

Chemodynamics of heavy metals in long-term contaminated soils: Metal speciation in soil solution

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Abstract

The concentration and speciation of heavy metals in soil solution isolated from long-term contaminated soils were investigated. The soil solution was extracted at 70% maximum water holding capacity (MWHC) after equilibration for 24 h. The free metal concentrations (Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}) in soil solution were determined using the Donnan membrane technique (DMT). Initially the DMT was validated using artificial solutions where the percentage of free metal ions were significantly correlated with the percentages predicted using MINTEQA2. However, there was a significant difference between the absolute free ion concentrations predicted by MINTEQA2 and the values determined by the DMT. This was due to the significant metal adsorption onto the cation exchange membrane used in the DMT with 20%, 28%, 44%, and 8% mass loss of the initial total concentration of Cd, Cu, Pb, and Zn in solution, respectively. This could result in a significant error in the determination of free metal ions when using DMT if no allowance for membrane cation adsorption was made. Relative to the total soluble metal concentrations the amounts of free Cd^{2+} (3%–52%) and Zn^{2+} (11%–72%) in soil solutions were generally higher than those of Cu^{2+} (0.2%–30%) and Pb^{2+} (0.6%–10%). Among the key soil solution properties, dissolved heavy metal concentrations were the most significant factor governing free metal ion concentrations. Soil solution pH showed only a weak relationship with free metal ion partitioning coefficients (K_p) and dissolved organic carbon did not show any significant influence on K_p .

Key words: Donnan membrane technique; free metal ion; heavy metals; partitioning coefficient; solubility; speciation

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Introduction

It is well recognised that the total heavy metal content of soils is a poor indicator of human and environmental health risks. Total metal loading has been found to overestimate risk and consequently the justification for contaminated site remediation (Naidu *et al.*, 2008). In an effort to minimise uncertainty in the decision making process, there has been a significant shift away from total metal loading to the bioavailable fraction which is defined by numerous researchers as the “degree to which a chemical in a potential source is free for uptake (movement into or onto an organism)” (Naidu *et al.*, 2008). Often, chemicals present in soil solution are defined as the most bioavailable metal fraction because this fraction is generally readily accessible by various biota including plants. Metals present in soil solution are also generally more mobile and thus pose greater potential risks to offsite receptors. Therefore, a thorough understanding of heavy metal composition in soil solution is essential for any study of phytotoxicity and phytoremediation because plants generally only uptake

heavy metal ions from the labile pool of the soil solution (Knight *et al.*, 1997; Holm *et al.*, 1998; Sauvé *et al.*, 2000a).

There is increasing evidence that labile metals complexed with chloride, sulphate and low molecular weight organic ligands presented in the soil solution influence metal uptake and concomitant toxicity (Smolders *et al.*, 1998; Zhang *et al.*, 2001). While it remains unclear whether plants predominantly uptake metals from soil solution as free metal ions or as complexed species, the free metal ion fraction is still extremely important in determining plant metal uptake (Knight *et al.*, 1997; Sauvé *et al.*, 2000b; Vulkan *et al.*, 2000). Hence, the investigation of free metal ions together with key chemical properties in soil solution is vital for further understanding the soil-root interface mechanisms.

Several techniques have been developed to speciate metals in solution, including ion selective electrodes (Mota, 1995), voltametric electrochemical method (Mota, 1995), cation exchange resin method (Holm *et al.*, 1995), diffuse gradients in thin films (Fitz *et al.*, 2003) and the Donnan membrane technique (DMT) (Temminghoff *et al.*, 2000). Of these, DMT has been used to separate free metal ions

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and mono-metric species from other complex species in solution without chemical interference from neutral and anionic species and without alternation of the equilibrium composition in the sample solution (Temminghoff *et al.*, 2000; Weng *et al.*, 2001a). In this technique, free cations are transported through a semi-permeable, negatively charged, cation exchange membrane until so-called "Donnan equilibrium" is reached (Temminghoff *et al.*, 2000). Moreover, through DMT the speciation of a range of metals can be determined simultaneously.

In this study, we applied DMT for the determination of metal speciation in the soil solution extracted from long-term contaminated soils containing a mixture of Cd, Cu, Pb and Zn. Soil solution composition was investigated at 70% maximum water holding capacity (MWHC) and the free metal ion activities in the soil solution were determined. In addition the influence of key soil solution properties on free metal ion composition was investigated.

1 Materials and methods

1.1 Soil samples and processing

Thirty one distinct soil samples were collected from 9 sites within the vicinity of the Pasminco Smelter, Lake Macquarie, NSW, Australia in March 2005. Lower air and water quality in this area had previously been attributed to elevated Pb concentrations in the soil (Morrison, 2003). Soils were sampled from sites within a 4-km

radius of the smelter including residential areas, public parks, playgrounds and recreational reserves and therefore represented a range of typical urban soil types. The sample location was well-mapped in our previous study (Kim *et al.*, 2009). Surface soils (0–10 cm) were collected using a soil auger (9 cm in diameter). The final soil sampled consisted of approximately 2 kg of bulked soil from three to four discrete core samples collected 1 m apart. Grass, leaves and roots presented in soil samples were discarded after gentle shaking to remove the soil attached around roots. All soils were air dried and sieved to < 2 mm using a stainless steel sieve and stored in plastic bags until analysis. The soil properties are shown in Table 1.

