Study on the chemical forms of heavy metals in the surface sediments of Ulsan Bay

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Contents of heavy metals (Cr, Cu, Zn, Cd, and Pb) in the sediments of Ulsan Bay were investigated by the sequential extraction methods that classifies heavy metals into five types of chemical forms: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter and residual. The analytes were determined by using an ICP-MS. Total Cr concentrations in the sediments were in the range of 41.6-96.4, Cu 60.7-680, Zn 189-1954, Cd 33.1-83.4, and Pb 138-567 mg/kg. Results of sequential fractionation indicates that relatively high proportion (~44%) of Cu is associated with organic matter. A large proportion of Pb is associated with three types of chemical forms: Fe-Mn oxides, organic matter, and residual. There were significant correlation in concentrations between the exchangeable components and total organic carbons. The heavy metals in the residual phase cannot be easily released to the environment since these are bound to the crystal lattice. But, reducible and organic phases carry a significant amount of most heavy metals. Therefore, there is potential danger of a substantial amount of metals becoming chemically mobile with environmental changes.

Key Word : heavy metal, sequential extraction, TOC, sediments, PCA

1. Introduction

The transfer of heavy metals from the land to the estuarine and coastal marine sediments is connected with adsorption and complexation processes by association with suspended particulates. For most coastal areas, concentrations of the natural trace metal can range over three orders of magnitude greater than those in the overlying water column. The transfer and distribution of heavy metals in sediment is dependent on the sources and input, hydrodynamic factor affecting flow, nature and amount of suspended solid and operation of certain biological process (Horowitz, 1985).

Metals are not necessarily fixed permanently in sediment, but may be recycled via biological and chemical agents, within both a sedimentary compartment and a water column. Contributions of anthropogenic heavy metals in coastal marine sediments are often introduced initially into the environment with solution and accumulated on fine grained suspended sediment. Heavy metal contaminants from anthropogenic sources may also be introduced in large particles.

The bioavailability and toxicity of heavy metals in the estuarine and coastal marine sediments depend not only on the total concentration but on the chemical forms. The availability of heavy metals depends greatly on the properties of the particle surface, on the types and strength of the bonds, and on external conditions such as pH, Eh,

salinity, and concentration of organic and inorganic complexation agents. Chemical extraction of sediment indicates the chemical forms of heavy metals associated with particulates. Precise characterization of such forms is difficult to undertake but selective chemical extraction procedures have been devised that at least give an approximation of the constituents with which the heavy metals are associated and of the potential for metal mobilization and biological uptake (Belzunce-Segarra, 1997).

Heavy metals can be retained in the sediment by several phases such as exchangeable, carbonates, Fe-Mn oxides, organic matter and residual. The retention of heavy metals in any phase depends on pH of sediment solutions, sediment constituents and the chemical type of that compound. In addition, at high pH sediment solutions, the retention of heavy metals by precipitation mechanism prevails, whereas the cation exchange mechanism become dominant at low pH sediment solutions (Yong, 1993).

Today, it is generally recognized that the particular behaviour of trace metals in environment is determined by their specific physicochemical forms rather than by their total concentration. Several chemical speciation and fractionation methods for heavy metal analysis in soils and sediments have been and are still being developed and applied.

In this study, we determined the heavy metal concentrations in the surface sediments of Ulsan Bay by using sequential extraction methods and we then classified the chemical forms of heavy metals, and examined the correlation between the contents of heavy metals and that of the total organic carbon.

2. Materials and Methods

2.1. Collection of sediment

Sixteen sampling sites were chosen at coastal areas from Hyundai Heavy Industrial Co. to On-san myon in Ulsan Metropolitan City. Samples of the surface sediment (0~10 cm depth) under 5 to 25 m depth of sea water were collected with a
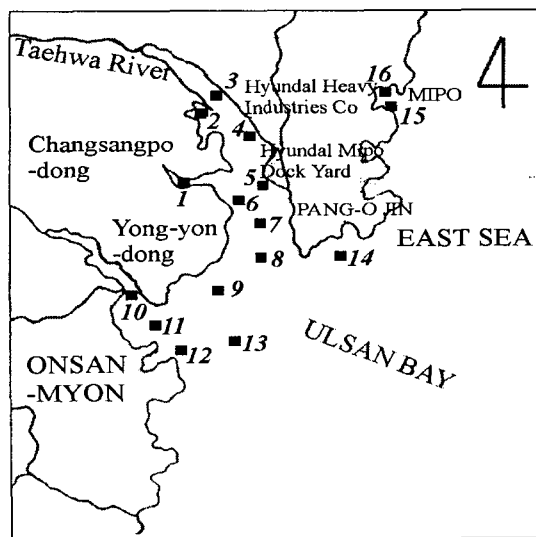

