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DISTRIBUTION OF TRACE METALS AND SEDIMENTS IN ESTUARIES OF THE KUM RIVER AND THE MANKYUNG RIVER

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ABSTRACT

To estimate the chemical mass balance of several kinds of trace metals in sea water, suspended matter and bottom sediments, sixty samples from the Kum and Mankyung estuaries were analyzed. In both estuaries, the distribution patterns of leachabl suspended trace metals and of bottom sediments were established to be similar. The relationship between the metal concentration and clay content of the sediments was found to be such that the metal concentration increases with an increase in clay content. A linear correlation was determined between pairs of leachable metals (Fe-Zn, Fe-Mn and Zn-Mn) in the Kum estuary. However, in the Mankyung estuary linear relationship does not exist. *Finally, it is suggested that the trace metals are reworking in the Kum* estuary and those in the Mankyung estuary are sinking.

INTRODUCTION

The fate of chemical constituents of water suspended particulate matter and bottom sediments in estuarine regions are subject to estuarine processes, There are many sources of trace metals in an estuary, such as aerosols (Turekian 1971), industrial wastes and excessive amounts of organic matter. Trace metals are largely associated with the particulate matter during transport from the river to the sea (Coonley et al 1971).

The process of flocculation of particulate matter may cause trace metals to sink (Postma 19 67). Adsorption by organisms, precipitation and complexation can also remove trace metals from the water column. Some of the trace metals leaving the estuary in the dissolved or colloidal form may be removed as coating on sand or other mineral grains in the marine environment.

The objective of this investigation is to quantify the distribution of copper, iron, manganese and zinc between the three phases: water, suspended particulate matter and bottom sediments as they move from the river through the estuary into the sea.

DESCRIPTION OF THE AREA OF INVESTIGATION

The study areas(35°50′-36°05N 126°30′-126° 45′E) are estuaries of the Kum and Mankyung rivers where they empty into the Yellow Sea (Fig 1). According to their geomorphological character, these two estuaries fall into a group known as drowned river valley estuaries(Prichard 1960). Many small islets and deep embayments support the submergence of the coast.

The total drainage area of the Kum river is about 11,500km². This estuary has the important port city of Kunsan with population of 160,000 and its associated industries. Among the industries are the Changhang metal refinery plant, two papermills, five veneer and plywood companies and two alcohol manufacturing companies. Near the river mouth there is an extensive submerged delta,

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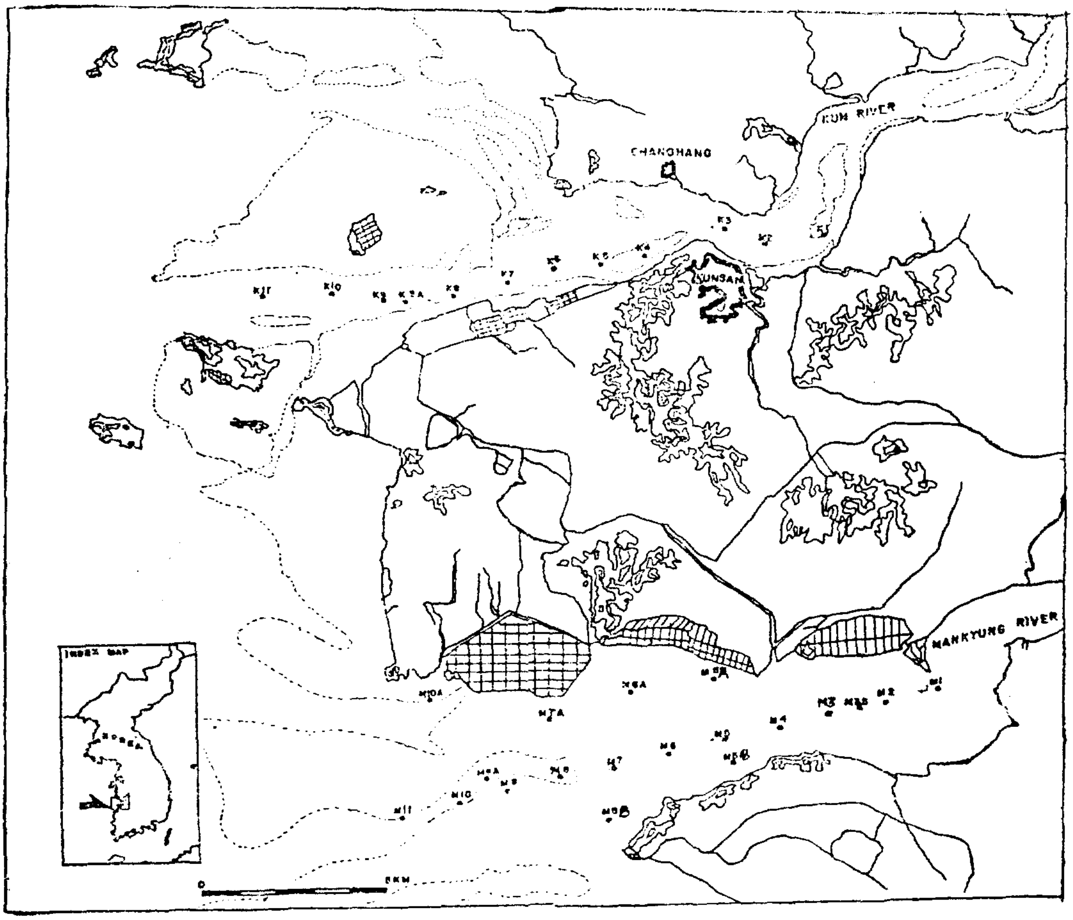

Fig. 1. Map of the area indicating sampling sites.

