Solid/solution partitioning and speciation of heavy metals in the contaminated agricultural soils around a copper mine in eastern Nanjing city, China

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Abstract

Solid/solution partition coefficient (K_d) and speciation of soil heavy metals can be used for predicting their environmental risks. The K_d values and solution speciation of soil Cu, Cd and Zn were analyzed in 40 samples of contaminated agricultural soils around Jiuhua copper mine in eastern Nanjing city, China. The K_d ranges (and mean values) for soil Cu, Cd and Zn are 703–7418 (3453), 37.3–3963 (940) and 319–17 965 (7244) L kg^{-1}, respectively, showing a large variability both for metals and soils. The results of differential pulse anodic stripping voltammetry (DPASV) indicates that 95.6% solution Cu is bound to dissolved organic ligands. About half of the dissolved Zn is DPASV-labile at pH < 6, while 92.1% solution Zn is in the form of organic complexes at pH > 6. DPASV-labile Cd is ranged from 22.6 to 98.7% with the mean value of 56.3%. Multiple linear regressions indicate that K_d, the dissolved and DPASV-labile concentrations of Cd and Zn are mostly influenced by the soil solution pH with R^2 of 0.50, 0.59 and 0.63, respectively for Cd, and 0.58, 0.72 and 0.64, respectively for Zn. Considering the second parameter of corresponding soil metal, the linear relationships of K_d with pH were improved with R^2 of 0.70 and 0.73 for Cd and Zn, respectively. However, the solubility of soil Cu was insensitive to pH. Only SOC shows a weak relationship to the dissolved Cu with R^2 of 0.21. As for its K_d, total soil Cu is the most significant factor. But for DPASV-labile Cu, no soil parameters were found to be good predictors.
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1. Introduction

As a result of increased input from industry, traffic and agriculture, the average soil heavy metal concentration in some industrialized areas has increased considerably [1], especially in the vicinity of mining and metallurgical industries [2–5]. It is accepted that total soil heavy metal concentration alone is not a good measure of bioavailability to determine the potential environmental and human health risks from soil contamination [6,7]. Therefore, the evaluation of the potential risks and toxicity of metals in soils requires an assessment of the proportion of the mobile and possibly bioavailable forms in the total metal. The relatively simple partitioning of metal between the fractions bound to soil solids and the part that is dissolved in the soil solution has been used [8,9]. This partitioning approach assumes that

dissolved metals are mobile and could possibly be taken up by adjacent plant roots or be detrimental to soil biota. The dissolved metal pool also reflects the soil metal fraction that could potentially be leached from the soil and contaminate groundwater or surface water.

Solid–solution partitioning is usually evaluated using the ratio of metal concentration in the particulate to liquid phases of soil, i.e. the partition coefficients (K_d) [10]. Although somewhat simplistic, the K_d approach is easy to integrate into various chemical models and allows estimation of metal dissolved in soil solution and prediction of metal mobility as well as potential leaching losses. For example, partition coefficients have been used to predict the maximum permissible total concentration of various toxicants in soil on the basis of the Dutch water quality criteria [11].

Risk assessment procedure usually requires an understanding of the transport of contaminants from source to receptor. Since heavy metals can be transported within soil in different forms, including free metal ions (hydrated ions), inorganic and organic

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complexes and those adsorbed to colloids, to estimate the mobility of metals in all these forms should be taken into account when K_d is measured [12]. Recent ecotoxicological studies revealed that metal speciation in the solution phase is one of the key factors that regulates metal uptake by plants as well as toxicity for soil and aquatic organisms [13]. For instance, many authors have shown unequivocally that metal toxicity in aquatic systems is controlled by free metal ions (free ion activity model, FIAM), such as Zn and Cu [14]. Except Cd, FIAM has also been approved in soil system, mainly for Cu [15–19].

The speciation discussed in this paper is not an attempt to categorize various forms of solid-bound metals, which is termed as fractions recommended by IUPAC [20], but instead tries to distinguish the species and amounts of metals dissolved in the soil solution. Some analytical techniques have been used to determine heavy metal speciation in aqueous solutions. They include potentiometric techniques utilizing ion-selective electrodes (ISE) [21], ion-exchange resins [22], cation-exchange membrane technique [23], chromatographic methods [24], competitive chelation [25], filtration and ultrafiltration [26], and dialysis [27]. Potentiometric techniques for the determination of free heavy metal ions were, until recently, mainly restricted to the Cu-ISE, especially in soil solution [16]. A potential drawback for dialysis techniques is that they may perturb the equilibrium in the sample solution if the ratio of sample solution to receiving dialysis solution is low. Chromatography techniques are mainly applied to the metals of varied valences [28] or to organometallic compounds [29]. In summary, determination of metal speciation in soil solution is not easy, with many analytical techniques suffering from chemical interferences, poor detection limits, and disturbance of solution equilibrium. Computational techniques rely on chemical equilibrium models such as GEOCHEM, MINEQL+, MINTEQA, or WHAM [30], where metal speciation is calculated using known solution composition and making significant assumptions regarding the interaction of metals with DOC. But some models may be limited by the estimate of the proportion of the total organic matter attributed to metal binding. Others are disadvantaged by the need for humic- and fulvic-metal stability constants, which are difficult to define and vary from soil to soil.

