

Effects of Acid Rain on Competitive Releases of Cd, Cu, and Zn from Two Natural Soils and Two Contaminated Soils in Hunan, China

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Abstract Leaching experiments of rebuilt soil columns with two simulated acid rain solutions (pH 4.6–3.8) were conducted for two natural soils and two artificial contaminated soils from Hunan, south-central China, to study effects of acid rain on competitive releases of soil Cd, Cu, and Zn. Distilled water was used in comparison. The results showed that the total releases were Zn>Cu>Cd for the natural soils and Cd>Zn»Cu for the contaminated soils, which reflected sensitivity of these metals to acid rain. Leached with different acid rain, about 26–76% of external Cd and 11–68% external Zn were released,

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but more than 99% of external Cu was adsorbed by the soils, and therefore Cu had a different sorption and desorption pattern from Cd and Zn. Metal releases were obviously correlated with releases of TOC in the leachates, which could be described as an exponential equation. Compared with the natural soils, acid rain not only led to changes in total metal contents, but also in metal fraction distributions in the contaminated soils. More acidified soils had a lower sorption capacity to metals, mostly related to soil properties such as pH, organic matter, soil particles, adsorbed SO_4^{2-} , exchangeable Al^{3+} and H^+ , and contents of Fe_2O_3 and Al_2O_3 .

Keywords acid rain · soil · leaching experiment · sequential extraction · Cu · Cd · Zn · China

1 Introduction

There is a growing public concern over the potential accumulation of heavy metals in agricultural soils in China owing to rapid urban and industrial development and increasing reliance on agrochemicals in the last several decades (Wong, Li, Zhang, Qi, & Min, 2002). Because of acidification processes triggered by acid rain, heavy metals are transported by the leachate via the groundwater to surface streams (Liciskó & Szebényi, 1999). Although cation exchange, surface adsorption, chelation with organic material, and

precipitation are important mechanisms for heavy metal mobility, acid rain water removes heavy metals which are weakly adsorbed in soils (Gong & Donahoe, 1997). Various soils show a very different behavior in sorption of heavy metals (Alumaa, Kirso, Petersell, & Steinnes, 2002), because the concentration of each heavy metal is always controlled by different parameters (soil pH, iron and aluminum oxide content, clay content, organic matter and cation exchange capacity) (Hernandez, L. Probst, A. Probst, & Ulrich, 2003). Various metals also exhibit different preferential leaching from soils. For example, the depletion sequence is Cd>Ni>Zn>Cu in some acid soils (Wilcke & Kaupenjohann, 1998). Although Cd abundance in lithosphere is quite low, it is a typical toxic element in soil to plants (Wang, 2000). Cu and Zn are necessary trace nutrient elements to plants and human being, but high contents of Cu or Zn in soil could result in accumulation in plants and subsequently inhibit growth of plants (Fan, 1991).

Hunan, a province in south-central China, is located in the center area of acid deposition (F. Wu, J. Wu, & Wang, 2000). Meanwhile, mining activities in Hunan have been conducted for more than 500 years, which has resulted in heavy metal contamination in soils, rivers, and crops in the mining areas, and even some environmental accidents (Liu, Probst, & Liao, 2005). However, there are few published reports on chemical behaviors of soil heavy metals influenced by acid rain in this area. We wonder how trace metals in the natural soils respond to acid rain, and what will happen if the soils are contaminated with heavy metals and exposed to serious acid rain. In this study, we conducted leaching experiments with two simulated acid rain solutions for two natural soils from Hunan and two artificial contaminated soils. The primary objectives of this study were to investigate effects of acid rain on competitive releases of Cd, Cu, and Zn from natural soils and from contaminated soils, and to compare changes in fractions of these metals in soil profile affected by

acid rain, because Cd, Cu, and Zn are main contaminating metals in Hunan mining areas and their ambience.

2 Materials and Methods

Two natural soil profiles were selected from the mountainsides, one from the suburb of Changsha (28°23'N, 113°17'E) in northern Hunan and the other from Chenzhou (25°48'N, 113°02'E) in southern Hunan. The soil from Changsha is red soil, marked as Soil A, and the main vegetation is China fir (*Cunninghemia lanceolata*). The soil from Chenzhou is yellow red soil, marked as Soil B, covering with mixed China fir (*Cunninghemia lanceolata*), Masson pine (*Pinus massoniana*), and bushes, and mining activities in Hunan mostly happen in this area. These two soils, both developed from Quaternary red clay (belonging to Allitic Udic Ferrisols in FAO system), are very typical soils in southern China. For each profile, the soil samples from three layers (20 cm for each layer, marked as topsoil, subsoil, and bottom soil, respectively) were collected, aired dried, and passed through a 2 mm sieve for further experiments.

