Evaluation of Extraction Techniques for the Determination of Heavy Metals in River Sediments

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Abstract

In order to distinguish whether heavy metal contents originate from a rock matrix or pollution, six different extraction techniques for copper, lead and cadmium were studied in Nagara River sediments in Gifu Prefecture, Japan. The extraction agents were hydrochloric-nitric acid mixture (1+1), 3N hydrochloric acid solution, 0.5N hydrochloric acid solution, 6M formic acid solution, 1N hydroxylamine hydrochloride plus 25% acetic acid solution and 0.05N ethylenediaminetetraacetic acid solution.

The comparison of the six extraction techniques was conducted on the basis of the heavy metal contents originating from pollution, which was estimated by subtracting background values from total contents. For copper, 3N hydrochloric acid is preferable, but in sediments with poor ignition loss, 0.5N hydrochloric acid and 6M formic acid are recommended. 1N hydroxylamine hydrochloride plus 25% acetic acid is suitable for lead and cadmium.

1. Introduction

Various extraction methods have been applied for the determination of heavy metals in aquatic sediments. In Japan, a sediment analytical method involving hydrochloric-nitric extraction is commonly employed for the evaluation of environmental pollution by heavy metals (WATER QUALITY BUREAU, Environmental Agency of Japan, 1975). Extraction with such a strong mineral acid assures highly effective extraction of heavy metals and is advantageous for the simultaneous determination of a large number of metals. On the other hand, a rock mineral can be partially attacked (AGEMIAN *et al.*, 1976), so it is difficult to evaluate strictly the degree of pollution by heavy metal only with the results obtained by the above method.

Some selective extraction methods using hydrochloric acid, ethylenediaminetetraacetic acid and hydroxylamine hydrochloride plus acetic acid were proposed by RAY *et al.* (1957), GOLDBERG *et al.* (1958) and CHESTER *et al.* (1967), in order to investigate the partitioning of trace elements in marine sediments. These methods were

applied for different environmental samples, e.g., river sediments (TADA *et al.*, 1976 a, b; AGEMIAN *et al.*, 1976; TADA *et al.*, 1979; LUONA *et al.*, 1981), lake sediments (OTSUKA, 1981), marine sediments (CHESTER *et al.*, 1967; ITO *et al.*, 1975, 1976; KITANO *et al.*, 1980 a, b) and soils (MAYNARD *et al.*, 1973; BRADSHAW *et al.*, 1974). Their heavy metal content and existing forms were also discussed. However, little effort has been made to ascertain the availability of extraction methods to distinguish between heavy metal contents originating from rock matrix and those from pollution (TADA *et al.*, 1976; AGEMIAN *et al.*, 1976). The aim of this work is mainly to demonstrate the effectiveness of different extraction methods by applying them to copper, lead and cadmium in river sediments.

2. Experimental

2-1. Sample collection and treatment

Figure 1 shows the river sediment sampling locations. One sediment sample was collected from each station in the Nagara River (Gifu Prefecture) in June 1981, and six samples were taken at St. 8. Sediment

Fig. 1. Location of sampling stations of the river sediments in the Nagara River.

samples were scooped from approximately 10 cm depth with a stainless-steel trowel and transported to the laboratory, where they were sieved to less than 2 mm and centrifuged at 3,000 rpm for 20 min.

2-2. Heavy metal extraction systems

Hydrochloric-nitric acid mixture (1+1) extraction (method A); 5 g of sediment was leached with 20 ml of boiling hydrochloric-nitric acid mixture (1+1) for 2 hrs (WATER QUALITY BUREAU, Environmental Agency of Japan, 1975).

3N hydrochloric acid extraction (method B); 10 g of sediment was leached with 30 ml of 3N hydrochloric acid in a water bath for 3 hrs (RAY *et al.*, 1957).

0.5N hydrochloric acid extraction (method C); 10 g of sediment was leached with 100 ml of 0.5 N hydrochloric acid and shaken for 8 hrs at room temperature (MAYNARD *et al.*, 1973).

