Depth Profiles of Heavy Metals in the Surface Sediments of Hôedong Reservoir

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We investigated the depth profiles of heavy metals in the surface sediments at Hôedong reservoir in Pusan. Sampling was done at the intervals of 50 m of drift along the water channel into the reservoir. All samples were analyzed with an ICP-AES. We determined the content of Zn, Pb, Cd, Mn, Cu, Cr, and Fe. The overall mean content of these heavy metals were observed to $(2.9\pm1.2)\times10^{-3}$, $(1.3\pm0.7)\times10^{-3}$, $(1.9\pm2.1)\times10^{-4}$, $(2.3\pm1.1)\times10^{-2}$, $(1.6\pm1.0)\times10^{-3}$, and $(4.5\pm2.6)\times10^{-4}$ ppm/ppmFe, respectively excluding iron data. Mean contents of Cu show an increasing trend toward the surface of sediments, while those of Cd show a decreasing trend, and those of Pb and Cr are relatively stable.

Comparing with the contents of heavy metals in soils at two sites of Kumjeong mountain, enrichment factors of heavy metals in the surface sediments were determined. Among heavy metals we investigated, copper showed the largest value of enrichment factor. Considering the maximum content of heavy metals in the surface sediment, the values of enrichment factors of Cu, Cd and Cr were significant, which were 22, 8.1 and 4.0, respectively.

In leaching experiment, it appeared that Pb, Cd, Cr, and Fe in sediments were hardly leached out into water. We also examined the effect of pH on the content of heavy metals.

Key Words : heavy metal, depth profiles, sediments, leaching rates

1. Introduction

Soil has very complicated compositions. So it shows various responses to the pollutants. When soil becomes once polluted, its effect maintained for a very long time. Especially, heavy metals once adsorbed in soil may exist semi-permanently as far as they are not artificially eliminated.

Surface sediments also can act as vast reservoirs of heavy metals. If heavy metals exist as soluble chemicals in sediments, these contaminants may have serious effect on human body because they may be accumulated through food chain. The relative toxicity of heavy metals to plants and animals can be classified as follows: Cd > (Cu, Pb) > (Mn, Zn) > (Fe, Cr) (Evans, 1989). They have low resolvability and diffusibility, so pollution level may increase as time goes on. Many species of heavy metals come in sediments through the second pollution by air, water, or wastes. They are not distributed uniformly because of complicated compositions of sediments (Environ. Agency, 1986).

In this study, depth profiles of heavy metals in the surface sediments of Hôedong reservoir was studied. For the surface sediments, there is concern that the release of heavy metals would occur as a result of resuspension events caused by water, wind and dredging.

The objectives of this work were, (1) to investigate depth profiles of heavy metals in sediments, (2) to find correlation between the content of each heavy metal in sediments, and (3) to investigate the effect of heavy metals in sediments on the water quality.

2. Material and Method

2.1. Sampling Method and Area

In the Hôedong reservoir located at Kum-jeong-gu Oryun-dong in Pusan Metropolitan City, one of the four accumulated areas was chosen as a sampling area in Jan. 1996. The best place among them was selected based on the possibilities of no direct contamination as the result of human activities. As shown in Fig. 1, three sampling sites were taken at the intervals of 50m along the stream whose entrance is connected to Chôlma-myôn. Site 1 and site 3 were digged down to 190cm, and site 2 was to 100 cm. Sampling was done at the intervals of 5 cm from surface to 100cm depth, and of 15cm from 100 to 190cm depth. The physical conditions of these sites were different each other. Sediments at site 1 was relatively dry and uniform compare with that of site 3. At site 3, sediments shows higher water contents and is less uniform compard with site 1. At site 2, sampling of sediments was impossible below 100 cm depth because of too much water content. Water content was determined by weighing the sediment sample before and after drying it.