Soil columns were rebuilt in washed PVC tubes (65 cm for the height and 7.1 cm for the diameter) according to the natural profiles. First, 1.1 kg of bottom soil was put into the column, and then followed by 1.0 kg of subsoil and 1.0 kg of topsoil. The height of each layer was about 20 cm, separating with a thin layer of sponge. According to the compositions of precipitation during the period of 1990–1998 in Chenzhou and Changsha (Wu et al., 2000), we prepared two simulated acid rain solutions for the leaching experiments, marked as AR2 and AR3, respectively, and distilled water (marked as AR1) was used in comparison. The pH and main compositions were given in Table 1. From AR1 to AR3, the pH values were decreased and total dissolved salts increased.

Table 1 pH values and major ion concentrations of simulated acid rain ($\mu\text{mol l}^{-1}$)

| Code | pH | Ca ²⁺ | NH ₄ ⁺ | Mg ²⁺ | K ⁺ | Na ⁺ | SO ₄ ²⁻ | NO ₃ ⁻ | Cl ⁻ |
|------|------|------------------|------------------------------|------------------|----------------|-----------------|-------------------------------|------------------------------|-----------------|
| AR1 | 5.74 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| AR2 | 4.56 | 52.40 | 57.50 | 4.94 | 7.29 | 13.70 | 80.65 | 20.81 | 21.06 |
| AR3 | 3.78 | 69.86 | 76.67 | 6.58 | 9.72 | 18.26 | 107.50 | 27.74 | 156.39 |

Two sets of leaching experiments were conducted, one for the natural soils and the other for the contaminated soils. In order to simulate contamination processes in the field, and to compare releases of the different metals from soils influenced by acid deposition on the same basis, the contaminated soils were prepared by adding 100 ml solution containing 200 mg of each metal Cd, Cu, and Zn (in the form of pure CdCl₂, CuCl₂, and ZnCl₂, respectively) evenly to the top of the natural soil column, and then equilibrated for 15 days. Calculated from annual about 1,500 mm precipitation in Hunan and about 50% evapotranspiration, each soil column was leached for 60 days with a total of 29.7 l simulated acid rain solution (495 ml for each day), which corresponded to the local precipitation of about 10 years. To simulate the field situation, an intermittent leaching process was adopted and the leaching rate was controlled at 30±5 ml h⁻¹, i.e. about 16 h for leaching and 8 h for drying each day. The leachates were collected every 6 days and 10 leachates were obtained from each column. All leachates were filtrated through 0.45 μm membrane and stored at 4°C. Meanwhile the soil samples from every 10 cm in the columns were collected, air dried, and stored for further analysis. The triplicate leaching experiments were conducted.

Basic physicochemical properties of the two natural soils (Table 2) and some soil parameters before leaching were determined according to Chinese standard methods for soil analysis (Lu, 1999). Contents of soil organic matter were determined by a volumetric method of K₂Cr₂O₇-heating, cation exchange capacity (CEC) and base saturation (BS) were determined by extracting with a 1.0 mol l⁻¹ NH₄OAc solution (pH 7.0). The total contents of soil heavy metals were determined directly by acid digestion using a mixture of HF/HNO₃/HClO₄/H₂O₂ on hot plates at atmospheric pressure. Following the operational procedures of Chao (1972), Tessier, Campbell, and Blasson (1979), Shuman (1982) and more recently, Leleyter and Probst (1999), heavy metal speciation in the soils was studied and divided into six fractions: exchangeable including water soluble (Ex), bound to manganese oxides (OMn), bound to organic matter (OM), bound to amorphous iron oxides (AOFe), bound to crystalline iron oxides (COFe), and residue (Res). Metals in the solutions were determined on atomic absorption spectroscopy with a graphite furnace (AAS, Shimadzu AA-6800), and the detection limit for Cd, Cu, and Zn was lower than 1 μg l⁻¹. Analysis uncertainties of metals on AAS were estimated by analyzing the replicated soil solutions, and the average standard deviations were about 5% for all metals.

Table 2 Basic physicochemical property of the natural soils

| Parameters | Soil A (Red soil) | | | Soil B (Yellow red soil) | | |
|--|--------------------------------|----------|----------|--------------------------|----------|----------|
| | 0–20 cm | 20–40 cm | 40–60 cm | 0–20 cm | 20–40 cm | 40–60 cm |
| Soil sampling site | Changsha | | | Chenzhou | | |
| pH value | 4.72 | 4.97 | 4.83 | 4.48 | 4.53 | 4.57 |
| Content of organic matter (g kg ⁻¹) | 21.99 | 18.46 | 16.10 | 20.87 | 5.26 | 4.54 |
| Cation exchange capacity (CEC, cmol kg ⁻¹) | 10.06 | 10.32 | 10.09 | 11.63 | 9.46 | 9.41 |
| Bases saturation (BS, %) | 14.40 | 11.75 | 12.47 | 12.54 | 10.95 | 12.32 |
| Content of adsorbed sulfate (g kg ⁻¹) | 10.97 | 8.19 | 8.32 | 16.32 | 18.25 | 16.40 |
| Content of exchangeable acidity | H ⁺ | 0.27 | 0.22 | 0.21 | 0.25 | 0.21 |
| (cmol kg ⁻¹) | 1/3Al ³⁺ | 4.07 | 4.26 | 4.49 | 4.89 | 4.96 |
| Content of soil particles (%) | >0.05 mm | 17.51 | 19.3 | 18.38 | 25.78 | 20.92 |
| | 0.05–0.02 mm | 6.27 | 7.15 | 8.16 | 6.19 | 8.22 |
| | <0.02 mm | 76.23 | 73.55 | 73.46 | 68.04 | 70.87 |
| Content of oxides (g kg ⁻¹) | Al ₂ O ₃ | 2.25 | 2.31 | 2.14 | 1.74 | 2.48 |
| | Fe ₂ O ₃ | 3.44 | 3.44 | 3.63 | 5.78 | 3.83 |
| Total content of heavy metals (mg kg ⁻¹) | Cd | 1.23 | 1.07 | 0.71 | 1.87 | 1.40 |
| | Cu | 32.99 | 21.01 | 22.42 | 21.22 | 17.93 |
| | Zn | 243.51 | 276.97 | 275.87 | 289.40 | 300.82 |

