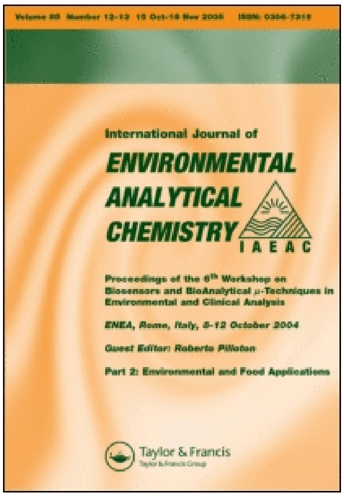

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Distribution of Heavy Metals in Water and Soil Solutions Based on Colloid-Size Fractionation

Weisheng Wang[a]; Bei Wen[a]; Shuzhen Zhang[a]; Xiao-Quan Shan[a]
[a] Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, China

To cite this Article Wang, Weisheng , Wen, Bei , Zhang, Shuzhen and Shan, Xiao-Quan(2003) 'Distribution of Heavy Metals in Water and Soil Solutions Based on Colloid-Size Fractionation', International Journal of Environmental Analytical Chemistry, 83: 5, 357 — 365

To link to this Article: DOI: 10.1080/0306731031000104704

URL: http://dx.doi.org/10.1080/0306731031000104704

Intern. J. Environ. Anal. Chem., Vol. 83, No. 5, pp. 357–365

DISTRIBUTION OF HEAVY METALS IN WATER AND SOIL SOLUTIONS BASED ON COLLOID-SIZE FRACTIONATION

WEISHENG WANG, BEI WEN,
SHUZHEN ZHANG and XIAO-QUAN SHAN*

Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences,
P.O. Box 2871, Beijing 10085, China

(Received 12 November 2002; In final form 17 February 2003)

The distribution of heavy metals Cr, Ni, Zn, Cu, Cd, and Pb among the truly dissolved (molecular weight cutoff < 1 kD), colloidal (1 kD–0.20 μm and 0.20–0.45 μm) and particulate (> 0.45 μm) fractions was investigated in the soil solution and surface water. In 15 soil solutions heavy metals were mainly present in the truly dissolved fraction (< 1 kD) with occasional exceptions. And a good correlation was also found between the concentrations of metals in the truly dissolved fractions and the cation exchange capacity of soils. As for the surface water samples, the distribution pattern was more complicated one depending on metal properties and sampling sites.

Keywords: Heavy metals; Colloid; Ultrafiltration; Distribution

INTRODUCTION

Colloids can be operationally described as particles suspended in water with characteristic dimensions between 1 nm and about 1 μm [1–4]. Organic or inorganic compounds may be present as or associated with colloids. A great deal of evidences indicate that colloids in natural water play an important role in regulating speciation, fate, transport, bioavailability, and toxicity of metals [5,6]. The key point is the concentration and size distribution of heavy metals in the dissolved, colloidal, and particulate fractions. However, the characteristics of colloidal particles in water and soil solutions are a Gordian knot of environmental chemistry [7]. The role of colloids in binding metals or nutrients has recently been studied in various aquatic systems [8–11]. The major part of these studies concerned marine and estuarine systems, whereas a little is known about freshwater.

There are some methods and strategies available for distribution of heavy metals among the dissolved, colloidal, and particulate phases. These methods include

---

*Corresponding author. Fax: +86-10-62923563. E-mail: xiaoquan@mail.rcees.ac.cn

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/0306731031000104704

centrifugation [10,12], ultrafiltration [2,8,10,13–15] and field-flow fractionation [16]. Among those techniques the ultrafiltration is the most popular one. However, this technique is suffered from some limitations such as sample contamination, especially poor mass balance etc. [17–19]. The size fraction ranging from greater than the molecular weight cutoff of 1 kD to 0.45 μm is operationally defined as colloidal fraction. The size fraction of molecular weight cutoff of <1 kD was regarded as the truly dissolved fraction, whereas the fraction of >0.45μm was defined as particulate [15].