However, voltammetric techniques have been successfully applied to metal speciation analysis [31–33]. Differential pulse anodic stripping voltammetry (DPASV), which as a classical method were initially used for speciation analysis of metals in water [34], has been introduced into the soil solution analysis recently, although mainly for Pb, Cd and Zn [35–37]. DPASV-labile metal represents the fraction of dissolved metal determined by DPASV. This fraction includes the free hydrated metal ions and the labile metal complexes, which dissociate very rapidly to yield the free metal ions [38]. DPASV involves two steps. The first step is the deposition of metal ions from the sample solution on a mercury electrode by reduction at negative (cathodic) potential. The amalgamated metals are measured in the second (stripping) step by applying a positive (anodic) potential scan and measuring the peak currents produced as the system reaches the oxidation potential of the metals. The process of metal accumulation in an organism by dissociation of labile

metals at a membrane surface, facilitated diffusion of the metal through the membrane and deposition in the cytosol, has obvious similarities to the process of DPASV electrodeposition [38]. The metal fraction that is bioavailable has been correlated well with the concentration of the DPASV-labile metal [18,38–40].

In this study, the solid/solution partitioning and speciation of heavy metals in the soils sampled around a Cu mine were explored, as well as their correlation with soil basic characteristics. For this purpose, the solid–solution partition coefficients (K_d) for Cu, Cd and Zn in the contaminated agricultural soils were analyzed, the metal speciation in the soil solutions were determined by DPASV, and the effects of simple soil properties (such as pH, total soil metal concentration, soil organic carbon, and clay content) on the solid–solution partitioning and speciation of Cu, Cd and Zn were evaluated.

2. Materials and methods

2.1. Soil samples

The site of this study is Jiuhua copper mine, which locates at latitude 32°04′N and longitude 119°05′E, in eastern Nanjing city, China. The mine stopped its mining activities 5 years ago. There are several villages closely distributed at the foot of the mine hill, and most of the farmlands around the mine are still cultivated with crops such as rice, vegetables and pastures. Forty agricultural soil samples (Luvisol) around the mine were collected from the surface layer (0–15 cm) in the autumn of 2004. The sampling map is shown in Fig. 1. Each soil sample was obtained by combining four subsamples within 3.0 m × 3.0 m area. The soils were air dried, and ground in an agate mortar to pass through a 2.0 mm sieve for analysis.
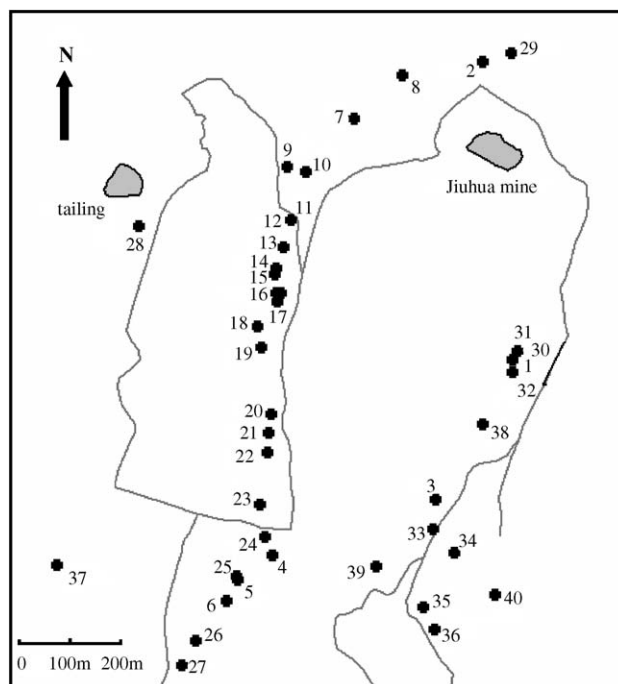

Fig. 1. The map of the soil sampling sites.

2.2. Analytical procedures

The solubility and speciation of metals were determined using 1:2 soil extracts with $10\,mmol\,L^{-1}$ KNO_3 to eliminate the effects of other salts on the total solution ionic strength. Taking example for one soil sample, 25 g of soil and 50 mL of $10\,mmol\,L^{-1}$ KNO_3 were added to a centrifuge tube. The tube was shaken for 2 h at 25 °C and then centrifuged for 5 min. The supernatant fluid was separated from the soil by filtering through a filter paper. The filtrates were passed through 0.22 μm cellulosic membranes before used to analyze the dissolved and labile Cu, Cd, and Zn. The electrical conductivity (EC), pH, and dissolved organic carbon (DOC) were measured also. A part of the extract was acidified with HNO_3 to determine the total dissolved metals.