1.2 Routine laboratory analysis

Soil pH and electrical conductivity (EC) were determined in a 1:5 of soil:water (W/V) of suspension using a combination pH-EC meter (smartCHEM-LAB, TPS, Australia) after 1 h equilibrium with shaking on an end-over-end shaker. Soil organic matter content was determined using the Walkely-Black method (Nelson and Sommers, 1996) and soil texture was determined using a micro-pipette method (Miller and Miller, 1987). Major exchangeable cations were determined by ion conductivity plasma mass spectrometer (ICP-MS) (7500c, Agilent, USA) following 1 mol/L NH₄OAc extraction. Soil (5 g, < 2 mm) was extracted with 1 mol/L NH₄OAc (50 mL, pH 7) (Sumner and Miller, 1996). Total dissolved organic carbon (DOC) was analysed using an automatic

Table 1 Characteristics of the soils studied

Site	No	pH	EC (µS/cm)	Clay (%)	OM (%)	DOC (mg/L)	Exchangeable cation (mg/kg)		
							Mg	K	Ca
LMa01	1	6.7	90	7.1	12.5	147	215	313	2500
	2	7.0	81	3.8	3.8	180	81	180	1200
	3	5.1	77	2.9	13.8	83	122	207	1150
	4	5.8	82	8.7	4.8	95	73.9	188	630
LMa02	1	7.3	340	11.1	3.1	60	190	151	1580
	2	7.5	52	12.8	3.4	29	235	94.7	1293
LMa03	1	6.5	30	3.0	17	118	60.7	108	390
	2	6.1	49	6.6	6.0	154	122	196	730
	3	5.8	41	6.9	8.0	260	103	133	750
	4	6.0	142	10.6	10.9	210	282	332	1003
	5	7.1	91	9.5	8.6	82	207	203	1520
LMa04	1	7.4	75	13.6	4.1	124	301	159	1309
	2	6.9	50	14.0	3.6	102	352	150	677
	3	6.5	60	19.9	4.2	149	525	159	690
	4	7.1	97	20.1	4.5	390	535	279	1090
LMa05	1	7.2	131	14.0	5.0	94	300	203	1590
	2	8.2	177	10.7	5.2	118	307	169	2300
	3	7.7	153	11.2	4.6	95	239	184	1820
LMa06	1	5.6	38	24.6	8.1	291	670	400	1510
	2	5.6	43	4.6	7.0	94	134	327	411
	3	5.2	36	19.8	3.7	154	313	183	332
LMa07	1	6.7	36	5.9	3.7	135	120	180	640
	2	6.9	46	7.2	6.2	110	145	162	830
	3	6.6	57	5.6	7.2	248	237	171	1010
LMa08	1	7.0	88	5.3	7.1	199	167	304	1650
	2	7.8	349	6.7	5.5	150	233	300	3500
	3	6.5	82	8.4	10.1	287	298	350	1760
	4	6.3	50	6.9	8.6	407	240	225	1600
LMa09	1	6.0	43	5.4	3.4	122	200	183	620
	2	5.7	40	5.9	2.5	82	158	122	450
	3	5.8	67	16.1	5.8	181	219	250	760

EC: electrical conductivity; OM: organic matter; DOC: dissolved organic carbon.

total organic carbon analyser (Model 1010, O.I. Analytical, USA) after extracting soil solution at 70% MWHC. Heavy metals in extracted solution were analysed using ICP-MS. Total heavy metal concentrations in soils were determined by ICP-MS following microwave (MARS5, CEM, USA) assisted *aqua regia* acid digestion in accordance with Method 3051H (USEPA, 1997). All digestions were conducted in triplicates and each batch included a standard reference material (Montana Soil SRM2711, Certificated by National Institute of Standards and Technology) and a blank to validate the digestion procedure.

1.3 Soil solution extraction and analysis

Soil solution was collected by centrifugation following equilibration of soils at 70% MWHC. Soil sample (20 g) was weighed into a 20-mL disposable plastic syringe where the syringe end had been plugged with acid washed glass wool to prevent the release of soil. The syringe was inserted in 50 mL centrifuge tube separated from the base by a PVC spacer (Thibault and Sheppard, 1992). Milli-Q water was added to the soil to obtain 70% of the MWHC and the soil was allowed to equilibrate for 24 h. The resulting soil paste was centrifuged at 2500 r/min for 25 min. The isolated soil solutions were filtered through 0.45- μm cellulose acetate disposable filters (MillexTM, Millipore, USA). Isolated soil solutions were used for the determination of pH, EC, DOC, and cation concentrations, while additional soil solution extractions were conducted for DMT speciation experiments.