Nowadays it is generally recognized that a description of the distribution only among the dissolved and particulate fractions is inadequate to predict the impact of metals in the environment. The aim of the present work was to use various membranes with different pore sizes to fractionate Cr, Ni, Zn, Cu, Cd, and Pb in fresh water and soil solution based on colloid-size fractionation.

EXPERIMENTAL SECTION

Sampling

Surface water samples were collected from rivers and reservoir around Beijing in June 2001. The Guanting Reservoir is situated in the northwest suburbs of Beijing and used for generation of electricity, irrigation, and source of drinking water for the city's inhabitants. Total capacity of the reservoir is about 2270 million m^3 and the catchment area is about 47 000 km^3. The water mainly comes from two rivers. Six sampling sites were chosen. PVC containers of 10 L were precleaned with 1 : 1 nitric acid for at least 48 h and then washed with deionized water several times. The surface water was drawn from about 30 cm depth. And then water samples were carried to lab and refrigerated [18]. The colloid-size fractionation was performed as soon as possible in lab.

The detailed information of soil solution extractions was reported previously [20,21]. Briefly, fifteen typical agricultural soils were collected around all China, representing different physical and chemical properties. All soils were taken from the surface layer (0–20 cm) of soils and air-dried. Soil properties of pH, organic matter (OM) and cation exchange capacity (CEC) are given in Table I. Duplicated 1.800 g of moist rhizosphere soil sample was weighed into a 50 mL polypropylene centrifuge tube, to

TABLE I Selected properties of soils

Sample	*Site*	*pH*	*CEC* (Cmol kg^{-1})	*OM* (%)
1	Jiamusi	5.97	27.03	4.30
2	Lanzhou	7.43	10.68	2.53
3	Shaanxi	8.25	25.88	1.75
4	Shanxi	7.92	21.86	4.12
5	Yuxi	4.45	25.78	1.37
6	Kunming	5.55	26.74	4.22
7	Shandong	5.94	30.20	3.62
8	Jiangxi	5.49	14.24	1.53
9	Shanghai	5.53	36.65	3.02
10	Hangzhou	7.05	19.76	3.28
11	Henan	7.73	18.12	2.03
12	Wuhan	7.27	53.98	2.37
13	Changsha	5.50	43.11	2.28
14	Hefei	6.71	24.95	2.09
15	Dongguan	7.45	15.92	1.37

which 30 mL of a mixture of acetic, formic, citric, and malic acid (2 : 2 : 1 : 1, molar ratio) at a total concentration of 0.010 mol L^{-1} was added. At the same time, subsamples were taken to determine the soil moisture content. Then the centrifuge tube was shaken by end-to-end at 30 rpm on a mechanical shaker for extraction of metals in soils. Shaking period was set 12 h. After shaking, the tubes were centrifuged at 4000 *g* for 30 min, and the supernatant was adopted for the further colloid-size fractionation.

Colloid-Size Fractionation Procedure

The supernatant of the extracted soil solutions and the fresh water samples were fractionated into three colloid-size ranges (Fig. 1). The soil solution and water were first filtered through a 0.45 μm cellulose acetate membrane. In order to determine the heavy metals in particulate fraction, the particulate matter of water collected was decomposed with the same procedure as that described by [22]. The filtrate obtained after filtration using a 0.45 μm membrane was then ultrafiltered successively through 0.20 μm membrane and molecular weight cutoff of 1 kD membrane using a homemade stirring ultrafilter.

