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HEAVY METALS IN THE NAGDONG ESTUARY

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ABSTRACT

In order to investigate water pollution of heavy metals in the Nagdong Estuary, samples were collected five times from August 1978 to April 1979 every other month, and analyzed for Cd, Cu, Pb and Zn by atomic absorption spectrophotometry.

The results showed no significant heavy metal pollution in most parts of the studied areas, except near the outfalls of the Sasang Industrial Complex. In general, the heavy metal contents were higher in the dry season than in the rainy season due to the dilution effect of river water flow. Distribution of heavy metals in the dissolved and the particulate fractions were also investigated.

INTRODUCTION

In Korea, due to rapid growth in industry and urbanization during the last two decades, transport of pollutants into coastal waters has been greatly increased through river inputs. In addition, many industrial complexes for heavy and chemical industries have been established near the coastlines, thereby increasing the pollution burden on coastal waters from various pollutants, especially from heavy metals.

Heavy metals are one of the critical pollutants to be monitored because of their potential toxicity to aquatic organisms, their persistence in the environment, and their tendency to be bioaccumulated through the marine food chain.

With a well-developed delta at its mouth, the Nagdong Estuary with annual discharge of about 63 billion tons of freshwater (Choe *et al.*, 1971), provided an suitable area for aquaculture of seaweeds over the last several decades. Furthermore, the Nagdong Estuary is now designated as one of the important "Natural Reserves" in Korea, since it is a suitable habitat for migratory birds of more than 125 species, including several rare ones.

However, in the Nagdong River watershed, the Gumi, Daegu and Sasang industrial complexes have been built, thus deteoriorating gradually water quality of the river as well as that of the estuary. Due to this water pollution, many laver culture farms were already deteoriorated, and the number of of migratory birds visiting the Nagdong Estuary has been rapidly decreasing.

The objectives of the present study were to determine pollution levels of heavy metals, such as Cd, Cu, Pb and Zn and, thus, to provide the basis for establishing pollution control measures in the Nagdong Estuary.

SAMPLING AND ANALYTICAL METHODS

Sampling Stations of heavy metals in the Nagdong Estuary are shown in Fig. 1. Surface samples were collected five times from August, 1978 to April, 1979 every other month at spring tide of the month. Samples collected with 5 *l*-Van Dorn water sampler were stored in 3.8 *l*-polyethylene bottles and transported to

