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Speciation of Some Heavy Metals in Surface and Core Sediments of Kyeonggi Bay, West Coast of Korea

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Chemical speciation of five heavy metals (Cr, Cu, Ni, Pb, Zn) has been analyzed from 37 surface and 2 core sediments of Kyeonggi Bay, using the modified sequential extraction method based on Tessier *et al.* (1979). The results show that heavy metals in the Kyeonggi Bay surface sediments are associated dominantly with the crystal lattice fraction. But in the polluted sediments of the Incheon North Harbor, the importance of the labile fractions increased while that of the lattice fraction decreased. In particular, the adsorbed and the easily reducible fractions showed a noticeable increase. In the core samples emerged a speciation pattern which differed significantly from that of the surface sediments. A sharp increase in the percentage of the reducible and organic/sulfide fractions and a decrease in the lattice fraction were observed. Throughout the vertical column, however, the metal contents in the lattice fraction showed stability while those of the labile fractions showed an upward increase. The strong association of heavy metals with the organic/sulfide fraction could be attributed in part to the sulfate reduction prevailing in the polluted harbor sediments.

INTRODUCTION

Coastal sediments act as sinks for materials, including metals, introduced from various land sources into the marine environment. Sediments can, therefore, reflect the current quality of the marine system, and the level of pollution in an environmental system can be evaluated by measuring the heavy metal contents of sediments (Salomons and Förstner, 1984). The metals, however, do not reside permanently in the sediment, but may be recycled into the water column when changes in biological and/or chemical conditions occur within the sedimentary deposits. In this respect, sediments can be regarded as a source of contaminants in a coastal ecosystem (Förstner, 1989).

Although the total content of metals can give some insight into the degree of pollution, it tells us little about bioavailability of the metals, or about their chemical and physical behavior under changing environmental conditions of the sediment. Various chemical association forms must be differentiated, as they become available under varying environmental conditions. The determination of the individual physicochemical forms of the heavy metal, which together make up its total concentration, in other words the speciation of the heavy metals in sediment, is usually performed by a sequential extraction technique (De Groot, 1995; Salomons and Förstner, 1984; Tessier *et al.*, 1979).

Kyeonggi Bay receives a vast quantity of domestic and industrial wastewaters from the Seoul metropolitan area through the Han River, from Incheon city and from various industrial plants located along the coastline. The marine environment of this bay is greatly affected by these waste inputs, which result in the accumulation of pollutants in the bottom sediments. However, due to the strong tidal currents that are very effective in dispersing these pollutants, the accumulation of pollutants in bottom sediments is observed only locally, in relatively calm water in harbors and in the vicinity of the coastal outfalls. A recent study by Lee *et al.* (1998) reported that high metal contents in bottom sediments occurred mostly in the Incheon North Harbor while other areas of the bay showed no noticeable increase in sedimentary metal contents, compared to the earlier report (Lee *et al.*, 1992). They also reported that except for those found in the harbor and outfall areas, heavy metals in the surface sediments were found to be dependent on the sediment grain size. The heavy metals that

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accumulate in harbor sediments are Ni, Cr, Zn and Cu (Lee *et al.*, 1998).

While the accumulation of heavy metals in harbor sediments is evident, it is important to understand the possible effects of these pollutants on the benthic biota and on the overlying waters. Since both the bioavailability and the remobilization of metals largely depend on their chemical forms, the first step towards understanding these will be the speciation of these heavy metals. As mentioned above, the sequential extraction method provides useful information on the specific physico-chemical forms of heavy metals in sediments (Malo, 1977; Rosental *et al.*, 1986; Schoer *et al.*, 1982). The purpose of the present paper is to report the results of heavy metal speciation in Kyeonggi Bay sediments and discuss the differences observed between the polluted harbor sediments and the other unpolluted sediments of the bay. We hope that these data will serve as useful basic information in understanding of the heavy metal behavior in polluted coastal sediments as well as in assessing the possible impact of these pollutants in this coastal ecosystem.

Study area

Kyeonggi Bay, located on the western coast of Korea, receives a large amount of fresh water and suspended sediments through the Han River, which drains the Seoul metropolitan area. Being the capital city of Korea, Seoul is the largest city in Korea with a population of about 11 million and possesses various industrial facilities in its peripheral areas. The Incheon Harbor, located in the middle of Kyeonggi Bay, is one of the largest harbors in Korea. On the north of the Incheon Harbor is located a waste dumping ground on a reclaimed intertidal area where most of the solid wastes originating from the entire metropolitan area are deposited. To the south of the harbor are two large industrial complexes: the Namdong and the Shihwa Industrial Complexes.

Kyeonggi Bay is separated from the offshore Yellow Sea waters by numerous islands and between these islands are developed the main tidal channel system. Most of these channels are developed in a NE-SW direction and their depths are between 10 and 30 meters. The surface sediments of Kyeonggi Bay consist of a wide variety of materials, ranging from gravelly sand to mud. The mean grain size of the surface sediments is in the range of 0.3–7.7 ϕ with an average value of. 4.4 ϕ. The distribution of the surface sediments in the bay is characterized by a general shoreward-fining pattern. Sands, which are the most dominant sediment type in the offshore area, extend along the main channel into the bay and within the bay are mixed with fine materials to a varying degree. Consequently, the sediment types change into silty sand and sandy silt progressively as they approach the shore (Lee *et al.*, 1992).

The tide in the bay is characterized by a semi-diurnal type and a macro-tidal ranges with a mean spring-tidal range of about 8 meters. During spring tides, the current velocities can attain a maximum of 1.8 m/sec during the flood and 2.3 m/sec during the ebb. The tidal prisms estimated at the main channel off the Incheon Harbor are estimated to be about 260–590 million cubic meters for the flood, and 200–470 million cubic meters for the ebb (Yi, 1972; Lee *et al.*, 1992).