In order to secure enough soil solution (100 mL) for each DMT determination, 25 replicates of syringe extractions for each sample were performed. Individual replicate solutions were isolated and bulked together to obtain at least 100 mL after filtering. The DMT speciation was performed within 2 h of soil solution collection.

1.4 Donnan membrane technique (DMT)

The DMT system used here was almost identical to that used by Temminghoff *et al.* (2000) including the negatively charged membrane (BDH, No. 55165 2U). However, in their study, conditions of donor (500 mL) and acceptor (17 mL) were used, while in this study 100 mL of donor and 8 mL of acceptor solution were used because of the relatively small volume of soil solution collected at 70% MWHC. Prior to applying DMT speciation to the soil solution of samples, DMT was validated using an artificially prepared solution. The measured free metal concentration was compared with the predicted free metal concentration calculated using MINTEQA2.

1.5 Validation of DMT

1.5.1 Establishing DMT equilibration time

In order to determine an appropriate equilibration time, 2 mmol/L $\text{Ca}(\text{NO}_3)_2$ donor solution (100 mL) was spiked with 200 $\mu\text{g/L}$ each of Cd, Cu, Pb, and Zn and 80 $\mu\text{mol/L}$ tri-sodium citrate and this solution was linked to 8 mL of the same background acceptor solution (2 mmol/L $\text{Ca}(\text{NO}_3)_2$) without the addition of metals or citrate, via PTFE peristaltic pump tubing. All metals were added as

their nitrate salts and citrate was added as an example of a typical soil solution ligand. Both donor and acceptor solutions were circulated through each side of the DMT apparatus at 2.5 mL/min and sub-samples were collected from both sides after 12 h equilibration. The same experiment was repeated further for 3 times with increasing equilibration time (24, 48, and 72 h).

1.5.2 Establishing the effect of ionic strength

In order to examine the effect of ionic strength on equilibration time, and therefore the speciation by DMT the above experiments were repeated in duplicates. During the experiments, 10 mmol/L $\text{Ca}(\text{NO}_3)_2$ was used as the background electrolyte and the sub-samples were collected following equilibration for ICP-MS analysis.

1.5.3 Comparing DMT result with MINTEQA2 calculation

Measured free metal ion fractions determined using the DMT were compared with values predicted using MINTEQA2. This comparison was conducted at a range of soil solution pH but with identical total metal solution composition as described above. After 24 h equilibration sub-samples were collected from both sides of the DMT apparatus and analysed for heavy metal contents and solution pH. The experiment was conducted in quadruplicates for each pH. The heavy metal concentration of the acceptor was assumed to be identical to the free metal ion concentration and the metal concentration in the donor solution was assumed to correspond to the total metal concentration in solution. The fraction of free metal ions was therefore calculated using the ratio of concentration in acceptor to concentration in donor. This calculation assumed that there was no degradation of the citrate ligand during the 24 h equilibration period. The fraction of free metal ions determined was compared with the values predicted by MINTEQA2, in which the concentrations of all metals and salts in the donor side were used as input data.

This experiment was repeated using only a single metal (Pb) with four different citrate (ligand) concentrations ranging from 0 to 160 $\mu\text{mol/L}$. The changes in the fractions of Pb^{2+} determined by DMT were compared with those predicted by MINTEQA2 as citrate concentration increase.

1.5.4 Mass balance and membrane adsorption test

While previous researchers have dismissed metal adsorption onto the cation exchange membrane as being negligible (Weng *et al.*, 2001a), mass balance studies demonstrated significant adsorption of metals onto the cation exchange membrane during equilibration. In order to quantify the amount of heavy metal loss in the system during equilibration, the composition of the solution for free metal ions described above was used in the DMT apparatus (200 $\mu\text{g/L}$ each metal and 80 $\mu\text{mol/L}$ citrate), with the solution pH fixed at 5.0. After each equilibrium, the total amount (μg) of heavy metals in both donor and acceptor solutions were subtracted from the initial amount of heavy metal added to the system.

Membranes were also soaked in 2 mmol/L $\text{Ca}(\text{NO}_3)_2$ solution of different pH to examine the change in the

adsorption capacity of the membrane as pH increase. After equilibration for 24 h the membranes were rinsed with Milli-Q water for three times and extracted with 100 mL of 0.1% HNO₃ for 1 h. The washing solution, 0.1% HNO₃, was analysed using ICP-MS to determine the Ca amount adsorbed by the membrane.

1.6 Soil solution speciation

Soil solutions were extracted from 31 long-term contaminated soil samples according to the method described above and analysed by DMT to determine free metal ion concentrations. The donor side consisted of extracted soil solutions (100 mL) without any added electrolyte, because soil solutions inherently have sufficient ionic strength for DMT determination. The concentration of Ca(NO₃)₂ in the acceptor solution was varied based on the ionic strength of each soil solution to minimise the differences between donor and acceptor solutions.