Reagents

All reagents used were of analytical grade or better. Stock solutions of each trace metals for sample analysis, 1000 μg mL^{-1}, were obtained from Research Center for Chinese

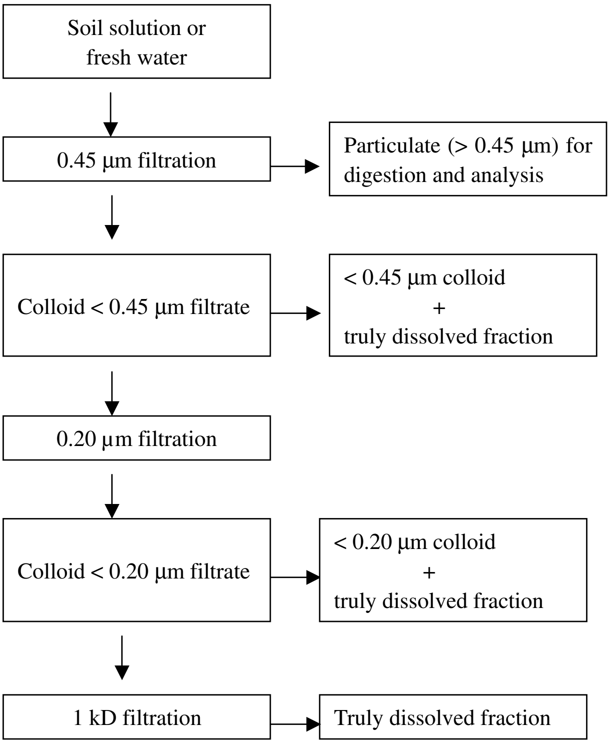

FIGURE 1 Fractionation procedure of heavy metals in soil solution and fresh water.

Standard Materials. High purity of water (18 MΩ cm) was obtained by double distillation of deionized water in a quartz still (Westdeutsche Quarzschmelze, Geesthacht, Germany). Nitric acid was purified by subboiling distillation in quartz still using ultrapure grade HNO_3 as feed. Prior to use, all beakers, calibrated flasks and other glassware were cleaned sequentially with tap water, neutral detergent, tap water, then dipped in nitric acid $(1+1)$ for 48 h and cleaned with double distilled deionized water before use.

Certified river water SLRS-4 samples were purchased from the Institute for National Measurement Standards, National Research Council of Canada.

Determination of Heavy Metals

Total concentrations of Cr, Ni, Zn, Cu, Cd, and Pb in various colloid-size fractions of soil solutions and water samples were determined by inductively coupled plasma mass spectrometry (VG PlasmaQuard 3, Fisons Instruments, UK). The operating conditions for the determinations were optimized with a solution of ^{115}In of 10 ng mL^{-1} in 2% nitric acid, which was also used as an internal standard to compensate for matrix suppression and signal drifting during analysis. All samples were performed duplicated.

Blank, Detection Limits and Certified Materials

The blank values for determinations were obtained by performing the colloid-size fractionation procedure using doubly distilled deionized water as sample. The detection limits were calculated based on three times the standard deviation of one run of 11 blank solutions. The blank values and the detection limits are given in Table II. In order to check the accuracy of ICP-MS determination certified reference river water SLRS-4 was used. However, a preconcentration procedure was adopted due to low content of heavy metals in water [23], and the determination values of heavy metals are given in Table III. There is a good agreement between the determination results and the certified values

TABLE II Blank and detection limits (ng L^{-1})

Element	*Blank*	*Detection limit*
Cr	25	17
Ni	319.7	29.8
Zn	129.8	89.3
Cu	9.3	11.6
Cd	6.4	6.4
Pb	48.8	13.6

TABLE III Determination of heavy metals in the certified river water SLRS-4*(ng mL^{-1})

Element	*Determination value*	*Certified value*
Cr	0.31 ± 0.03	0.33 ± 0.02
Ni	0.63 ± 0.05	0.67 ± 0.08
Zn	0.98 ± 0.07	0.93 ± 0.10
Cu	1.87 ± 0.09	1.81 ± 0.08
Cd	0.14 ± 0.01	0.12 ± 0.002
Pb	0.086 ± 0.003	0.086 ± 0.007

*Seven times, preconcentration by chelate fiber.