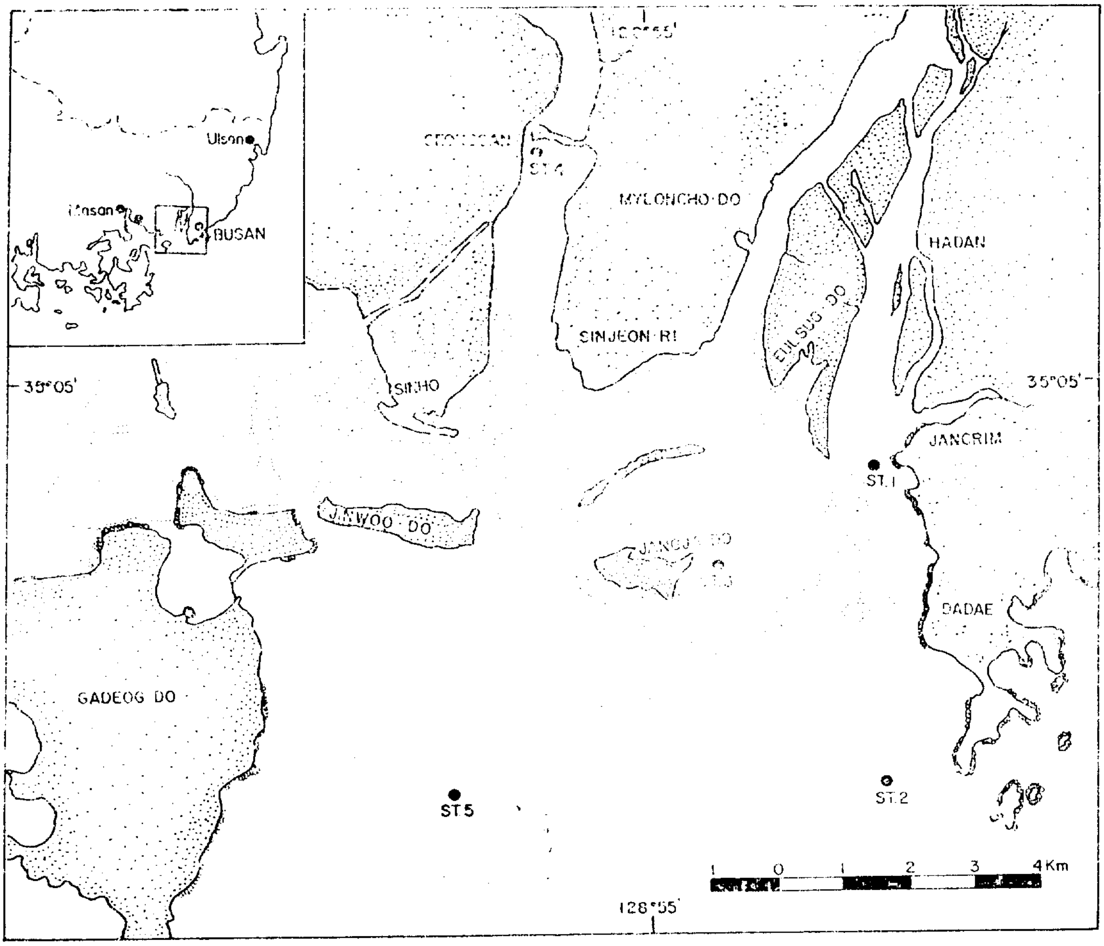

Fig. 1. Sampling stations of the Nagdong Estuary

the laboratory for analysis.

In laboratory, samples were filtered on HA type Millipore membrane filters with pore size 0.45μm and diameter 47mm. Heavy metals in the filtrate and the suspended solids were than analyzed by separate analytical methods. The contents of heavy metals in the filtrate were reported as "Dissolved" metals and those in the suspended solids as "Particulate" metals. The sum of concentrations of the metals in both dissolved and particulate fractions was reported as "Total" metals.

Analytical procedure for the determination of dissolved Cd, Cu, Pb and Zn is as follows. Pour 800ml of the filtered seawater sample into an one liter roundbottom flask, and two drops of methyl orange and 5ml of Fe(III) solution(100 mg/l), and adjust the pH approximately to 3. Add 15ml of the citrate buffer and finally 5ml of 5% APDC solution. Shake the flask for one min., let stand for half an hour, and filter. The precipitate is collected on a filter and transferred into a 10-ml test tube with a stopper. Dissolve the precipitate by adding in 5 ml of 1:5 HNO_3 in an oven at 60°C. The sample solution is then aspirated into the air-acetylene burner for the atomic absorption measurement. The precise analytical procedure is referred to the previously published paper(Lee *et al.*, 1980). Particulate metals were determined according to the EPA analytical manual(EPA, 1974).

Measurements were made with an Instrumentation laboratory (II) Model 251 Atomic Absorption Spectrophotometer. IL hollow-cathode lamps (Cd, Cu, Pb and Zn) and deuterium lamp for background correction were used as ligh sources.

RESULTS AND DISCUSSION

In the present study, heavy metals were studied for dissolved, particulate and total fractions. Table 1 shows the ranges and means for the bimonthly and total heavy metals for all stations. The ranges and means of heavy metals at each station are given in Table 2. Table 3 describes distribution of heavy metals between the dissolved and particulate fractions in the Nagdong Estuary. For convenience, the survey period was devided into two parts, dry season and rainy season, where the dry season includes October, December and February, and the rainy season, April and August.