3 Results

3.1 Competitive Releases of Soil Heavy Metals Affected by Acid Rain

When the pH values decreased from 5.7 to 3.8 in simulated acid rain solutions, the accumulative releases

Fig. 1 Effects of acid rain on accumulative releases of Cd (above), Cu (middle), and Zn (below) from the natural soils and the contaminated soils. "N" was the natural soils and "C" the contaminated soils. AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). The accumulative release presented the sums of metal contents in the leachates and 10 leachates were collected during the leaching process

of heavy metals (the sum of metal contents in the 10 leachates) increased significantly (Fig. 1). For the natural soils, the release trends of Cd, Cu, and Zn were almost linearly increased with increasing in leaching volumes ($R^2 > 0.990$; $n = 10$, $\rho_{0.01} = 0.585$). The final releases for these three metals were Zn (1.2–2.2 mg) > Cu (0.86–1.5 mg) > Cd (0.26–0.38 mg),

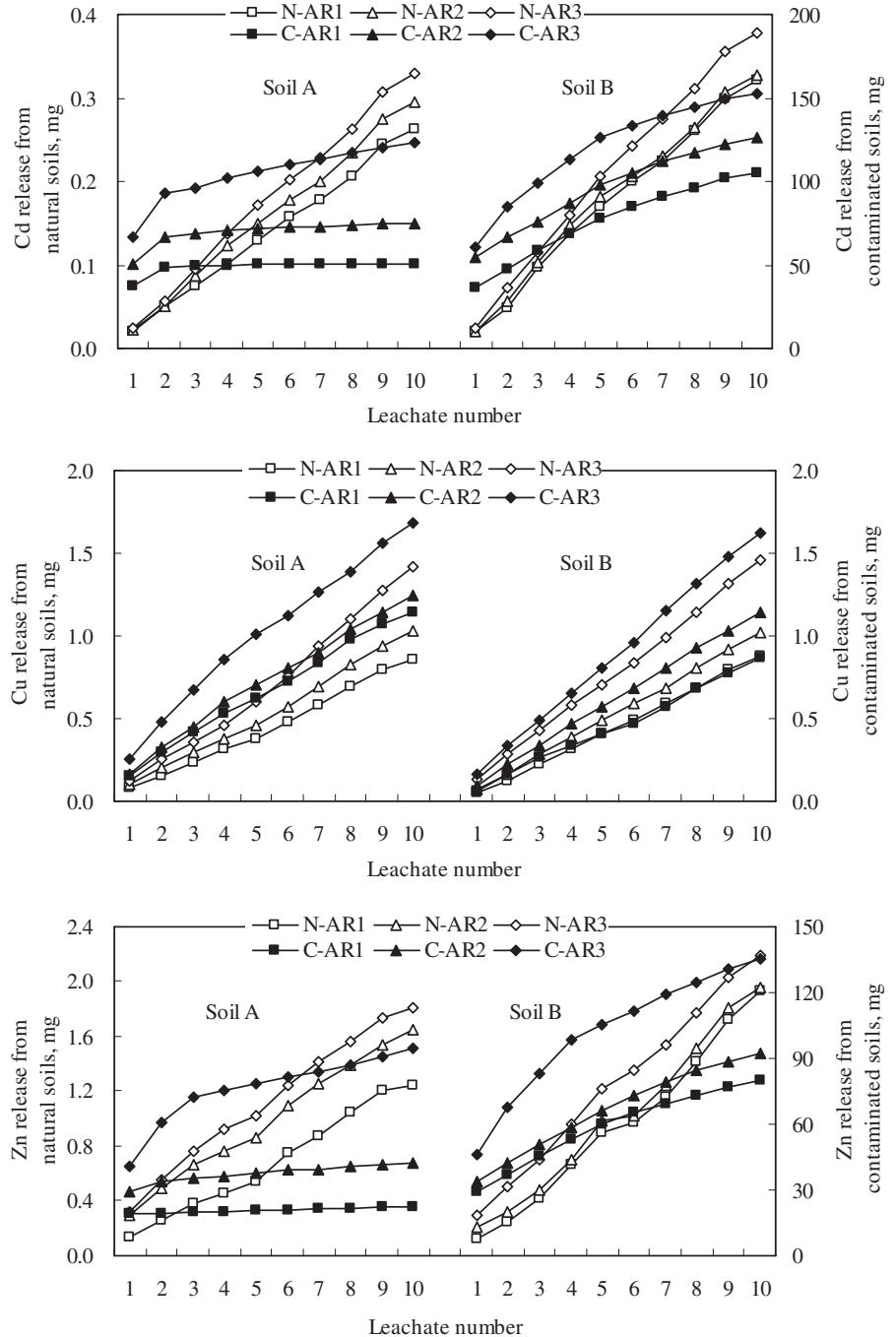
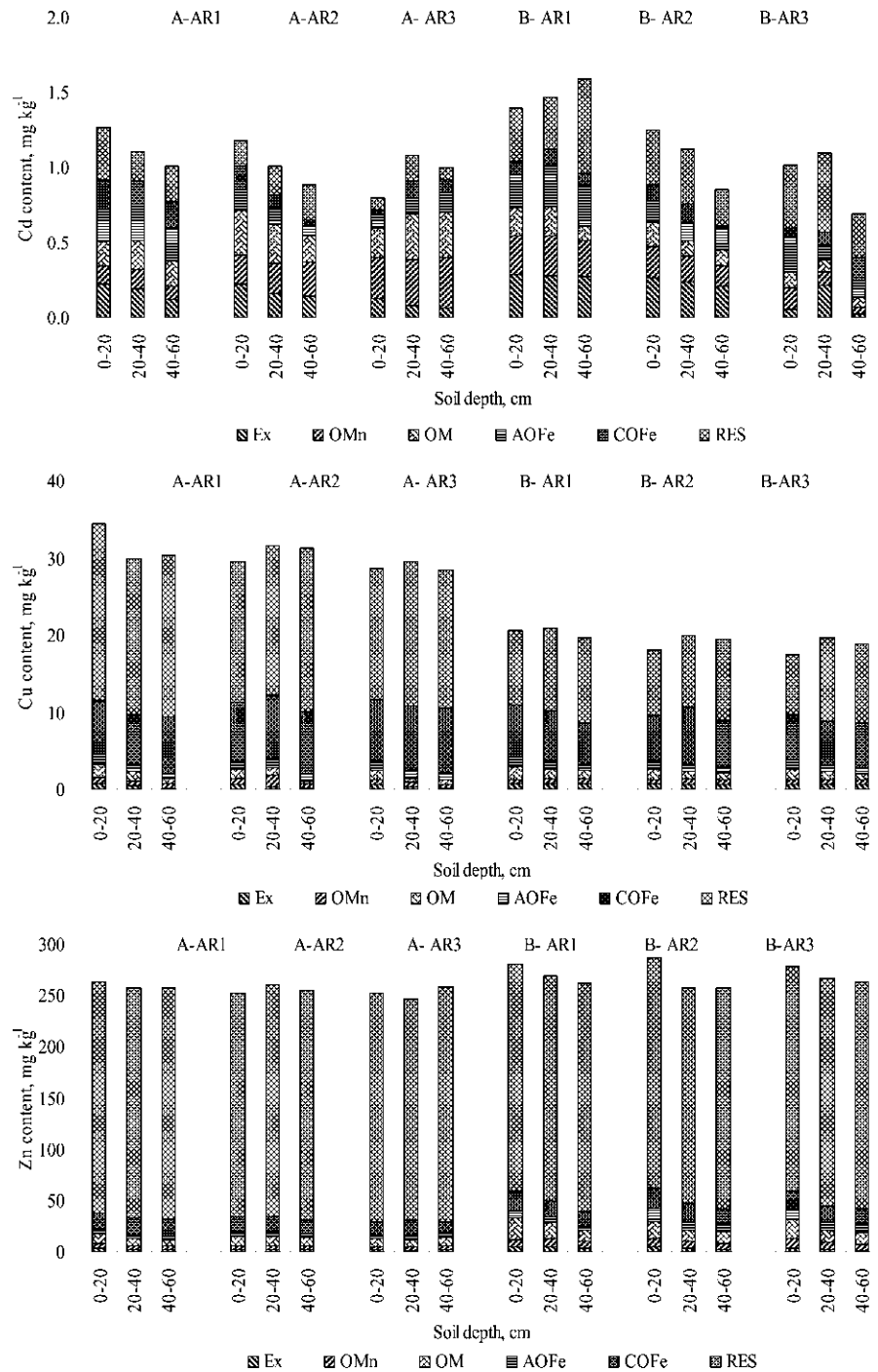