Sediments were collected by using a clay auger (cf. Cole Parmer #E-99026-10) and stored in a polyethylene bag. Sample preparation steps are as follows: air dry, mildly grind to pass through a 2mm standard sieve, homogenize, and finally store in a 250ml polyethylene bottle.
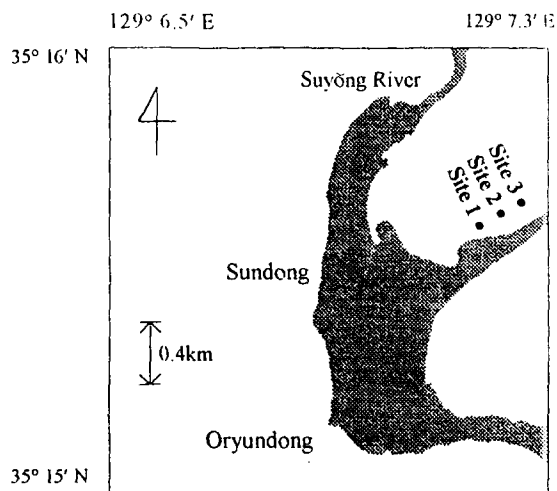

Fig. 1. The sampling sites in the Hôedong Reservoir

2.2. Leaching Experiments

Two specific samples of sediments were chosen for leaching experiment, the largest amount of heavy metals was found in one sample and the smallest in the other. In this study, leaching experiment is not a major part. Thus, the tendency of leaching of heavy metals into water was investigated with only two specific sediments.

Three aliquots of sediments were provided, 5g each and added 100ml of about 0.01 N NaNO$_3$. In order to see the effect of pH of water to the extent of leaching rate, one sample was kept at the original pH, and the others were adjusted to the original pH$\pm$1, respectively(Allen et al., 1995; Jackson et al., 1984; Bürgisser et al., 1973). Then, it was shaken for two hours before measuring the final pH and the content of heavy metals leached into water.

2.3. Analysis

The reagents were analytical grade from Junsei Co. To provide a sample solution, 25ml of

aqua-regia was added to about 5g of exactly weighed sediments, and shook it in a temperature controlled shaking bath at 30℃ for two hours. Then, the sample was filtered into a 100ml volumetric flask and filled with distilled-deionized water. The deionized water was provided with Millipore Water System. The content of Zn, Pb, Cd, Mn, Cu, Cr, and Fe was measured with an inductively coupled plasma atomic emission spectrometer (ICP-AES) (Japan, Seiko spectra 1200A) (Steven et al., 1996).

To obtain the recovery factors, standard solutions for atomic absorption (Katayama Chemical, Japan) of each heavy metal were used. In order to estimate the contents of heavy metals in sediments, calibration curves were plotted by using the standard solutions and experimental contents of heavy metals were calculated through interpolation or sometimes extrapolation from the calibration curve. These processes were performed by the computer system of the ICP spectrometer. Four data points were adopted in the calibration curve, three from the standard solutions of each heavy metal in different concentrations and the other one is the blank.

To obtain the enrichment factors of each heavy metal, soils in the Kumjeong mountain was taken as a reference. Soil was taken from two sites: one from north and the other from east side of that mountain where pollution level may be considered very low.

2.4. Data handling

All the data in this paper are relative content to the content of Fe in each sample as follows:

relative content =

$$\frac{\text{content of each heavy metal (ppm)}}{\text{content of Fe (ppm)}} \pm \text{s} \quad (2.1)$$

where $\text{s} = \dfrac{\text{content of each heavy metal(ppm)}}{\text{content of Fe(ppm)}} \times$

$\sqrt{\{\text{rsd(others)}\}^2 + \{\text{rsd(Fe)}\}^2}$ and rsd indicates the relative standard deviations. The actual reason we did not use the absolute content but used the relative value is that we made an agreement with the Water Works Headquaters Pusan Metropolitan City. The contents of heavy metals in the Hôedong reservoir may lead to very sensitive problems to the citizens. Thus, before obtaining permission to take the surface sediments of that reservoir, we came to an agreement not to disclose the absolute contents. So we selected the iron content as a normalization factor. Since iron was most abundant and most uniformly distributed among the heavy metals we studied. Iron also has been shown to be an important carrier phase for metals in sediments. The behavior of iron in sediments during early diagenesis can have a profound effect on the behavior of metals in sediments (Santschi, et al, 1990).