RESULT AND DISCUSSION

Distribution of Metals in Colloid-size Fractions of Soil Solutions

The range and mean values of metals in 15 soil solutions in the truly dissolved (< 1 kD), and in 1 kD–0.20 μm and 0.20–0.45 μm of colloidal fractions are presented in Table IV. For all metals Cr, Ni, Zn, Cu, Pb, and Cd the average metal concentrations in the different fractions decreased in the following order: truly dissolved form including free metal ions, organic and inorganic complexes (< 1 kD) > colloidal fraction of 1 kD to 0.20 μm > colloidal fraction of 0.20–0.45 μm.

Distributions of metals among the colloidal fractions of 0.20–0.45 μm and 1 kD–0.20 μm and truly dissolved fraction (< 1 kD) in a percentage form are presented in Fig. 2. It should be pointed out that the metal concentrations in filtrate after filtrating with 0.45 μm membrane were referred as total concentration of metals in aqueous phase. Heavy metals Cr, Ni, Zn, Cu, Pb, and Cd in different soil solution fractions exerted a different distribution pattern. In 15 soils, Cr concentrations in truly dissolved, colloidal fractions of 1 kD–0.20 μm and 0.20–0.45 μm were ranged 62–92%, 5–30% and 0–8%, respectively. Ni, Pb, and Cd exhibited a similar distribution pattern as Cr with a few exceptions. Cu and Zn showed similar distribution pattern among the 15 soils to some extent, the percents of Cu and Zn in colloidal fraction of 1 kD–0.20 μm varied significantly.

It must be considered that the results reported here were obtained by using 10 mmol L^{-1} mixed organic acid as an extractant. Organic acids can complex with metals and transfer metals from fraction associated with colloids to the truly dissolved fraction. And rhizosphere soil distinguishes from bulk soil due to the exudation of low molecular weight organic acids by plant roots and organisms present there [24]. Considering this aspect we used low molecular weight organic acids in the present study as an extractant to investigate the metal distribution among various colloidal fractions, which may represent the real-world situation of metals in soil solutions. It may be helpful to know which part of metals in soil solution is more easily available to plant.

A correlation was achieved between the metal concentrations in the truly dissolved fraction and CEC of 15 soils (Table V). However, no correlation was found between the metal concentrations in truly dissolved fraction and soil pH or organic matter of 15 soils. This may indicate that the amounts of metals in the truly dissolved fraction were mainly affected by soil CEC. It was also found that there was no correlation between the concentrations of metals in the colloidal fractions of 1 kD–0.20 μm or

TABLE IV The mean and range of metal concentrations (ng mL^{-1}) in the truly dissolved and colloidal fractions in 15 soil solutions

	Truly dissolved (< 1 kD)		*Colloid* (1 kD–0.20 μm)		*Colloid* (0.20–0.45 μm)	
	mean	*range*	*mean*	*range*	*mean*	*range*
Cr	165.6	89.25–410.2	46.02	2.60–161.0	8.07	0.55–28.30
Ni	520.8	124.5–1070	81.24	2.85–192.3	35.54	0.70–187.1
Zn	1543	72.22–6848	213.2	13.07–706.2	96.05	6.83–277.0
Cu	351.8	38.94–826.0	191.8	7.86–439.0	90.35	2.20–509.0
Pb	127.4	16.50–275.0	51.56	0.36–341.6	26.58	2.05–110.2
Cd	24.09	2.81–79.84	8.26	0.13–57.77	1.62	0.05–5.60