6 M formic acid extraction (method D); 10 g of sediment was heated with 50 ml of 6 M formic acid in a water bath for 1 hr (RAY *et al.*, 1957).

1N hydroxylamine hydrochloride plus 25% acetic acid extraction (method E); 5 g of sediment was leached with 60 ml of hydroxylamine hydrochloride and 140 ml of 35% acetic acid and shaken for 4 hrs at room temperature (CHESTER *et al.*, 1967).

0.05N ethylenediaminetetraacetic acid extraction (method F); 5 g of sediment was leached with 100 ml of 0.05N ethylenediaminetetraacetic acid and shaken for 8 hrs at room temperature (MAYNARD *et al.*, 1973).

2-3. Apparatus

Measurements of copper, lead and cadmium were made with a Hitachi, Model 308, atomic absorption spectrophotometer equipped with a triple-slot air-acetylene burner. Air and acetylene pressure were 1.8 and 0.5 kg·cm⁻², respectively. Perkin-Elmer Intensitron lamps were used for the determination.

2-4. Extraction procedure of heavy metals

For determining heavy metals, the DDTC-MIBK extraction method was used (WATER QUALITY BUREAU, Environmental Agency of Japan, 1975).

2-5. Ignition loss

Ignition loss data were obtained from weight loss by ignition to 550°C for 2 hrs (WATER QUALITY BUREAU, Environmental Agency of Japan, 1975).

3. Results and Discussion

3-1. Comparison of extractabilities of heavy metals in sediments by different extraction systems

Applying six extraction methods described in 2-2. for the samples collected from St. 8, copper, lead and cadmium were analyzed and analytical results of these metals were given in Table 1. The metal contents determined by the method A were the highest in every sediment sample. The extractabilities of each metal calculated from the basis of the results with method A were summarized in Table 2.

Table 1. Analytical results of heavy metals in the river sediments of the Nagara River (St. 8) using different extraction system.

Metal	Ignition loss (%)	A	B	C	D	E	F
Copper ($\mu\text{g}\cdot\text{g}^{-1}$)	1.0	7.71	5.39	3.17	4.06	3.19	3.28
	1.0	7.07	4.65	3.89	3.11	3.28	2.81
	1.3	11.2	7.69	5.57	6.07	5.13	7.80
	1.7	11.9	7.87	7.40	6.58	4.25	4.36
	2.3	15.5	13.8	9.39	10.8	8.40	7.10
	4.5	33.2	30.4	24.6	24.0	15.6	18.5
	(1.7)	(12.4)	(9.27)	(6.99)	(7.12)	(5.57)	(5.87)
Lead ($\mu\text{g}\cdot\text{g}^{-1}$)	1.0	8.88	6.15	3.69	3.81	0.90	2.30
	1.0	8.91	6.81	3.94	3.07	2.30	2.04
	1.3	9.23	8.47	6.12	5.75	4.89	4.02
	1.7	11.2	10.1	7.27	5.19	6.31	4.48
	2.3	13.3	10.3	8.69	5.79	7.74	5.75
	4.5	20.6	17.3	16.0	14.6	12.7	10.9
	(1.7)	(11.4)	(9.28)	(6.69)	(5.56)	(4.30)	(4.18)
Cadmium ($\mu\text{g}\cdot\text{g}^{-1}$)	1.0	0.26	0.20	0.11	0.09	0.06	0.07
	1.0	0.25	0.16	0.07	0.10	0.03	0.04
	1.3	0.37	0.18	0.13	0.12	0.01	0.08
	1.7	0.32	0.20	0.12	0.13	0.10	0.09
	2.3	0.39	0.22	0.21	0.17	0.19	0.10
	4.5	0.55	0.36	0.30	0.35	0.07	0.28
	(1.7)	(0.34)	(0.21)	(0.14)	(0.14)	(0.05)	(0.09)

Values in parentheses denote geometric mean.

