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PARTITIONING OF HEAVY METALS IN SEDIMENTS FROM JINHAE BAY, KOREA

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鎭海灣 堆積物 中의 重金屬 分布

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Abstract: Sediments were collected from eight stations in Jinhae Bay and heavy metals were fractionated into the adsorbed, reducible, oxidizable and residual fractions. Cd, Cu, Pb and Zn in each fraction were determined by atomic absorption spectrophotometry.

Cd was shown to be mainly in the adsorbed form, Cu in the oxidizable and residual fractions, and Pb and Zn mainly in the reducible fractions, The total concentrations of Cu, Pb and Zn in sediments decreased gradually with increasing distance from the head of the bay, and the relationship of linear regression was obtained.

要約: 진해만 퇴적물 중의 중금속 분포를 조사하기 위하여 8개의 조사점에서 시료를 채취하여 흡착부분, 환원부분, 산화부분 및 잔류부분으로 중금속을 분류하였다. 본 조사 결과로는 Cd은 흡착부분에, Cu는 산화 및 잔류부분에, Pb와 Zn는 환원부분에 주로 분포되어 중금속에 따라 큰 차이를 보여주었다. 또 Cu, Pb 및 Zn의 농도는 내만에서 외양으로 갈수록 농도가 뚜렷이 감소되는 선형회귀곡선을 얻었다.

INTRODUCTION

Once heavy metals are introduced into the marine environment by the various transporting agents, the surrounding water, suspended matter including living biota and bottom sediments serve as their principal reservoirs (Brewer and Spencer 1975, Katz and Kaplan 1981). And coastal marine sediments are good indicators of geochemical and environmental changes including transport of pollutants, especially heavy metals, through river inputs (Goldberg 1978).

Since the Masan-Changwon area is the location of near-sea industrial complexes, its industrial and domestic wastewaters flow into Jinhae Bay. The presence, however, of narrow channels restricts flushing of the bay water, thus causing serious pollution problems and damages to aquaculture and fishing in the bay (Lee *et al.* 1981).

In the present study, partitioning of heavy metals was determined in sediments of Jinhae Bay and was related to man's activities in the Korean coastal environment.

MATERIALS AND METHODS

Sampling stations in Jinhae Bay are shown in Fig. 1. Samples were collected at eight stations with a Ekman snapper in August, 1980, put into plastic bags, frozen, freeze-dried and ground with a mortar.

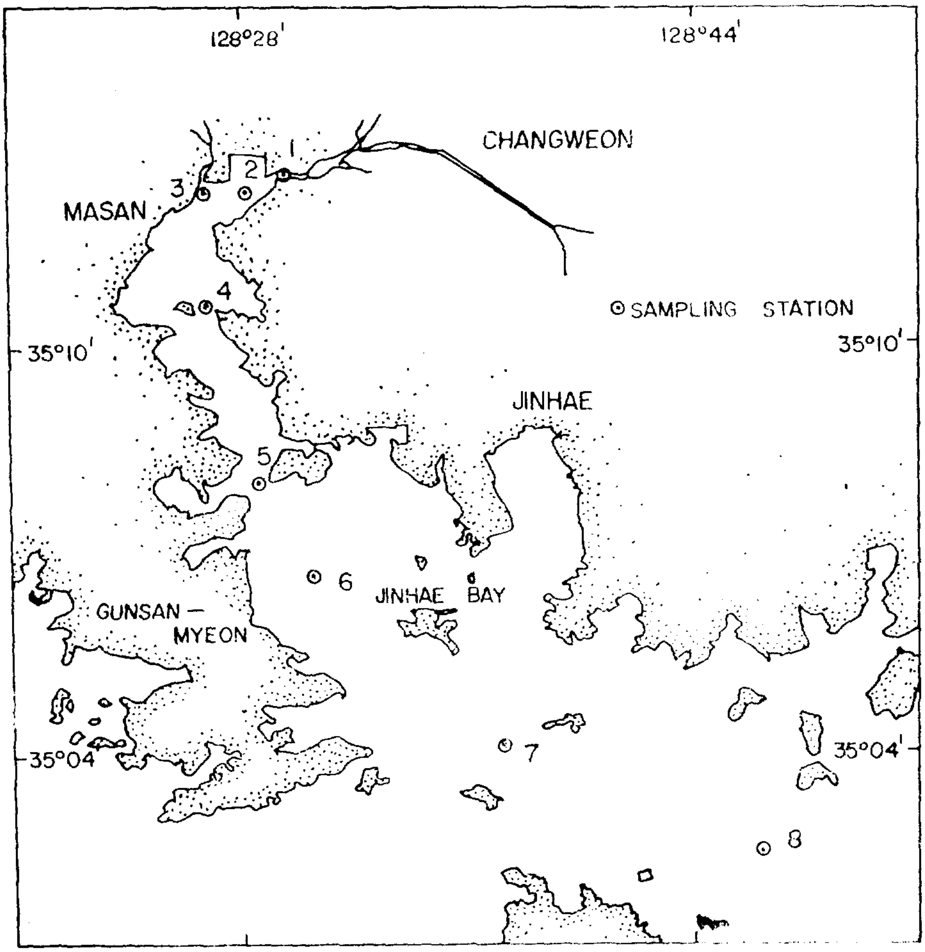

Fig. 1. Sampling stations in Jinhae Bay.

