Fractionation of heavy metals in surface sediments of Taihu Lake, East China

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Abstract

The BCR (European Communities Bureau of Reference) three-step sequential extraction procedure was applied to fractionate heavy metals in the sediment of Taihu Lake. For the determination of total metal concentration of the sediments, sample digestion was achieved by using HF/H₂O₂/HNO₃ (2/1/1) acid mixture in a microwave-irradiated closed vessel system. The concentrations of Cd, Ni, Cr, Zn, Cu and Pb in various extracts solutions were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). The results obtained from the BCR three-step sequential extraction indicated relatively high mobility of Zn, Cu, Pb and Ni in the sediments while Cd and Cr were poorly mobile. Enrichment of heavy metals was found in the sediments collected in the northern parts of Taihu Lake. In the sediments collected in the southern and western sides of the Lake, heavy metal concentrations were relatively low. The relationship between total organic carbon (TOC) and heavy metals concentrations in the sediments is discussed.

1. Introduction

Sediment constitutes the most important sink of metals and other pollutants, it can act as a non-point source and have the potential to release the sediment-bound metals and other pollutants to overlying waters, and in turn adversely affects aquatic organisms.

As the third largest freshwater lake of China with water surface area of 2334 km², the Taihu Lake region holds 0.4% of the nation's total area, 2.9% of the nation's population, and more than 14% of the gross domestic production (GDP). The Lake is an important source of drinking water for the residents living nearby, and also for freshwater fisheries. The lake has been contaminated by industrial and household effluent combined with agricultural run-off, and for decades, the water quality of the lake has been deteriorating (Jin & Ye 1999).

Total metal analysis may provide information concerning possible enrichment of heavy metals in sediment, but it is often assumed that heavy metals with different forms have different bioavailability and toxicity to plants and animals. When the possible biological effects of trace metals in sediments need to be evaluated, additional studies are required. However, very little information is available on the heavy metal fractionation status in the sediment of Taihu Lake.

The objective of this study was to determine the concentration, distribution and fractionation of heavy metals in the sediment of Taihu Lake.

Microwave-assisted acid solubilization has been proved to be the most suitable method for the digestion of complex matrices such as sediments and soils (USEPA 1995; Kingston 1998). This method shortens the digestion time, reduces the risk of external contamination and uses smaller

quantities of acids, thereby improving detection limits and the overall accuracy of analytical method.

Among various sequential extraction procedures (Matzner & Prenzel 1992; Gupta *et al.* 1996; McGrath 1996) in fractionation of heavy metals in soil, those described by Tessier *et al.* (1979) and Salomons and Forstner (1984) have received wide application. In the late 1980s, measurements and testing program (formerly BCR) organized a project for studying mobility and availability of metals in sediments which reached a compromise between analysis time and the amount of information obtained.

In the present study, the sequential extraction procedure designed by the BCR was applied to determine the solid-phase distribution of trace metals in sediments of Taihu Lake. The microwave digestion technique was used to digest the sediment samples for the estimation of total metal contents. The leachable parts from sequential extraction were determined by ICP-AES analysis. The relationship between trace metal partitioning and TOC content in sediment was also investigated.

2. Materials and methods

2.1. Sampling

Twelve sediment samples were collected with a Van Veen grab in Taihu Lake in November 2000 as shown in Figure 1. At each sampling site, 1 kg

of sediment was collected and stored in polyethylene bags.

2.2. Sample preparation

Sediment samples were freeze-dried by a Yamato freeze dryer, homogenized and sieved (2 mm). pH of the sediment samples was determined according to Folsom *et al.* (1981).

2.3. Total metal concentration analysis

0.1 g sediment sample was put in a Teflon PFA microwave vessel, adding 4 mL HF/H₂O₂/HNO₃ (2/1/1) acid mixture, and left in contact with the acid solution for 4 h. The vessel was then sealed and heated in the microwave oven. After cooling, the clear solution obtained was quantitatively transferred into a 50 mL flask and brought to volume with deionized water and analyzed by ICP-AES.