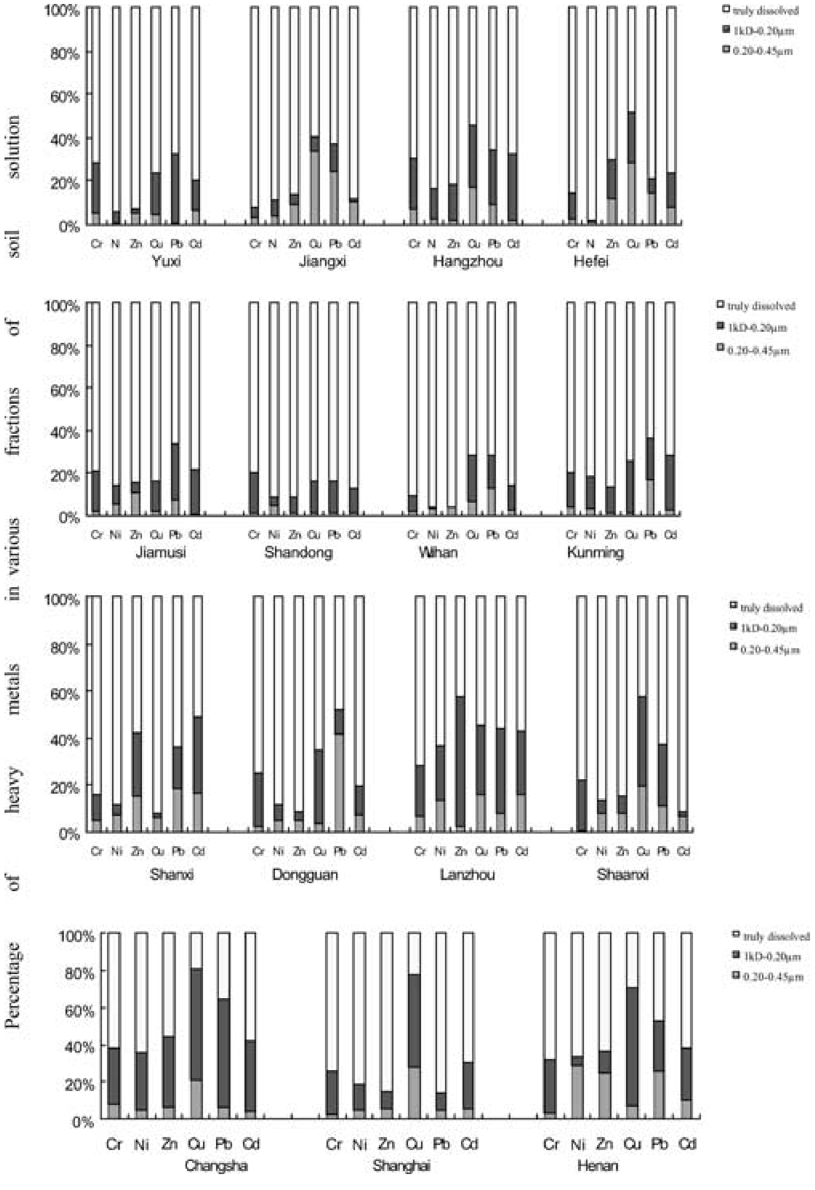

FIGURE 2 Distribution of heavy metals among 15 soil solutions.

0.20–0.45 μm and pH or CEC or OM of soils. It indicated that it is difficult to establish relationship between soil properties and metal distribution among different colloidal fractions.

Distribution of Metals Among Different Colloidal Fractions and Particulate in Fresh Water

The concentration ranges and means of Cr, Ni, Zn, Cu, Cd, and Pb in the truly dissolved (< 1 kD), colloidal fractions of 1 kD–0.20 μm and 0.20–0.45 μm, and particulate

TABLE V Correlation coefficients between the metal concentrations in three fractions of soil solutions and properties of 15 soils