The pH was measured using a pH meter (REX, pHS-3B) with a glass electrode. EC was measured with a conductometer (REX, DDS-11A). DOC was measured by a colorimetry at $\lambda = 490\,nm$ after oxidized by a Mn(III)–pyrophosphate complex in the presence of concentrated H_2SO_4, and calibrated by the absorbance of oxalic acid solutions after oxidized [41]. DPASV measurements were performed with a CHI 660A electrochemical workstation (Shanghai Chenghua Instrumental Company, Shanghai, China). The electrolytic cell made of poly (methyl methacrylate) was equipped with a three-electrode system. A hanging mercury drop electrode (HMDE) was used as a working electrode. The reference electrode was a saturated Ag/AgCl electrode and the auxiliary electrode was a Pt-coil. It is important to avoid any chloride leakage from the reference electrode into the test solution, because chloride seriously suppresses the stripping wave of Cu. So a double-junction reference electrode with a low leakage rate was used. The outer filling solution of the reference electrode $(0.01\,mol\,L^{-1}$ $KNO_3)$ was changed daily. Oxygen dissolved in solution interferes with Cu determination severely, so the samples were deaerated by bubbling pure N_2 (99.999%) for 20 min before determination. And the cell was sealed so that a positive pressure of nitrogen could be maintained over the surface of the samples.

Theoretically, Cu, Cd and Zn can be determined simultaneously by DPASV, but sometimes Zn–Cu intermetallic compounds maybe formed inside the mercury drop if Zn and Cu are codeposited. So we measure Cu alone, Cd and Zn together. As for Cu, the detection parameters of −0.4 V reduction potential, 90 s deposition time (with stirring) followed by a 30 s homogenization period (without stirring) were used. Cu stripping was then done by scanning potential (without stirring) from −0.45 to +0.15 V and the Cu current peak appeared at +0.045 V. As for Cd and Zn, the parameters of a reduction potential of −1.3 V, 1 min deposition time and 30 s rest period were used. Two current peaks for Zn and Cu appeared at −0.985 and −0.565 V, respectively, in the voltammograms. The DPASV-labile metal was quantified using peak height calibration of their corresponding nitrate salts solutions $(0.01\,mol\,L^{-1}$ $KNO_3)$. All voltammetric measurements were made in a clean room controlled at 20 °C. Total dissolved Cu and Zn were determined by atomic absorption spectrometry (AAS, Hitachi 180-80), and Cd using AAS-graphite furnace.

The total metal concentration of the soils was analyzed by digesting the soils with a mixture of HF, $HClO_4$ and HNO_3 with a ratio of 3:1:1 at 240 °C and determined by AAS with corresponding wavelengths recommended by the spectrophotometer manufacturer. The quality assurance of the analytical procedure was checked by routinely analyzing certified reference materials (GSS-1 and GSS-6) and including blanks in digestion batches. The certified standard samples were included at every stage of analysis. The variation in determining the concentration of the standard samples was 95.9 ± 1.3, 97.5 ± 2.8 and $98.3 \pm 7.7\%$ for Cu, Cd and Zn, respectively. Soil organic carbon (SOC) was determined by titration with $FeSO_4$ after oxidized by $K_2Cr_2O_7$ and concentrated H_2SO_4 in the condition of external heat. Clay content was determined by a LS 230 laser diffraction particle analyzer (Beckman Coulter).

2.3. Data statistic

The data are summarized using mean values, standard deviations, coefficients of variation (ratio of the standard deviation to the mean) and the ranges. Statistical analyses (linear regressions and stepwise multivariate general linear models) were carried out using SAS software. The K_d, soluble and DPASV-labile concentration of soil metals were analyzed by multiple linear regressions to evaluate the effects of soil properties on metal partitioning and speciation. Model was performed by stepwise selection with a significant level of 0.05 for variables. All data used for regression were log-transformed in order to normalize their distribution.

3. Results and discussion

The samples cover a wide range of total soil metal concentration with Cu from 280 to $1931\,mg\,kg^{-1}$, Cd from 0.13 to $2.84\,mg\,kg^{-1}$, and Zn from 27.4 to $704\,mg\,kg^{-1}$. The Cu, Cd and Zn concentrations in the natural soil were 23.4, 0.11, and $71.8\,mg\,kg^{-1}$, respectively. Soil solution pHs vary from 5.45 to 7.87. The SOC content is in the range of 1.3–3.1%, DOC varied from 6.4 to $109\,mg\,C\,L^{-1}$ and the clay content ranged from 9.3 to 17.3%. The statistic data of the concentration of total soil metal, soluble (KNO_3 extraction) and DPASV-labile metal, soil solution pH, soil clay content, DOC and SOC content are summarized in Table 1.

3.1. Soluble soil metal concentration

Soil solution is normally obtained either by extraction with a dilute salt solution (soil/solution = 1:2) or using the saturated-paste technique [19], or from field moist soils, using centrifugation and/or filtration [36]. In the present study, soil samples were extracted with $10\,mmol\,L^{-1}$ KNO_3 solution similar to [42]. The KNO_3 was necessary to maintain a minimum and constant ionic strength for reproducible DPASV determinations.

