

Mobility and speciation of Cd, Cu, and Zn in two acidic soils affected by simulated acid rain

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Abstract: Through a batch experiment, the mobility and speciation of heavy metals (Cd, Cu, Zn) in two acidic forest soils from Hunan Province were studied. The results showed that the release and potential active speciation of Cd, Cu, and Zn in the tested contaminated red soil (CRS) and yellow red soil (CYRS) increased significantly with pH decreasing and ion concentrations increasing of simulated acid rain, and these effects were mainly decided by the pH value of simulated acid rain. Cd had the highest potential risk on the environment compared with Cu and Zn. Cd existed mainly in exchangeable form in residual CRS and CYRS, Cu in organically bound and Mn-oxide occluded forms, and Zn in mineral forms due to the high background values.

Keywords: batch experiment; heavy metals; mobility; speciation; acid rain

Introduction

Contamination of soil heavy metals has long been a problem in industrialized areas. Many processes, such as direct dumping of industrial waste derived from ore extraction and manufacturing, chemical weathering of mine tailings and landfills, and the atmospheric deposition of materials resulting from burning fossil fuels and smelting ore, could bring metals into the surface environment and significantly enriched in surface horizons (Hernandez, 2003). The chemical behaviors of soil heavy metals are greatly affected by acid deposition mostly due to cation exchange in soils with H^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ coming from acid deposition (Probst, 2000). Hunan province, in the central south of China, is an area with lots of non-ferrous metals mines. With the rapid development of mining and smelting industries, many toxic metals were introduced into the soil and harmful to the plants and human (Wang, 2002). Hunan is also a center area of acid rain in southern China. With increasing emission of SO_2 , acid rain became more serious, and the most important chemical processes of soil metals were accelerated. However, there were not enough data on the mobility and chemical speciation of heavy metals in contaminated soils affected by acid rain. In this study, a six-step chemical speciation extraction scheme was used to evaluate the environmental mobility and speciation of external Cd, Cu and Zn affected by simulated acid rain in contaminated soils.

1 Materials and methods

1.1 Soil

The two typical soils (0—20 cm) were collected from Hunan Province. Red soil (RS) was collected from the artificial forest mountains in Changsha suburbs, which was developed from quaternary red clay. Yellow red soil (YRS) was collected from the mineral mountains in Chenzhou area, which was developed from sandstone. They belonged to Allitic Udic Ferrisols, acidic, variable charges, low CEC, low base saturation and high exchangeable Al saturation (Table 1).

Table 1 Basic physico-chemical properties of the tested soils

Item	RS	YRS
pH value	4.72	4.48
Content of OM, g/kg	21.99	20.87
CEC, cmol/kg	10.06	11.63
Bases saturation, %	14.40	12.54
Content of exchangeable acidity, cmol/kg		
H^+	0.27	0.25
$1/3Al^{3+}$	4.07	4.89
$H^+ + 1/3Al^{3+}$	4.34	5.14
Content of soil particles, mm, %		
2—0.25	7.07	15.22
0.25—0.05	10.44	10.56
0.05—0.02	6.27	6.19
0.02—0.002	43.86	34.02
< 0.002	32.37	34.02
Total content of heavy metals, mg/kg		
Cd	1.23	1.87
Cu	22.33	15.12
Pb	19.82	49.47
Zn	281.54	287.87
Cr	127.76	79.85

1.2 Simulated acid rain

In the sampling areas, the annual rainfall was around 1500 mm, and the pH of rainfall was about 3.50—4.50. The simulated acid rains were designed according to the average pH values and main ion composition of rain water during the period 1991—1996 in Hunan Province. AR1 was deionized water that saturated with CO_2 in air and stand for the normal rain. AR2 was similar to the acid rain in Chenzhou area and AR3 in Changsha area, respectively (Table 2).