Fraction	*Element*	*pH*	*CEC*	*OM*
Truly dissolved fraction (< 1 kD)	Cr	−0.49[a]	0.58[b]	−0.30
	Ni	−0.21	0.53[b]	0.28
	Zn	0.07	0.48[a]	−0.25
	Cu	−0.15	0.49[a]	0.03
	Pb	−0.72[b]	0.49[a]	−0.39
	Cd	−0.48[a]	0.62[b]	−0.05
Colloid (1 kD-0.20 μm)	Cr	−0.48[a]	0.05	−0.32
	Ni	−0.37	0.15	0.35
	Zn	−0.11	0.05	−0.04
	Cu	−0.21	0.38	−0.08
	Pb	−0.43	0.38	−0.19
	Cd	−0.37	0.46[a]	0.06
Colloid (0.20–0.45 μm)	Cr	−0.52[b]	0.08	−0.22
	Ni	0.29	−0.11	0.00
	Zn	0.05	0.33	−0.40
	Cu	−0.26	0.34	−0.04
	Pb	0.06	−0.24	−0.50[a]
	Cd	−0.36	0.30	−0.35

a, b significance at 10% and 5% levels, respectively.

TABLE VI Mean and range of metal concentrations (ng mL^{-1}) in the truly dissolved, colloidal and particulate fractions of 6 fresh water samples

	Dissolved (< 1 kD)		*Colloid* (1kD–0.20 μm)		*Colloid* (0.20–0.45 μm)		*Particulate* (> 0.45 μm)	
	Mean	*Range*	*Mean*	*Range*	*Mean*	*Range*	*Mean*	*Range*
Cr	2.05	1.86–2.26	1.58	0.03–2.88	0.68	0.06–1.32	0.55	0.26–1.26
Ni	2.68	2.06–3.12	0.45	0.11–0.65	0.23	0.08–0.65	0.52	0.26–1.02
Zn	5.68	4.82–7.01	2.17	0.41–5.08	2.63	0.13–6.39	4.28	1.80–7.03
Cu	1.95	1.19–3.50	0.72	0.13–1.08	2.82	0.23–5.91	0.77	0.36–1.68
Cd	0.10	0.09–0.12	0.02	0–0.14	0.01	0–0.04	0.01	0–0.04
Pb	0.62	0.30–0.95	0.89	0.05–4.37	2.80	0.11–12.52	0.76	0.25–1.73

(> 0.45 μm) of 6 fresh water samples are presented in Table VI. High truly dissolved (< 1 kD) concentrations of Ni (2.1–3.1 ng mL^{-1}), Zn (4.8–7.0 ng mL^{-1}), Cu (1.2–3.5 ng mL^{-1}), Pb (0.3–0.9 ng mL^{-1}) and Cd (0.1 ng mL^{-1}) were detected at all 6 sampling sites. The values observed were higher than those that had been determined at other sites. [7,17,25–27]. The increased concentrations of heavy metals were probably due to environmental pollution.

The distributions of heavy metals in the truly dissolved (< 1 kD), colloidal fractions of 1 kD–0.20 μm and 0.20–0.45 μm and particulate (> 0.45 μm) are presented in Fig. 3. Here, the sum of metal concentrations in filtrate after filtrating with 0.45 μm membrane and in particulate phase was used as total concentration. The results demonstrated that heavy metals were not homogeneously distributed over the various size fractions, suggesting that size fraction exercises a determining influence on the partitioning of heavy metals. Cd, Ni, Cr, and Zn were found mainly in the truly dissolved fraction (< 1 kD). Cu was mainly present in 0.20–0.45 μm colloidal (average 38%) and truly dissolved