Free metal ions in solution were calculated using Eq. (1) when the charge-corrected ratios of the cation activities in the donor and acceptor solutions are equal:

$$\frac{C_{M^{2+}A}}{C_{M^{2+}D}} = \frac{C_{K^+A}^2}{C_{K^+D}^2} \quad (1)$$

where, $C_{M^{2+}D}$ and $C_{M^{2+}A}$ are the free metal concentrations in the donor and acceptor solutions, respectively, and C_{K^+D} and C_{K^+A} are the potassium (K) concentrations in the donor and acceptor solutions, respectively (Weng *et al.*, 2003). Potassium was used as the reference cation because K is naturally present as free or very weakly complexed metal in soil solution (Weng *et al.*, 2001a). The reproducibility of DMT was initially tested using three different bulk soils in triplicates (not considered in this study). This was an important initial step because the present soils studied were not available in sufficient quantity to allow replicate analysis.

1.7 Data analysis

All data were statistically analysed using SPSS 12.0.1 to examine interrelations between metal concentrations extracted at 70% MWHC and for studying the influence of soil properties on metal composition in soil solution. All data were processed after being log-transformed to normalize the distribution of data.

2 Results and discussion

2.1 Soil solution composition

The range of DOC concentrations (29–407 mg/L, Table 1) was similar to the range (18–631 mg/L) reported by Nolan *et al.* (2003), who isolated soil solution at the water holding capacity from several contaminated soils. However, Oste *et al.* (2002) reported much lower DOC concentrations (only up to 17.9 mg/L) when a low soil/solution ratio was used.

The soluble fractions of Cd, Cu, Pb, and Zn were generally less than 1% of the total heavy metal content of the soil. This is consistent with the results reported by

Nolan *et al.* (2003), who showed that soluble Cu, Pb, and Zn were less than 1% of total heavy metals in contaminated soils. This suggested that most of the heavy metals were present in bound forms associated with clay particles, such as Fe/Mn oxidehydroxides or organic matter (Table 2) (Maskall and Thornton, 1998; Krishnamurti and Naidu, 2000).

2.2 Speciation of metal using DMT

2.2.1 Establishing DMT equilibration time

As discussed in the methods section, the optimum condition for Donnan system was established prior to soil solution speciation of field samples. These preliminary studies indicated that an equilibration time of 24 h was sufficient and beyond this time there was no change in free metal ions concentration in the acceptor solution (data not shown). This was in good agreement with the study of Temminghoff *et al.* (2000). Based on this observation all solutions were subsequently equilibrated for 24 h using DMT.

2.2.2 Comparing DMT and MINTEQA2

The effect of pH, ionic strength and nature of ligand ions on Donnan speciation were investigated and compared with MINTEQA2 simulations. In general, there was a highly significant relationship between the DMT and the MINTEQA2 prediction, and Donnan free ion activities were found to be less than those predicted by MINTEQA2 (Table 3). Correlation coefficients were 0.94, 0.80, 0.99 and 0.96 for Cd, Cu, Pb and Zn, respectively. The low ionic activities for the Donnan system were attributed to metal loss via adsorption to the membrane during equilibration of the DMT system.

Speciation of soluble Pb was further tested in the presence of increasing concentrations of ligand (citrate), but in the absence of any other competing metals, using DMT and MINTEQA2 (Table 4). Not surprisingly free Pb decreased with increasing citrate for both DMT and MINTEQA2. Similar to earlier studies using pure system, MINTEQA2 predicted free Pb concentrations were 2–6 folds higher than that obtained using DMT. Moreover, the amount of Pb lost during the equilibration was significantly higher than when using a mixed metal spiked solution (the amount of Pb lost was lower in the presence of other metal ions) (Tables 4 and 5).

2.2.3 Metal loss in DMT system

Since the cation exchangeable membrane used in DMT has a negatively charged surface and sulphonic (–SH) functional groups (Temminghoff *et al.*, 2000), it can potentially be responsible for the difference in mass balance due to the adsorption of cations from solution during DMT determination. The identical DMT analysis with and without membrane was performed to test whether there was any loss of metals to the DMT system as a whole or to the membrane. This comparison confirmed that in the absence of membrane there was no significant metal loss (data not shown) indicating that the membrane was responsible for metal loss. The amount of metal loss increased with an