3. Results and Discussion

3.1. Analysis of heavy metal contents

For the standard solutions of Zn, Pb, Cd, Mn, Cu, Cr, and Fe, the recovery factors of each heavy metal obtained from the ICP spectrometer we used were >99%, respectively.

The maximum content of Zn, Pb, Cd, Mn, Cu, and Cr are 5.4×10^{-3}, 3.2×10^{-3}, 9.7×10^{-4}, 4.7×10^{-2}, 3.6×10^{-3}, and 1.3×10^{-3} ppm/ppmFe, respectively. We are more interested in the content of Pb, Cd, Cu and Cr because of their well known toxicity. Thus, depth profiles of only these four heavy metals are given in Table 1 and illustrated in Figures 2a~2d. Of these four heavy metals, copper is most highly contained in sediments,

Table 1. Contents of Pb, Cd, Cu, and Cr in the surface sediments of the Hôedong reservoir

depth (cm)	relative content (ppm/ppmFe)			
	Pb($\times 10^3$)	Cd($\times 10^4$)	Cu($\times 10^3$)	Cr($\times 10^4$)
5	1.4±0.9	1.9±1.9	2.4±0.8	4.4±2.2
10	1.3±0.7	1.8±1.7	2.0±0.7	4.5±1.7
15	1.3±0.6	1.5±1.3	2.4±0.3	3.9±0.7
20	1.3±0.7	1.7±0.9	2.2±0.6	7.2±4.9
25	1.0±0.4	1.5±1.6	2.0±1.4	3.8±1.6
30	1.0±0.5	1.6±1.1	1.6±0.8	4.0±0.7
35	1.2±0.6	1.6±1.2	1.9±0.2	3.5±0.8
40	1.3±0.6	1.4±1.2	2.5±0.5	4.1±1.2
45	1.9±1.4	1.6±1.2	3.5±1.2	4.2±1.1
50	1.0±0.7	1.4±0.9	2.1±1.4	4.6±2.9
55	1.1±0.8	1.3±0.7	2.0±1.2	4.1±2.7
60	1.1±0.7	1.3±0.6	1.5±1.2	6.9±5.3
65	1.2±0.5	1.2±0.9	1.1±0.5	3.6±2.0
70	1.5±0.5	1.5±1.0	1.6±0.7	3.5±0.7
75	1.4±0.4	1.6±1.1	1.5±0.9	3.5±0.7
80	1.2±0.5	1.4±1.1	1.5±0.7	3.4±1.2
85	0.79±0.39	1.2±0.9	1.2±0.6	5.1±2.9
90	0.82±0.38	0.61±0.32	0.97±0.35	3.7±1.6
95	0.90±0.52	0.74±0.32	0.96±0.39	3.7±1.8
100	1.0±0.4	0.59±0.18	1.1±0.2	3.7±0.8
115	2.3±1.0	4.7±4.1	1.2±0.2	5.3±1.5
130	2.0±0.6	3.6±2.9	0.67±0.25	7.6±2.9
145	2.8±0.8	1.4±0.7	0.63±0.16	3.3±1.3
160	1.5±0.2	5.3±5.2	0.85±0.09	4.3±0.7
175	1.8±0.1	8.6±0.5	0.81±0.38	6.1±0.9
190	1.9±0.1	8.2±0.6	1.1±0.1	6.3±0.7

and lead is the next. Fortunately, these were not leached out from sediments, except Cu, into water. This observation will be discussed in the following section.

