

Sequential Extraction of Some Heavy Metals in Haihe River Sediments, People's Republic of China

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Metals can not be always fixed by sediments permanently, and they may be recycled via the biological and chemical agents, both within the sedimentary compartment and back to the water body. The changes in the environment conditions, such as acidification, redox potential conditions or increases in the organic ligand concentrations can cause the trace elements mobilization. As a sink and source, sediment constitute reservoir of the bioavailable trace elements and plays an important role in the geo-chemical cycles. So the investigation of heavy metal concentration in sediments is very important. However, the total concentration of metals can not provide sufficient information because the mobility, bioavailability and toxicity of metals depends not only on their total concentration but on the physicochemical form in which they occur.

Sequential extraction (SE) proposed by Tessier et al (1979) and Kersten (1986) provides more information about mobility, bioavailability and toxicity of metals. Following these two basic schemes, some modified procedures including the BCR method (Ure, 1993) were developed with the different sequences of reagents used or the modified operational conditions. In this study, the exchangeable fraction and the carbonate fraction were considered respectively. A developed five-step sequential extraction procedure was proposed based on the BCR and Kersten scheme. According to the proposed method, metals in sediments were separated into five different fractions, which could be described as exchangeable, carbonate, iron and manganese oxides, sulfides and organic matter, residue fractions. This sequential extraction scheme can provide the information about the extent that trace metals bound to the binding sites in sediments and help us in understanding geochemical processes of trace metals.

Haihe River is a famous river in north China and locates in Tianjin area. Tianjin city has a long history as an industrial city with a population of 9.16 million. Haihe River receives input of industrial, domestic and agricultural effluents from the cities and sends them into the Bohai Sea at the Tanggu influx. In our study, eight sampling sites were selected along Haihe River and the sediment samples were submitted to the proposed sequential extraction procedure to obtain the distribution patterns of metals. The sampling locations for the study were indicated in Figure 1.

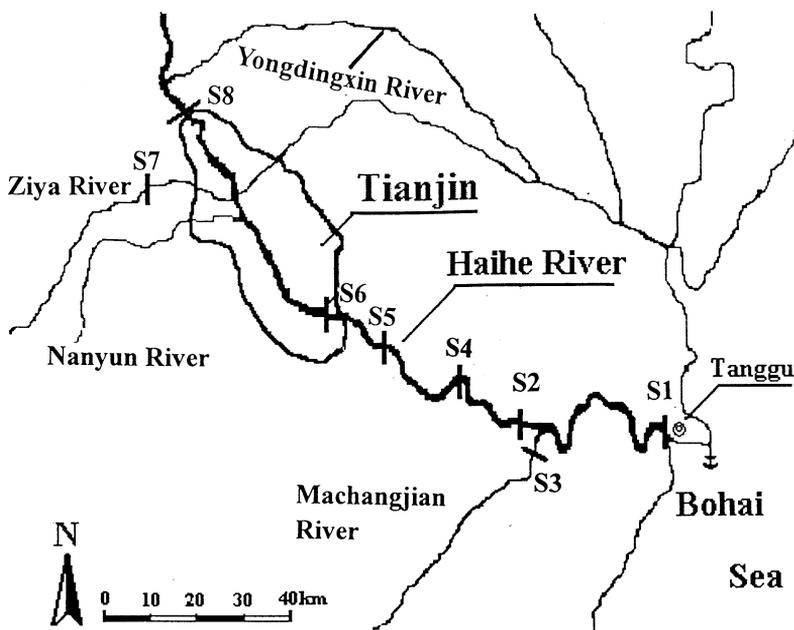


Figure 1. Map of study area and sampling sites.

MATERIALS AND METHODS

Elements were determined by graphite furnace atomic absorption spectrometry using a Hitachi Z5700 Polarized Zeeman spectrometer, equipped with single element hollow-cathode lamps and autosampler. Zeeman background correction was used for all analyses in the experiment. Palladium modification (200 mg l^{-1}) was preferred for the determination of cadmium and lead. Analytes were determined at the following wavelengths (nm): Cd 228.8; Cu 327.4; Mn 280.1; Co 240.7; Ni 232.0; Pb 283.3.

A horizontal rotator shaker was used for the extraction. The extract was centrifuged at 4000 r/min for 20 min by using a centrifuge. All the glass containers used in the experiment were marinated in 50% (V/V) nitric acid and rinsed with deionized water three times. The extracts from the samples were stored in PTFE tubes at 4°C in a refrigerator before analysis.