Table 2 Concentrations of heavy metals in soil and extracted solution

Site	No.	Cd		Cu		Pb		Zn	
		Total (mg/kg)	Soluble ($\mu\text{g/L}$)	Total (mg/kg)	Soluble ($\mu\text{g/L}$)	Total (mg/kg)	Soluble ($\mu\text{g/L}$)	Total (mg/kg)	Soluble ($\mu\text{g/L}$)
LMa01	1	65	77	404	272	4960	285	3966	5640
	2	12	11	90	98	1407	24	627	1516
	3	86	273	564	204	5886	362	6329	29845
	4	16	217	131	178	1609	324	1173	30320
LMa02	1	10	47	732	88	15912	15	1440	2961
	2	14	15	1484	102	31016	20	2773	1196
LMa03	1	3.1	12	71	183	2446	89	346	3038
	2	8.3	35	108	216	2698	266	768	5415
	3	16	55	101	164	1623	440	1291	5990
	4	11	45	76	177	1195	421	1073	5590
	5	19	14	461	79	38395	9.0	2440	2957
LMa04	1	0.4	1.0	7.6	20	81	15	44	76
	2	0.5	8.1	7.2	18	42	30	42	111
	3	0.5	1.2	6.4	20	55	15	46	138
	4	0.3	1.4	7.1	28	50	34	41	72
LMa05	1	1.1	1.7	236	86	3851	18	547	636
	2	1.1	0.8	790	180	12340	13	1680	146
	3	1.6	2.0	421	155	7348	10	1046	594
LMa06	1	3.5	13	44	35	662	38	235	2970
	2	3.1	3.2	43	36	231	19	156	468
	3	1.7	12	11	23	165	68	108	1265
LMa07	1	1.6	1.7	518	177	14461	11	663	1357
	2	1.3	1.7	1177	214	28854	23	3141	2421
	3	1.2	1.9	565	240	11543	29	1236	1943
LMa08	1	1.3	2.2	594	221	21384	85	6370	2194
	2	1.0	1.6	204	93	8164	7.9	762	460
	3	1.7	2.1	78	87	3627	24	386	2962
	4	1.1	0.9	10	28	307	20	79	446
LMa09	1	0.1	0.6	7.1	36	5.3	11	7.9	109
	2	0.1	0.9	6.1	27	53.7	13	9.0	156
	3	0.2	1.9	11	39	229.7	33	47	1241

Total: *Aqua regia* extractable concentration; soluble: 70% MWHC extractable concentration.

Table 3 Fraction of free metal ions in solution with different pH values determined using DMT and MINTEQA2 (%)

pH	Cd		Cu		Pb		Zn	
	DMT ^a	MTQ2 ^b	DMT ^a	MTQ2 ^b	DMT ^a	MTQ2 ^b	DMT ^a	MTQ2 ^b
3.2	96 (2)	98.9	66 (3)	94.0	71 (4)	95.1	81 (2)	98.7
4.2	92 (2)	97.7	50.1 (0.6)	31.8	52 (8)	88.9	80 (3)	89.8
5.2	89 (2)	95.5	8.4 (0.4)	7.1	21.1 (0.5)	80.2	52 (2)	69.5
6.0	86 (1)	95.0	1.8 (0.1)	5.6	18 (1)	78.1	47 (1)	65.3

^a Fraction of free metal ions using DMT; ^b fraction of free metal ions using MINTEQA2. The numbers in parenthesis are standard deviation.

increase in cation affinity of the functional groups of the membrane in the order of $\text{Pb} > \text{Cu} > \text{Cd} > \text{Zn}$, reflecting a higher adsorption of Pb and Cu by the cation exchange membrane (Table 5). The fractions of metal loss relative to the initial concentration were 20.1% (3.9 μg), 28% (5.5 μg), 44% (6.0 μg) and 8% (1.7 μg) for Cd, Cu, Pb, and Zn, respectively.

The capacity for cation adsorption onto the membrane was pH dependent and increased with increasing pH (Fig. 1). This result suggested that there may be a significant uncertainty in the application of DMT to environmental samples which have significantly different pH values. Through soil column DMT, Oste *et al.* (2002) showed a good agreement between measured free metal ions and calculated values by a NICA-Donnan model. However, there was no suggestion of any metal loss in the DMT system during equilibration. Weng *et al.* (2001a) calculated that the proportion of Cu lost relative to the total Cu concentration in soil was 0.16% and 0.002% for two

Table 4 Fraction of Pb^{2+} determined using DMT and MINTEQA2 in solutions having different concentration of citrate, and Pb loss during DMT equilibration

Citrate ($\mu\text{mol/L}$)	pH	Initial conc. ^a ($\mu\text{g/L}$)	DMT ^b (%)	MTQ2 ^c (%)	Pb loss (%)
0	5.5	181.5	39 (4)	95.3	73.9 (0.02)
40	5.8	181.5	16.6 (0.1)	84.8	63.4 (0.4)
80	5.8	181.5	10.1 (0.4)	76.4	57 (1)
160	6.0	181.5	7.5 (0.8)	62.7	51.7 (0.3)

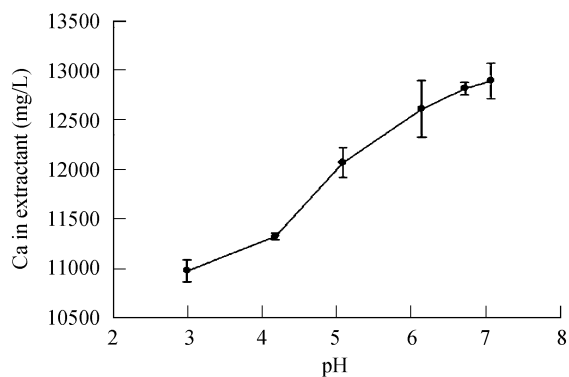
^a Initial concentration of Pb before DMT equilibration; ^b Pb^{2+} fraction determined using DMT; ^c Pb^{2+} fraction determined using MINTEQA2. The numbers in parenthesis are standard deviation.