MATERIALS AND METHODS

Ninety surface sediment samples were collected from Kyeonggi Bay, in December 1995, using a van-Veen type grab sampler. At the same time, two sediment core samples, with 30 and 50 cm of length

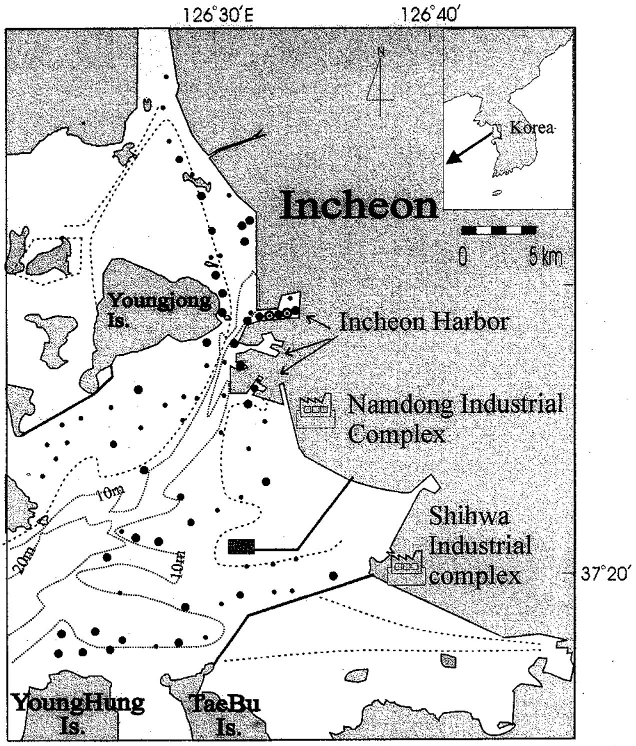

Fig. 1. Map showing the study area and the sample sites. ·: Samples for total concentrations of heavy metals, •: Samples for heavy metal speciation, ◉: Core samples

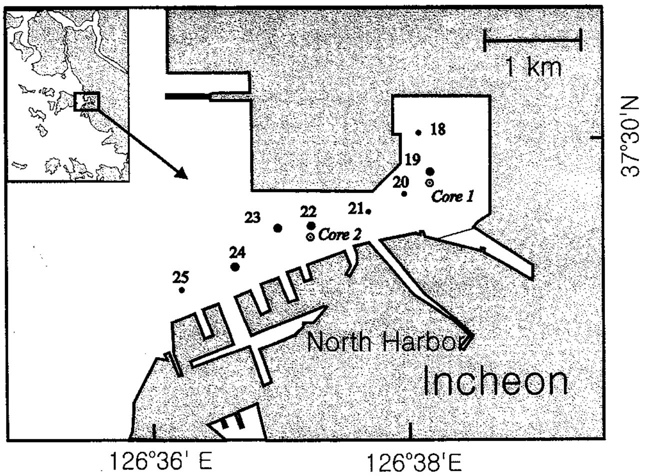

Fig. 2. Map showing the sample sites in the Incheon North Harbor, Kyeonggi Bay. •: Samples for total concentrations of heavy metals, •: Samples for heavy metal speciation, ◉: Core samples

each, were also collected from the polluted Incheon North Harbor using a gravity corer (Fig. 1 and Fig. 2).

For all the sediment samples collected, analyses were done for their grain-size, organic carbon contents and contents of nine metals (Al, Fe, Mn, V, Co, Ni, Cr, Zn and Cu). The result of these analyses has already been reported in our previous paper (Lee *et al.*, 1998). For the purpose of the present study, we selected 37 surface sediments and two core sediments and analyzed 5 heavy metals (Cr, Cu, Ni, Pb and Zn) for their speciation, using a modified Tessier's sequential extraction method (Tessier *et al.*, 1979). In this method, five fractions have been distinguished by sequential leaching with 1M CH_3COONH_4 (adsorbed), 1M CH_3COONa (easily reducible), 0.04 M NH_2OH-HCl (reducible), H_2O_2 and 3.2 M CH_3COONH_4 in 20% HNO_3 (organic/ sulfide), and HF-HNO_3-$HClO_4$ mixed solution (lattice fraction), respectively. Leached solution from each fraction was analyzed by atomic absorption spectrophotometry (Perkin-Elmer 3110). Accuracy and precision were checked with BCSS-1 (a SRM of Canadian NRC). The accuracy was generally in good agreement with the certified values of SRM, as shown in Table 1. The precision was evaluated by triplicate analysis of SRM.

Table 1. Results of SRM analysis (in μg/g).

Elements	Measured values	Certified values
Cr	113 ± 15	123 ± 14
Cu	21 ± 3	19 ± 3
Ni	48 ± 6	55 ± 4
Pb	22 ± 3	23 ± 3
Zn	97 ± 3	119 ± 12

RESULTS AND DISCUSSION

General characteristics of sediments from the harbors

As reported in the previous paper (Lee *et al.*, 1998), the heavy metal contents of Kyeonggi Bay sediments are generally dependent on the sediment grain size, as can be seen in Fig. 3. However, for Cr, Cu, Zn and Pb, there are some samples which do not follow this general tendency and have higher contents than those expected from their mean grain sizes. These are all from the Incheon North Harbor area.