For analysis of heavy metals in sediments, four grams of each sample were taken and analyzed using modified sequential leaching techniques of Gibbs (1973) and Burrows and Hulbert (1975). This technique involves a series of extractions of heavy metals in sediments with distilled water (adsorbed fraction) with hydroxylamine hydrochloride in acetic acid (reducible fraction), with hydrogen peroxide (oxidizable fraction), and finally with hydrofluoric acidnitric acid (residual fraction).

The concentrations of heavy metals, cadmium (Cd), copper(Cu), lead(Pb) and zinc(Zn), were determined by flame atomic absorption spectrophotometry with an Instrumentation Laboratory Model 251 with deuterium background correction.

RESULTS AND DISCUSSION

The results of a four-stage analysis of sediments are shown in Tables 1-4 for Cd, Cu, Pb and Zn, respectively, The labile adsorbed fraction is readily removed by washing with distilled water. The reducible fraction is dissolved with hydroxylamine hydrochloride and consists of carbonates and iron-manganese oxides. Hydrogen peroxide dissolves oxidizable species of sulfides and organic complexes. And finally the residual fraction, environmentally inert, of primarily silicates is extracted with a hydrofluoric acidnitric acid mixture (Burrows and Hulbert 1975).

Most of Cd, 55 to 88% (mean, 71%) of the total Cd, in sediments was concentrated in the labile adsorbed fraction, whereas 10 to 33% (mean, 25%) of the total Cd was coprecipitated with oxides (Table 1). The oxidizable fraction accounted for 2 to 18% (mean, 4%) of the total Cd and no Cd remained in the residual fraction. Burrows and Hulbert (1975) reported that Cd was only in the oxidizable fraction prior to weathering and in the residual fraction after weathering.

The total Cd was variable from station to station and lowest at St. 4 and highest at St. 7 without showing any gradual change from the head of the bay. The mean total Cd, 0.24 μg/g dry wt. in sediments of Jinhae Bay from this study was lower than that of Lee and Lee (1983), or that of Israeli coast (Roth and Hornung 1977), but similar to the mean Cd reported by Bowen (1979).

Partitioning of Cu in sediments of Jinhae Bay (Table 2) showed a different distribution from that of Cd (Table 1). Very little Cu was found in the adsorbed form, whereas 31 to 79% (mean, 55%) of the total Cu was associated with the oxidizable fraction. The residual fraction accounted for 15 to 58% (mean, 29%) of the total

Table 1. Partitioning of Cd in sediments of Jinhae Bay (μg/g dry wt.).

Fraction / Station	Adsorbed	Reducible	Oxidizable	Residual	Total
1	0.03	0.03	0.01	0	0.07
2	0.22	0.05	0.03	0	0.30
3	0.09	0.05	0.02	0	0.15
4	0.03	0.02	0.01	0	0.06
5	0.23	0.13	0.01	0	0.37
6	0.27	0.03	0.01	0	0.31
7	0.30	0.10	0.01	0	0.41
8	0.16	0.05	0.01	0	0.22
Mean	0.17	0.06	0.01	0	0.24
% Mean	70.8	25.0	4.2	0	100.0

Table 2. Partitioning of Cu in sediments of Jinhae Bay (μg/g dry wt.).

Fraction / Station	Adsorbed	Reducible	Oxidizable	Residual	Total
1	0.1	11.3	13.6	11.9	36.9
2	0.1	0.7	41.0	10.4	52.2
3	0.1	18.2	56.3	19.3	93.9
4	0.3	9.9	7.7	6.7	24.6
5	0.5	0.4	11.3	7.0	19.2
6	0.1	0.7	8.0	7.7	16.5
7	0.2	1.0	4.9	7.5	13.6
8	0.2	0.8	4.1	6.8	11.9
Mean	0.2	5.4	18.4	9.7	33.6
% Mean	0.5	16.0	54.7	28.8	100.0

Cu and 1 to 40% (mean, 16%) was found in the reducible fraction. These results suggest that most of Cu in sediments of Jinhae Bay was in the non-labile form and binding with organic complexes may be one of the major mechanisms restricting Cu mobility in Jinhae Bay.

The total Cu was highest at St. 3(94 μg/g), where the Masan industrial and domestic wastewaters enter the bay, and lowest at St. 8 (12 μg/g), farthest to the open ocean. This result is similar to that of Lee and Lee (1983). The mean levels of total Cu in the present study (33.6 μg/g dry wt.) were nearly the same as the mean Cu concentration for marine sediments reported by Bowen(1979).