Fig. 1. The sampling sites in Ulsan Bay.

grab sampler. The sampling locations are shown in Figure 1. Samples from sites 1, 2, 11, and 12 were black in colour and sample from site 11 smelled strongly of organic solvents. A large portion of samples from site 13, 14 was sands. Each sample taken was about 150 g and placed in a polyethylene bag, and transported to the laboratory, and was stored at 4℃ until analysis.

2.2. Sample preparation

Sediment samples were air dried at room temperature for a week and extraneous materials such as twigs, shells, rocks, etc. were removed. They were, then, hand ground in porcelain mortar and sieved through a 2-mm sieve.

2.3. Sequential extraction

The five step sequential extraction method of Tessier (1979) was followed to determine the partitioning of the trace metals: Cr, Cu, Zn, Cd, and Pb. At the end of each extraction, the extractable fraction was separated from the residue by centrifugation at 10,400 rpm for 30 min. The supernatant was transferred to the polyethylene bottle using a Pasteur pipet and stored at 4℃ prior to analysis. Before starting the next extraction step, the residue was washed with 10 ml distilled and deionized water, shaken for 30 min and centrifuged at the same operational conditions. The supernatant was removed and discarded. Each of the five steps of sequential extraction was carried out as follows:

(1) Exchangeable: About 1 g of the exactly weighted sediment was extracted into 10 ml of 1 M $MgCl_2$ solution (pH 7.0) with continuous shaking for 1 h at room temperature.

(2) Bound to Carbonates: The washed residue from

the first fraction was shaken continuously for 5 h at room temperature with 10 ml of 1 M sodium acetate solution(NaOAc) adjusted to pH 5.0 with acetic acid(HOAc).

(3) Bound to Fe-Mn Oxides: The washed residue from the second extraction was heated at 96 ± 3℃ for 6 h with 20 ml of 0.04 M hydroxylamine hydrochloride($NH_2OH \cdot HCl$) in 25% (v/v) acetic acid. In this step, sample containers were shaken manually at regular intervals.

(4) Bound to organic matter: Into the washed residue from the third step, added 3 ml of 0.02 M nitric acid(HNO_3) and 5 ml of 30% hydrogen peroxides(H_2O_2) adjusted to pH 2.0 with nitric acid, and then the mixture was heated to 85 ± 2℃ for 2 h with occasional shaking. A second 3 ml aliquot of 30% hydrogen peroxides(pH 2 with HNO_3) was added and the sample was heated again to 85 ± 2℃ for 3 h with occasional shaking. The solution was allowed to cool for 3 h to room temperature and 5 ml of 3.2 M ammonium acetate solution(NH_4OAc) in 20% HNO_3 was added. The volume was adjusted to 20 ml with 20% (v/v) HNO_3 and the mixture was shaken continuously for 30 min.

(5) Residual: The residue from the fourth step was digested with a mixture of 2 ml conc. perchloric acid($HClO_4$) and 10 ml of hydrofluoric acid(HF) in a platinum crucible placed on hot plate. When the solution was completely dried a second portion of 1 ml $HClO_4$ and 10 ml HF was added and again the mixture was evaporated to near dryness. Finally, 1 ml $HClO_4$ was added and heated until white fumes appeared. The final residue was dissolved in 12 N hydrochloric acid(HCl), filtered (Whatman No. 2) and diluted to 50 ml.

2.4. Total organic carbon analysis

The wet oxidation method of Walkley-Black is the most widely used method for determining organic carbon in soils, organic sediments and wastes (Walkley, 1934). Modifications based on that method are very frequently applied (Tyurin, 1936). Although they have disadvantages of measuring only the oxidizable carbon(OXC) not the total organic carbon(TOC). Generally, OXC values determined are between 75 and 85% of the TOC values (Navarro, 1991; Navarro, 1993; Heanes, 1984; Yeomans, 1988).