The average heavy matal contents of 8 surface sediment samples collected from the Incheon North Harbor are as high as 136 μg/g for Cr, 138 μg/g for Cu, 33 μg/g for Ni, 38 μg/g for Pb and 260 μg/g for Zn. When we look at the inner part of the harbor, the degree of enrichment of heavy metal contents reaches a even higher level. The average content of the 4 surface sediments collected from the inner part of the harbor (St. 18, 19, 20, 21) is 214 μg/g for Cr, 251 μg/g for Cu, 40 μg/g for Ni, 56 μg/g for Pb and 420 μg/g for Zn. Compared to the average contents of these metals in the entire Kyeonggi Bay sediments, which are 70 μg/g for Cr, 25 μg/g for Cu, 25 μg/g for Ni, 24 μg/g for Pb and 92 μg/g for Zn, the above values obtained from the harbor sediments are significantly high and prove the polluted nature of these sediments (Table 2). The grain size of the harbor sediments are uniformly fine and the mean grain size ranges between 5.5–7.8 ϕ, with the finest sediments in the central part of the harbor. However, the contents of heavy metals increase toward the inner part of the harbor, suggesting the source of these contaminants to be in the landward side of the harbor (Fig. 4).

Speciation of heavy metals in surface sediments

Among the 37 surface sediment samples analyzed for heavy metal speciation, 4 samples (St. 19, 22, 23, 24) were from the polluted Incheon North Harbor area (the Harbor sediments) and the remaining 33 samples from the rest of the Kyeonggi Bay area excluding the polluted harbor (the Bay sediments). The result of heavy metal speciation in surface sediments is shown in Table 3.

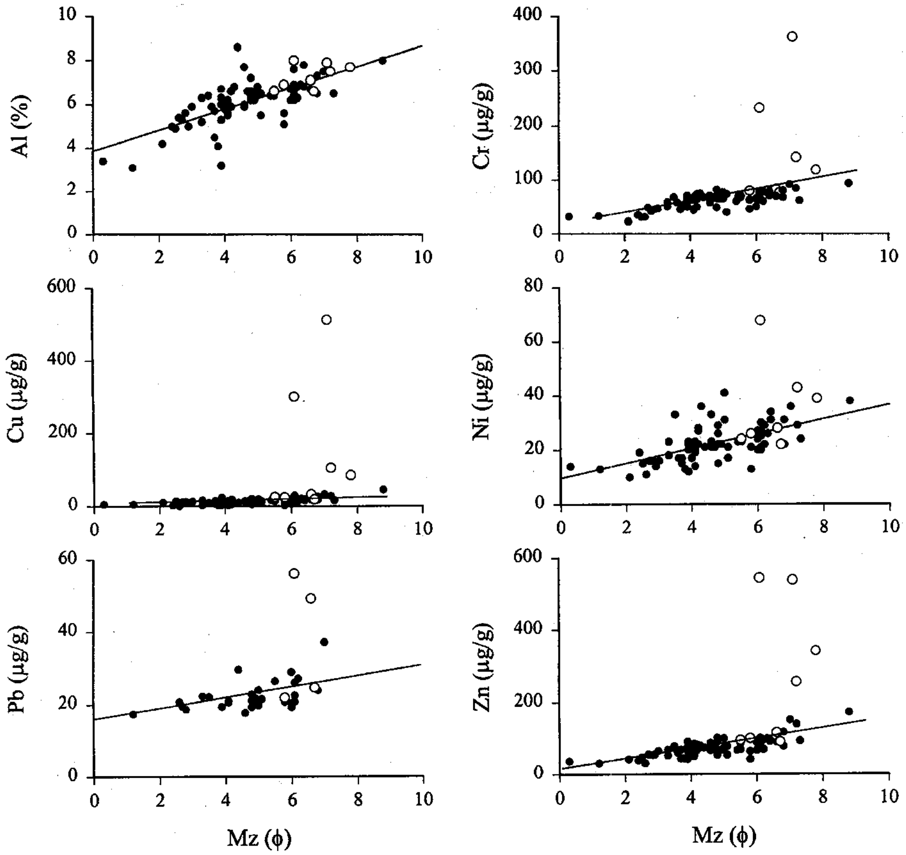

Fig. 3. Relationships between the heavy metal contents and the mean grain size in surface sediments of Kyeonggi Bay. Open circles are sediment samples from the Incheon North Harbor.

Table 2. The average heavy metal contents in surface sediments of the entire Kyeonggi Bay (n = 90), of the Incheon North Harbor (n = 8) and of the inner part of the North Harbor (n = 4). (in µg/g)

Metals	Cr	Cu	Ni	Pb	Zn
Entire Kyeonggi Bay	70	25	25	24	92
Incheon North Harbor	136	138	33	38	260
Inner part of the North Harbor	214	251	40	56	420

In the Bay sediments, all five metals showed their strong association with the crystal lattice fraction, comprising on the average more than half of the total heavy metal contents. The average contribution of the crystal lattice fraction in total heavy metal contents of the Bay sediments was 90.1% for Cr, 79.5% for Ni, 67.8% for Pb, 66.3% for Zn and 51.4% for Cu. The adsorbed fraction was important for Cu (av. 14.1%) and Zn (10.9%), and was of relatively minor importance for Pb (6.5%), Ni (4.4%) and Cr (2.5%). The easily reducible (or carbonate) fraction was important for Pb (15.6%), Cu (13.8%) and Zn (9.8%), but less important for Ni (5.5%) and Cr (2.7%). The reducible fraction was shown to be important only for Cu (10.8%) and of minor importance for Zn (6.2%) and Pb (3.6%). For Cr and Ni, the reducible fraction has not been detected at all. The organic and/or sulfide fraction was relatively important for Ni (10.6%) and Cu (9.9%), and less important for Zn (6.9%), Pb (6.4%) and Cr (4.7%).