A, nitric-hydrochloric acid (1+1); B, 3N hydrochloric acid; C, 0.5N hydrochloric acid; D, 6M formic acid; E, 1N hydroxylamine hydrochloride+25% acetic acid; F, 0.05N ethylenediaminetetraacetic acid.

Table 2. Percentage of extraction of heavy metals by six extraction methods.

Metal	Metal, $\mu\text{g}\cdot\text{g}^{-1}$ by method A, B, C, D, E or F Metal, $\mu\text{g}\cdot\text{g}^{-1}$ by method A $\times 100$					
	A	B	C	D	E	F
Copper	100	75 $\pm$ 11	57 $\pm$ 10	58 $\pm$ 10	45 $\pm$ 6	48 $\pm$ 11
Lead	100	82 $\pm$ 8	60 $\pm$ 13	50 $\pm$ 13	44 $\pm$ 19	38 $\pm$ 11
Cadmium	100	64 $\pm$ 7	43 $\pm$ 9	44 $\pm$ 9	22 $\pm$ 15	29 $\pm$ 11

Data for copper, lead and cadmium from Table 1 referred to the results with hydrochloric-nitric acid method.

A, hydrochloric-nitric acid; B, 3N hydrochloric acid; C, 0.5N hydrochloric acid; D, 6M formic acid; E, 1N hydroxylamine hydrochloride+25% acetic acid; F, 0.05N ethylenediaminetetraacetic acid.

The percentage of extraction in these methods were in the order $A>B>D\geq C>F>E$ for copper, $A>B>C>D>E>F$ for lead, and $A>B>D\geq C>F>E$ for cadmium. Among the method C, E and F, which are well used as the selective extraction methods, the method C showed higher values

than other methods, but there was no noticeable difference between the methods E and F.

3-2. Availability of extraction methods for heavy metals in sediments originating from pollution

Heavy metal contents originating from

pollution in river sediments may be estimated by subtracting background values from total contents. In general, background values of heavy metals in river sediments have been analogized by heavy metal contents in sediments from non-polluted areas of the same watershed under the hypothesis that the geology of the survey area is similar to that of the non-polluted area (OKADA *et al.*, 1977; KUBO *et al.*, 1977). In the previous study, the present authors investigated the background values of heavy metals in Nagara River sediments using the hydrochloric-nitric acid extraction method, and revealed that the background values of copper, lead and cadmium were $3.5 \mu\text{g}\cdot\text{g}^{-1}$, $6.4 \mu\text{g}\cdot\text{g}^{-1}$ and $0.24 \mu\text{g}\cdot\text{g}^{-1}$, respectively (SHIMOKAWA *et al.*, 1980 a).

These data could not be strictly regarded as background values because hydrochloric-nitric acid does not liberate all of the metals from the silicate matrix. However, they are sufficient to estimate the heavy metal contents originating from pollution when total contents are obtained by the same technique. Thus, the method's lack of extractability can be deleted in the calculating process.

Hence, the copper, lead and cadmium contents in sediments originating from pollution were estimated from the data shown in Table 1, column 2 and the background values described above; then the heavy metal contents obtained by different extraction methods were compared to the estimated values. It is apparent

Fig. 2. Relations of copper by different extraction methods and ignition loss in sediments.

A, hydrochloric-nitric acid; B, 3N hydrochloric acid; C, 0.5N hydrochloric acid; D, 6M formic acid; E, 1N hydroxylamine hydrochloride+25% acetic acid; F, 0.05N ethylenediaminetetraacetic acid; G, A—background value (estimated from the analytical data of sediments in the upper reach of the Nagara River)

from Table 1 that heavy metal contents generally increase with increasing ignition loss. The measured and estimated pollutant values (Y) were found to be related to ignition loss (X) in the following form at 1% significance $Y=AX+B$ empirically. Then, a comparison of the six extraction methods was made on the basis of the above relationship.