different soils. However, calculation of metal loss relative to the total soil concentration is misleading and makes the loss of metal seem insignificant, when in reality significant loss of metal from soil solution may be occurring. Since DMT is a tool for speciation of cations in solution, it is more appropriate to express the metal loss relative to the

Table 5 Heavy metal ion loss after DMT equilibration

Metal	Initial conc. ^a ($\mu\text{g/L}$)	Donor ^b ($\mu\text{g/L}$)	Acceptor ^c ($\mu\text{g/L}$)	Free metal (%)	Mass loss (μg)	Fraction of loss (%)
Cd	196	147 (1)	130 (1)	88.7 (0.7)	3.9 (0.2)	20.1 (0.9)
Cu	198	142 (4)	12.2 (0.2)	8.6 (0.3)	5.5 (0.4)	28 (2)
Pb	138	76 (2)	16.0 (0.1)	21.1 (0.3)	6.0 (0.2)	44 (1)
Zn	216	191 (2)	98 (2)	51.1 (0.3)	1.7 (0.2)	8 (1)

^a Initial concentration of Pb before DMT equilibration; ^b metal concentration in donor side after DMT equilibration; ^c metal concentration in acceptor side after DMT equilibration. The numbers in parenthesis are standard deviation.

**Fig. 1** Change of Ca absorption to the membrane with increasing pH.

total solution phase concentration rather than the total soil metal concentration. Metal loss can be compensated by using soil column DMT (Weng *et al.*, 2001a). During soil column DMT equilibration a column of soil is continually connected to the donor side of the DMT apparatus. Under this condition metal loss should be minimal since the change of equilibrium due to the membrane adsorption of Cu^{2+} would drive continual replenishment of Cu^{2+} from the solid phase to compensate for any solution Cu^{2+} loss until the cation exchange membrane is saturated and an alternate equilibrium is established. However, when using soil column DMT, a lower soil/solution ratio is required for circulation of solution in the DMT system, which probably makes the soil solution composition different from the field soils having field moisture contents.

Given the significant loss of metal ions via sorption to the Donnan membrane system reported here, while the current DMT technique may not be appropriate for determining absolute values of free metal ions, it does allow the establishment of trends in the fraction of free metal ions to be monitored relative to changes in solution properties. Indeed, DMT may be an excellent tool for speciation of metals in solution samples enriched with high concentrations of metals. In such solution loss of metals via sorption would be insignificant.

2.2.4 Reproducibility of DMT

The reproducibility and mass balance of the DMT were examined using soil solutions extracted from three bulk soils (PP01 and PP02 from a smelting area in Australia, Ko01 from a shooting range in Korea), prior to the speciation of the soil solutions from field samples. In three different soil solutions, the reproducibility of speciated free metal ions was reliable with the relative standard

deviation being better than 20%. However, the metal loss was significant and varied with the soil analysed. Of the three soils analysed, the greatest metal loss was observed in Ko01 which had the lowest soil solution ionic strength (Table 6).

Table 6 Reproducibility and metal loss in determination of free metal ions in soil solution extracted by 70% MWHC using DMT

Metal	Sample	pH	Initial conc. ($\mu\text{g/L}$) ^a	M^{2+} (%) ^b	Metal loss (%)
Cd	PP01	8.1	1.4 (0.2)	34 (1)	29 (1)
	PP02	8.0	14.0 (0.3)	6.4 (0.2)	2 (2)
	Ko01	6.4	38.6 (0.6)	45 (1)	41 (3)
Cu	PP01	8.1	69 (5)	0.8 (0.2)	24 (6)
	PP02	8.0	610 (10)	0.05 (0.01)	2.9 (0.8)
	Ko01	6.4	11.6 (0.5)	1.9 (0.3)	23 (2)
Zn	PP01	8.1	70 (10)	35 (6)	36 (2)
	PP02	8.0	890 (20)	4.3 (0.7)	1 (1)
	Ko01	6.4	29 (1)	66 (2)	22 (4)
Pb	PP01	8.1	70 (10)	1.1 (0.4)	54 (5)
	PP02	8.0	108 (3)	0.5 (0.4)	3 (3)
	Ko01	6.4	3.2 (0.7)	10 (1)	70 (10)

^a Pb concentration in extracted soil solution; ^b fraction of M^{2+} by DMT. The numbers in parenthesis are standard deviation.