1.3 Batch experiment

The two soil samples (0—20 cm) were air-dried and ground to pass through a 2 mm sieve, and treated with 200 mg/kg of Cd, Cu, and Zn in the form of complex chloride solution (standing for CRS and CYRS, respectively). After equilibrium of 15 d under natural conditions, these polluted soils were air-dried, pass through 2 mm sieve again. They would be used in the batch experiment. 150 ml artificial acid rain solution was added into 30 g air-dried soil samples (CRS and CYRS), and the mixture was agitated 15 min per 12 h. After 48 h, the mixture was centrifugally separated. The

centrifugal solution was passed through a 0.45 μm filter, acidified to pH less than 2.0, and refrigerated in 4 $^{\circ}\text{C}$ condition for further analysis. These processes were repeated 5 times. The experiment was conducted in triplicates at room temperature 25 $^{\circ}\text{C}$.

Table 2 pH values and ion concentrations of simulated acid rain

Acid rain	Unit: $\mu\text{mol/L}$		
	AR1	AR2	AR3
pH	5.74	4.56	3.78
SO_4^{2-}	0	80.65	107.50
NO_3^-	0	20.81	27.74
Ca^{2+}	0	52.40	69.86
NH_4^+	0	57.50	76.67
Mg^{2+}	0	4.94	6.58
K^+	0	7.29	9.72
Na^+	0	13.70	18.26

1.4 Analysis

The main soil parameters have been analyzed following classical methods (Lu, 1999): Soil pH was measured with Mettler Toledo 320 pH Meter, and the ratio of soil to water was 1:2.5; the exchangeable hydrogen, exchangeable Al and acidity were extracted with 1 mol/L KCl solution; soil organic matter was determined with potassium dichromate method. A six-step sequential speciation scheme, composed of exchangeable (including water-soluble), Mn oxide-occluded, organically bound, amorphous Fe oxide occluded, crystalline Fe oxide occluded, and mineral, based on the works of Tessier (Tessier, 1979), Chao (Chao, 1972), and Shuman (Shuman, 1982), was used for species analysis of soil heavy metals. The available contents of metals were determined in extracts of 0.1 mol/L HCl solution. Concentrations of heavy metals were determined by atomic absorption spectrophotography (Shimadzu, AA-6800 AAS) using the standard addition technique. The average standard deviations were less than 5% for all metals, and the differences between the sums of various species and the total contents of soil heavy metals were less than 10%.

2 Results

2.1 Release of metals

Continuously extracting with the same simulated acid rain, the releasing of heavy metals in CRS and CYRS was $\text{Cd} > \text{Zn} > \text{Cu}$. With decreasing pH in simulated acid rain, the release of heavy metals in CRS and CYRS increased obviously, and the effects of acid rain were $\text{AR3} > \text{AR2} > \text{AR1}$ (Fig. 1). According to this sequence, it was easy to find that desorption of metals was influenced by decreasing pH and increasing ion concentrations of simulated acid rain. When the pH of simulated acid rain changed from 5.74 to 3.78, the desorption ratio of Cd increased from 29.25% to 57.08%, of Zn from 23.77% to 38.65%, and of Cu from 5.76% to 19.66%, respectively. Especially the releases of Cu treated with AR3 (pH 3.78) (Fig. 1), the desorption content of copper was 1.95, and 1.66 times in CRS compared to AR1 (pH 4.56) and AR1 (pH 5.74), respectively. At the same time, the desorption content of copper was 1.63, and 1.49 times in CYRS, respectively. The analysis of linear regression between pH values and desorption quantities of Cd, Cu, and Zn by Duncan's showed that the relationships were remarkable ($n = 18$, $R^2 = 0.5571^{**}$, 0.6601^{**} , 0.6185^{**}). The acidity of simulated acid rain increased the releasing potential of metals in soils.