In Figure 2, mean contents of Cu show a increasing trend toward the surface of sediments, while those of Cd show a decreasing trend, and those of Pb and Cr are relatively stable. In the range of surface to 100cm depth, it should be noted that contents of Cu is clearly in increasing trend toward the surface of sediments, whereas those of Pb, Cd and Cr are relatively constant.
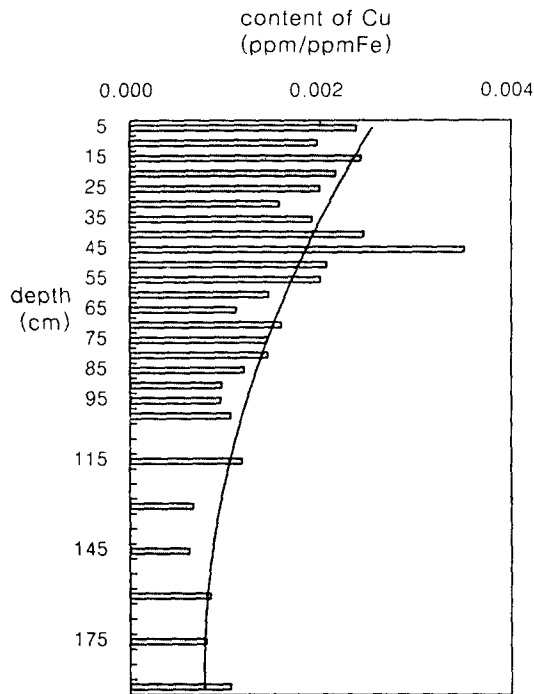

Fig. 2a.

Fig. 2b.

content of Cu
(ppm/ppmFe)

content of Cr
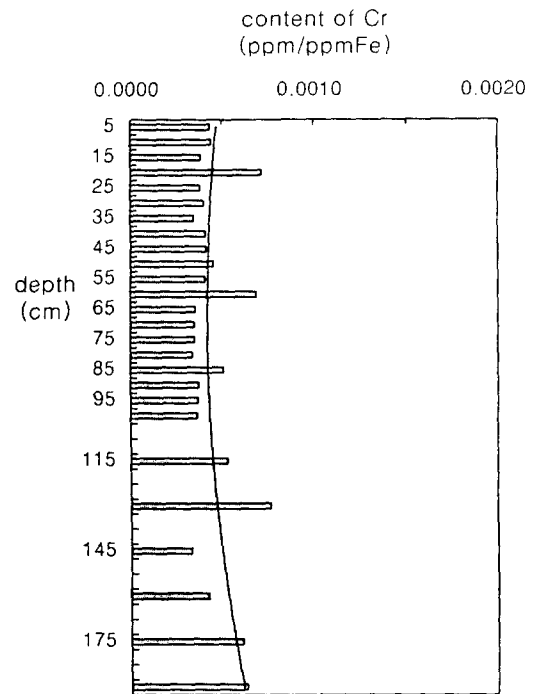(ppm/ppmFe)
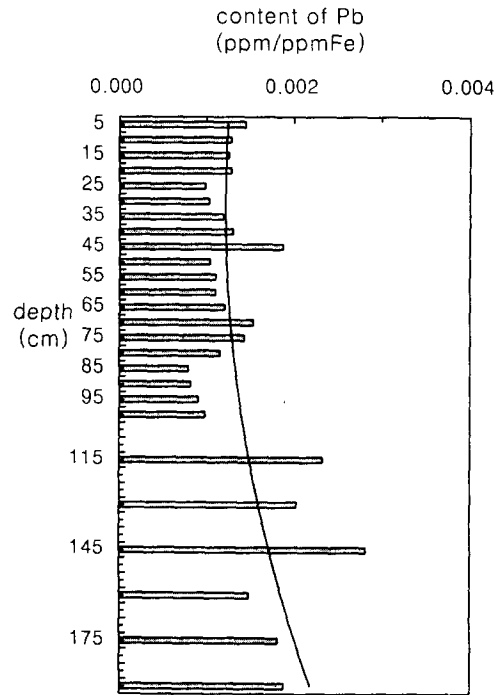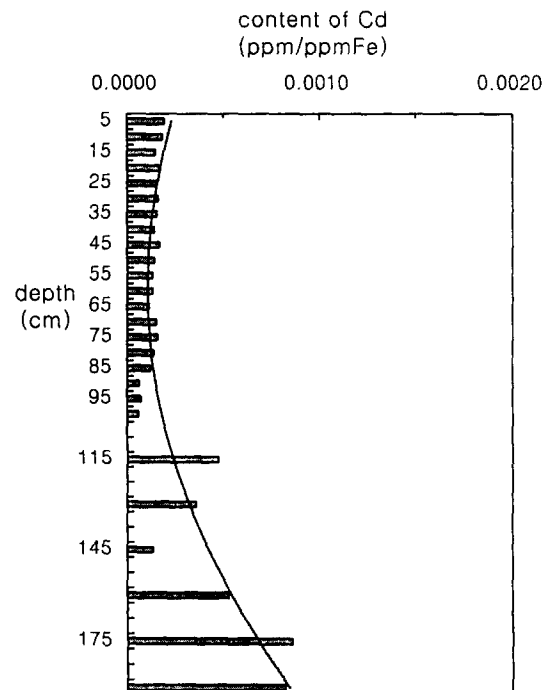
Fig. 2c   **Fig. 2d**