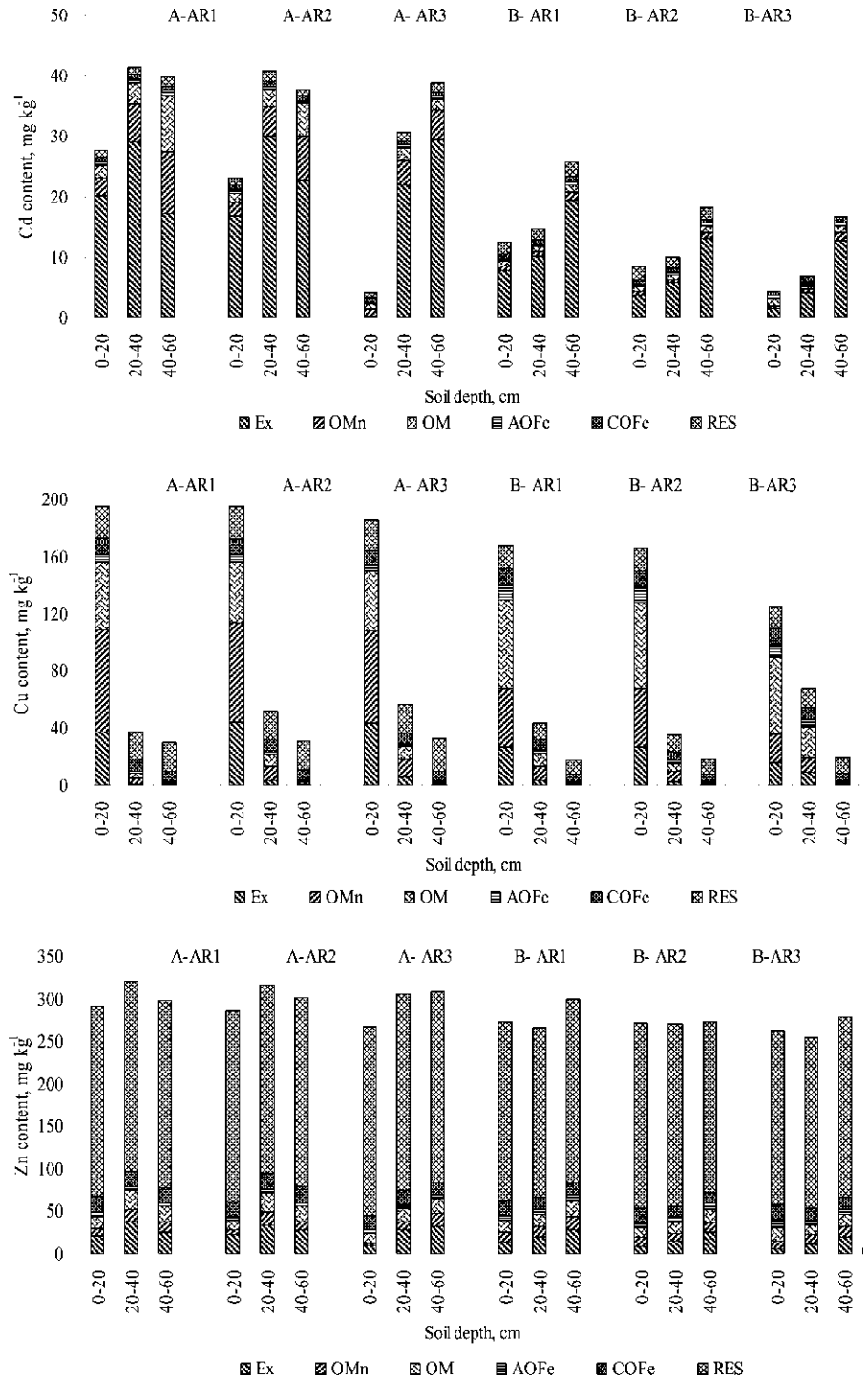
Fig. 2 Effects of simulated acid rain on fraction contents of Cd (*above*), Cu (*middle*), and Zn (*below*) in the natural soils. A meant Soil A (*left*), B meant Soil B (*right*). AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). Ex: exchangeable; OMn: bound to manganese oxides; OM: bound to organic matter; AOfFe: bound to amorphous iron oxides; COFe: bound to crystalline iron oxides; Res: residue



and this sequence corresponded to soil metal contents. Compared with Soil A, the releases of Cd and Zn were higher from Soil B due to higher soil total contents of Cd and Zn; however, Cu releases were almost the same in the two soils, although Soil A had higher Cu content

than Soil B (Table 2). For the contaminated soils, the accumulative releases were greatly enhanced for Cd (51–153 mg) and Zn (22–136 mg) owing to external addition, but not for Cu. Cu releases from the contaminated soils (0.87–1.69 mg) were almost the

Fig. 3 Effects of simulated acid rain on fraction contents of Cd (*above*), Cu (*middle*), and Zn (*below*) in the contaminated soils treated with 200 mg of each element. A meant Soil A (*left*), B meant Soil B (*right*). AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing). Ex: exchangeable; OMn: bound to manganese oxides; OM: bound to organic matter; AOFc: bound to amorphous iron oxides; COFe: bound to crystalline iron oxides; Res: residue



same as those from the natural soils, and there were no obvious differences between the two soils. This meant that the sorption capacity of these two soils to Cu was great. The release sequence in the contaminated soils

was $Cd > Zn > Cu$, showing that external Cd in soils was the most sensitive to acid rain, followed by Zn. Most external Cu was adsorbed by soils and did not show sensitivity to acid rain.