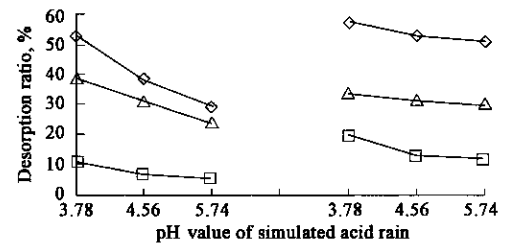


Fig.1 Desorption ratios of heavy metals from CRS (left) and CYRS (right) affected by simulated acid rain
 \diamond Cd; \square Cu; \triangle Zn

2.2 Releasing potential and speciation distribution of metals

The tested soils contaminated by external metals in a short period, the speciation of Cd and Cu in the residual CRS and CYRS existed mainly in mobile and unstable forms (Table 3). For Zn, it had a lot of mobile and unstable forms, but the stable forms were important because of high background value in the tested soils and most part of background Zn was stable forms. After continuous extracting, the release of Cd and Zn in CYRS was greater than in CRS. The contents of Cd in the residual CRS and CYRS were much lower than Cu and Zn, showing a higher mobility of Cd than Zn and Cu in the tested soils. Some studies showed that the static properties of Cd^{2+} were more than of Zn^{2+} in the single divalent ion solution system like as Zn^{2+} or Cd^{2+} solution system, in contrary, the static properties of Zn^{2+} were more than of Cd^{2+} in the complex divalent ions solution system like as the Zn^{2+} - Cd^{2+} solution system. In this experiment, the results showed that the leaching of Cd was higher than of Zn and Cu in complex divalent ions solution system like as Cd^{2+} - Cu^{2+} - Zn^{2+} solution system.

Table 3 Speciation distributions of metals in residual CRS and CYRS after continuous extracting

Metals	CRS			CYRS			
	AR1	AR2	AR3	AR1	AR2	AR3	
Cd	Ex -	62.56	60.96	43.44	22.83	20.88	10.72
	OMn -	7.87	4.53	4.24	1.94	1.87	1.44
	OM -	9.93	6.42	5.06	2.52	2.46	0.97
	AOfFe -	0.00	0.00	0.00	0.00	0.00	0.00
	COFe -	0.06	0.17	0.28	0.06	0.34	0.00
	Min -	0.00	0.00	0.00	0.00	0.00	0.00
Cu	Ex -	19.83	19.65	24.55	10.38	11.26	9.68
	OMn -	76.73	78.91	80.74	51.21	52.67	47.02
	OM -	73.45	66.43	72.90	89.57	92.40	84.88
	AOfFe -	17.68	18.59	16.40	24.24	27.34	25.70
	COFe -	36.45	35.72	31.16	33.72	36.82	35.90
	Min -	31.89	30.98	27.70	23.51	24.42	23.51
Zn	Ex -	43.11	41.03	32.02	14.99	13.82	8.41
	OMn -	17.10	15.31	11.89	9.69	9.93	6.96
	OM -	14.28	23.63	17.42	33.97	33.03	24.12
	AOfFe -	4.03	3.75	3.75	6.92	7.49	6.51
	COFe -	20.76	23.66	22.42	24.44	25.60	25.56
	Min -	153.60	165.08	199.20	178.91	140.26	131.69

Notes: The data were the average values of triplicates, mg/kg. Ex -, OMn -, OM -, AOfFe -, COFe - and Min - stand for the speciation of exchangeable (including water-soluble), manganese oxide-occluded, organically bound, amorphous Fe oxide occluded, crystalline Fe oxide occluded and mineral, respectively

Compared to Cd, Cu presented higher values in residual soils and showed a less release. According to the speciation content of manganese oxide-occluded and organically bound, Cu was significantly affected by the content of CEC and organic matter in soil. Compared to Zn, the content of Cu in residual soils was lower and mainly decided by its background values in soils.