The most prominent characteristics of the speciation of Cr in the surface sediments of Kyeonggi Bay are therefore the overwhelming dominance of the lattice fraction and the absence of the reducible fraction. The organic, adsorbed and carbonate fractions are only of minor importance. For Cu, the contribution of the 4 labile fractions (i.e., the adsorbed, easily reducible, reducible and organic/sulfide fractions) are equally significant. For Ni, among the labile fractions, only the organic/sulfide fraction contributed in any significant proportion. The reducible fraction is absent. For Pb, only the easily reducible fraction showed a significant contribution, and for Zn, both the adsorbed and easily reducible fractions were

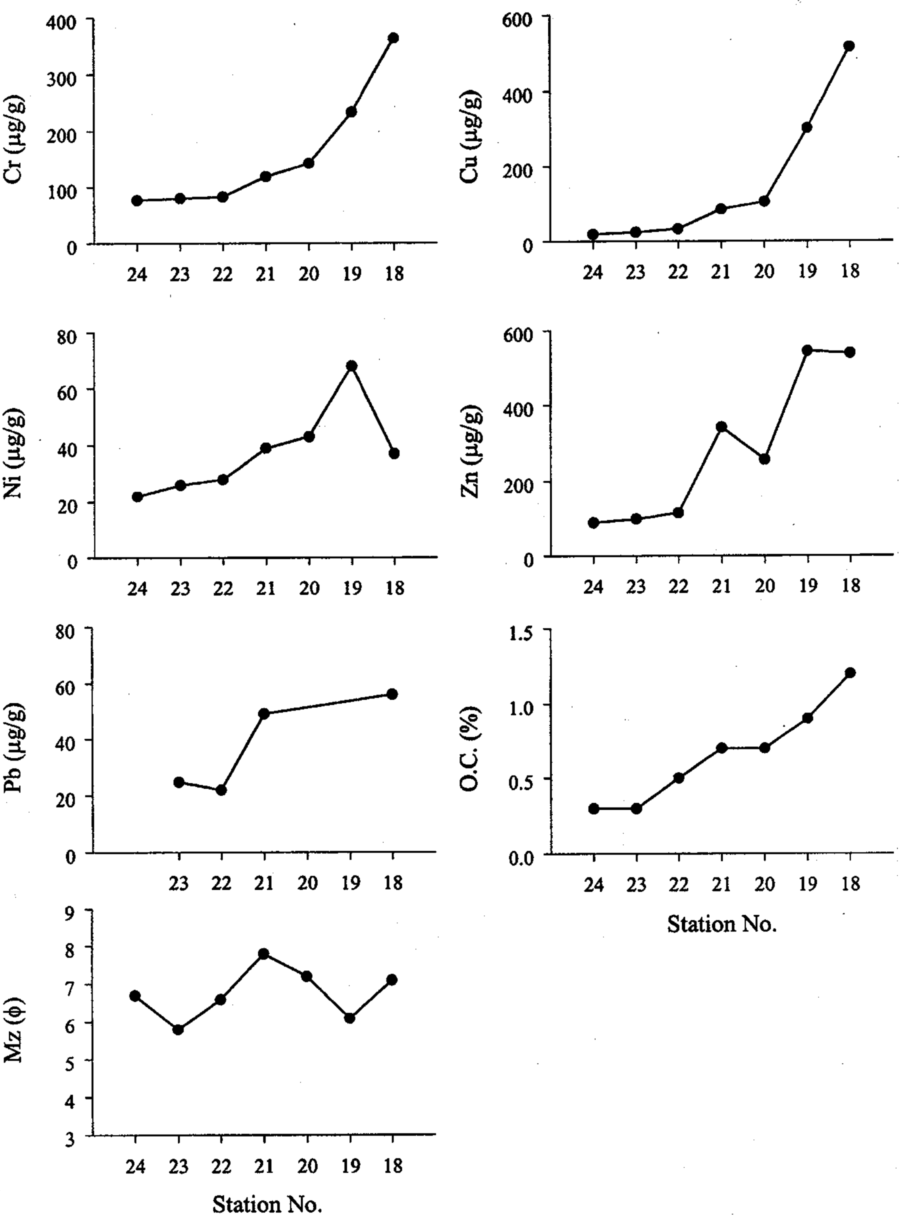

Fig. 4. Lateral variations of the heavy metal contents within the Incheon North Harbor area. St. 24 is located near the mouth of the Harbor and St. 18 in the innermost part of the Harbor.

shown to be important (Table 4).

In the Harbor sediments (n=4), however, there emerged a different speciation pattern. Compared to that of the Bay sediments, the contribution of the lattice fraction decreased noticeably, while that of the labile fractions increased. This increase in contribution occurred in the easily reducible and organic/sulfide fractions for Cr, in the adsorbed fraction for Ni, in the easily reducible fraction for Pb, and in the adsorbed and easily reducible fractions for Zn. For Cu, the increase in contribution was observed for all of the 4 labile fractions, although that of the reducible fraction was less prominent (Table 4).

Considering that the Harbor sediments are significantly enriched in heavy metals whereas the Bay sediments remained relatively unpolluted with respect to these metals, the difference in speciation pattern observed between the Bay and the Harbor sediments can be interpreted as the result of the accumulation of pollutant metals in the harbor area. Many authors have suggested that the metal contaminants introduced from man's activity usually exist in labile fractions which are relatively unstable (Fillipek and Owen, 1979; Kitano *et al.*, 1980; Förstner and Wittmann, 1981; Salomons and Förstner, 1984; etc.). Consequently, a clear decrease of the lattice fraction is expected with increasing overall metal contents as was observed in the present study. Since labile frac-

Tabel 3. Results of heavy metal speciation in surface sediments of Kyeonggi Bay (in %). AF = adsorbed fraction, ERF = easily reducible fraction, RF = reducible fraction, OF = organic/sulfide fraction, LF = lattice fraction, ND = not detected.