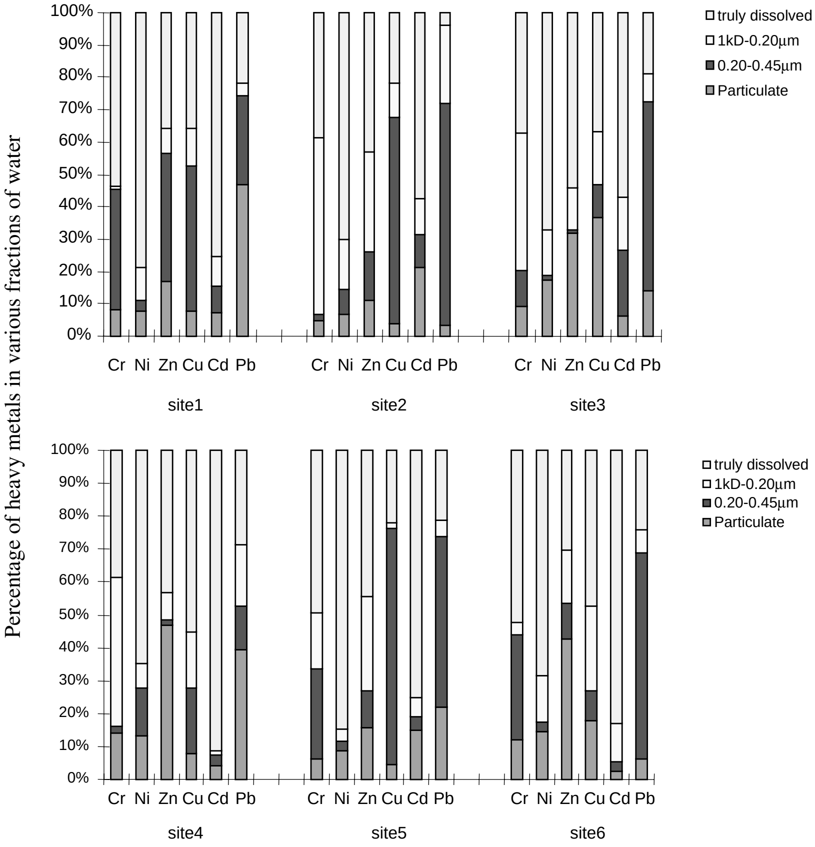

FIGURE 3 Distribution of heavy metals in fresh water among 6 sampling sites.

(average 34%) fractions. Unlike other metals, Pb was mainly found in colloidal fraction of 0.20–0.45 μm with the average value of 41%.

It is believed that particle reactive element (e.g., Pb) would have very small truly dissolved fractions. On the other hand, elements such as Cd that form strong chloride anion complexes should have larger fractions in the truly dissolved pool. And for metals Cu, Ni, and Zn that form strong organic complexes, ligand competition between high and low molecular weight ligands may control the outcome of the size distribution [15]. The results of the present study approved the above observation that there was only a few percentage of Pb in the truly dissolved fraction (< 1 kD), and Cd was mainly existed in the truly dissolved fraction (< 1 kD). While the distribution of Cr, Cu, Zn, and Ni among different colloidal fractions varied from one element to another, and also varied among different sampling sites. The reason for this was probably due to the effect of organic ligands in water.

CONCLUSION

Based on the above study one may concluded that the distribution of heavy metals among various colloidal-size fractions was related to the soil and metal's properties.

A correlation existed between the metal concentration in the truly dissolved form and the cation exchange capacity of the soils. It was understood that the truly dissolved form of heavy metals was easily available by plants. And the cation exchange capacity of the soils was correlated with the bioavailabililty. Therefore, the relationship between the truly dissolved form of heavy metals in soil solutions and the cation exchange capacity of the soils would exist. In water, dominant Ni and Cd were existed in the truly dissolved fraction (<1 kD), whereas Pb was primarily occurred in the particulate (>0.45 μm) and colloidal (1 kD–0.20 μm) fraction, respectively.

Acknowledgment

This study was supported by the Chinese Academy of Science (KZCX2-410) and the National Basic Research Development Programme (G1999045710).