We determined the OXC by first treating a 0.5 g sample with 0.5 M HCl and then drying it overnight in an oven. It was then poured into a 250 ml of erlenmeyer flask and 10 ml of 1 N potassium dichromate ($K_2Cr_2O_7$) and 20 ml concentrated sulfuric acid (H_2SO_4) was added. The mixture was shaken vigorously for 30 sec and we let it stand for 30 min. Then added 10 ml of 85% phosphoric acid(H_3PO_4) and 0.2 g of sodium fluoride(NaF). The excess dichromate was titrated with 0.5 N Fe^{2+} solution [$Fe(NH_4)_2(SO_4)_2$]. A blank was also run with 10 ml of $K_2Cr_2O_7$ and 20 ml of concentrated H_2SO_4. The OXC content, expressed as a percentage in the extract, can be calculated by the expression:

$$\%OXC = (B-S) \times (M \text{ of } Fe^{2+}) \times 100 \times 12/(w \times 4000)$$

where B and S are the volume(ml) of the $Fe(NH_4)_2(SO_4)_2$ solution, W is the weight of the extract sample, and 12/4000 is milliequivalent weight of carbon in 1 g of sample.

2.5. Trace metal analysis

All apparatus were carefully washed with 5% nitric acid prior to use. The reagents were of analytical grade and water was of the ultra-high purity. Trace metal concentrations were determined by Inductively Coupled Plasma Mass Spectrometer (Hewlett Packard model 4500, ICP-MS). In order to estimate the contents of heavy metals in sediment, calibration curves were plotted by using standard solutions. These processes were performed by the computer system of the ICP-MS. Four data points were adopted in the calibration curve, three from the standard solutions of multi-elements in different concentrations and the other one is the blank. Triplicate samples were analyzed.

2.6. Principal component analysis

Details of the methods and goals for the use of PCA with environmental and geochemical data are provided by Jöreskog et. al. (Jöreskog, 1976) and Legendre (Legendre, 1983). PCA was used in this study to determine if there were significant spatial differences in the distribution pattern of heavy metals present in the sediments. Difference in the pattern of heavy metals within or between sampling sites may reflect variation in the anthropogenic sources or environmental transport of metals.

PCA was used to take the data from the original five-dimensional space (five metals in sediments) and project them onto a two-dimensional plane that retains most of the information on the original data. This was done by calculating vectors(eigenvectors or principal axes) along which the five-dimensional data point on a principal axis is called a principal component. In the new coordination system, sediment samples have similar profiles of metals plot out near each other. This plot of the samples can often give a better indication of the similarity of heavy metal patterns in the sediment samples than comparison between individual metals (James, 1995).

Table 1. Total concentrations of heavy metals in the surface sediments of Ulsan Bay (mg/kg).

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	96.4 ± 0.4	137 ± 0.3	587 ± 1	34.5 ± 0.1	198 ± 1
site 2	86.6 ± 0.2	174 ± 0.4	1954 ± 4	33.8 ± 0.1	243 ± 1
site 3	50.8 ± 0.1	98.7 ± 0.3	189 ± 0.3	33.1 ± 0.04	179 ± 2
site 4	62.1 ± 0.4	105 ± 0.1	221 ± 0.3	33.2 ± 0.1	155 ± 1
site 5	60.4 ± 0.2	185 ± 1	585 ± 13	37.6 ± 0.1	205 ± 1
site 6	57.0 ± 0.3	75.8 ± 0.1	223 ± 0.3	33.2 ± 0.04	139 ± 1
site 7	46.3 ± 0.2	71.8 ± 0.6	1059 ± 1	33.3 ± 0.04	156 ± 1
site 8	59.5 ± 0.2	92.2 ± 0.1	654 ± 0.5	33.2 ± 0.02	180 ± 1
site 9	41.6 ± 0.1	60.7 ± 0.2	536 ± 1	34.5 ± 0.03	162 ± 1
site 10	74.1 ± 0.4	137 ± 1	1473 ± 13	57.9 ± 0.9	186 ± 1
site 11	72.0 ± 0.4	154 ± 0.4	888 ± 5	53.7 ± 0.2	568 ± 2
site 12	57.7 ± 1.1	680 ± 4	1021 ± 5	83.4 ± 0.2	506 ± 1
site 13	55.5 ± 1.3	70.1 ± 0.3	474 ± 2	40.1 ± 0.1	260 ± 1
site 14	50.8 ± 0.4	76.1 ± 1	449 ± 8	38.2 ± 0.3	200 ± 1
site 15	57.5 ± 0.3	187 ± 0.5	640 ± 1	37.9 ± 0.04	251 ± 1
site 16	47.6 ± 0.2	183 ± 0.4	541 ± 1	35.7 ± 0.04	207 ± 1
Average	61.0 ± 0.3	155 ± 1	781 ± 4	40.8 ± 0.2	237 ± 0.4