Table 1. Ranges and bimonthly mean concentrations of heavy metals in the Nagdong Estuary. Unit: $\mu g/l$

Element	Fraction	1978					
		August		October		December	
		Range	Mean	Range	Mean	Range	Mean
Cd	DIS	0.09—0.35	0.18	0.08—0.73	0.42	0.07—1.19	0.05
	PAR	0.03—0.07	0.04	0.02—0.39	0.16	0.02—0.14	0.07
	TOT	0.12—0.39	0.22	0.10—1.08	0.58	0.11—1.33	0.57
Cu	DIS	1.2—1.9	1.5	0.4—1.2	0.8	0.7—1.4	1.1
	PAR	0.1—0.4	0.2	0.1—0.2	0.2	0.2—0.6	0.4
	TOT	1.3—2.3	1.7	0.6—1.4	1.0	0.9—2.0	1.5
Pb	DIS	<0.5	<0.5	0.8—1.6	1.2	1.4—2.8	2.0
	PAR	<0.5	<0.5	<0.5	<0.5	<0.5—1.2	0.7
	TOT	0.5	0.5	1.1—1.9	1.5	1.7—3.1	2.7
Zn	DIS	5.0—15.0	9.0	4.9—37.0	15.0	6.3—13	10.1
	PAR	0.3—2.7	1.2	0.4—2.2	1.3	0.8—3.2	2.4
	TOT	5.9—17.7	10.2	5.2—39.2	16.3	7.1—15.9	12.5

Element	Fraction	1979				Total	
		February		April			
		Range	Mean	Range	Mean	Range	Mean
Cd	DIS	0.15—1.90	0.68	0.08—0.45	0.17	0.07—1.90	0.38
	PAR	0.02—0.13	0.06	0.02	0.02	0.02—0.39	0.07
	TOT	0.23—1.94	0.74	0.10—0.47	0.19	0.10—1.94	0.45
Cu	DIS	0.7—1.9	1.1	1.5—3.7	2.1	0.5—3.7	1.3
	PAR	0.2—1.3	0.5	0.4—2.3	1.1	0.1—2.3	0.5
	TOT	0.9—3.2	1.6	1.9—6.2	3.2	0.6—6.2	1.8
Pb	DIS	<0.9—3.9	1.8	<0.5—5.5	2.0	<0.5—5.5	1.4
	PAR	<0.5—1.1	0.6	0.7—4.1	2.1	<0.5—4.1	0.8
	TOT	0.9—4.2	2.4	1.2—9.6	4.0	0.5—9.6	2.2
Zn	DIS	3.1—38.0	18.6	9.3—19.0	14.9	3.1—38.0	13.6
	PAR	0.7—5.3	2.5	2.0—6.6	4.7	0.3—6.6	2.5
	TOT	3.8—43.3	21.1	11.3—25.4	19.5	3.8—43.3	16.1

Table 2. Ranges and mean concentrations of heavy metals at each station. Unit: μg/l

Element	Fraction	St. 1 Range	St. 1 Mean	St. 2 Range	St. 2 Mean	St. 3 Range	St. 3 Mean	St. 4 Range	St. 4 Mean	St. 5 Range	St. 5 Mean
Cd	DIS	0.09—1.90	0.79	0.10—0.63	0.32	0.09—1.19	0.50	0.07—0.69	0.28	0.08—0.16	0.12
	PAR	0.02—0.04	0.03	0.02—0.20	0.10	0.02—0.14	0.07	0.02—0.39	0.11	0.02—0.04	0.02
	TOT	0.12—1.94	0.82	0.12—0.72	0.42	0.11—1.33	0.57	0.11—1.08	0.39	0.10—0.20	0.14
Cu	DIS	1.2—3.7	2.1	0.9—2.0	1.5	0.9—1.7	1.3	0.6—1.5	1.0	0.5—1.7	1.0
	PAR	0.2—2.5	1.1	0.1—1.3	0.6	0.1—0.7	0.4	0.1—0.4	0.2	0.1—0.4	0.2
	TOT	1.4—6.2	3.1	1.0—3.3	2.1	1.3—2.4	1.7	0.8—1.9	1.2	0.6—2.0	1.3
Pb	DIS	<0.5—5.5	2.5	<0.5—1.8	0.8	<0.5—1.9	1.2	<0.5—3.9	1.9	<0.5—2.8	1.0
	PAR	<0.5—4.1	1.4	<0.5—3.0	1.0	<0.5—1.7	1.0	<0.5—0.8	0.6	<0.5—0.7	0.5
	TOT	0.5—9.6	3.9	0.5—3.5	1.8	0.5—3.3	2.2	0.5—4.4	2.3	0.5—3.3	1.4
Zn	DIS	13.0—38.0	26.5	12.0—19.0	14.8	5.0—17.0	10.8	3.1—17.0	8.6	4.9—20.0	9.3
	PAR	1.3—6.6	3.9	0.6—6.4	3.0	0.9—5.3	3.1	0.3—3.1	1.8	0.4—2.0	1.0
	TOT	14.3—43.3	30.4	12.6—25.4	17.8	5.9—20.1	13.9	3.8—20.1	10.4	5.3—20.9	10.3