Figure 2 shows the relationship of copper contents and ignition loss in sediments. Analytical results by the method B were in good agreement with the estimated values over the whole range of ignition loss. With methods C and D, a fair agreement was recognized in the range of lower ignition loss (less than 2%), but in the range of higher ignition loss the measured values

were somewhat lower than the estimated ones. The method A gave higher values, whereas methods E and F gave lower values, than the estimated values.

Figure 3 shows the relationship of lead contents and ignition loss in sediments. Methods D and E were preferable in the overall range of ignition loss. Methods A, B and C gave higher than the estimated values in the whole range of ignition loss, but the method F generally gave lower values in the higher range of ignition loss.

Figure 4 shows the relationship of cadmium contents and ignition loss in sediments. Results of the method E were approximately in accord with the estimated values. All but the method F extraction method gave higher than the estimated

Fig. 3. Relations of lead by different extraction methods and ignition loss in sediments.

A, hydrochloric-nitric acid; B, 3N hydrochloric acid; C, 0.5N hydrochloric acid; D, 6M formic acid; E, 1N hydroxylamine hydrochloride+25% acetic acid; F, 0.05 N ethylenediaminetetraacetic acid; G, A—background value (estimated from the analytical data of sediments in the upper reach of the Nagara River)

Fig. 4. Relations of cadmium by different extraction methods and ignition loss in sediments.

A, hydrochloric-nitric acid; B, 3N hydrochloric acid; C, 0.5 N hydrochloric acid; D, 6M formic acid; E, 1N hydroxylamine hydrochloride+ 25% acetic acid; F, 0.05 N ethylenediaminetetraacetic acid; G, A—background value (estimated from the analytical data of sediments in the upper reach of the Nagara River)

values. In fact, method F gave appreciably lower values in the range of higher ignition loss.

3-3. Application of some extraction methods to the sediments from several stations in the Nagara River

Table 3 gives a description of sediment samples collected from 7 stations in the

Nagara River. The linear relationships between the estimated pollutant value (Y) and the ignition loss (X) obtained from the data for St. 8 were as follows; $Y = 7.21X - 3.26$ for copper, $Y = 3.08X - 0.63$ for lead, $Y = 0.080X - 0.039$ for cadmium. The estimated pollutant values in the sediments from the sampling stations except St. 8

Table 3. Description of sediment samples.

Station	Sample location	Distance from coastline	Sediment type	Ignition loss (%)
1	Wago Bridge	112	Sand	1.6
2	Mino Bridge	75	Silty sand	1.6
3	Aikawa Bridge	59	Fine sand	1.0
4	Goudo Bridge	45	Silty sand	2.9
5	Nagara Bridge	39	Fine sand	1.4
6	Nannou Bridge	28	Silty sand	3.0
7	Tokai Bridge	22	Anaerobic mud	3.1

could be calculated by substituting the ignition loss values listed in Table 3 in the above equations. Then, on the basis of these estimated pollutant values, the effectiveness of methods C and E was studied, because they were commonly used for the determination of metals originating from polluted water. The copper, lead and cadmium results were illustrated in Figs. 5, 6 and 7, respectively.

In Fig. 5, the measured values by the method C were in good agreement with estimated values. The results do not conflict

with the information obtained in 3-2. because the ignition loss of sediment samples was relatively low (less than 3%). Method E showed lower than the estimated values for all sediment samples.

In Fig. 6, the estimated values were

Fig. 5. Distribution of copper in sediments of the Nagara River with two extraction methods.

●, copper contents with 0.5N hydrochloric acid; ◐, copper contents with 1N hydroxylamine hydrochloride + 25% acetic acid; ○, estimated copper contents originating from pollution.

Fig. 6. Distribution of lead in sediments of the Nagara River with two extraction methods.

●, lead contents with 0.5N hydrochloric acid; ◐, lead contents with 1N hydroxylamine hydrochloride + 25% acetic acid; ○, estimated lead contents originating from pollution.