2.3 Free metal ion chemistry

2.3.1 Fraction of free metal ions in solution by DMT

The proportion of free metal ions in soil solution determined by DMT varied with atomic number. Thus, Cd and Zn had high fractions of free metal ions ranging from 3%–52% (average = 28%) and 11%–72% (average = 38%), respectively (Table 7). For Cu and Pb, 0.2%–30% and 0.6%–10% of the soluble pool existed as free ions with an average of 3.9% and 3.5%, respectively, implying that most of the Cu and Pb in soil solution existed as organo-metal complexes, whereas Cd and Zn occurred substantially in the free ion forms (McBride *et al.*, 1997; Nolan *et al.*, 2003). The proportions of free Cd, Cu and Pb observed here were significantly lower than the values observed by Oste *et al.* (2002) who showed 70%–100% of Cd, 5%–50% of Cu, and 11%–97% of Pb. This may be attributed to the different concentration of DOC in the soil solution of Oste's study. They reported DOC concentrations below < 17.9 mg/L in all their samples while the DOC in the present study ranged from 29 to 407 mg/L. High affinity of Pb^{2+} and Cu^{2+} for DOC and concomitant maintenance of a low corresponding free metal ions was demonstrated previously (Sauvé *et al.*, 2000b).

Table 7 Fraction of free metal ions in soil solution determined using DMT (%)

Site	No.	Cd	Cu	Pb	Zn
LMa01	1	44	0.6	1.2	54
	2	44	1.1	2.7	51
	3	51	1.8	6.3	53
	4	49	1.7	5.9	55
LMa02	1	52	2.7	8.9	72
	2	47	1.4	2.9	53
LMa03	1	16	0.4	3.3	21
	2	32	0.3	1.0	42
	3	51	0.9	2.6	70
	4	26	0.5	0.8	38
	5	45	2.5	5.4	58
LMa04	1	17	16	8.2	25
	2	3.0	8.6	1.0	15
	3	16	9.3	4.2	20
	4	14	6.5	4.5	11
LMa05	1	30	30	5.2	35
	2	12	0.7	3.9	11
	3	20	0.6	5.9	27
LMa06	1	39	2.4	3.4	55
	2	35	1.2	2.0	35
	3	47	3.1	3.2	60
LMa07	1	20	0.4	4.0	24
	2	22	0.3	0.8	40
	3	20	0.2	0.6	23
LMa08	1	16	0.6	0.6	34
	2	14	16	10	35
	3	23	0.7	0.8	35
	4	14	2.0	0.6	26
LMa09	1	10	1.7	1.8	15
	2	28	5.9	8.1	42
	3	22	3.5	0.9	43

2.3.2 Factors influencing on free metal ions in soil solution

In order to investigate the relationship between free metal ion dynamics and soil solution properties, free metal

ion partitioning coefficients (K_p) were calculated using Eq. (2).

$$K_p = \frac{C_{M_S}}{C_{M_F}} \quad (2)$$

where, C_{M_S} ($\mu\text{g/L}$) was the metal concentration in the extracted soil solution and C_{M_F} ($\mu\text{g/L}$) as the free metal ion concentration in solution.

The most significant factor among soil solution properties influencing free metal ion concentrations was the dissolved metal concentrations of Cd, Pb, and Zn (Fig. 2), which respectively accounted for up to 98%, 61%, and 96% of the variability in ion activities in solution. In particular, free ion concentrations of Cd and Zn were strongly dependent on the dissolved concentration of these metals.

There was no significant influence of DOC on K_p of Cd (data not shown; $r^2 = 0.13$, $p > 0.1$) and Zn ($r^2 = 0.05$, $p > 0.1$) while soil solution pH showed only a weak relationship with K_p of Cd (data not shown; $r^2 = 0.19$, $p < 0.1$) and Zn ($r^2 = 0.15$, $p < 0.1$). There was no relationship between free and soluble Cu (Fig. 2). This suggested that most of the Cu ions existed as Cu-ligand complexes which is dominant in solution phase. Similar to Cd and Zn, free Pb concentration was significantly related to soluble Pb (Fig. 2).

Metal distribution in soil solution is predominantly correlated with soil pH and DOM (Sauvé *et al.*, 2000b; Weng *et al.*, 2002; Qin *et al.*, 2004). However, in the present study, there was no effect of soil solution pH on K_p of either Cu or Pb. According to the simulation study reported by Weng *et al.* (2001b) using the NICA-Donnan model, Pb adsorption onto Fe hydroxides is strong while the negatively charged sites on DOC have little influence on