A five step sequential extraction procedure was developed and applied to determine the concentration of Cd, Mn, Cu, Co, Ni and Pb in the river sediments. The sequential extraction procedure is illustrated as follows:

20 ml $1\text{M NH}_4\text{OAc}$ at initial pH 7 was added to 0.5 g dry sediment in a 50ml centrifuge tube. The mixture was shaken for 2 h at room temperature.

20 ml volume 1M NaOAc buffered to pH 5.0 with HOAc was added to the residue from the above step and stirred for 5h at room temperature.

The residue from step two was extracted with 20ml 0.1M NH₄OH-HCl (adjusted to pH 2 with HNO₃). The tube was then shaken for 16h at room temperature.

5 ml 30% H₂O₂ (pH 2.0 adjusted with HNO₃) was added to the residue from step three. The digestion procedure lasted for 1h at room temperature with occasional manual shaking. Then the centrifuge tube was put into a 85°C water bath for 1h. A second 5 ml aliquot of H₂O₂ was added and the tube was again heated to 85°C for 1h. 20ml 1M NH₄OAc (adjusted to pH 2.0 with HNO₃) was added to the cool, moist residue. Then the tube was shaken for 16h at room temperature.

The residue from step four was freeze-dried and 0.1000 g (dry weight) of residue was weighted into a 30ml Teflon container with seal and then 2 ml concentrated HNO₃, 0.5 ml HF were added in sequence. The container was heated at 180°C for 8 h.

At the end of each extraction step, the extract was separated by centrifugation and 10 ml deionized water was used to wash the residue by shaking for 15min. Then the tube was centrifuged, and the supernatant was decanted. To obtain the total concentration of elements in the samples, the total digestion procedure similar with the fifth step was applied. Compared to the fifth step extraction, 2 ml hydrogen peroxide was added to accelerate destruction of organic components in samples during the total digestion procedure.

RESULTS AND DISCUSSION

In order to evaluate the recovery and precision of the extraction procedure, a stream sediment reference material (GBW07310) was employed during the course of sequential extraction. Table 1 and Table 2 indicate that the proposed sequential extraction procedure is repeatable and reliable with acceptable standard deviation and good recoveries (93.8-118.8%). The results of the Haihe river sediment samples obtained from the proposed sequential extraction scheme are listed in Table 3.

Exchangeable fraction (F1): The metals in this fraction mean that they can be released easily by ion-exchange process. Usually the weakly-sorbed metal species, particularly those retained on the sediment surface by relatively weakly electrostatic interactions, are included in this operation fraction. Heavy metal concentration in the exchangeable fraction play a very important role in the evaluation of environment and always act as a pollution indicator (Forstner and Wittmann, 1979) for its environmental mobility and bioavailability. In our experiment, most of elements studied in this fraction were in very small section. For example, although 50.48 μg g⁻¹ lead was found at sampling site S5, the concentration occurred in the exchangeable fraction was only 0.01 μg g⁻¹ (account for 0.02% of total concentration).

The proportion of the exchangeable fraction was Cd 2.4-6.5%, Cu 0.6-4.1%, Co 0-1.3%, Ni 0.8-4.2% respectively. Relative higher proportion in this fraction was

found in distribution of Mn, which 5.8-13.0% of the total concentration was found in exchangeable fraction. The results from the study indicate that the river was not polluted seriously according to Forstner and Wittmann's criterion. The distribution patterns agree with the observation of Suriya and Branica(1995). In their study, the distribution of Cd, Pb and Cu in the exchangeable fraction was negligible. The similar results were also obtained by Stalikas et al. (1999) who used 0.05M EDTA solution as the extraction reagent for metals in the exchangeable fraction and found that the concentrations of metals in the phase were very low in general.

Carbonate fraction (F2): The metals occurred in this fraction may be thought to have been present as co-precipitated with carbonate minerals and is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5. In this work, a buffered acetic acid and sodium acetate was applied to achieve the information of the metal concentration in this

Table 1. Standard deviation of the proposed five-step sequential extraction procedure ($\mu\text{g g}^{-1}$ dry weight, n=5).