Dissolved metal concentration varied from 147 to $701\,\mu g\,L^{-1}$ for Cu, 0.38 to $24.8\,\mu g\,L^{-1}$ for Cd and 20.2 to $1269\,\mu g\,L^{-1}$ for Zn, covering a range of two to three orders of magnitude. To identify the parameters that best predicted log (dissolved metal),

Table 1
The statistical data of the soil samples and the corresponding soil extracts by 10 mmol L^{-1} KNO$_3$

Parameters	Units	Minimum	Maximum	Median	Mean	S.D.	CV
pH		5.45	7.87	7.38	7.22	0.57	0.08
Clay	%	9.30	17.3	13.3	13.6	1.76	0.13
SOC	%	1.30	3.10	2.20	2.20	0.39	0.17
DOC	mg C L^{-1}	6.40	109	41.7	43.1	26.8	0.62
Total soil Cu	mg kg^{-1}	280	1931	1085	1062	330	0.31
Total soil Zn	mg kg^{-1}	27.4	704	314	321	142	0.44
Total soil Cd	mg kg^{-1}	0.13	2.84	1.20	1.20	0.60	0.49
Dissolved Cu	μg L^{-1}	147	701	322	340	128	0.38
Dissolved Zn	μg L^{-1}	20.2	1269	40.9	113	220	1.95
Dissolved Cd	μg L^{-1}	0.38	24.8	1.30	3.20	4.70	1.47
DPASV-labile Cu[a]	μg L^{-1}	0.7	33.5	11.7	12.6	9.2	0.73
DPASV-labile Zn	μg L^{-1}	0.4	735	2.9	36.9	132	3.58
DPASV-labile Cd	μg L^{-1}	0.5	15.2	2.1	3.5	4.0	1.17

Mean: arithmetic mean; S.D.: standard deviation; CV: coefficient of variability; $N = 40$.

[a] N for DPASV-labile Cu, Zn and Cd are 23, 31 and 13, respectively, because the other samples contained the concentration below the detection limit.

Table 2
Dataset of the soil samples and the corresponding soil extracts by 10 mmol L^{-1} KNO$_3$

No.	Soil						0.01 M KNO$_3$ soil extract				
	pH	OM (%)	Clay (%)	Cu (mg kg^{-1})	Zn (mg kg^{-1})	Cd (mg kg^{-1})	pH	EC (ms cm^{-1})	Cu (μg L^{-1})	Zn (μg L^{-1})	Cd (μg L^{-1})
1	6.71	3.2	13.0	922	492	1.7	7.11	1.14	258	104	5.1
2	7.76	3.9	13.6	1091	511	1.9	7.72	1.20	360	28	1.2
3	6.48	2.6	11.6	847	704	2.8	6.13	1.10	253	392	8.2
4	6.89	3.5	16.2	986	242	0.9	6.73	1.15	147	50	1.3
5	7.14	4.9	13.8	1931	460	1.4	7.49	1.32	545	58	1.7
6	7.40	4.3	12.9	978	193	0.6	7.64	1.53	442	35	1.1
7	6.87	3.9	13.7	1752	288	1.3	6.98	1.23	236	41	0.8
8	6.48	3.7	15.1	1089	289	0.4	6.91	1.20	322	128	2.3
9	7.04	4.9	9.3	1558	246	0.8	7.23	1.24	349	33	0.6
10	7.99	3.8	12.6	948	217	1.6	7.65	1.21	267	32	0.5
11	7.96	3.3	11.7	1399	344	2.4	7.66	1.41	268	22	0.6
12	7.52	3.9	11.9	1136	239	1.4	7.51	1.42	271	24	1.0
13	7.88	4.3	12.5	1350	278	1.1	7.44	1.40	331	21	1.3
14	6.93	4.7	11.8	1268	199	1.4	7.26	1.74	334	36	2.3
15	6.83	4.6	12.3	1063	142	0.7	7.20	1.86	225	34	1.3
16	6.98	4.2	13.2	1085	148	0.7	7.20	1.61	209	23	0.9
17	6.68	3.4	12.4	1032	152	0.9	7.35	1.80	176	57	1.5
18	7.88	4.4	13.7	1414	314	1.6	7.70	1.20	574	20	0.8
19	6.23	3.5	13.2	1105	179	0.3	7.08	2.25	325	212	7.0
20	6.92	4.1	12.2	1213	342	1.4	7.64	2.34	361	95	4.6
21	7.19	4.0	12.4	1342	415	1.3	7.47	1.46	367	52	1.3
22	6.99	3.3	10.5	1203	389	1.3	7.61	1.64	311	53	2.4
23	6.25	3.5	13.3	1251	277	0.6	6.81	2.22	250	210	5.8
24	6.68	4.3	14.1	1089	299	1.2	7.41	1.40	227	54	2.8
25	6.77	4.7	15.8	1240	333	0.9	6.95	2.02	697	80	1.0
26	7.24	5.3	14.8	1078	351	1.3	7.52	1.76	497	24	1.3
27	6.91	3.5	17.3	966	435	1.2	7.36	2.42	249	41	3.5
28	7.64	4.2	14.6	989	27	0.1	7.62	1.33	304	22	0.6
29	7.87	2.3	16.9	668	156	0.5	7.71	1.26	181	20	0.5
30	8.55	4.0	13.3	1073	327	1.6	7.87	1.21	701	23	1.0
31	7.71	3.9	12.7	1126	453	1.5	7.80	1.26	443	30	1.2
32	6.36	3.3	14.1	802	448	1.2	6.38	1.21	280	176	6.3
33	6.86	3.9	12.8	1138	657	2.1	6.96	1.19	379	86	2.5
34	7.58	3.7	13.2	854	417	1.8	7.66	1.19	285	27	0.8
35	6.28	3.4	15.2	674	349	1.2	7.56	1.36	394	22	1.0
36	5.54	3.8	15.7	1087	504	2.0	6.26	1.37	417	631	15.4
37	6.64	3.9	13.6	660	405	0.9	5.45	1.81	440	1269	24.8
38	8.03	2.7	13.4	280	150	0.4	7.64	1.17	399	28	0.9
39	7.48	5.1	17.1	355	235	0.9	7.38	1.76	293	34	0.4
40	5.61	3.2	16.6	430	242	0.5	5.60	1.68	237	195	11.7