3. Result and Discussion

3.1. Total metal concentrations

Heavy metal concentrations in the sediments are shown in Table 1. The average concentrations of heavy metals in the sediments were high, particularly in samples from sites 1, 2, 10, 11, and 12. The distribution trend of these sites is different from those of the other sampling sites. Overall mean contents of Cr, Cu, Zn, Cd, and Pb in the sediments are 61.0, 155, 718, 40.8, and 237 mg/kg, respectively. Total contents for Cr and Cu were higher than limitation values(Cr 30, Cd 30 mg/kg) for soil pollution management and Cu and Pb were lower. The high values for Cr are observed in samples from sites 1, 2, 10, and 11 and the other metals have high values in samples from sites 10, 11, and 12. Especially, the maximum content of Cu is observed in the sample from site 12 with 680 mg/kg. Samples from sites 13 and 14 are found to be below average concentration for most of the metals.

3.2. Total organic carbon analysis

Sediment TOC concentrations are shown in Table 2. Contents for total organic carbon was in the range of 0.18~2.69% with mean of 1.21%. The lowest content is observed in sample from

Table 2. TOC contents in the surface sediments of Ulsan Bay (%).

Sampling site	Total Organic Carbon(TOC)
site 1	2.69 ± 0.11
site 2	2.29 ± 0.05
site 3	0.77 ± 0.03
site 4	1.06 ± 0.02
site 5	1.38 ± 0.05
site 6	1.50 ± 0.03
site 7	1.23 ± 0.06
site 8	1.45 ± 0.04
site 9	0.48 ± 0.11
site 10	1.45 ± 0.02
site 11	1.75 ± 0.17
site 12	0.75 ± 0.04
site 13	0.32 ± 0.01
site 14	0.18 ± 0.03
site 15	1.38 ± 0.05
site 16	0.74 ± 0.04
Average	1.21 ± 0.04

site 14 which is coarse-grained like sand, and the highest one is most strongly influenced by discharge from wastes of human activities. Organic carbon is valuable in that it accounts for the presence of adsorbed organic ligands, which can bind metals to sediment particles (James, 1995). Especially, correlation of between TOC and exchangeable metals is significant positively. TOC has been shown to be an important carrier phase for metals in the sediments.

3.3. Sequential extraction analysis

Having considered in some detail the analytical performance of the proposed sequential extraction procedure, we shall now briefly comment on the heavy metals partitioning in the sediment samples studied by their chemical forms. The proportions of each heavy metal were expressed as a concentration with mg/kg and a percentage of the sum of fractions.

The values of sequential extraction analysis of heavy metal contents in the sediments can be seen in respect to the 'partitioning' of heavy metal retention capability in the sediments. It is accepted that the method does not identify exactly the total proportions of heavy metals retained by the different sediment constituents or as different phases in the sediments studied (Yong, 1993). However, this should not be the evaluation of the capability of a particular type of sediments.

Fraction 1. Exchangeable

Concentrations of exchangeable Cr, Cu, Zn, Cd, and Pb are shown in Table 3. Each content of metals with the exception of Pb in the samples from sites 1 and 2 was higher than the other sites. And exchangeable fraction accounts below 10% of the total metal concentration, but chromium was about 19%. There is a significant

correlation between this fraction and TOC. This fact indicates that absorbed organic binding sites on the sediment particles are an important carrier phase for these metals. There is a difference between correlation and causation, and it is possible that organic carbon from anthropogenic sources covaries with anthropogenic metal pollution within and between sampling sites and does not affect metal binding to sediment particles. However, a relationship between organic carbon and metal content has been shown in sediments at other locations (James, 1995). The exchangeable components are ready to affect water column directly by exchanging metals for neutral salts and electrolytes at natural conditions.