3.2 Effects of Acid Rain on Metal Distribution in the Natural Soils

The fraction distribution of Cd, Cu, and Zn in the natural soils affected by simulated acid rain was given in Fig. 2. For Cd, six fractions were basically evenly distributed in the both soils. Ex forms were decreased from the topsoil to the bottom soil in Soil A and from AR1 to AR3, but no special pattern was observed for the other fractions. For Cu, the most important fractions were Res and COFe forms. Affected by acid rain (AR2 and AR3), Res forms in the topsoil were lower than those in the subsoil or bottom soil, probably due to mineral dissolution at lower pH. But for the Ex, OM, and AOFe forms of Cu, the contents were generally declined from the topsoil to the bottom soil. For Zn, Res form was the dominant fraction. Because the final releases accounted for only 0.15–0.24% compared with the total contents in the soils, there were no significant changes for Zn among the different treatments of simulated acid rain solutions. After leaching, the total contents of Cd and Zn were higher in Soil B than in Soil A, and those of Cu had a reverse result of Cd and Zn.

3.3 Effects of Acid Rain on Metal Distribution in the Contaminated Soils

Compared with the natural soils, the contaminated soils had different fraction distributions, especially for Cd and Cu (Fig. 3). The most important Cd fraction was Ex form, followed by OMn and OM forms in Soil A and Res form in Soil B. Because of leaching process, the total contents and Ex fraction increased generally from the topsoil to the subsoil or bottom soil, indicating a higher migration of Cd in soil profiles accompanied with leachates. From AR1 to AR3, the total Cd contents were obviously decreased, particularly in the topsoil, showing a higher sensitivity of external Cd to acid rain. Most Cu content was found in the topsoil where it was regularly distributed among the different fractions. Only a small part of external Cu was transferred to the lower soil layers, showing a greater sorption capacity to Cu for these two soils, so that a clear sequence of Cu contents was obtained as topsoil > subsoil > bottom soil. The Cu contents of Ex, OMn, and OM forms enhanced quite a lot because of addition of external Cu. With

increasing in acidity and total dissolved salts in acid rain, the total Cu content decreased in the topsoil and increased in the subsoil or bottom soil. In the two contaminated soils, residue Zn (Res) was still the dominant fraction, but the other fractions increased to different degrees. Exchangeable Zn (Ex) was the second important form, and increased from the topsoil to the bottom soil in most cases, especially in Soil B, demonstrated that Ex Zn, mostly coming from the external source, was sensitive to acid rain and easily transferred through soil columns. Compared with Soil B, the total contents of Cd, Cu, and Zn were all higher in Soil A, further implying a greater sorption capacity to heavy metals for Soil A.

3.4 Comparison between Metal Releases and Contents in Soils

Under the affection of simulated acid rain, the final releases of Cd, Cu, and Zn from the natural soils were all increased from AR1 to AR3 (Fig. 1), and accounted for 7.8–10.7%, 1.1–2.5%, and 0.15–0.24% in the total contents of Cd, Cu, and Zn, respectively (Table 3). It was clear that increasing acidity in acid rain resulted in increasing metal releases from the natural soils. In the contaminated soils, the total contents enhanced 200 mg for each element due to addition of external sourced heavy metals. In these cases, the final releases of Cd and Zn were greatly increased with treatments of acid rain, and accounted for 25–75% and 2.2–12.2% of the total Cd and Zn, respectively. Because most of soil Cd came from the external source (around 98%), these percentages for Cd were almost the same as for the external Cd. However, due to only a small part soil Zn coming from the external source (around 19%), the percentages increased to 11–47% for Soil A and 40–68% for Soil B when compared with the external added Zn. From this point, the releases of Cd and Zn from the contaminated soils due to affection of acid rain were mostly from the external source. Although a large part soil Cu came from the external source (72–77%), the final releases of Cu from the contaminated soils were only slightly higher than those from the natural soils (Fig. 1), accounting for 0.3–0.6% of the total Cu or 0.4–0.8% of the external sourced Cu. These percentages were much lower than those for Cd and Zn. A comparison between final metal releases

Table 3 Comparison between the final metal releases from the natural and contaminated soils affected by acid rain and the metal total content in the corresponding soils, and ratios of the final releases from the contaminated soils to those from the natural soils