After continuously extracting, the content of metals in residual soils decreased and the unstable speciation content increased significantly with the acidity increasing of simulated acid rain (Table 3). The exchangeable fractions of Cd, Cu, and Zn in CRS and CYRS increased extensively, especially for Cd and Zn. The main speciation of Cd in residual polluted soils was exchangeable forms, and the content of Cd was 43.44–62.56 mg/kg in CRS and 10.72–22.83 mg/kg in CYRS, respectively. The secondary form was Mn oxide-occluded and organically bound. For Zn, the most important fractions existed in mineral and exchangeable in CRS, accounting for 153.60–199.20 mg/kg and 32.02–43.11 mg/kg, respectively; but in CYRS, the form of Zn existed mainly in mineral and organically bound, accounting for 131.69–178.91 mg/kg and 24.12–33.97 mg/kg, respectively. However, the rate of exchangeable Cu was not obviously different, and the most part of Cu existed organically bound and Mn oxide-occluded forms, and the contents were 66.43–73.45 mg/kg and 76.73–80.74 mg/kg in CRS, and 84.88–92.40 mg/kg and 47.02–52.67 mg/kg in CYRS. These indicated that active forms of Cu were released by simulated acid rain, and unstable forms were activated. Most part of Cu in residual was unstable and its ecological effects were increased probably. In short, the speciation of metals was generally changed, showing heavy metals in these soils to be easily transferred by acid rain.

Due to ion exchange of cations in acid rain with soil heavy metals, or due to some other chemical processes in soil, acid rain would lead to release of metals from soils and motivate transferring of metals speciation, and probably cause more serious harmful effects on vegetation.

3 Discussion

The effects of acidity and ion concentrations of acid rain on metals in acidic soils indicated that heavy metal concentrations in soil solutions were controlled by pH of acid rain and ion exchange reaction, the pH of acid rain was the main factor for the mobility and releases of heavy metals in soils. If heavy metals were absorbed into the soil or released from the soil, the complex reaction should happen among heavy metal ions, basal cations and anions in soil. However, it was not clear for the reaction between metal ions and soil complex sites. So it was not easy to explain the chemical mechanisms of different metals. As we have known, the pH of acid rain was the main factor for the mobility and speciation of metals in soil, but it was difficult to decide which one was the other controlling factor for the mobility and chemical speciation of heavy metals in soil. It might be mainly determined by the factors such as H^+ , Al^{3+} or anions. With decreasing pH and increasing ion concentrations of simulated acid rain, the releasing ratio of Cd, Cu, and Zn in the soils was increased. Therefore, the effects of acid rain not only resulted in the release of soil heavy metals, but also led to the release of Ca^{2+} and Mg^{2+} and toxic Al^{3+} (Liao,

1994; 1997), meaning that soil acidification and contamination of heavy metals happened simultaneously and the ecological effects were increased significantly.

Decreasing pH of simulated acid rain, the releasing potential of metals increased in acidic soils, and moved to the unstable forms, especially for Cd. So the speciation of metals was useful for us to understand the chemical mechanisms in acidic soils by acid rain. However, it is unclear about diffused in the kinetics and reaction mechanisms on speciation transferring of metals in soils. Maybe, the column experiment or field plots could catch more available information to demonstrate the problems. And more, to explore the environmental hazard behavior of metals in soils from bio-availability, mobility and environmental points of view, further field investigation is required.

4 Conclusions

On the basis of this batch experiment, acid rain was mainly factor for the release of Cd, Cu, and Zn in the tested soils (CRS and CYRS). The releasing potential of Cd, Cu, and Zn was $Cd > Zn > Cu$, which indicated that Cd had higher potential risk on environment. With pH decreasing and ion concentration increasing of simulated acid rain, concentrations of Cd and Zn were higher than that of Cu in the soils affected by acid rain. The main fraction of soil Cd was exchangeable in residual CRS and CYRS. The unstable Cu was transferred immediately and the most part of Cu existed mainly in organically bound forms, and implied mobilization potential of this element affected obviously by acid rain. Zn existed mainly in mineral form due to the high background value.

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