Table 3. The mean concentrations for exchangeable fraction of heavy metals in the surface sediments of Ulsan Bay (mg/kg)

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	12.0	7.34	12.9	3.79	14.9
site 2	11.9	7.43	8.28	3.70	14.4
site 3	11.3	5.53	5.26	3.07	14.6
site 4	11.9	5.96	6.38	2.93	20.8
site 5	11.3	6.37	5.56	2.91	14.6
site 6	11.2	5.93	6.00	3.35	16.6
site 7	11.2	6.97	7.03	2.96	16.2
site 8	10.9	7.14	6.14	2.92	14.7
site 9	11.1	5.70	4.96	3.10	15.5
site 10	10.9	6.60	8.14	3.02	14.3
site 11	10.9	7.51	5.50	3.06	16.3
site 12	9.88	6.42	5.92	3.23	15.2
site 13	10.9	5.32	5.25	2.93	14.7
site 14	10.9	5.48	4.54	2.89	14.3
site 15	10.6	6.64	11.9	3.07	14.5
site 16	10.7	6.83	9.11	3.00	14.7
Average	11.1	6.45	7.05	3.12	15.4

Fraction 2. Metals bound to carbonates

Concentrations of metals bound to carbonates are shown in Table 4. This fraction shows similar distribution to that of the exchangeable. In the

samples from sites 1, 15 and 16, relatively great contents of metals are observed. The observed concentrations represent an appreciable proportion of the total contents: 8.4~14.7% Cr; 2.4~18.8% Cu; 0.2~27.6% Zn; 3.4~9.2% Cd; 6.6~15.3% Pb.

Table 4. The mean concentrations for carbonates fraction of heavy metals in the surface sediments of Ulsan Bay (mg/kg).

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	10.3	12.7	162	3.03	20.4
site 2	8.73	19.0	70.1	3.11	19.9
site 3	6.14	11.9	3.99	2.90	19.0
site 4	6.18	12.0	14.0	2.80	18.0
site 5	6.24	12.0	9.04	2.81	18.1
site 6	6.22	13.0	8.42	2.78	16.6
site 7	6.22	10.6	3.29	2.81	19.1
site 8	6.21	11.6	6.08	2.83	20.1
site 9	6.10	11.4	4.72	2.81	18.2
site 10	6.24	9.58	18.4	2.91	23.9
site 11	6.43	12.1	20.6	2.84	46.2
site 12	6.46	16.3	30.4	2.85	77.4
site 13	6.08	9.19	1.89	2.84	17.2
site 14	6.70	6.00	0.77	2.87	18.2
site 15	6.80	13.9	156	2.94	26.5
site 16	6.54	21.0	82.2	2.86	22.2
Average	6.73	12.6	37.0	2.88	25.1

Fraction 3. Metals bound to Fe-Mn oxides

With the exception of chromium, the trace metal levels in fraction 3 are relatively high and represent a large fraction of the total metal contents. The observed concentrations represent an appreciable proportion of total contents: 1.1~17.8% Cr, 1.5~18% Cu, 2.9~34.7% Zn, 6.9~17.4% Cd, and 14.7~40.4% Pb. In the samples from sites 1, 2, 15, and 16, Cr and Zn concentrations are higher than those in the other samples. Assuming that $Fe(OH)_3$ and MnO_2 are representative empirical formulas for the Fe and Mn oxides, respectively, and that the observed trace metals originated only from Fe-Mn oxides, one can

calculate the trace metal concentrations in the Fe-Mn oxides phases. Table 5 shows the concentrations of heavy metals in Fe-Mn oxides phase. Lead is associated with the more mobile phase to a considerable extent, in particular with the Fe-Mn oxides (15~40%). On the average, approximately 29% of the total Pb occurs in this fraction. Lead compounds are soluble at low pH and at high pH, such as those induced by solidification and stabilization treatments.

Table 5. The mean concentrations for Fe-Mn oxides fraction of heavy metals in the surface sediments of Ulsan Bay (mg/kg).