Fig. 7. Distribution of cadmium in sediments of the Nagara River with two extraction method.

●, cadmium contents with 0.5 N hydrochloric acid; ◐, cadmium contents with 1N hydroxylamine hydrochloride + 25% acetic acid; ○, estimated cadmium contents originating from pollution.

intermediate between the values measured by method C and those by method E, but rather near the values by method E. The results were almost consistent with those shown in Fig. 3.

In Fig. 7, the method E showed good conformity with the estimated values, but the results mostly coincide with those shown in Fig. 4.

For the selective extraction of lead and cadmium in sediments originating from pollution, methods D and E using a weak extracting agent would be preferable. For copper, methods using a stronger extracting agent (e.g., method B or C) are required. It may be due to the fact that copper can be strongly complexed with organic compounds (SCHNIZER *et al.*, 1967).

Acknowledgements

We would like to thank Mr. S. NISHIWAKI, President of the Gifu Prefectural Research Institute for Environmental Pollution, for his valuable suggestions and publication permission.

摘 要

岐阜県長良川の底質中の銅、鉛およびカドミウムについて、硝酸-塩酸混液 (1 + 1) 抽出法、3 N 塩酸溶液抽出法、6 M 蟻酸溶液抽出法、1 N 塩酸ヒドロキシルアミン + 25% 酢酸溶液抽出法および 0.05 M EDTA 溶液抽出法を用いて、それぞれの金属元素を定量し、汚染由来推定重金属量 (同河川上流部底質の分析値をバックグラウンド値として算出) と比較し、各抽出法の汚染由来重金属抽出法としての有効性を検討した。

銅は、3 N 塩酸抽出法による測定値がもっとも汚染由来重金属量と一致した。また、強熱減量の少ない (1 ~ 2%) 試料については、0.5 N 塩酸あるいは 6 M 蟻酸によっても比較的良好な結果が得られた。鉛は、6 M 蟻酸抽出法および 1 N 塩酸ヒドロキシルアミン + 25% 酢酸抽出法が他の抽出法に比して優れていた。カドミウムは、1 N 塩酸ヒドロキシルアミン + 25% 酢酸法が他の抽出法に比して優れていた。

References

- AGEMIAN, H. A. and S. Y. CHAU (1976) : Evaluation of extraction techniques for the determination of metals in aquatic sediments. *Analyst*, 101: 761-767.
- BRADSHAW, P. M. D., I. THOMPSON, B. W. SMEE and J. O. LARSON (1974) : The application of different analytical extractions and soil profile sampling in exploration geochemistry. *J. Geochem. Explor.*, 3: 209-225.
- CHESTER R. and M. J. HUGHES (1967) : A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chem. Geol.*, 2: 249-262.
- GOLDBERG, E. D. and G. O. S. ARRHENIUS (1958) : Chemistry of Pacific pelagic sediments. *Geochim. Cosmochim. Acta.*, 13: 153-212.
- ITO, K., S. KOJIMA and Y. NARUSE (1975) : Heavy metals pollution of bottom muds in Nagoya Harbour. *Nagoya-shi Kogai Kenkyu Shoho*, 4: 45-54. (in Japanese)
- ITO, K., Y. NARUSE, S. KOJIMA and T. HASEGAWA (1976) : Behavior of heavy metals in water and bottom sediments in Nagoya Port. *Nagoya-shi Kogai Kenkyu Shoho*, 5: 53-57. (in Japanese)