2.4. BCR three-step sequential extraction procedure

The sequential extraction protocol proposed by the BCR (Ure *et al.* 1992) was applied to fractionate heavy metals of Cd, Ni, Cr, Zn, Cu and Pb. This protocol produced three independent fractions. They are B1: acetic acid extractable fraction or exchangeable fraction, B2: acidic hydroxylamine extractable metals or acid reducible fraction, and B3: acidic hydrogen peroxide extractable metals or organic fraction. The residual metals B4 were also determined by the same method as total

Fig. 1. Map of Taihu Lake showing sampling locations.

metal concentration analysis. The insoluble residue (B4) represents the portion of metals bound to silicate lattice or crystalline iron and manganese oxides.

For the BCR extraction, the first step was to shake the sediment sample with 40 mL 0.11 mol L⁻¹ acetic acid (HOAc; pH 2.9) for 16 h, followed by centrifugation and collection of the supernatant. The solid was rinsed with deionised water and centrifuged again. The residue was then shaken with 40 mL 0.1 mol L⁻¹ hydroxylamine hydrochloride (NH₂OH-HCl; pH 2) for 16 h, before repeating the centrifugation and rinse as in the first step. The third step involved digesting with 10 ml 30% (w/v) hydrogen peroxide for 1 h at room temperature, adding a further 10 mL H₂O₂ and digesting for 1 h at 85 °C. The solution was then reduced to a few mL before adding 50 mL 1 mol L⁻¹ ammonium acetate (NH₄Ac; pH 2) to the residue and shaking for 16 h. The supernatant was collected after centrifugation.

2.5. Technical details

TOC of sediments were determined by Tocometer (Tekmar-Dohrmann Apollo 9000, USA). Microwave oven (CEM MDS 2000, USA) was used to digest the samples. The operating frequency of the oven was 2450 MHz, maximum power was about 600 W. Cd,

Ni, Cr, Zn, Cu and Pb concentrations were determined by ICP-AES (Jarrell-Ash Icap 9000, USA).

Stock standard solutions of Cd, Ni, Cr, Zn, Cu and Pb (1000 ± 2 mg L⁻¹ in 5% HNO₃) were obtained from National Standard Materials Center of China. All other chemicals were of analytical grade. Glassware used was cleaned by soaking in a 1:1 (v/v) nitric acid solution overnight and then rinsed with deionized water.

3. Results and discussions

3.1. Total concentrations of heavy metals in sediment

Total concentrations of Cd, Ni, Cr, Zn, Cu, and Pb determined in the sediments of Taihu Lake are presented in Table 1. Sampling sites T6 and T12 can be considered as unpolluted with no special inputs, the increase in agricultural and industrial activities combined with human wastes, were connected with metal levels found in the north of Taihu Lake. This increase was particularly significant for Cu, Zn and Ni in the most urban and industrial stations (T1–T2). The sequence of heavy metal concentrations was north bank > south bank > west bank > center of the Lake. This result demonstrate that the effluent from a larger city (Wuxi) contained larger amounts of heavy

Table 1. Total metal concentrations in surface sediments of Taihu Lake.