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	17.2	14.3	127	5.74	60.2
site 2	13.3	14.0	66.7	5.80	54.5
site 3	1.28	15.9	65.8	5.74	48.3
site 4	3.48	18.8	53.6	5.76	55.3
site 5	2.26	18.1	277	5.88	67.4
site 6	2.04	10.9	31.4	5.69	50.2
site 7	2.33	11.1	30.9	5.68	50.3
site 8	3.49	10.7	37.5	5.77	54.7
site 9	2.33	9.61	19.7	5.69	46.4
site 10	4.95	10.0	51.6	5.82	75.2
site 11	3.98	14.5	73.1	5.82	83.4
site 12	2.82	10.1	51.8	5.75	153.9
site 13	0.62	10.0	20.9	5.80	48.5
site 14	1.01	8.94	25.0	5.68	45.0
site 15	6.07	21.0	190	5.76	77.7
site 16	4.57	15.1	119	5.76	75.4
Average	4.48	13.3	77.5	5.76	65.4

Fraction 4. Metals bound to organic matter

Levels of copper, zinc, and lead found in fraction 4 are relatively high. The concentrations of metals bound to organic matter are shown in Table 6. In the samples from sites 1 and 2, concentrations of heavy metals are higher than those in the other samples. Generally, copper is more strongly associated with the organic matter fraction than any of the other metals due to its

high affinity for soluble organic ligands (Carolyn, 1987). Cu concentrations in this fraction was in the range of 22~84% with a mean percentage of 44%. Very small proportions of Cu was observed in the other potentially mobile phase with most of the remaining copper being present in the residual phase (average value 28% Cu). For the other heavy metals, the observed concentrations represent an appreciable proportion of the total metal contents: 2% Cr, 10% Zn, 16% Cd, and 25% Pb, on the average.

importance of fraction 5 illustrates clearly the difficulty of distinguishing between background and anomalous levels of heavy metal contamination when only total metal contents are determined. These metals from residual fraction are not expected to be released in the overlying water over a reasonable time span under the conditions normally encountered in nature.

Table 6. The mean concentrations for organic matter fraction of heavy metals in the surface sediments of Ulsan Bay (mg/kg).

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	19.5	77.3	51.0	6.45	60.2
site 2	19.1	101	43.7	6.19	64.1
site 3	11.2	42.6	25.1	5.95	46.9
site 4	11.2	36.2	20.1	5.88	44.1
site 5	10.9	77.0	108	6.12	38.9
site 6	11.2	22.8	62.9	5.86	47.9
site 7	11.5	24.5	19.0	6.27	54.1
site 8	12.0	37.9	42.4	6.18	58.6
site 9	9.72	16.5	19.1	5.84	44.4
site 10	11.5	40.8	33.4	5.95	57.4
site 11	12.5	73.5	80.4	6.14	60.4
site 12	9.86	568	327	6.92	65.8
site 13	10.1	15.7	12.8	6.47	48.1
site 14	9.01	20.6	20.8	6.04	44.6
site 15	12.5	117	48.0	6.16	53.5
site 16	10.7	113	47.8	6.21	49.2
Average	12.0	86.5	60.1	6.16	52.4

Table 7. The mean concentrations for residual fraction of heavy metals in the surface sediments of Ulsan Bay (mg/kg).

Sampling site	Cr	Cu	Zn	Cd	Pb
site 1	37.4	25.9	234	15.5	42.3
site 2	33.4	33.2	1766	15.0	90.4
site 3	20.9	22.8	89.2	15.4	50.0
site 4	29.3	31.6	127	15.8	16.7
site 5	29.7	71.4	185	19.9	66.1
site 6	26.3	23.2	115	15.6	7.22
site 7	15.0	18.7	999	15.6	16.0
site 8	26.8	24.9	562	15.5	32.0
site 9	12.4	17.5	488	17.0	37.9
site 10	40.5	70.3	1361	40.2	15.1
site 11	38.2	46.8	708	35.9	361
site 12	28.6	78.6	606	64.7	193
site 13	27.8	29.9	433	22.0	131
site 14	23.2	35.1	398	20.7	77.5
site 15	21.6	28.7	234	19.9	78.4
site 16	15.0	27.1	283	17.9	45.3
Average	26.6	36.6	537	22.9	78.8

Fraction 5. Residual metals

Concentrations of Cr, Zn, and Cd observed in fraction 5 are higher than those observed in any of the preceeding extractions. The concentrations of these five metals are shown in Table 7. Overall mean concentrations in residual fraction are 26.6, 36.6, 537, 22.9, and 78.8 mg/kg for Cr, Cu, Zn, Cd, and Pb. This overwhelming