Table 3. Dissolved and particulate fractions of heavy metals in the Nagdong Estuary. Unit: %

Element	Dissolved	Particulate
Cd	84.4	15.6
Cu	73.8	26.2
Pb	64.2	35.8
Zn	84.6	15.4

1. Cadmium

1) Dissolved Cd

The range and mean concentrations of dissolved Cd are 0.07～1.90 μg/l and 0.38 μg/l, respectively. As shown in Table 1, the bimonthly mean concentrations of dissolved Cd in dry season are much higher than those in rainy season. Table 2 shows that the mean concentration of dissolved Cd at St. 1(0.79 μg/l) is the greatest and that at St. 5(0.12 μg/l) is the lowest among stations The dissolved fraction, as given in Table 3, accounts cn the average for 84.7% of the total Cd and, therefore, it greatly affects the characteristics of total Cd.

The mean value of the dissolved Cd of the present study is much higher than that of the lower stream of the Nagdong River, 0.14 μg/l (Lee *et al.*, 1978), or that of ocean water, 0.11 μg/l (Goldberg, 1963).

2) Particulate Cd

The range and mean concentrations of particulate Cd are 0.02～0.39μg/l and 0.07μg/l, respectively. Bimonthly variation of the particulate Cd is much like that of the dissolved Cd, and the contents are higher in dry season than in rainy season. The mean concentration of St. 4(0.11 μg/l) is the highest and that of St.5 (0.02μg/l) is the lowest among stations. However, it should be noted that, in spite of the largest value of dissolved Cd, St. 1 is comparatively lower in the particulate Cd content. The particulate fraction only shares 15.3% of the total Cd on the average.

The mean concentration of the particulte Cd of this study is nearly the same as that of the lower stream of the Nagdong River (0.05 μg/l).

3) Total Cd

The range and mean concentrations of total Cd are 0.10～1.94 μg/l and 0.45 μg/l, respectively. As mentioned above, most of the total Cd contents are contributed by the dissolved fraction. Therefore, the characteristics of the total Cd depend greatly on those of the dissolved Cd. The bimonthly mean concentrations of the total Cd are much higher in dry season than in rainy season. Of the stations, the mean concentration of total Cd at St. 1(0.82 μg/l) is the highest.

The mean value of total Cd of the present study(0.45μg/l) is higher than those of the lower stream of the Nagdong River(0.19μg/l), and Northeast Pacifiic water(0.006 μg/1, Bruland *et al.*, 1978), but much lower than those of the Israel coastal area(0.94 μg/l, Roth and Hornung, 1977) or the water quality standards of the U.S.A. for Cd for seawater aquatic life (5μg/l, EPA, 1976).