Distribution of Pb in Jinhae Bay sediments showed that most Pb, 52 to 85% of the total Pb(mean, 80%), was deposited in the reducible fraction, whereas 1 to 42% of the total Pb(mean, 12%) was in the oxidizable fraction with 2 to 20% in the residual(Table 3).

Less than 4% of the total Pb was located in the adsorbed fraction, as it was reported with polluted sediments (Burrows and Hulbert 1975), but Pb in other fractions did not agree between two studies. The results suggest that coprecipitation with Fe-Mn oxides immobilizes most of available Rb in sediments of Jinhae Bay.

Table 3. Partitioning of Pb in sediments of Jinhae Bay (μg/g dry wt.).

Station \ Fraction	Adsorbed	Reducible	Oxidizable	Residual	Total
1	0.3	44.2	5.1	3.6	53.2
2	0.2	13.7	10.9	1.1	25.9
3	0.2	37.6	3.9	0.8	42.5
4	0.1	25.0	2.7	1.4	29.2
5	0.4	17.5	2.5	0.7	21.1
6	0.8	13.7	0.6	3.6	18.7
7	0.6	12.8	0.2	2.8	16.4
8	0.2	13.7	0.8	1.4	16.1
Mean	0.4	22.3	3.3	1.9	27.9
% Mean	1.4	79.9	11.8	6.9	100.0

Table 4. Partitioning of Zn in sediments of Jinhae Bay (μg/g dry wt.).

Station \ Fraction	Adsorbed	Reducible	Oxidizable	Residual	Total
1	0.1	74.5	18.1	13.3	106.0
2	0.2	37.3	16.0	16.7	70.2
3	1.9	76.9	15.8	16.1	110.7
4	0.6	59.6	14.6	13.3	88.1
5	1.0	42.7	25.7	14.6	84.0
6	0.6	17.8	16.4	22.4	57.2
7	1.9	18.3	12.0	16.1	48.3
8	1.9	16.4	12.4	14.6	45.3
Mean	1.0	42.9	16.4	15.9	76.2
% Mean	1.3	56.3	21.5	20.9	100.0

The range and mean contents of the total Pb of the bay were 16 to 53 μg/g and 28 μg/g dry wt. respectively. The total Pb was highest at St. 1 (53 μg/g) and, then, St. 3 and lowest at St. 8 (16 μg/g). The mean of the total Pb in sediments of this study (28 μg/g) was higher than the mean level for marine sediments (19 μg/g) reported by Bowen(1979) but lower than that by Lee and Lee(1983).

Out of the total Zn, 30 to 70% (mean, 56%) was associated with the reducible fraction(Table 4). The oxidizable and the residual fractions accounted for similarly 10 to 30% (mean 21%) of the total Zn. Less than 5% was found in the adsorbed, as was the case of polluted sediments reported by Burrows and Hulbert (1975). As was the case with Pb, Zn in sediments was mainly coprecipitated with Fe-Mn oxides in Jinhae Bay and very little was in available form.

The total Zn in sediments was highest at St. 3 (111 μg/g) and lowest at St. 8 (45μg/g dry wt.), as was the case with Cu and Pb. The mean level of the total Zn in this study (76 μg/g dry wt.) was lower than that for marine sediments reported by Bowen (1979) or that of Lee and Lee(1983) for sediments in Jinhae Bay.

Concentrations of the total Cu, Pb and Zn, except Cd, were highest at the head of Jinhae Bay and decreased gradually with increasing distance from the head of the bay. The linear relationship between heavy metal concentration and the distance from the head of the bay is shown in Table 5, where data from St. 1, 2 and 3 are excluded because of some dredging activities. Linear correlation coefficients were all signifficant at the 99% level and linear regression was obtained with concentration (Y) of heavy metals on the distance (D). Similar relationship was reported by Lee and Lee (1983), although in their study the total Cd contents showed the same trend as total Cu, Pb and Zn. This relationthip showed that the sources of heavy metals are inputs of domestic and indust rial wastewaters and heavy metals are readily distributed in sediments as various forms of the adsorbed, reducible, oxidizable and residual fractions.

Table 5. The relationship between heavy metal concentration(in μg/g dry wt) and the distance from the head of Jinhae Bay (in Km).

Metal	R	Regression
Cu	−0.097**	Y=25.11−0.57D
Pb	−0.898**	Y=28.18−0.56D
Zn	−0.941**	Y=95.79−2.23D

** Significant at the 99% level.

CONCLUSIONS

Heavy metals, Cd, Cu, Pb and Zn, in Jinhae Bay sediments showed each a different distribution in the adsorbed, reducible, oxidizable and residual fractions.

Cd in Jinhae Bay sediments was mainly in the adsorbed form, whereas Cu was in the oxidizable and residual fractions. And both Pb and Zn were mainly in the reducible fractions.

The total concentrations of Cu, Pb and Zn in sediments decreased linearly with increasing distance from the head of the bay.

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