Fig. 2. Overall mean contents of Pb, Cd, Cu, and Cr and their trend of a variation

Table 2. Overall mean, range and enrichment factors of Zn, Pb, Cd, Mn, Cu, Cr, and Fe in the surface sediments of the Hoedong reservoir.

Metals	Mean content*	Range* (min~max content)	Ratio of max/min	Mean enrichment factors wrt Kumjeong Mt	Range of enrichment factors (min~max factor)
Zn	$(2.9\pm1.2)\times10^{-3}$	$(1.2\sim6.1)\times10^{-3}$	5.1	0.81	$0.33\sim1.7$
Pb	$(1.3\pm0.7)\times10^{-3}$	$(0.21\sim3.8)\times10^{-3}$	18	0.61	$0.098\sim1.8$
Cd	$(1.9\pm2.1)\times10^{-4}$	$(0.30\sim9.9)\times10^{-4}$	33	1.6	$0.24\sim8.1$
Mn	$(2.3\pm1.1)\times10^{-2}$	$(0.13\sim3.9)\times10^{-2}$	30	0.34	$0.020\sim0.60$
Cu	$(1.6\pm1.0)\times10^{-3}$	$(0.38\sim4.4)\times10^{-3}$	12	7.9	$1.8\sim22$
Cr	$(4.5\pm2.6)\times10^{-4}$	$(0.058\sim1.4)\times10^{-3}$	24	1.4	$0.18\sim4.3$
Fe	1.0 ± 0.4	$0.65\sim1.9$	2.9	1.3	$0.83\sim2.4$

* : relative contents compared with respect to the mean content of Fe, ppm/ppm Fe

Overall mean contents, range of contents of heavy metals relative to the mean iron content and enrichment factors with respect to the content of each heavy metal in the Kumjeong mountain are shown in Table 2. Ratios of max/min contents of Pb, Cd, Mn, and Cr are 18, 33,

Table 3. The effect of pH on the content of leached heavy metals

	initial pH[1]	final pH[2]	contents of heavy metals in the leached solution, ppm/ppmFe				
			Zn	Mn	Fe	Cu	Pb, Cr, Cd
	4.4	4.5	0.19	2.0	1.0	0.076	ND[3]
Site 1 depth: 60 cm	5.4 (original pH)	4.5	0.15	2.0	1.0	0.054	ND
	6.5	4.5	0.16	2.3	0.98	0.067	ND
	4.1	4.3	0.47	2.1	1.0	0.076	ND
Site 2 depth: 55 cm	5.3 (original pH)	4.3	0.56	2.0	1.0	0.054	ND
	6.5	4.4	0.39	2.3	0.98	0.067	ND