Station	Cr					Cu				
	AF	ERF	RF	OF	LF	AF	ERF	RF	OF	LF
4	2.0	2.3	N.D.	5.0	90.8	20.1	16.2	9.5	7.8	46.3
6	3.7	3.3	N.D.	8.4	84.6	17.3	18.2	9.2	9.2	46.1
8	3.1	3.1	N.D.	5.1	88.8	16.8	12.8	7.3	9.5	53.6
9	5.2	5.7	N.D.	6.7	82.4	18.5	15.7	8.9	9.7	47.2
10	1.7	1.7	N.D.	3.9	92.7	14.0	10.3	10.3	7.3	58.2
13	2.6	3.1	N.D.	7.0	87.2	17.8	15.2	11.3	10.4	45.2
15	1.9	2.3	N.D.	4.3	91.4	10.6	16.2	15.0	6.9	51.5
16	2.1	1.2	N.D.	2.7	94.0	14.3	14.9	10.8	8.3	51.7
17	3.5	4.3	N.D.	6.2	86.0	18.5	13.7	8.1	8.8	50.9
19	11.1	20.3	N.D.	19.8	48.8	2.0	40.6	17.7	25.3	14.4
22	5.0	10.1	N.D.	6.0	78.8	34.4	19.8	10.4	16.7	18.8
23	3.6	4.7	N.D.	6.9	84.9	25.4	17.6	11.6	12.2	33.2
24	3.3	4.2	N.D.	5.5	87.0	19.6	14.5	10.1	12.5	43.3
26	2.1	3.5	N.D.	4.6	89.8	18.3	10.8	9.7	9.7	51.5
28	1.4	3.0	N.D.	4.6	91.0	15.4	13.4	8.9	12.5	49.8
31	3.9	4.6	N.D.	6.6	84.9	24.3	14.6	9.6	12.4	39.1
32	2.0	2.6	N.D.	3.4	92.1	14.4	10.2	11.8	10.2	53.4
37	1.8	2.6	N.D.	3.8	91.7	15.1	23.9	13.4	10.8	36.8
42	2.3	2.9	N.D.	4.4	90.3	9.5	14.6	11.0	8.0	57.0
49	2.3	1.0	N.D.	5.0	91.6	5.0	13.3	9.9	3.3	68.6
56	2.7	4.4	N.D.	9.4	83.5	22.5	13.3	12.5	10.8	40.9
57	3.2	1.4	N.D.	4.5	90.9	9.2	14.8	18.4	0.0	57.6
60	4.3	1.8	N.D.	6.1	87.8	15.1	12.8	13.9	5.8	52.3
61	4.6	3.6	N.D.	5.6	86.1	19.8	16.8	10.4	8.4	44.7
67	2.4	2.2	N.D.	6.0	89.4	12.2	21.2	11.6	10.3	44.6
73	1.3	3.0	N.D.	3.4	92.3	12.2	11.8	9.8	13.5	52.6
75	3.5	2.9	N.D.	6.7	86.8	12.8	19.2	10.3	11.5	46.1
76	1.0	2.2	N.D.	2.7	94.0	10.2	8.8	8.1	10.2	62.5
77	1.1	1.3	N.D.	1.6	96.0	11.4	9.9	12.9	12.2	53.7
79	1.7	2.9	N.D.	3.8	91.7	10.7	16.1	11.5	15.7	46.0
81	1.6	1.6	N.D.	1.2	95.6	11.2	12.8	11.2	10.4	54.3
85	2.7	3.0	N.D.	3.5	90.8	19.9	14.1	11.7	12.4	41.9
86	2.0	2.4	N.D.	3.7	91.9	8.4	6.1	9.1	13.7	62.7
87	1.7	2.6	N.D.	3.6	92.0	10.2	8.8	9.5	11.0	60.5
88	2.2	2.9	N.D.	4.0	91.0	7.2	9.5	8.7	11.9	62.7
89	1.9	2.4	N.D.	3.1	92.6	11.1	14.1	12.1	12.1	50.7
90	2.1	2.5	N.D.	3.5	91.9	11.2	11.2	10.3	11.2	56.2
Min.	1.0	1.0		1.2	48.8	2.0	6.1	7.3	0.0	14.4
Max.	11.1	20.3		19.8	96.0	34.4	40.6	18.4	25.3	68.6
Avg.	2.8	3.5		5.2	88.5	14.8	14.8	11.0	10.6	48.8

tions are chemically unstable, they are more accessible for short-term geochemical processes, such as remobilization and biological uptake, than the detrital (lattice) component. The accumulation of pollutant heavy metals, especially for Cu, Pb and Zn, appears to occur in Kyeonggi Bay sediments mainly in the adsorbed and easily reducible fractions. These are the most unstable forms among the labile fractions and, therefore, can be easily released into the overlying waters by small changes in environmental conditions of the bay area.

Speciation of heavy metals in core sediments

The total contents of heavy metals analyzed in the two core sediment samples, collected from the Incheon North Harbor, were in the range of 44.7–106.7 μg/g for Cr, 17.3–84.6 μg/g for Cu, 11.6–33.2 μg/g for Ni, 27.3–57.8 μg/g for Pb and 49.0–339.3 μg/g for Zn. The higher values occurred in the upper part of the core and the lower values in the lower part. The heavy metal contents therefore generally showed an increasing trend as they moved upward

Tabel 3. (continued).