Table 3
The linear regression equations of log (dissolved metal) ($\mu g \, L^{-1}$) against soil solution pH, log (total metal), log SOC and log (clay content) ($N = 40$)

Log (dissolved)	Constant	Parameters	R^2
Cu=	2.20 ± 0.10 (<0.0001)	$+0.88 \pm 0.28$log SOC (0.0033)	0.205 (0.0033)
Cd=	4.49 ± 0.57 (<0.0001)	-0.59 ± 0.08pH (<0.0001)	0.593 (<0.0001)
Zn=	6.44 ± 0.47 (<0.0001)	-0.65 ± 0.07pH (<0.0001)	0.723 (<0.0001)
Zn=	5.46 ± 0.66 (<0.0001)	-0.62 ± 0.06pH (<0.0001) $+0.31 \pm 0.15$log (total Zn) (0.0461)	0.752 (<0.0001)

The values in parentheses are the p (level of significance) values for individual parameters.

multiple regressions were performed using a stepwise selection of the following parameters: pH, log (total metal), log SOC and log clay, which are listed in Table 2. Thus, a better empirical understanding of the soil factors that influence log (dissolved metal) can be developed. The results are shown in Table 3. For dissolved Cu, except log SOC, no other variable met the significant level of 0.05. For Cd, only pH met this level. For Zn, both pH and log (total Zn) met this level.

The dissolved metal has been shown previously to be a function of pH, total soil metal, and the metal adsorption capacity of soil. Recently, a competitive adsorption model to predict trace metal solubility in contaminated soils was proposed: log (dissolved metal) $= a + b$ pH $+ c$ log (total metal) $+ d$ log SOM [43]. It was derived from a semi-mechanistic approach, which assumes that free metal ions and H^+ compete for adsorption sites of the soil. Such a model has been applied to predict the solubility of Cu ($R^2 = 0.611$), Cd ($R^2 = 0.884$) and Zn ($R^2 = 0.618$) in a wide range of soils [43], which are obtained from a compiled dataset incorporating both spiked and field-collected contaminated soils.

In this study, the linear relationship of dissolved Cd and Zn with soil solution pH alone could explain up to 59.3% of variability in log (dissolved Cd) and 72.3% in log (dissolved Zn). However, the regressions of Cd and Zn were not improved significantly by further considering the parameters of log SOM and/or log clay. The results are similar to other studies which had reported that pH was more important than any other single property in predicting Zn and Cd solubility while SOM did not have much effect [44,45], and sometimes there was poorer correlation to total [46]. Copper showed different behaviors from Cd and Zn. Only log SOC explained 20.5% of variability in log (dissolved Cu). There are no good regressions between log (dissolved Cu) and the soil pH or total Cu, which is consistent with the known insensitivity of Cu solubility to pH [47,48].

3.2. Solid/liquid metal partitioning

A partition coefficient, K_d (total soil metal concentration/dissolved metal concentration) is usually used to describe the distribution of metal between the solid and aqueous phases

in environmental risk and fate models. K_d also can be defined as the ratio of exchangeable metal relative to metal in soil solution [49], the ratio of sorbed metal to dissolved metal under equilibrium conditions [50], or the ratio of the total soil metal relative to metal in soil water extracts [19]. The fractions of soil metal dissolved in solution varied widely. In many cases, poor relationships were observed between soluble metals (mg L^{-1}) and total soil metals (mg kg^{-1}) because of their dependence on the kinds of metal as well as on the soil characteristics. Thus, the study of soil–water partitioning of heavy metals has become a hot issue [50,51].