2. Copper

1) Dissolved Cu

The range and mean concentrations of dissolved Cu are 0.5~3.7 μg/l and 1.3 μg/l, respectively. Table 1 shows that the bimonthly mean concentrations of dissolved Cu are higher in rainy season that in dry season. This trend is shown to be opposite to the case of Cd. As for the difference for each stations(Table 2), the mean concentration of dissolved Cu at St. 1(2.1 μg/l) is the greatest among the stations. On the contrary, the bimonthly mean contents of Sts. 4 and 5 are the same(1.0μg/l) and the smallest of all stations. The dissolved fraction accounts for 73.8% of the total Cu on the average, as given in Table 3, and it greatly affects the characteristics of total Cu.

The mean concentration of the dissolved Cu of this study is about the same as that of the lower stream of the Nagdong River, 1.48μg/l (Lee *et al.*, 1978).

2) Particulate Cu

The range and mean concentrations of particulate Cu are 0.1~2.3μg/l and 0.5μg/l, respectively. The mean concentration of the particulate Cu was much higher in April than any other months. Among the stations, St. 1 is the highest(1.1μg/l) and Sts. 4 and 5 are equally the lowest (0.2μg/l). It should be emphasized that St. 1, which is located near the outfall of the Sasang Industrial Complex, is over five times higher than Sts. 4, 5 in the particulate Cu content. The particulate fraction only shares 26.2% of the total Cu.

The mean concentration of the particulate Cu of this study is nearly same as that of the lower stream of the Nagdong River(0.42μg/l).

3) Total Cu

The range and mean concentrations of total Cu are 0.6-6.2 μg/l and 1.8 μg/l, respectively. As previously mentioned, most of the total Cu contents are contributed by the dissolved fraction, Consequently, the distrubution patterns of the total Cu are much like those of the dissolved Cu. The bimonthly mean concentrations of total Cu are comparatively higher in rainy season than in dry season. It is quite interesting that the seasonal variation of total Cu is just opposite to that of Cd. The mean concentration of total Cu at St. 1(3.1 μg/l) is much higher than that of any other stations.

The mean value of total Cu of the present study is nearly the same as those of the lower stream of the Nagdong River(1.90 μg/l), and Irish Sea(Roth and Hornung, 1977), but much lower than those of the Dokai Bay(8.3 μg/l, Sakino *et al.*, 1980) or the water quality standards for Cu for seawater aquatic life in the U.S.A.(50 μg/l).

3. Lead

1) Dissolved Pb

The range and mean concentrations of dissolved Pb are 0.5-5.5 μg/l and 1.4 μg/l, respectively. Table 1 shows that the mean concentration of dissolved Pb in August(0.5 μg/l) is the lowest among the five periods of survey. St. 1 which has the highest contents of Cd and Cu is also highest among all stations in dissolved Pb, as shown in Table 2. Table 3 shows that the dissolved fraction of Pb in the Nagdong

Estuary accounts for 64.2% of the total Pb on the average. Compared with that of Cd or Cu, this is much lower value, but it is expected that dissolved Pb will still influence the distribution characteristics of the total Pb.

The mean concentration of dissolved Pb of this study is higher than that of the lower stream of the Nagdong River, 0.5 μg/l(Lee *et al.*, 1978), or ocean water,0.03 μg/l(Goldberg, 1963)

2) Particulate Pb

The range and mean concentrations of particulate Pb are 0.5-4.5 μg/l and 0.8 μg/l, respectively. The mean concentration of particulate Pb in April(2.1 μg/l) is the highest among the five periods of survey. Of the stations, St. 1 has the highest particulate Pb contents, as the case of the dissolved Pb. The particulate Pb contributes only 35.8%of the total Pb contents, and does not greatly affect the characteristics of the total Pb. However, it should be noted that the fraction of particulate Pb is higher than that of Cd(15.6%) or Cu(26.2%).

The mean concentration of the present study is slightly lower than that of the lower stream of the Nagdong River(1.1 μg/l).

3) Total Pb

The range and mean concentrations of total Pb are 0.5-9.6 μg/l and 2.2 μg/l, respectively. The bimonthly mean concentration of total Pb in April(4.0 μg/l) is the highest and that in August(0.5 μg/l) is the lowest during the study period. Of the stations, St. 1 is much higher than any other stations in the mean contents of the total Pb, while St. 2 is the lowest. It should be noted that the mean contents of Pb as well as Cd and Cu are the highest at St. 1 which is located near the outfall of the Sasang Industrial Complex.