Sampling sites	Latitude	Longitude	pH	Concentration (mg kg ⁻¹)					
				Cr	Cu	Zn	Cd	Ni	Pb
T1	31° 32' 14"N	120° 13' 17"E	7.17	162.1	102.2	370.3	6.2	121.4	388.3
T2	31° 32' 00"N	120° 12' 04"E	7.40	146.2	68.2	209.4	8.9	89.6	495.4
T3	31° 30' 09"N	120° 12' 02"E	7.25	85.6	33.4	141.9	4.9	41.9	286.6
T4	31° 28' 43"N	120° 11' 48"E	7.43	141.7	52.1	206.0	6.8	65.3	443.5
T5	31° 26' 45"N	120° 11' 24"E	7.41	136.4	42.0	135.1	8.4	63.3	482.6
T6	31° 24' 59"N	120° 11' 16"E	7.40	95.7	31.2	78.3	3.9	40.3	258.9
T7	31° 20' 15"N	120° 10' 53"E	7.45	91.0	28.6	113.3	4.8	35.4	269.2
T8	31° 11' 29"N	119° 55' 32"E	7.23	106.1	34.5	156.5	7.3	46.5	408.1
T9	30° 59' 15"N	120° 07' 51"E	7.22	86.2	9.7	75.9	4.6	36.8	329.2
T10	31° 01' 43"N	120° 08' 10"E	7.16	102.1	34.3	137.2	5.7	42.1	384.3
T11	31° 03' 36"N	120° 08' 51"E	7.23	126.2	47.5	150.4	6.3	46.3	404.2
T12	30° 58' 46"N	120° 13' 23"E	7.16	84.4	31.9	71.6	4.8	33.5	336.5
Mean			7.29	113.6	44.6	153.8	6.05	55.2	373.9

metals than a smaller city (Huzhou), and that the center of the Lake was relatively clean.

3.2. Fractionation of heavy metals in sediments

Concentrations of heavy metals in the sediments of Taihu Lake in the four fractions are summarised in Figure 2, and compared to the total metal concentrations. The mass balance agreed within $\pm 7\%$

for Cd, Cr, Cu, and within $\pm 9\%$ for Ni, Pb and Zn. The extractable fractions of heavy metals in 0.11 mol L^{-1} acetic acid were very low for Cr (1.05%), moderate for Pb, Cd and Cu (4.6–10.5%) and relatively high for Ni and Zn (13.7–13.9%). More than 25% of the total Zn and Ni were released in the B2 fraction, the portions in this fraction for other heavy metals were 3.03% for Cr, 21.5% for Pb, 14% for Cu and 18.75 % for Cd. Ni,

Fig. 2. Distribution of heavy metal speciation in the sediments of Taihu Lake.

Cu, Cd, Pb and Zn released in the B3 fraction varied from 17.47 to 26.01%, while Cr was smaller (10.4%). In the B4 fraction, Cr took up the highest percentage of 85.4%, Cu and Cd the second (75.10%), Zn, Pb and Ni took up the lowest percentage of 41.72–53.44%. Copper can easily complex with organic matter because of the high formation constant of organic–Cu compounds (Stumm & Morgan 1981). In this study, Cu was primarily present in the residual fraction (B4) or associated with the organic fraction (B3), this result agrees with those found in the literature (Tessier *et al.* 1979). In agreement with several other papers (Tuin & Tels 1990) is the high variability that was found for the chemical forms of Zn associated with the different sediment fractions. The increase in the levels of the most bioavailable forms (B1&B2) of Ni and Zn in T1 and T2 was associated with industrial or, specifically, urban activities. Similar variations in the percentages, corresponding to the different fractions extracted from sediments, being dependent upon the economic activity of the area has been previously described in the literature. Cd had been a cause of concern due to its hazardous environmental implications, however the low content of Cd (below 5%) as B1 form indicates that Cd may not easily be taken up by living organisms.

It is assumed that the total organic carbon (TOC) can serve as a matrix on particle surfaces for complexing metals. Seidemann (1991) found a strong correlation between the percentage of TOC and metal pollution in sediment of an urban estuary. However, the relationship between the concentrations of heavy metals in different fractions and TOC is not well documented. In this study, the correlation matrix analysis between the TOC of sediment and the concentrations of heavy metals in total, and in B1, B2 and B3 fractions were carried

out and tabulated in Tables 2 and 3, respectively. (the concentration data are not shown). It can be seen that in the first matrix, Ni and Cu have the highest correlation with TOC ($r = 0.88$ – 0.93). The coefficient of TOC and metal concentrations for Zn and Cr are smaller ($r = 0.73$ – 0.79). Cd and Pb concentrations have no significant correlation with TOC. The first matrix also shows that Cr has a high coefficient with all the other five heavy metals ($r > 0.73$). Cu has a high coefficient with Zn and Ni ($r > 0.95$), Zn was significantly correlated only with Ni ($r = 0.93$), while Cd was significantly correlated only with Pb. The significant correlations may be related to the similar source and distribution pattern of these metals.