1) The original pH and adjusted pH with HNO_3 or NaOH solution, see text
2) The pH value measured after shaking the solution for two hours
3) none detected

30, and 24 respectively, which indicate that these metals are distributed very ununiformly along depth of the sediments. The values of mean enrichment factors show that the contents of Zn, Pb and Mn are less in the surface sediments of Hôedong than those in soils of Kumjeong mountain, but the maximum contents of Zn and Pb are higher. Cu shows the largest value of enrichment factor, which may imply that, among the heavy metals we determined, copper is most seriously contaminated in this reservoir. Cd shows the second largest value of enrichment factor. Maximum values of enrichment factors of Cu and Cd are 22 and 8.1, respectively.

3.2. Effect of pH on leaching of heavy metals

The content of heavy metals in the leached solution was investigated to test the correlation between the pH of leaching water and the content of heavy metals leached from sediments into water. The standard procedure to determine pH of soil is as follows: take 5g of air dried soil into a 50ml beaker and add 25ml of distilled water, and leave it for an hour by stirring it occasionally with a glass rod(Nat'l Inst., 1988). This value of pH was considered as the original

pH of sediments in this study.

It is a general trend that the solubility of metals increases as pH of the solution decreases. In Table 3, some metals show negative trends of solubility when pH values change. In this experiment, pH was adjusted to the original pH$\pm$ 1 to see the effect of pH on the amount of heavy metals being leached. But, regardless of the initial pH values adjusted, the final pH was nearly the same after shaking the leaching water for two hours. The contents of leached heavy metals also gave no systematic variation and show very little difference as pH changes. So it is hard to give any definite conclusion about correlation between the initial pH and contents of heavy metals leached out.

The leaching rate was calculated to see whether or not the contaminated sediments directly affect quality of water above it. As shown in Table 4, Fe showed low leaching rate, and Cd, Cr and Pb were not leached out. This indicates that Cd, Cr and Pb in the surface sediments of the Hôedong reservoir do not lead to contamination of the water over sediments. For copper which showed the highest enrichment factor, leaching rate was 2.9 and 8.2%. In case of Zn, however, leaching rate was quite high. Thus, each heavy metal adsorbed in sediments may

affect the water quality at different levels according to its leaching rate. Fe, Pb, Cd, and Cr in sediments of the Hôedong reservoir may not contaminate water of this reservoir. But Zn, Mn and Cu may have significant effect on water quality of this reservoir.

Table 4. Leaching rates(%) of heavy metals from sediments in the range of 55~65cm depth at site 1 and 50~60cm depth at site 2

	Zn	Mn	Fe	Cu	Pb, Cd, Cr
site 1*	35	13	0.11	2.9	ND
site 2**	13	1.6	0.10	8.2	ND

* : The depth in which the largest content of heavy metal was observed
** : The depth in which the smallest content of heavy metal was observed
ND : none detected

3.3. Correlation of distribution of heavy metals

According to the t-test with the observed contents of heavy metals in this study, the r value has significance if r exceeds 0.50 at 95% confidence level(Miller and Miller, 1988; Yang et al., 1995). Thus, when r exceeds 0.50, the distribution of two metals has significant correlation. The correlation coefficients of the content of each heavy metal to another one from the three sites are shown in Table 5.