A number of studies have tried to explain the mobility of heavy metals in soils based on the multiple regression analysis of soluble metal concentration versus soil properties such as total soil metal concentration, soil pH, soil organic matter (SOM) content, cation exchange capacity (CEC), texture, $CaCO_3$ content, phosphorus content, and Fe and Al oxides [46,52,53]. Most of these multivariate regression exercises aim to infer the relationships between metal solubility and soil properties, while some studies aim to develop predictive metal solubility algorithms. And some authors have successfully shown a correlation of metal solubility with some soil physicochemical characteristics [53,54]. In a critical review on partitioning of metals in contaminated soils, total soil metal concentration, solution pH, and SOM in a semi-mechanistic model were used to predict dissolved metal concentration in the contaminated soils [43]. Solid–solution partitioning study on real contaminated soils, however, is a neglected area.

In the present study, K_d (L kg^{-1}) is calculated as the ratio of total soil metal (mg kg^{-1}) relative to that extracted with 10 mmol L^{-1} KNO_3 (mg L^{-1}). The ranges and mean values for K_d in this study (Cu 703–7418, 3453; Cd 37.3–3963, 940; Zn 319–17 965, 7244 L kg^{-1}, see Table 4) are considerably lower than those reported (Cu 6.8–82 850, 4799; Cd 0.44–192 000, 2869; Zn 1.4–320 000, 11 615 L kg^{-1}) in a compilation of 70 studies collected from different polluted sites [43], but the indicated order of metal mobility in the soils (Cd > Cu > Zn) is consistent.

The K_d values cover three orders of magnitude for Cd and Zn and two orders for Cu. A multiple linear regression was used

Table 4
The statistical data of soil metal partitioning coefficients (K_d, L kg^{-1}, $N = 40$)

Element	Minimum	Maximum	Median	Mean	S.D.	CV (%)	log (mean)
Cu	703	7418	3396	3453	1451	0.42	3.54
Cd	37.3	3963	720	940	863	0.92	2.97
Zn	319	17965	6739	7244	5085	0.70	3.86

Table 5
The linear regression equations of log K_d (L kg^{-1}) against soil solution pH, log (total metal), log SOC and log (clay content) ($N = 40$)

Log K_d	Constant	Parameters	R^2
Cu=	0.93 ± 0.44 (0.0438)	$+0.86 \pm 0.15$ log (total Cu) (<0.0001)	0.468 (<0.0001)
Cu=	0.70 ± 0.41 (n.s.)	$+1.04 \pm 0.15$ log (total Cu) (<0.0001) $- 0.91 \pm 0.31$ log SOC (0.0060)	0.567 (<0.0001)
Cd=	-1.67 ± 0.72 (0.0269)	$+0.61 \pm 0.10$ pH (<0.0001)	0.498 (<0.0001)
Cd=	-1.52 ± 0.57 (0.0114)	$+0.59 \pm 0.08$ pH (<0.0001) $+ 0.82 \pm 0.17$ log (total Cd) (<0.0001)	0.696 (<0.0001)
Zn=	-0.29 ± 0.56 (n.s.)	$+0.56 \pm 0.08$ pH (<0.0001)	0.576 (<0.0001)
Zn=	-2.46 ± 0.66 (0.0006)	$+0.62 \pm 0.06$ pH (<0.0001) $+ 0.69 \pm 0.15$ log (total Zn) (<0.0001)	0.728 (<0.0001)

The values in parentheses are the p (level of significance) values. n.s.: no significance for $p > 0.05$.

to predict log K_d by a stepwise selection of the parameters pH, log (total metal), log SOC and log clay. The results are shown in Table 5. For Cu, except log (total Cu) and log SOC, no other variable met the significant level of 0.05. The regression equation could explain 56.7% of the variability of the K_d, which is better than those described by others in which regressions only explained 42% of the variability of the K_d with pH and DOC [17], 28.8% with pH only, 41.9% with pH and SOM [43], 21% with pH alone, 27% with pH and SOC [46].

For Cd and Zn, both pH and log (total metal) met the significant level of 0.05, as shown in Fig. 2. The linear relationship between log K_d and pH explains 49.8% and 57.6% of the variability in K_d values for Cd and Zn, respectively. The results are consistent with the studies in which K_d values for Cd and Zn can be predicted by soil pH [42,50,55]. The linear regression coefficients of log K_d with soil pH in this study (Cd 0.61, Zn 0.56) are comparable to those reported in previous metal partitioning studies (Cd 0.59 [42]; Zn 0.62 [43]). In many other cases, the use of second parameter of total soil metal content and/or organic matter content could improve the predictive capacity of the regression model [46,51]. In this case, the variability in K_d values could be improved to 69.6% for Cd and 72.8% for Zn by using log (total soil metal) as a second parameter.