In the fractions of extractable forms of heavy metals in 0.11 mol L^{-1} acetic acid (water-soluble, exchangeable and carbonate-bound), a significant correlation ($r > 0.90$) has been identified among Cr, Zn, and Ni with TOC. There was also a significant correlation between Cr–Zn (0.957), Cr–Ni (0.973) and Zn–Ni (0.982). In the B2 fraction, extractable in hydroxylamine hydrochloride (heavy metals bound to iron and manganese oxides and hydroxides), a significant correlation ($r > 0.90$) has been identified between Zn, Ni with TOC. There was also a significant correlation between Zn and Ni (0.983). In the third moderately soluble fraction (heavy metals bound to organic matter and sulfides), a significant correlation ($r > 0.90$) has been observed among Cr, Cu, Zn, Ni and Pb with TOC, there were also significant correlations between Cr–Cu (0.996), Cr–Zn (0.995), Cr–Pb (0.938), Cu–Zn (0.992), Cu–Ni (0.992), Cu–Pb (0.941) and Zn–Ni (0.980). It is clear that in the third fraction more metals had significant correlations with TOC than that in the first and second fractions.

Table 2. Correlation matrix of TOC and total metal concentration.

Total	TOC	Cr	Cu	Zn	Cd	Ni
Cr	0.7342					
Cu	0.8820	0.8726				
Zn	0.7946	0.8392	0.9457			
Cd	0.4523	0.7296	0.4456	0.4473		
Ni	0.9263	0.8994	0.9760	0.9327	0.5569	
Pb	0.4029	0.7633	0.4747	0.4464	0.9443	0.5512

Table 3. Correlation matrix of TOC and metal concentrations (B1, B2 and B3 fractions).

	TOC	Cr	Cu	Zn	Cd	Ni
<i>B1</i>						
Cr	0.9371					
Cu	0.2197	0.1755				
Zn	0.9591	0.9573	0.2061			
Cd	0.1450	0.3043	0.4469	0.1306		
Ni	0.9612	0.9732	0.2130	0.9822	0.1587	
Pb	-0.092	0.1889	-0.0412	0.0627	0.5859	0.0207
<i>B2</i>						
Cr	0.3364					
Cu	-0.3187	0.2341				
Zn	0.9519	0.4844	-0.2336			
Cd	0.2570	0.1517	-0.1752	0.3801		
Ni	0.9452	0.4635	-0.2187	0.9827	0.4013	
Pb	-0.5863	0.3869	0.3043	-0.4221	-0.1162	-0.4517
<i>B3</i>						
Cr	0.9615					
Cu	0.9498	0.9958				
Zn	0.9607	0.9950	0.9918			
Cd	0.1999	0.2728	0.2472	0.2472		
Ni	0.9265	0.9839	0.9919	0.9800	0.2407	
Pb	0.9031	0.9379	0.9407	0.9527	0.3410	0.9357

4. Conclusions

1. The total concentrations of heavy metals in the sediments collected in the northern parts of the Taihu Lake were higher than that concentrations in the southern and western sides of the Lake.
2. The portions of heavy metals, based on BCR three-step sequential extraction procedure, indicates relatively high mobility of Zn, Cu, Pb and Ni in the sediments: Cr and Cd were mainly in the B4 fractions and hence poorly mobile.
3. The relationship between the concentrations of heavy metals to each other suggest that Zn, Cu and Ni probably came from the same kind of pollution source.
4. In the B3 fraction more metals had significant correlations with TOC than those of the B1 and B2 fractions, which indicates that the identification of the third fraction as the partition of heavy metals bound to organic matter and sulphides is reasonable.

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