Element	Fraction				
	F1	F2	F3	F4	F5
Cd	0.082 ±	0.24 ±	0.34 ±	0.16 ±	0.19 ±
	0.009	0.058	0.028	0.006	0.026
Cu	0.120 ±	1.01 ±	0.07 ±	1.62 ±	17.06 ±
	0.016	0.062	0.005	0.19	1.06
Co	0.030 ±	0.41 ±	3.26 ±	8.01 ±	5.34 ±
	0.006	0.05	0.27	0.36	0.28
Ni	0.195 ±	1.40 ±	10.45 ±	7.95 ±	11.26 ±
	0.019	0.106	1.23	0.69	0.65
Mn	8.13 ±	101.30 ±	318.36 ±	106.57 ±	556.60 ±
	0.69	8.25	12.97	9.65	39.85
Pb	0.023 ±	0.38 ±	11.01 ±	7.26 ±	10.56 ±
	0.002	0.021	1.6	0.63	0.87

Table 2. Recovery of the proposed five-step sequential extraction procedure ($\mu\text{g g}^{-1}$ dry weight, n=5).

Element	Total	Reference value	Recovery ^a (1)	Recovery ^b (2)
Cd	1.05 ± 0.087	1.12 ± 0.12	96.4	93.8
Cu	23.15 ± 1.24	22.6 ± 2.0	85.9	102.4
Co	18.17 ± 0.56	15.3 ± 1.7	93.9	118.8
Ni	29.89 ± 1.68	30.2 ± 2.6	104.6	99.0
Mn	1009.90 ± 69.45	1013 ± 44	108.0	99.7
Pb	28.14 ± 1.32	27 ± 3.0	103.9	104.2

^aRecovery (1) = $(C_{F-1}+C_{F-2}+C_{F-3}+C_{F-4}+C_{F-5})/C_{\text{Total}}$, given in percentage (%)

^bRecovery (2) = $C_{\text{Total}}/C_{\text{Reference value}}$, given in percentage (%)

Table 3. Sequential extraction results for the sediment samples from Haihe River ($\mu\text{g g}^{-1}$ dry weight).

Site	Fraction	Cu	Mn	Co	Ni	Pb	Cd
S1	F1	1.52	79.92	0.18	1.07	0.04	0.05
	F2	2.55	199.23	1.97	3.63	1.25	0.10
	F3	0.12	56.77	1.92	5.03	0.23	0.22
	F4	2.67	36.13	2.99	9.92	3.70	0.44
	F5	40.26	485.26	14.56	15.62	30.11	0.76
S2	F1	0.46	64.02	0.09	0.38	0.02	0.04
	F2	0.82	114.23	1.28	1.80	1.21	0.10
	F3	0.02	22.62	1.66	2.87	0.06	0.14
	F4	1.02	35.25	1.77	5.28	3.02	0.15
	F5	25.68	592.36	12.38	24.88	26.02	0.61
S3	F1	0.52	76.50	0.07	1.40	0.01	0.03
	F2	0.91	200.00	1.52	4.19	1.34	0.09
	F3	0.02	41.91	1.29	3.99	0.07	0.21
	F4	1.04	24.03	1.66	7.03	3.32	0.11
	F5	28.89	456.66	12.86	19.26	14.01	0.60
S4	F1	1.27	92.70	0.21	1.05	0.01	0.04
	F2	1.31	193.25	1.75	3.11	1.39	0.11
	F3	0.09	40.31	2.11	4.23	0.39	0.12
	F4	0.22	24.70	2.10	5.96	2.17	0.38
	F5	28.06	359.87	9.56	16.42	12.85	1.01
S5	F1	0.82	85.27	0.12	0.72	0.01	0.06
	F2	0.93	137.18	1.02	1.81	0.98	0.14
	F3	0.04	24.21	1.55	1.90	0.07	0.22
	F4	1.51	32.99	1.52	5.34	3.07	0.15
	F5	26.33	408.89	11.45	24.65	46.35	0.35
S6	F1	1.01	91.29	0.17	1.44	0.01	0.09
	F2	1.24	132.21	1.81	4.36	1.69	0.16
	F3	0.01	24.50	1.76	5.35	0.16	0.20
	F4	0.48	25.83	1.57	6.55	4.12	0.38
	F5	36.21	468.77	12.36	16.24	26.27	1.32
S7	F1	0.82	30.65	ND ^a	0.29	0.02	0.05
	F2	0.08	57.09	0.36	1.10	1.49	0.17
	F3	0.06	15.45	0.68	1.51	0.03	0.13
	F4	1.33	28.48	1.69	8.76	3.62	0.08
	F5	26.89	401.22	11.55	22.31	21.13	0.46
S8	F1	0.23	112.29	0.12	1.26	0.03	0.07
	F2	1.44	200.91	2.36	4.51	1.03	0.13
	F3	0.03	44.25	2.02	4.97	0.06	0.21
	F4	1.34	31.88	2.02	7.43	2.79	0.18
	F5	32.01	621.36	16.23	28.56	30.44	0.66