Station	Ni					Pb				
	AF	ERF	RF	OF	LF	AF	ERF	RF	OF	LF
4	4.2	7.3	N.D.	9.8	78.7	3.8	15.4	0.2	7.7	72.9
6	6.9	4.8	N.D.	8.4	79.9	8.4	21.0	4.1	6.0	60.5
8	4.5	4.1	N.D.	7.5	84.0	8.7	14.7	5.9	2.4	68.4
9	0.2	5.0	N.D.	11.5	83.2	0.0	23.9	5.3	10.2	60.7
10	7.5	7.0	N.D.	8.5	77.0	4.4	9.4	3.8	5.2	77.1
13	3.4	7.3	N.D.	11.3	78.0	3.2	11.0	2.6	5.1	78.1
15	6.1	9.3	N.D.	11.6	72.9	4.4	16.8	3.3	7.7	67.7
16	4.8	9.0	N.D.	11.0	75.3	8.2	16.6	1.6	3.5	70.0
17	6.8	3.6	N.D.	10.9	78.7	5.4	18.0	4.6	4.8	67.2
19	27.9	13.1	N.D.	6.3	52.7	17.1	45.4	2.6	6.0	28.9
22	8.6	6.7	N.D.	6.8	77.9	10.8	37.0	12.4	4.0	35.9
23	1.1	4.8	N.D.	9.0	85.1	0.0	24.1	6.5	9.0	60.4
24	2.3	4.9	N.D.	8.1	84.7	6.8	17.6	6.3	7.1	62.2
26	3.1	5.5	N.D.	9.7	81.6	2.6	15.8	5.5	8.9	67.3
28	4.0	4.0	N.D.	9.1	82.9	10.1	18.3	5.3	4.2	62.2
31	5.0	4.7	N.D.	8.2	82.1	13.6	16.0	2.4	6.5	61.5
32	0.6	5.7	N.D.	12.2	81.5	4.5	13.8	3.6	6.1	71.9
37	2.9	5.6	N.D.	7.0	84.5	5.9	13.8	3.0	5.6	71.8
42	2.9	5.8	N.D.	10.2	81.1	3.0	15.5	4.2	6.4	70.9
49	4.0	4.3	N.D.	10.9	80.8	3.8	11.7	2.0	6.4	76.1
56	7.1	7.1	N.D.	18.4	67.5	12.1	20.5	5.3	7.1	55.0
57	3.5	4.0	N.D.	19.5	72.9	15.7	7.3	4.0	4.8	68.2
60	5.3	6.3	N.D.	15.0	73.4	3.3	4.9	4.1	7.4	80.3
61	2.8	5.9	N.D.	13.5	77.9	1.1	22.9	2.5	6.7	66.8
67	3.9	7.7	N.D.	11.3	77.1	4.0	21.8	4.3	8.9	60.9
73	1.4	4.7	N.D.	8.7	85.2	0.0	20.0	2.8	8.7	68.4
75	4.4	6.8	N.D.	13.0	75.8	9.9	23.8	1.6	7.0	57.7
76	5.3	3.1	N.D.	7.8	83.8	4.2	13.0	4.2	6.0	72.5
77	2.5	4.2	N.D.	6.6	86.7	2.5	15.0	11.0	4.3	67.2
79	1.4	5.8	N.D.	8.4	84.4	0.0	26.1	2.7	7.2	64.0
81	3.5	5.0	N.D.	9.3	82.2	0.0	16.0	3.6	13.6	66.8
85	16.8	3.4	N.D.	11.0	68.9	29.1	12.5	2.3	5.0	51.1
86	3.4	7.0	N.D.	8.6	81.0	7.1	11.8	3.7	5.6	71.8
87	3.3	7.2	N.D.	7.4	82.1	4.8	13.6	1.5	4.9	75.3
88	5.1	2.5	N.D.	10.9	81.5	7.7	11.0	4.1	5.4	71.9
89	3.2	3.2	N.D.	11.3	82.2	8.9	10.1	3.2	7.9	69.8
90	7.0	3.8	N.D.	10.8	78.5	14.7	12.9	1.1	5.6	65.8
Min.	0.2	2.5		6.3	52.7	0.0	4.9	0.2	2.4	28.9
Max.	27.9	13.1		19.5	86.7	29.1	45.4	12.4	13.6	80.3
Avg.	5.0	5.7		10.3	79.0	6.8	17.3	4.0	6.5	65.5

in the vertical sediment column, the maximum content appearing in the surface sediment (Fig. 5). Core 1, located in the inner part of the harbor, had on the whole higher contents of all the 5 heavy metals than Core 2 which was collected from the outer part of the harbor.

Heavy metal speciation from core sediments showed a remarkably different pattern from surface sediments (Table 5). Cr in the organic/sulfide fraction increased greatly (av. 18.9% in Core 1 and 37.6% in Core 2) compared to that in surface sediments (9.5% in the Harbor sediments). The lattice fraction was still the dominant component for Cr in core sediments and the reducible fraction, which did not occur for Cr in surface sediments, contributed 6.4% and 4.8% in Core 1 and 2, respectively. The importance of the adsorbed and the easily reducible fractions was greatly reduced. For Cu, the organic/sulfide fraction became the dominant fraction (66.8% in Core 1 and 58.8% in Core 2). The importance of the reducible fraction increased and that of the lattice fraction decreased for Cu in core sediments. The adsorbed

Tabel 3. (continued).

Station	Zn				
	AF	ERF	RF	OF	LF
4	14.8	11.6	6.5	6.7	60.4
6	14.5	12.3	6.2	6.6	60.5
8	10.5	6.9	3.4	3.9	75.3
9	15.6	12.0	5.8	5.4	61.2
10	9.8	7.8	5.2	6.7	70.4
13	11.9	9.5	6.8	6.9	64.8
15	5.8	7.6	6.0	6.8	73.8
16	11.3	11.3	6.6	7.0	63.7
17	16.1	9.1	4.4	5.9	64.5
19	0.8	35.4	9.8	8.5	45.6
22	58.2	12.2	3.8	2.6	23.2
23	21.3	11.7	6.5	6.0	54.4
24	15.0	10.7	6.2	6.6	61.6
26	12.4	9.9	5.8	7.8	64.2
28	13.0	9.7	5.2	6.1	66.0
31	26.4	11.1	6.0	6.6	49.9
32	12.0	9.4	5.9	6.9	65.9
37	13.9	9.5	4.9	5.7	66.0
42	7.9	11.3	6.4	6.8	67.5
49	6.0	9.6	6.2	7.0	71.2
56	16.0	11.2	7.8	7.4	57.6
57	12.5	9.8	8.5	7.2	62.0
60	13.5	9.4	7.7	7.5	62.0
61	12.5	13.2	7.3	6.9	60.1
67	8.1	10.7	7.4	7.7	66.1
73	10.3	8.6	6.3	7.1	67.6
75	11.7	13.4	7.5	7.8	59.6
76	7.1	8.5	5.4	6.1	72.8
77	7.3	9.0	6.7	7.5	69.4
79	8.1	11.0	6.2	7.3	67.4
81	8.0	9.4	6.2	7.0	69.4
85	10.4	10.8	7.2	8.3	63.4
86	4.3	8.1	6.4	7.4	73.8
87	5.8	8.2	5.3	7.2	73.6
88	6.1	7.3	5.0	6.7	74.9
89	7.4	8.8	5.7	7.8	70.4
90	7.8	8.8	5.4	6.9	71.1
Min.	0.8	6.9	3.4	2.6	23.2
Max.	58.2	35.4	9.8	8.5	75.3
Avg.	12.3	10.7	6.2	6.8	64.1