References

[1] C. Haisch, J. Liermann, U. Panne and R. Niessner, *Anal. Chim. Acta*, **346**, 23–35 (1997).
[2] W.-X. Wang and L. Guo, *Environ. Sci. Technol.*, **34**, 4571–4576 (2000).
[3] M.L. Wells and E.D. Goldberg, *Limnol. Oceanogr.*, **39**, 286–302 (1994).
[4] M.L. Wells, G.J. Smith and K.W. Bruland, *Mar. Chem.*, **71**, 143–163 (2000).
[5] B.D. Honeyman and P.H. Santschi, In: J. Buffle (Ed.), *Environmental Particles*, *IUPAC Environmental Analytical Chemistry Series*, Vol. 1, pp. 379–423. Lewis Publishers, London (1992).
[6] Ö. Gustafsson and P.M. Gschwend, *Limnol. Oceanogr.*, **42**, 519–528 (1997).
[7] M.M. Shafer, J.T. Overdier, J.P. Hurley, D. Armstrong and D. Webb, *Chem. Geol.*, **136**, 71–97 (1997).
[8] G. Benoit, S.D. Oktay-Marshall, A. Cantu, E.M. Hood, C.H. Coleman, M.O. Corapcioglu and P.H. Santschi, *Mar. Chem.*, **45**, 307–336 (1994).
[9] K.K. Bertine and R. VernonClark, *Mar. Chem.*, **55**, 189–204 (1996).
[10] H. Grout, M.R. Wiesner and J.Y. Bottero, *Environ. Sci. Technol.*, **33**, 831–839 (1999).
[11] B.S. Lartiges, S. Deneux-Mustin, G. Villemin, C. Mustin, O. Barrès, M. Chamerois, B. Gerard and M. Babut, *Wat. Res.*, **35**, 808–816 (2001).
[12] D. Perret, M.E. Newman, J.C. Nègre, Y. Chen and J. Buffle, *Wat. Res.*, **28**, 91–106 (1994).
[13] J.L. Guentzel, R.T. Powell, W.M. Landing and R.P. Mason, *Mar. Chem.*, **55**, 177–188 (1996).
[14] S.A. Sañudo-Wilhelmy, I. Rivera-Duarte and A.R. Flegal, *Geochim. Cosmochim. Acta*, **60**, 4933–4944 (1996).
[15] L.-S. Wen, P.H. Santschi, G. Gill and C. Paternostro, *Mar. Chem.*, **63**, 185–212 (1999).
[16] M. Hassellöv, B. Lyvén and R. Beckett, *Environ. Sci. Technol.*, **33**, 4528–4531 (1999).
[17] L. Sigg, H. Xue, D. Kistler and R. Schönenberger, *Aquat. Geochem.*, **6**, 413–434 (2000).
[18] L.-S. Wen, M.C. Stordal, D. Tang, G.A. Gill and P.H. Santschi, *Mar. Chem.*, **55**, 129–152 (1996).
[19] J.M. Greenamoyer and S.B. Moran, *Mar. Chem.*, **55**, 153–163 (1996).
[20] Z.W. Wang, X.Q. Shan and S.Z. Zhang, *Anal. Chim. Acta*, **441**, 147–156 (2001).
[21] X.Q. Shan, Z.W. Wang, W.S. Wang, S.Z. Zhang and B. Wen, *Anal. Bioanal. Chem*, **375**, 400–407 (2003).
[22] S.Z. Zhang and X.Q. Shan, *At. Spectrosc.*, **19**, 140–144 (1997).
[23] B. Wen and X. Q. Shan, *Anal. Bioanal. Chem.*, **374**, 948–954 (2002).
[24] D.L. Jones, *Plant Soil*, **205**, 25–44 (1998).
[25] A.M. Shiller, *Geochim. Cosmochim. Acta*, **61**, 4321–4330 (1997).
[26] H.L. Windom, J.T. Byrd, R.G. Smith Jr. and F. Huan, *Environ. Sci. Technol.*, **25**, 1137–1142 (1991).
[27] A.M.L. Kraepiel, J.F. Chiffoleau, J.M. Martin and F.M.M. Morel, *Geochim. Cosmochim. Acta*, **61**, 1421–1436 (1997).