3.3. Speciation of metals in the extracted soil solution

Heavy metals exist in soil solution as free metal ions, inorganic and organic complexes which bound to various ligands such as Cl$^-$, SO$_4^{2-}$, PO$_4^{3-}$ and dissolved organic ligands [56]. The proportion of the soluble metal bound to soluble organic ligands can be estimated by simply subtracting inorganic metal species (as DPASV-labile metal) from the soluble metal. The concentrations of DPASV-labile Cu, Zn and Cd and the correlations with their respective soluble metal are presented in Fig. 3. It should be pointed out that only part of the soil samples was included in the figure, because the others had the DPASV-labile metal concentration below the detection limit.

The results show that about 95.6% of the soluble Cu existed as non-labile forms. Organic complexes of Cu were found to be the most dominant species, ranging from 88.4 to 99.8%. For Zn, about half of the dissolved Zn was DPASV-labile at pH < 6. But organic complexes became important and dominated completely at pH > 6, ranging from 76.1 to 99.3% with the mean value of 92.1%, as shown in Fig. 4. For Cd, DPASV-labile Cd is in the range of 22.6–98.7% with the mean value of 56.3%. It was earlier demonstrated that Cu was almost exclusively present

in organically complexed form in soil solutions [19,46,57] and that Zn–DOM complexes were quite significant in soil solutions [19,36]. However, the results of Cd speciation in soil solution varied greatly in references. For example, most of the dissolved Cd was free one in Ref. [23]; free Cd^{2+} was accounted for 65% of the dissolved Cd in Ref. [58], 22–86% (mean 49%) for con-
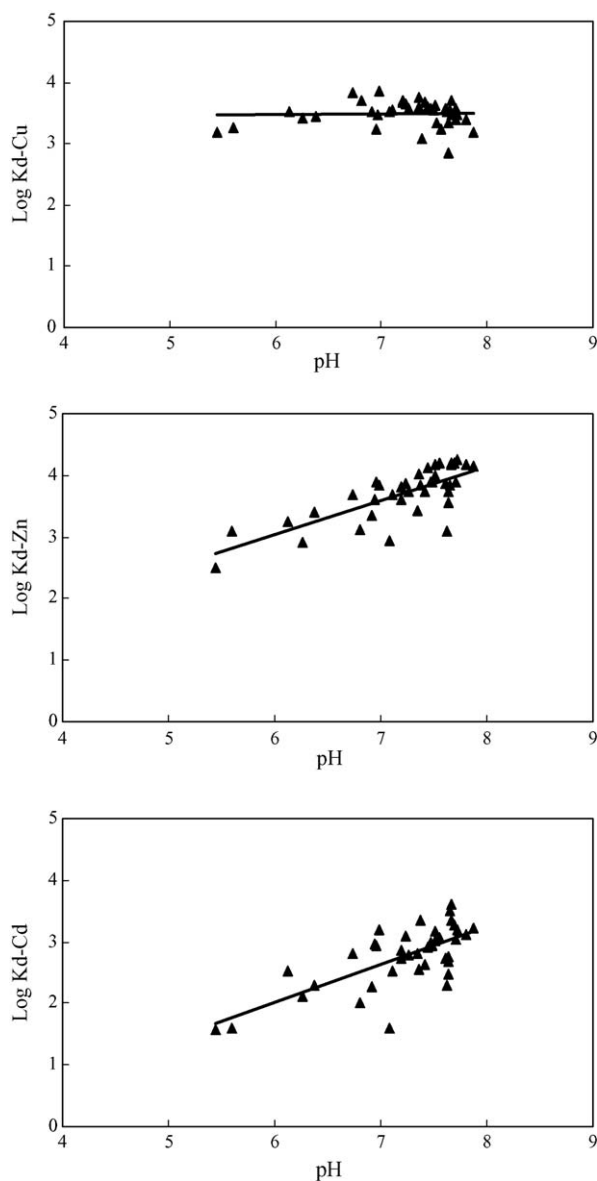

Fig. 2. Linear regressions of log K_d for Cu, Zn and Cd against soil solution pH.

Table 6
The linear regression equations of DPASV-labile metal concentration (μg L^{-1}) against soil solution pH, log (total metal), log SOC and log DOC

Log (DPASV-labile)	Constant	Parameters	R^2	N
Cu=	-0.81 ± 1.64 (n.s.)	-0.52 ± 0.30log DOC (0.0976) $+ 0.35 \pm 0.23$pH (0.1431)	0.185 (0.1295)	23
Cd=	5.39 ± 1.18 (0.0008)	-0.73 ± 0.17pH (0.0013)	0.626 (0.0013)	13
Zn=	7.65 ± 0.98 (<0.0001)	-0.98 ± 0.14pH (<0.0001)	0.640 (<0.0001)	31