The mean concentration of this survey(2.2 μg/l) is higher than that of the lower stream of the Nagdong River(1.6 μg/l), but much lower than those of Israel coast(6.4 μg/l, Roth and Hornung, 1977) and the Dokai Bay(40.8 μg/l, Sakino *et al.*, 1980) or the water quality standards for Pb for seawater aquatic life(50 μg/l) in the U.S.A.

4. Zinc

1) Dissolved Zn

The range and mean concentrations of dissolved Zn are 3.1-38.0 μg/l and 13.6 μg/l, respectively. In geneal, the bimonthly mean concentrations of dissolved Zn are higher in rainy season than in dry season, as shown in Table 1. Such seasonal variation of dissolved Zn is much like that of dissolved Cd, but just opposite to that of dissolved Cu. Table 2 shows the mean concentration of dissolved Zn at St. 1 (26.5 μg/l) is the greatest and that at St. 4 (8.6 μg/l) is the smallest. As given in Table 3, the dissolved fraction of Zn accounts for 84.6% of the total Zn on the average and, therefore, it greatly affects the characteristics of total Zn.

The mean contents of dissolved Zn of the present study are higher than those of the lower stream of the Nagdong River, 5.7 μg/l(Lee *et al.*, 1978) or ocean water, 5 μg/l(Goldberg, 1963).

2) Particulate Zn

The range and mean concentrations of particulate Zn are 0.3-6.6 μg/l and 2.5 μg/l, respectively. The mean concentration of partiuclate Zn in April(4.7 μg/l) is two to four times higher than that in any other months. However, there is no evidence of seasonal variation of particulate Zn between the dry and the rainy seasons. Of the stations, St. 1(3.9 μg/l) is the highest in particulate Zn contents, while St. 5(1.0 μg/l) is the lowest. The particulate fraction of Zn only shares 15.4% of the total Zn on the average. Thus, it is expected that particulate Zn is not so important as dissolved

Zn in its influence upon the characteristics of total Zn.

The mean contents of particulate Zn of this survey are higher than those of the lower stream of the Nagdong River(1.5 μg/l).

3) Total Zn

The range and mean concentrations of total Zn are 3.8-43.3μg/l and 16.1 μg/l, respectively. The bimonthly mean concentrations of total Zn are slightly higher in rainy season than in dry season. In February, the total Zn contents is greater than any other months, while August is the smallest. St. 1 is the highest in the mean concentration of total Zn(30.4 μg/l) as Cd, Cu and Pb, while St.5(10.3 μg/l) is the lowest among the stations.

The mean contents of total Zn of this study are more than twice as much as those of the lower stream of the Nagdong River(7.2 μg/l). But it is much lower than those of the Israel coast(38.3 μg/l, Roth and Hornung, 1977) or the water quality standards for Zn for seawater aquatic life(100 μg/l) in the U.S.A..

CONCLUSIONS

The bimonthly mean concentrations of Cd and Zn are higher in dry season than those in rainy season, while the seasonal variation of Cu is just opposite to Cd and Zn. In the case of Pb, there is no evidence of seasonal variation between the dry and the rainy seasons.

Of the stations, St. 1 showed much higher heavy metal contents than any other stations. The higher concentrations of heavy metals at St. 1 are greatly attributed to the wastewaters from the outfalls of the Sasang Industrial Complex.

The dissolved fractions of metals in the Nagdong Estuary are much higher than those of particulate metals on the average. Therefore, they influence the characteristics of the total metals considerably more than the particulate fraction.

In general, the heavy metal contents of the Nagdong Estuary are higher than those of the lower stream of the Nagdong River(Lee *et al.*, 1978), or ocean water(Goldberg, 1963), but much lower than those of the Israel coast, the Dokai Bay or the heavy metal stantards for seawater aquatic life in the U.S.A..

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