^a ND : not detected.

fraction. The concentration range was as follows: Cd 0.09-0.17 $\mu\text{g g}^{-1}$, Cu 0.08-2.55 $\mu\text{g g}^{-1}$, Co 0.36-2.36 $\mu\text{g g}^{-1}$, Ni 1.10-4.51 $\mu\text{g g}^{-1}$, Mn 57.09-200.91 $\mu\text{g g}^{-1}$, Pb 0.98-1.69 $\mu\text{g g}^{-1}$. The proportion of this fraction in the total concentration was about 10% for Cd and Co, 0.3-5.4% for Cu, 3.2-12.8% for Ni, 1.9-8.3% for Pb. The relative higher proportion was also found for element Mn, which 10.7-27.2% of total concentration occurred in the F2 carbonate fraction. Carbonates were regarded as inefficient metal carrier phases (Sigg, 1987), so high concentration of Mn in this fraction maybe result from the poor selectivity of the reagent used for Mn and the dissolution of Mn in hydrous oxides.

Iron-manganese oxides (F3): It is well established that iron and manganese oxides exist as nodules, concretions, cement between particles, or simply as a coating on particles; these oxides are excellent scavengers for trace metals and are thermodynamically unstable under anoxic conditions. By controlling the Eh and pH of reagents, dissolution of some or all the metal-oxide phases can be released. In our experiment 0.1M $\text{NH}_4\text{OH} \cdot \text{HCl}$ (HNO_3 , pH=2.0) was used. A very small proportion 0.02-0.3% and 0.1-2.3% was found in this fraction for Cu and Pb respectively. Similar proportion range was found for Co (4.8-13.4%) and Ni (4.4-15.8%). The variation of proportion distribution according to sampling sites for Cu, Co and Ni was not significant. Compared to the exchange fraction and the carbonate fraction, proportion of Cd in the reducible fraction increased (7.2-24.2%) and the proportion of Mn decreased (2.7-6.6%). It should be noticed that the distribution of Cd in the reducible fraction with sampling positions varied evidently. The lowest proportion of Cd (7.2%) was found at S4 and the highest proportion (24.2%) was found at S5. So significant difference existing between the two neighbor sites indicate that S5 was influenced by anthropologic pollution more seriously.

Sulfides and organic matter fraction (F4): In sediments, trace metals may be associated with the organic matters, such as living organisms, organic coatings on inorganic particles and biotic detritus. Under the oxidizing conditions, the organic materials may be destroyed and the trace metals associated with them may be released into the environmental water system. Metals in this fraction are more stable and difficult to take part in the geochemical cycle. It is not to say that metals in this fraction do not pose threaten to environment. The metals in this fraction always act as a sink and reservoir for pollution. In this study, the small proportions of the total concentration were found in this fraction for Cu (0.7-5.7%) and Mn (3.0-5.3%) in the sediments from Haihe River. As to Co and Pb, about 10% of the total concentration occurred in this fraction and the relative higher proportion occurred to Cd (8.7-28.0%) and Ni (15-28.1%). It was found that the higher proportion of the total concentration was present in this fraction in the lake sediments for Co, Ni, Pb and Mn each by Tokalioglu et al. (2000). That Cu occurred in forms of the stable organic complexes and the metal sulfides in the lake sediments was also indicated in his paper, but, in our study, only very small proportion Cu (0.7-5.7%) of Cu was in the sulfides and organic matter fraction.

Residue fraction (F5): Metals in the residue fraction are safer to environment for

their lowest mobility and bioavailability. Primary and secondary mineral containing metals in the crystalline lattice constitute the bulk of this fraction. To leach elements in this fraction is more difficult, because the structure of the crystalline lattice must be destroyed sufficiently. In this experiment, the aim was obtained by using of a strong acid HF. The results showed that the metals studied could be extracted completely. From the sequential extraction results, most of the metals occurred in the residue fraction accounted for a large proportion of the total concentration except for Cd. The results agree with the observation obtained by Martin et al (1998) who found that approx. 70-80% of the total Ni and 60% of the total Cu were in the residue fraction in the river sediments.

From this study, the proposed five-step sequential extraction procedure is reliable and repeatable. Although the influence of non-corresponding reagents on other sediment components can not be ignored during the whole sequential extraction procedure, the method can supply more information about the mobilization and bioavailability of metals and can help us to understand the metal recycles further. The results of the experiment indicate that Haihe River was not polluted with studied heavy metals seriously with the moderate concentration and the large proportion of total concentration in the residue fraction, excepted for the element Cd.

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