3.4. Principal component analysis

PCA analysis incorporates the data from all the metals in all the sediments into one unified comparison and may reveal groupings of samples (or metals) with similar spatial behavior. The score plot (the plot of the samples in the new space defined by the first two pricipal axes) of the concentrations in exchangeable fractions is shown in Figure 2. Spatially, samples from similar geographical locations form clusters around the

hypothetical end members. The highly contaminated samples from sites 1 and 2 have positive loadings along the second principal component, and negative loadings along the first principal component. Also, relatively the least contaminated sites including samples from sites 13 and 14 have positive loadings along first and second principal components. The less contaminated samples have negative loadings along the second principal component. This group is less polluted than highly contaminated samples from sites 1 and 2. From these results, we can classify them into three groups by the levels of the contamination. Also, a possible explanation is that there was a point source of contamination. Highly contaminated sites 1 and 2 are located in low flow rate of the tides and surrounded by residential areas. Also, these areas have low depth, about 10 m. And sites 10, 11, and 12 are located near to Onsan-industrial base, in particular with Cu, Zn, and Pb. Sites 15 and 16 are located in near Hyudai-Heavy Industrial Co. The least contaminated sites 13 and 14 are much deeper than any other sites, and most of the sample from these sites were sandlike forms. The PCA showed that sediments from different sites have characteristic five-dimensional
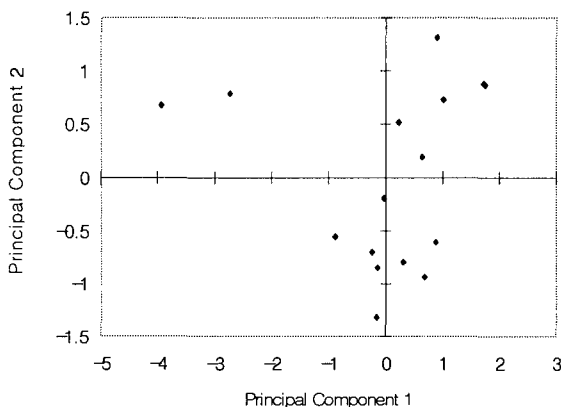
Fig. 2. Principal component score plot of exchangeable fraction in the surface sediments of Ulsan Bay.

'fingerprints' based on the concentrations of heavy metals. These fingerprints can be used to study the transport and fate of metals in Ulsan-Bay. The metals are effectively retained in the sediments, and processes such as early diagenetic release of metals or sediment transport apparently do not lead to a homogeneous distribution throughout the bay.

4. Conclusion

The heavy metals in the surface sediments in Ulsan Bay are associated primarily with detrimental input from soils and weathered rocks from the land, and secondly, with industrial wastes and wastes from livings. The average relative partitioning(%) of Cr, Cu, Zn, Cd and Pb among the five chemical phases in the sediments are followed in order of increasing;

Cr : Residual > Organic Matter > Exchangeable > Carbonates > Fe-Mn Oxides,

Cu : Organic Matter > Residual > Fe-Mn Oxides = Carbonates > Exchangeable,

Zn : Residual > Fe-Mn Oxides > Organic Matter > Carbonates > Exchangeable,

Cd : Residual > Organic Matter > Fe-Mn Oxides > Exchangeable = Carbonates,

Pb : Fe-Mn Oxides > Residual > Organic Matter > Carbonates > Exchangeable.

The exchangeable phase takes the smallest share of total metals. In the carbonates phase, the percentage of Zn and Cd are low: 5.9 and 7.5%, respectively. In the Fe-Mn oxides phase, only the presence of Pb(29.4%) is an important part of total Pb. Also, the presence of Cu(44%) in organic matter phase is an important part of total Cu. The metals in the residual phase cannot be easily released to the environment since the metals are

bound to the crystall lattice. But, since the reducible and organic phases carry a significant amount of most metals, there exists potential danger of a substantial amount of metals becoming chemically mobile with environmental changes.

In this study, multivariate technique PCA was performed to examine the level of contamination of metals present within individual samples. The PCA score and variable loading plots simplified the data from five dimension to two dimensions. The data showed spatial variation of the metals in Ulsan Bay based on the chemical type of metal present. We have divided three groups by contaminating levels of 16 sediment samples.

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