The values in parentheses are the p (level of significance) values. N is the number of data points.
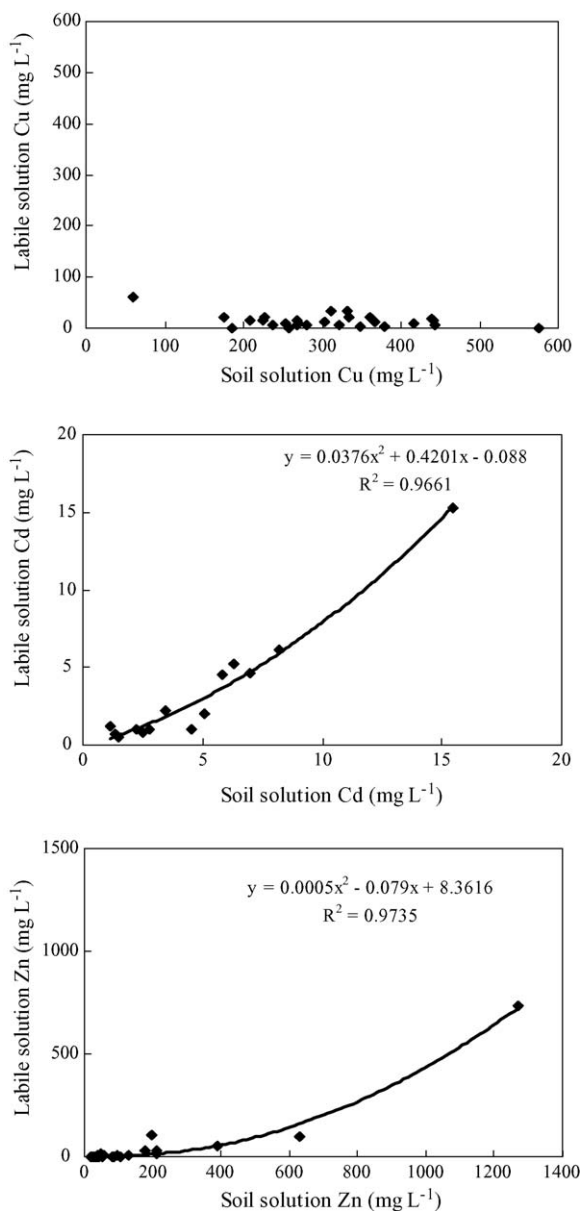
Fig. 3. Dependence of the DPASV-labile Cu, Zn and Cd concentration on corresponding soluble metals concentration.
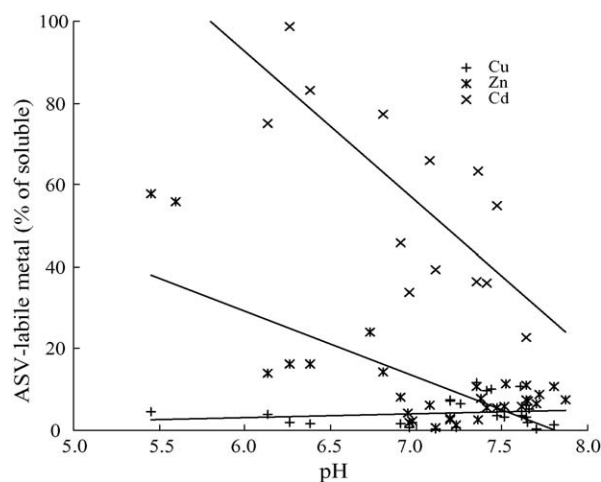

Fig. 4. Dependence of log (DPASV-labile metal/soluble metal) on soil solution pH.

did not improve these regressions significantly. As shown in the equations, DPASV-labile Cd and Zn are mainly influenced by solution pH, similar to other reports [46,58,59]. And pH alone could explain 63 and 64% variability in DPASV-labile Cd and Zn, respectively. DOC may influence the soil solution speciation. Increasing concentration of DOC can increase the formation of organic metal complexes, while the solubility of metals may also increase [37,60].

4. Conclusions

Solid/solution partition coefficient (K_d) and speciation of soil heavy metals have been successfully used to predict the environmental risks in the contaminated agricultural soils around Jiuhua copper mine in eastern Nanjing city, China. The concentrations of DPSAV-labile Cu, Zn and Cd in the soils are different. Although soluble Cu concentration is high, the free Cu ions concentration with mean value of 12.6 μg L^{-1} is low, because most of Cu is bound to SOC. While the ratio of DPASV-labile Cd to total soluble Cd is high, but the free Cd concentration with mean value of 3.5 μg L^{-1} is low due to the lower total soluble Cd concentration in the soil. However, for soil Zn, it has a high concentration of soluble Zn and also a high ratio of DPASV-labile Zn to soluble one with the average DPASV-labile Zn concentration of 36.9 μg L^{-1}. Because the critical values of free metal ions in soil solution are not available until now, it is necessary to further explore the relationship of free metal ions in soil solution with their environmental effect.

taminated soils, and 59–102% (mean 75%) for agriculture soils were found in Ref. [46].

Multiple regression analysis of log (DPASV-labile metal) with soil pH, log (total metal) and log SOC or log DOC is shown in Table 6. For Cu, no variable met the significance level of 0.05. For Cd and Zn, only pH met this level. Adding other parameters

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