and easily reducible fractions were, unlike the surface sediments, negligible for Cu in core sediments. Ni was associated mainly with the organic/sulfide (26.4% in Core 1 and 53.9% in Core 2) and the lattice fractions (44.2% in Core 1 and 32.3% in Core 2). The reducible fraction, which was also absent for Ni in surface sediments, made up on the average 23.0% and 9.2% of total Ni in Core 1 and Core 2, respectively. For Pb, the contributions from the reducible and the organic/sulfide fractions increased while those of the lattice and the easily reducible fractions decreased greatly. For Zn, the organic/sulfide fraction became the dominant component in core sdiments, as was the case for Cu, and contributed 63.9% and 56.4% of the total Zn content in Core 1 and Core 2, respectively. Zn in the lattice fraction decreased greatly while that in the reducible fraction increased compared to the surface sediments.

When we look at the content rather than the percentage of heavy metals, another interesting feature emerges (Fig. 5 and Fig. 6). The content of each metal in the lattice fraction remains within a relatively constant range through the whole vertical column of the sediment core, even though their relative contributions vary depending on the total contents. On the contrary, the contents of metals in the organic/sulfide and the reducible fractions increase upward (toward the surface) in the sediment cores. This upward increasing trend is particularly prominent for Cr, Cu and Zn. It is therefore evident that the surface enrichment of these metals in the Harbor sediments is due to the increased amount of the organic/sulfide and the reducible fractions.

A strong association of heavy metals with the organic/sulfide fraction indicates that a large part of these metals exist in core sediments as various metal sulfide complexes or as organic bound chemical species. The distinction between the sulfide and organic forms of metals can not be made with the present method of sequential leaching. However, since these are all stable forms under an anoxic environment, they can tell us that the sediment below the surface layer is generally in oxygen-depleted condition. The depletion of dissolved oxygen will lead to sulfate reduction in the sediment pore waters, and we could observe the sulfate reduction in pore waters of our sediment core samples. And the pH values observed from pore waters of our sediment cores were in the range of 7.1–7.8. The pH in pore waters under reducing environment is normally buffered in the range of 6.9–8.3 and, if sulfide minerals form, can be changed further into narrower range by the remnant of sulfides in pore (Ben-Yaakov, 1973; Millero, 1986). Though additional data such as H_2S and alkalinity are lacking, it will be reasonable to conclude from the above facts that the formation of sulfide minerals occurs and thereby controls the speciation pattern of heavy metals in the polluted harbor sediments. And it is also possible that heavy metals associated with other fractions might change into organic/sulfide fraction as burial proceeds (Förstner, 1989).

Table 4. Average values of heavy metal speciation of the Harbor sediments compared to that of the Bay sediments (in %). AF = adsorbed fraction, ERF = easily reducible fraction, RF = reducible fraction, OF = organic/sulfide fraction, LF = lattice fraction.

	AF	ERF	RF	OF	LF
Cr (Bay)	2.5	2.7	0	4.7	90.1
(Harbor)	5.7	9.9	0	9.5	74.9
Cu (Bay)	14.1	13.8	10.8	9.9	51.4
(Harbor)	20.4	23.1	12.5	16.7	27.4
Ni (Bay)	4.4	5.5	0	10.6	79.5
(Harbor)	10.0	7.4	0	7.5	75.1
Pb (Bay)	6.5	15.6	3.6	6.4	67.8
(Harbor)	8.7	31.0	6.9	6.5	46.9
Zn (Bay)	10.9	9.8	6.2	6.9	66.3
(Harbor)	23.8	17.5	6.6	5.9	46.2

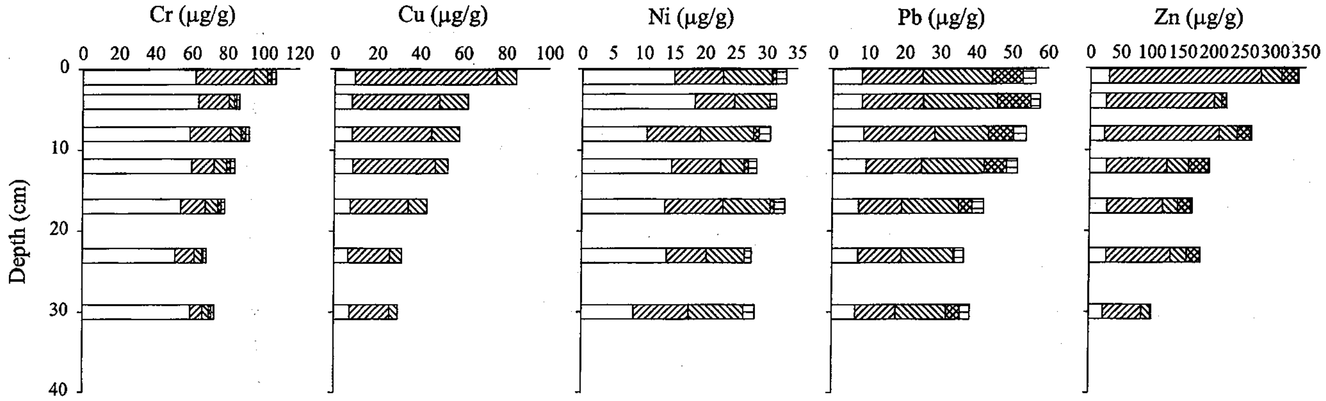

Fig. 5. Vertical distribution of heavy metal speciation in Core 1. (▤ adsorbed fraction; ▩ easily reducible fraction; ▧ reducible fraction; ▨ organic/sulfide fraction; ☐ lattice fraction.