| Items | Soil A | | | Soil B | | |
|---|--------|------|------|--------|------|------|
| | Cd | Cu | Zn | Cd | Cu | Zn |
| <i>For the natural soils</i> | | | | | | |
| Release (AR1)/Total content, % | 8.53 | 1.09 | 0.15 | 7.84 | 1.47 | 0.21 |
| Release (AR2)/Total content, % | 9.58 | 1.31 | 0.20 | 8.04 | 1.71 | 0.22 |
| Release (AR3)/Total content, % | 10.69 | 1.80 | 0.22 | 9.24 | 2.46 | 0.24 |
| <i>For the contaminated soils</i> | | | | | | |
| Release (AR1)/Total content, % | 25.1 | 0.40 | 2.20 | 51.6 | 0.30 | 7.20 |
| Release (AR2)/Total content, % | 37.0 | 0.40 | 4.10 | 61.8 | 0.40 | 8.30 |
| Release (AR3)/Total content, % | 60.7 | 0.60 | 9.20 | 74.8 | 0.60 | 12.2 |
| Release (AR1)/External addition, % | 25.5 | 0.60 | 11.1 | 52.6 | 0.40 | 40.0 |
| Release (AR2)/External addition, % | 37.5 | 0.60 | 21.2 | 63.1 | 0.60 | 46.2 |
| Release (AR3)/External addition, % | 61.6 | 0.80 | 47.2 | 76.3 | 0.80 | 67.8 |
| <i>Ratios of the releases of the contaminated soils to those of the natural soils</i> | | | | | | |
| AR1 | 193.9 | 1.3 | 17.9 | 328.6 | 1.0 | 41.4 |
| AR2 | 254.4 | 1.2 | 25.7 | 384.4 | 1.1 | 47.1 |
| AR3 | 374.1 | 1.2 | 52.3 | 404.5 | 1.1 | 61.8 |

from the contaminated soils and from the natural soils showed that 194–405, 18–62, and 1.0–1.3 times higher releases could be resulted in for Cd, Zn, and Cu, respectively, by the treatments of simulated acid rain solutions. This implied that for the external sourced heavy metals, the sorption capacity of the two tested soils was $Cu \gg Zn > Cd$. In other words, acid rain would remove most external Cd out from the soils, but has no special effects on movement of soil Cu and most external Cu (<99%) would be retained inside the soils.

4 Discussion

A regression analysis indicated that the accumulative releases of heavy metals (ARHM) in the 10 leachates from the contaminated soils were significantly exponentially proportional to the accumulative releases of total organic carbon (ARTOC) in the leachates: $ARHM (mg) = a \times [ARTOC (mg)]^b$, where a and b were constants (Table 4). This showed that the release of soil metals was controlled by the contents of total organic carbon to a great extent, and was similar to the results of Strobel, Hansen, Borggaard, Andersen, and Raulund-Rasmussen (2001) and Tipping et al. (2003). Special low values of coefficient a for Cu indicated that Cu was highly associated with soil

organic matter and not released into soil solution. The correlation coefficients were much higher than the level of $\rho_{0.01}$ ($n=10$, $\rho_{0.01}=0.585$) for all three elements and for all three acid rain treatments, resulting in possibility in some cases to evaluate heavy metal releases from measuring TOC contents in soil solutions.

Exchangeable fractions and total amounts of heavy metals in the contaminated soils after leaching were correlated with contents of Fe_2O_3 , Al_2O_3 , adsorbed SO_4^{2-} , exchangeable Al^{3+} or H^+ in the soils (Table 5). These relationships clearly exhibited the similar chemical behaviors for soil Cd and Zn, but quite different from Cu. Exchangeable Cd or Zn and total Cd or Zn were significantly negatively proportional to total contents of Fe_2O_3 , adsorbed SO_4^{2-} , and exchangeable Al^{3+} , and significant positive relationships between total amounts of soil Cd or Zn and total contents of Al_2O_3 were also obtained, which was similar to the results of Hernandez et al. (2003). Exchangeable Al^{3+} might markedly reduce metal sorption, for instance Cd and Zn, due to its strong affinity for the sorption sites (Phillips, 1999) and strong competition with other metals. Contrast to Cd and Zn, exchangeable Cu and total Cu had only significantly positive linear relationships with exchangeable H^+ among various characteristics in the soils. Meanwhile, exchangeable Cu and total Cu were

Table 4 Relationships between the accumulative releases of heavy metals and total organic carbon in the leachates from the contaminated soils treated with different simulated acid rain

| ARHM (mg) = a × [ARTOC (mg)] ^b | | | | | | | |
|---|--------------|-----------------------|-------|-----------------------|-----------------------|-------|-----------------------|
| Simulated acid rain | Heavy metals | Soil A | | | Soil B | | |
| | | a | b | R ² (n=10) | a | b | R ² (n=10) |
| AR1 | Cd | 28.1 | 0.126 | 0.722** | 5.47 | 0.645 | 0.994** |
| | Cu | 7.10×10 ⁻³ | 1.02 | 0.997** | 8.73×10 ⁻⁴ | 1.50 | 0.988** |
| | Zn | 14.1 | 0.088 | 0.916** | 4.55 | 0.625 | 0.992** |
| AR2 | Cd | 27.9 | 0.210 | 0.803** | 13.1 | 0.502 | 0.969** |
| | Cu | 2.89×10 ⁻³ | 1.25 | 0.995** | 2.13×10 ⁻³ | 1.40 | 0.991** |
| | Zn | 14.4 | 0.220 | 0.973** | 6.31 | 0.592 | 0.966** |
| AR3 | Cd | 18.9 | 0.396 | 0.937** | 11.1 | 0.605 | 0.990** |
| | Cu | 2.74×10 ⁻³ | 1.35 | 0.989** | 2.51×10 ⁻³ | 1.47 | 0.990** |
| | Zn | 6.87 | 0.556 | 0.931** | 6.84 | 0.686 | 0.982** |

ARHM meant the accumulative release of each heavy metal in the 10 leachates, and ARTOC the accumulative release of total organic carbon in the 10 leachates. AR1, AR2, and AR3 were different simulated acid rain solutions (pH ranging from 5.7 to 3.8 and total dissolved salts increasing)

** meant very significant ($n=10$, $\rho_{0.01}=0.585$)

positively related to contents of Fe₂O₃ and exchangeable Al³⁺, although not significantly, which was also different from Cd and Zn.