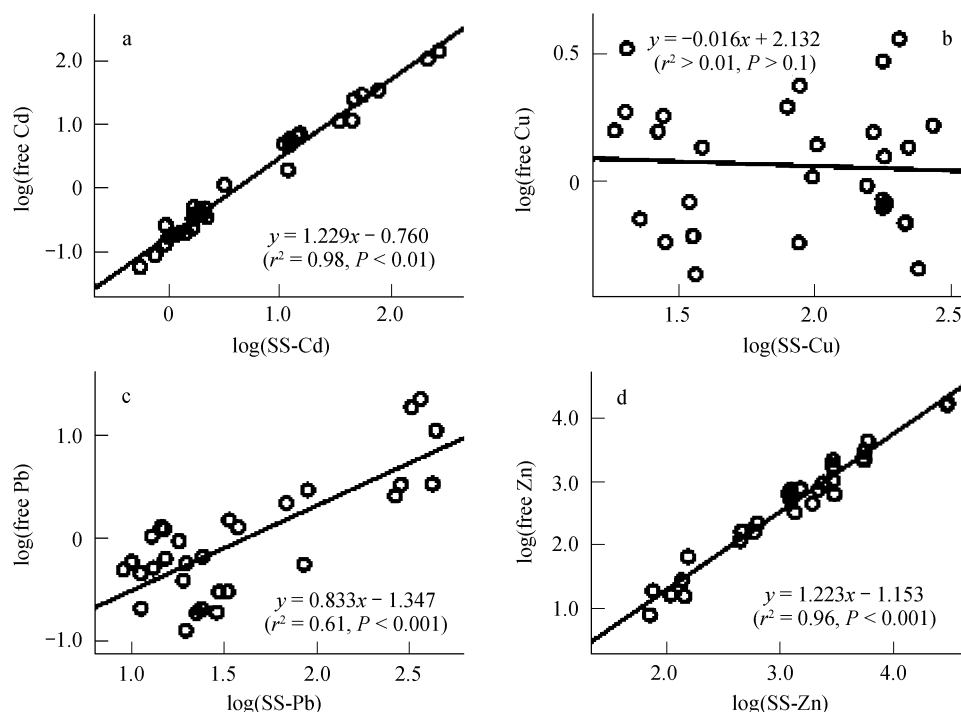


Fig. 2 Relationship between soil solution metal concentrations (SS-M) and free metal concentrations (free M) in soil solutions.

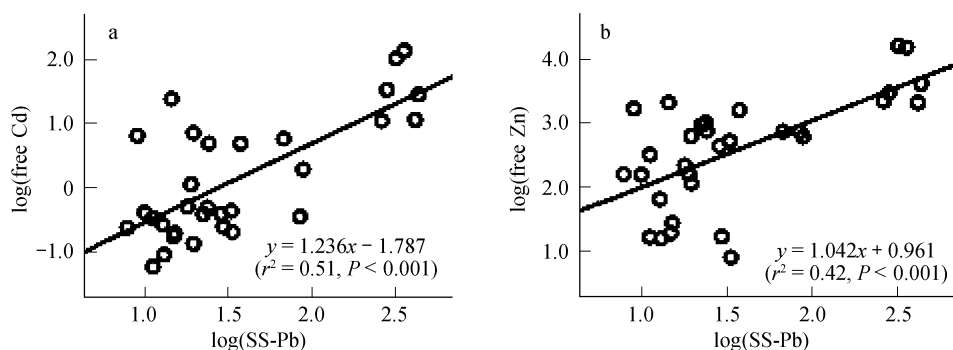


Fig. 3 Relationship between Pb concentration in soil solution (SS-Pb) and free metal ion concentration of Cd (a) and Zn (b).

the Pb^{2+} activity. In addition, Weng *et al.* (2002) explained that even though DOC affects the solubility of metals to a considerable extent, it does not contribute significantly to the control of metal activity as indicated through NICA-Donnan simulation.

2.3.3 Competition effect of heavy metals

Sites contaminated with a mixture of heavy metals pose significantly new challenges towards an understanding of the risk that such systems posed to our environment. As shown in this study, correlation studies demonstrated there were significant relationship between Pb (that had the greatest affinities for binding) and other heavy metals. Thus, a unit increase in Pb resulted in a unit increase in Cd and Zn in soil solution which enhanced the bioavailability of these metals (Fig. 3). This result suggests that the effect of multi metals on bioavailability needed to be considered while addressing environment soils.

3 Conclusions

Soil solution composition and heavy metal speciation were investigated using soil solution extracted at 70% MWHC from long-term contaminated soils, together with key soil solution properties. The Donnan Membrane Technique was used to determine the free metal ion concentration after validating the technique using a synthetic soil solution. It was evident from these studies that:

(1) Soluble fractions of Cd, Cu, Pb, and Zn were less than 1% (W/W) of the total concentrations, with Cd and Zn having higher solubility than either Cu or Pb.

(2) The proportions of free metal ions determined by DMT and calculated by MINTEQA2 were in good agreement but the absolute value for Pb^{2+} was 2–6 folds lower in DMT due to metal loss during the DMT equilibration with the largest loss for Pb being attributed to adsorption of Pb onto the cation exchange membrane. This can be a significant source of error in the determination of free metal ions by DMT. The cation adsorption capacity of the membrane was increased with solution pH. This loss can be countered by connecting the DMT to a soil column capable to establish an equilibrium following metal loss to the membrane. However, this technique is not always possible due to the techniques requirement of a low soil/solution ratio which is not observed under field

moisture conditions.

(3) The proportions of both free Cu^{2+} and Pb^{2+} were low, on average only 3.9% and 3.5%, respectively, indicating that most of the dissolved Cu and Pb existed as ligand complexes. In comparison the proportions of free Cd^{2+} and Zn^{2+} were much higher, averaging 28.2% and 37.7%, respectively.

(4) Free metal ion activities were governed by the metal concentration and competing metal ions in soil solution rather than soil solution pH and DOC concentration.

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