- KITANO, Y. and R. FUJIYOSHI (1980 a) : Selective chemical leaching of cadmium, copper, manganese and iron in marine sediments. *Geochem. J.*, 14: 113-122.
- KITANO, Y. and R. FUJIYOSHI (1980 b) : Partitioning of cadmium, copper, manganese and iron into mineral and organic fractions in core sediments from the Osaka Bay. *Geochem. J.*, 14: 289-301.
- KUBO, K., M. TOUOKA, S. NAGAYAMA and K. MIYATA (1977) : Studies on heavy metals of river sediments in Kumamoto Prefecture. *Kumamoto-ken Eisei Kogai Kenkyu Shoho*: 45-48. (in Japanese)
- LUONA, S.N. (1981) : A statistical assessment of the form of trace metals in oxidized estuarine sediments employing chemical extractants. *Sci. Total Environ.*, 17: 165-196.
- MAYNARD, D.E. and W.K. FLETCHNER (1973) : Comparison of total and partial extractable copper in anomalous and background peat samples. *J. Geochem. Explor.*, 2: 19-24.
- NARUSE, Y., R. ANDO, F. TSUCHIYAMA and K. BANNO (1980) : Heavy metals pollution in rivers of Nagoya City. *Nagoya-shi Kogai Kenkyu Shoho*, 10: 27-28. (in Japanese)
- OGURA, H., I. YARITA, S. KOBAYASHI and J. NAKAJIMA (1979) : Mechanism of metal accumulation of sediments of Edogawa and Murata rivers. *Suishitsu Odaku Kenkyu*, 2: 173-180. (in Japanese)
- OKADA, K., T. YAMAMOTO, Y. TAKADA, K. KUSUNOKI, M. MIYAHISA and Y. SOGA (1977) : Proposal and tentative plan of environmental maps. *Kogai to Taisaku*, 13: 12-19. (in Japanese)
- OTSUKA, H. (1982) : Forms of heavy metals in the settling matter from a man-made lake. *Jap. J. Limnol.*, 43: 28-39. (in Japanese)
- RAY, L., H.R. GAULT and C.G. DODD (1957) : The separation of clay minerals from carbonate rocks. *Am. Mineralogist*, 42: 681-686.
- SCHNIZER, M. and S.I.M. SKINNER (1967) : Organo-metallic interaction in soils. *Soil Sci.*, 104: 247-252.
- SHIMOKAWA, K., H. TAKADA, Y. YASUDA, N. WATANABE and Y. OSE (1979 a) : Particle size distribution of river sediments (I). *Suishitsu Odaku Kenkyu*, 2: 85-88. (in Japanese)
- SHIMOKAWA, K., H. TAKADA, N. WATANABE, Y. YASUDA and Y. OSE (1979 b) : Particle size distribution of river sediments (II). *Suishitsu Odaku Kenkyu*, 2: 152-156. (in Japanese)
- SHIMOKAWA, K., H. TAKADA, N. WATANABE, N. HARA, H. MORI, Y. YASUDA and Y. OSE (1980 a) : Correlation between heavy metals, ignition loss and clay in bottom sediments of the lower reach of Nagara River. *Suishitsu Odaku Kenkyu*, 3: 37-42. (in Japanese)
- SHIMOKAWA, K., H. TAKADA, N. WATANABE, H. MORI, N. HARA, Y. YASUDA and Y. OSE (1980 b) : Correlation between cation-exchange capacity and ignition loss, clay fraction or heavy metal content in bottom sediments from the Nagara River. *Suishitsu Odaku Kenkyu*, 3: 181-186. (in Japanese)
- TADA, F., T. TAKASHIMA, N. KAWAGUCHI, H. DOI and S. SUZUKI (1976 a) : Distribution of heavy metals in bottom mud of river (V). *J. Hyg. Chem.*, 22: 339-344. (in Japanese)
- TADA, F., K. YAMAZAKI, T. TAKASHIMA and S. SUZUKI (1976 b) : Distribution of heavy metals in bottom mud of river (IV). *Jap. J. Limnol.*, 37: 100-107. (in Japanese)
- TADA, F. and S. SUZUKI (1979) : Distribution of heavy metals in bottom mud of river (VII). *Jap. J. Limnol.*, 40: 153-161.
- WATER QUALITY BUREAU, ENVIRONMENTAL AGENCY OF JAPAN (1975) : *Measuring Method for Bottom Sediments*. (in Japanese)
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Accepted: 12 January 1983