Soil B had a lower sorption capacity to heavy metals than Soil A. In the natural soil profiles, Soil B had lower pH values, organic matter, base saturation, and soil particles smaller than 0.02 mm, but higher contents of adsorbed SO₄²⁻ and exchangeable Al³⁺,

compared with Soil A (Table 2), indicated that Soil B had been more acidified. The lower sorption capacity to heavy metals for Soil B could probably be a consequence of these characteristics, because metal solubility was controlled by soil characteristics such as pH, organic matter content, soil mineralogy (Martínez & Motto, 2000). Therefore, we could speculate that plants and groundwater in Chenzhou

Table 5 Relationships between the contents of exchangeable and total heavy metals and the soil parameters in the contaminated soils treated with different simulated acid rain

| Soil parameters | Relations | $n=36$, $\rho_{0.01}=0.178$ | | | | | |
|---|----------------|------------------------------|----------|---------|----------|---------|----------|
| | | Ex. Cd | Total Cd | Ex. Cu | Total Cu | Ex. Zn | Total Zn |
| Total Fe ₂ O ₃ , g kg ⁻¹ | R ² | 0.491** | 0.576** | 0.028 | 0.073 | 0.531** | 0.490** |
| | +/- | - | - | + | + | - | - |
| Total Al ₂ O ₃ , g kg ⁻¹ | R ² | 0.157 | 0.201** | 0.105 | 0.102 | 0.094 | 0.273** |
| | +/- | + | + | + | + | + | + |
| Adsorbed SO ₄ ²⁻ , g kg ⁻¹ | R ² | 0.293** | 0.345** | 0.131 | 0.128 | 0.184** | 0.408** |
| | +/- | - | - | - | - | - | - |
| Exchangeable Al ³⁺ , mg kg ⁻¹ | R ² | 0.370** | 0.567** | 0.016 | 0.021 | 0.325** | 0.461** |
| | +/- | - | - | + | + | - | - |
| Exchangeable H ⁺ , mg kg ⁻¹ | R ² | 0.066 | 0.074 | 0.532** | 0.551** | 0.090 | 0.040 |
| | +/- | - | - | + | + | - | - |

There were a total 36 contaminated soil samples, including two sets of soil columns (Soil A and Soil B, treated with three simulated acid rain solutions AR1, AR2, and AR3, and each soil column with six layers 10 cm for each layer)

+ meant the positive relations, - the negative relations, and ** very significant at the level of $\rho_{0.01}=0.178$ ($n=36$)

where Soil B collected were more fragile to suffer complex contamination of heavy metals and acid rain.

5 Conclusions

Under the effects of acid rain, the release sequences were Zn>Cu>Cd in the natural soils corresponding to soil metal contents and Cd>Zn»Cu in the contaminated soils, indicating that different metals had different sorption and desorption behaviors. With increasing in leaching volumes and in acidity (and total dissolved salts) of acid rain, more metals were released. In the contaminated soils, about 26–76% of external Cd and 11–67% external Zn were removed by simulated acid rain, but more than 99% of external Cu was adsorbed by the soils. The enhanced Cd in the soils was mostly exchangeable, and gradually moved down through the soil columns; however, most enhanced Cu including the fractions bound to exchangeable, manganese oxides, and organic matter was found in the topsoil. Residue Zn was still dominant in the contaminated soils after leaching, but total and exchangeable Zn increased quite a lot. Except the acidity of acid rain, the accumulated releases of heavy metals (ARHM) were closely correlated with the accumulative releases of total organic carbon (ARTOC) in the leachates, and an equation $ARHM(mg)=a \times [ARTOC(mg)]^b$ could be used to quantify metal desorption under acid rain influence. Soil sorption capacities to heavy metals were related to soil properties, such as pH, organic matter, base saturation, soil particles, adsorbed SO_4^{2-} , exchangeable H^+ and Al^{3+} , contents of Fe_2O_3 and Al_2O_3 . Generally, the soil having been more acidified had a lower sorption capacity to heavy metals, for instance Soil B from Chenzhou area in southern Hunan, China, where mining activities have been conducted. Some environmental accidents happened in 1985 in this area, and a recent field investigation showed contamination of heavy metals in the local soils and crops (Liu et al., 2005). Therefore, we could deduce that crops and groundwater in this area were fragile to soil heavy metals, especially Cd and Zn, because these two elements were very sensitive to acid rain.

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