Table 5. Average values of heavy metal speciation in Core 1 and Core 2 sediments (in %). AF = adsorbed fraction, ERF = easily reducible fraction, RF = reducible fraction, OF = organic/sulfide fraction, LF = lattice fraction.

	Metals	AF	ERF	RF	OF	LF
Core 1	Cr	2.3	2.1	6.4	18.9	70.2
	Cu	--	--	16.6	66.8	16.5
	Ni	5.0	1.4	23.0	26.4	44.2
	Pb	6.4	11.0	35.0	30.9	16.6
	Zn	0.7	8.9	12.4	63.9	14.2
Core 2	Cr	0.3	--	4.8	37.6	57.3
	Cu	0.2	0.8	24.3	58.8	15.9
	Ni	4.5	--	9.2	53.9	32.3
	Pb	2.9	16.4	20.4	34.7	25.6
	Zn	1.3	0.1	24.4	56.4	17.8

CONCLUSIONS

Speciation of five heavy metals (Cr, Cu, Ni, Pb and Zn) in surface sediments of Kyeonggi Bay can be characterized by an overall dominance of the crystal lattice fraction. Among the labile fractions, each metal showed different degree of assocation with various fractions. The adsorbed fraction showed important for Cu and Zn, the easily reducible fraction for Cu, Pb and Zn, the reducible fraction for Cu and the organic/sulfide fraction for Cu and Ni. In contrast to this, the Harbor sediments, which were relatively enriched in heavy metals, showed somewhat different speciation patterns. The importance of the lattice fraction decreased on the whole, while the percentage of the labile fraction showed an increase. The easily reducible fraction showed an increase in almost all the metals while the adsorbed fraction increased in Cu and Ni and Zn, and the organic/sulfide fraction in Cu.

In the core samples, the speciation pattern emerged with remarkably different characteristics from those of the surface sediments. The most significant differences are the sharp increase in the percentages of the reducible and organic/sulfide fractions and the

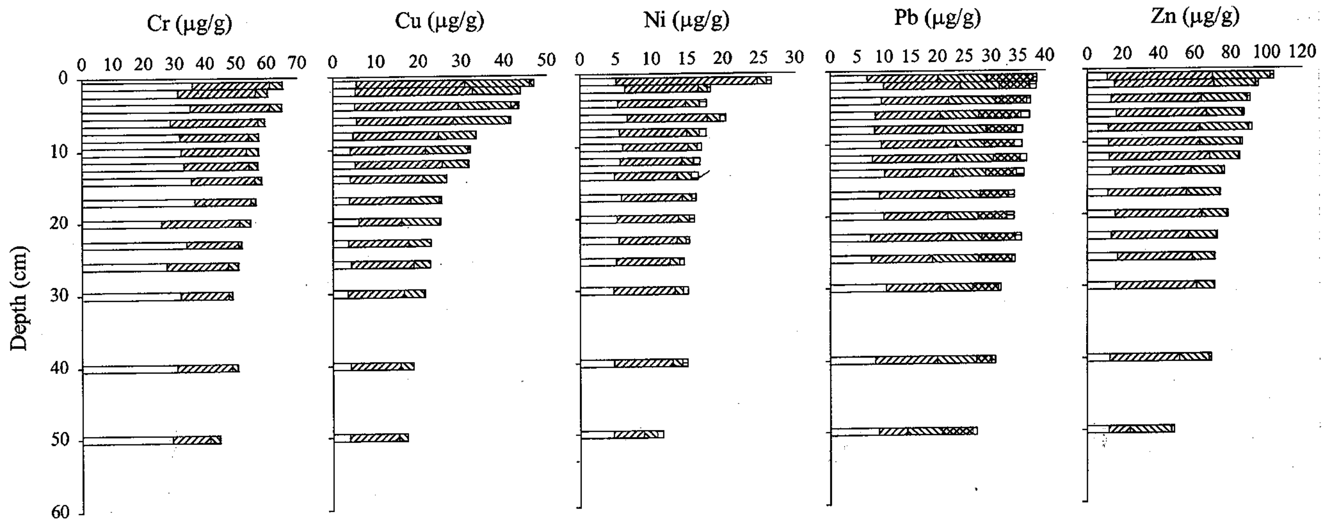

Fig. 6. Vertical distribution of heavy metal speciation in Core 2. (▤ adsorbed fraction; ▩ easily reducible fraction; ▧ reducible fraction; ▨ organic/sulfide fraction; ▭ lattice fraction.

decrease in the lattice fraction. The metal contents in the lattice fraction, however, remain relatively stable through the whole vertical column but those in the organic/sulfide and reducible fractions showed an upward increasing pattern. Consequently it can be concluded that the increased amount of the organic/sulfide and reducible fractions is responsible for the surface enrichment of these metals in the polluted harbor. In addition, the dominance of the organic/sulfide fraction can be attributed in part to the sulfate reduction and subsequent sulfide mineral formation under the anoxic condition of the polluted harbor sediments.

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