As shown in Table 5, there are higher correlations in site 2 compared with those in the other two sites. At site 2, the water content is much higher than that of other sites. The water content in sediments is about 57% at site 2, and those of site 1 and 3 are about 39% and 43%, respectively. Water would transport chemical species in sediments to different depths. This may lead to higher correlation at site 2 along the depth than those in the other sites. As a reference, the correlations between relative contents

Table 5. Correlation of the contents of each heavy metal according to depth of the three sites

Site 1	Zn	Pb	Cd	Mn	Fe	Cu	Cr
Zn	1.00	0.30	0.51	-0.08	-0.37	0.80	0.59
Pb		1.00	0.09	-0.22	0.52	-0.04	0.53
Cd			1.00	-0.33	0.20	0.36	0.40
Mn				1.00	0.14	0.16	-0.28
Fe					1.00	0.54	0.68
Cu						1.00	0.38
Cr							1.00

Site 2	Zn	Pb	Cd	Mn	Fe	Cu	Cr
Zn	1.00	0.75	0.82	0.34	0.75	0.71	0.84
Pb		1.00	0.87	0.05	0.79	0.59	0.86
Cd			1.00	0.03	0.98	0.44	1.00
Mn				1.00	0.03	0.22	0.05
Fe					1.00	0.28	0.97
Cu						1.00	0.48
Cr							1.00

Site 3	Zn	Pb	Cd	Mn	Fe	Cu	Cr
Zn	1.00	0.24	0.11	0.11	0.52	0.45	0.72
Pb		1.00	-0.07	0.37	0.25	0.70	-0.02
Cd			1.00	-0.05	-0.08	-0.26	0.10
Mn				1.00	0.50	0.41	0.04
Fe					1.00	0.39	0.42
Cu						1.00	0.13
Cr							1.00

of Cr and Fe from the three sites are shown in Figure 3.
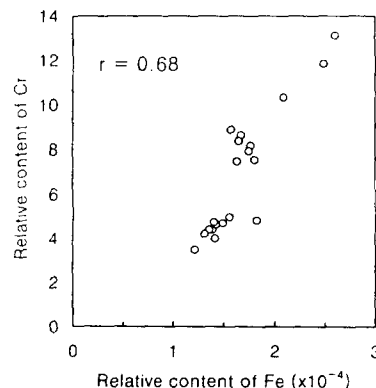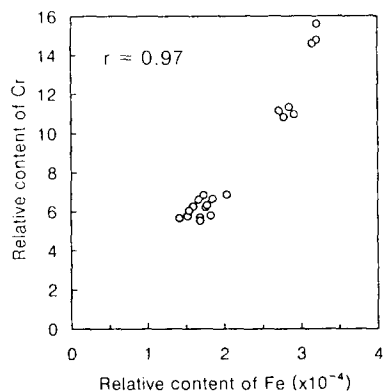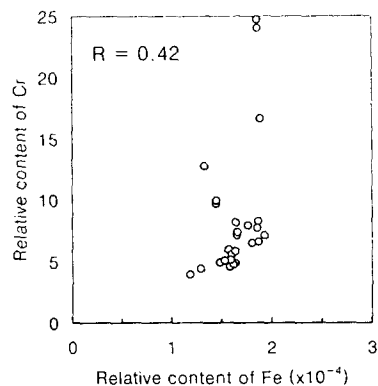

Fig. 3a.

Fig. 3b

Fig. 3c.

Fig. 3. Correlation between relative contents of Cr and Fe from the three sites

4. Conclusion

In this work, we investigated depth profiles of heavy metals, the effect of heavy metals in sediments on the water quality, and correlation between the distribution of each heavy metal. Among heavy metals we investigated, copper showed the largest value of enrichment factor. Considering the maximum content of heavy metals in the surface sediments, the values of enrichment factors of Cu, Cd and Cr were significant, which were 22, 8.1 and 4.0, respectively. Mean contents of Cu show an increasing trend toward the surface of sediments, while those of Cd show a decreasing trend, and those of Pb and Cr are relatively stable.

Each heavy metal at site 2 has better correlation each other, this may be resulted from the higher water content in sediments at this site. In natural situation (i.e. pH 4-5), Pb, Cd, Cr, and Fe were hardly leached out but Zn is relatively highly leached. Therefore Pb, Cd, Cr, and Fe in sediments have little or no effect on water quality over sediments. Each heavy metal may affect the water quality over sediments at different levels according to its leaching rate.

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