on the changes in free metal ion concentration and DOC concentration over time. Concentration of DOC did not vary much over the incubation time. Therefore, we can expect that the changes in total soluble Cu and Cd concentrations will follow the changes in free Cu^{2+} and Cd^{2+} concentrations.

5. Conclusions

The addition of rice straw led to decreased free Cu^{2+} , free and soluble Cd concentration but to increased soluble Cu concentration. The effects of rice straw on metal distribution are probably mainly caused by its indirect effects on soil pH and DOC concentration, rather than by the adsorption capacity of rice straw itself. Compared to humic substances that present as stable soil organic matter, the metal adsorption capacity of fresh organic materials such as rice straw is much weaker. The ageing effects are stronger for Cd than for Cu, probably because that more Cd is adsorbed to clay minerals than Cu does. Response of metal distribution to organic matter incorporation in soil may differ depending on the affinity of metal to the initial and added organic matter.

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