The area drained by the Mankyung river is smaller in supply area than that of Kum river. These two areas are composed of pre-cambrian rocks and associated granite. Alluvial flates, comprised of interbedded silts and sands are common to both estuaries.

The areas are dominated by a diurnal tide having a ratio of amplitudes(W_1+K_1/M_2+S_2) of approximately 0.2 knot and its direction of flood tide is 110° with maximum speed of 1.7 knot and the ebb tide has a direction of 219° with a current speed of 2.8 knot(Kim 1970).

METHODS

All samples from the Kum and Mankyung esturies were taken in the periods 9th to 10th September 1967. The sampling stations at 1.5km intervals are parallel to the river streams. Thirty stations, including two north and four south stations in the Mankyung estuary, were occupied in these.

Surface suspended matter and sea water sample were obtained by means of a polypropylene bucket. Immediately after collection $1.5l$ aliquots were isolated from the buckets and stored in acid soaked polyethylene bottles at 0°C. In the laboratory the samples were filtered under pressure of vaccum through pre-weighed 0.45μm millipore membrane filter. The filtrate was frozen to 0°C immediately after filtration and kept in acid soaked polyethylene bottles until anayzed.

The particulate matter remaining on the filter was dried at 40°C. The filters were reweighted and the residues were leached with 0.1N HCl for 18 hours. According to the method of Duinker et al(1974) 1500g of bottom sediments were obtained with a Dietz-LaFond snapper and sealed in plastic bags. In laboratory the portions of the sediment samples were dried in oven at 20~30°C for 20 hours. After grinding in a mortar crucible the sediment samples were leached with strong HCl(1) and HNO_3(3) for 24 hours and then filtered.

The remainder of the subsamples were used for grain size analysis of sediment. The particles coarser than sand were classified by dry sieve method, and the particles finer than sand were analysed by the pipette method.

All the pre-treated samples were analysed with a Perkin-Elmer 303 atomic absorption spectrophotometer for Cu, Fe, Mn and Zn.

In addition to trace metal analysis salinity and pH were also determined. Salinity measurement were made by titration with silver nitrate, *p*H with a Fisher *p*H meter using electrodes and Beckmen *p*H buffer directly on board.

RESULTS AND DISCUSSION

1. *p*H and salinity

The values of *p*H and salinity for the investigated area are presented in Fig 2. The *p*H ranges from 7.4 to 8 for the Kum estuary which is somewhat lower than the open ocean. The Mankyung estuary had a *p*H range of 7.35 to 8.35. This region may be characterized as a tidal pools or small bays rather than an estuary(Horn 1969). Similar *p*H and dissolved oxygen(4.28~6.53 cc/*l*) values were reported by Fisheries research & Development Agency(1972) in the Kum estuary.

Not only the longitudinal distribution but also the lateral and vertical distribution as a function of time should also be dealt with in estuarine dynamic studies.

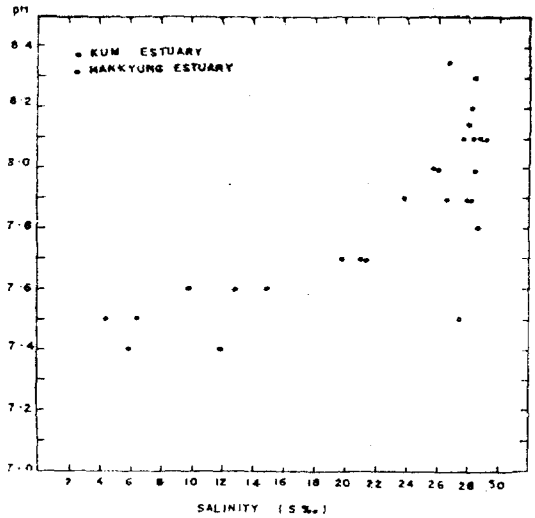

Fig. 2. Relation between *p*H and Salinty for investigated area.

A detailed investigation was not carried out in these areas because of time and some limitations. However, some gross features were determined. Kum estuary has an average salinity of about 15.6‰. It has large variability influenced by seasonal fluctuation with a high of 20.2‰ in January and a low of 9.7‰ in September. The salinity in the Mankyung estuary is usually higher than upper Kum inlet (Choi et al. 1975). Salinity in the Kum estuary ranges systematically from 4.29‰ at station K1 to 26.60‰ at K11 and those in Mankyung estuary range from 25.61‰ to 29.17‰ showing a relatively small contribution of Mankyung river water.

2. Textural analysis of sediment

The moment parameters(table 2) are calculated with the method of Folk(1968).

The grain size of the bottom sediments of the Kum estuary are ranged from silt to medium sand(1.9-5.47ϕ). But most samples in the Mankyung estuary are composed of very fine sands and a few samples are composed of silt

Table. 1. Distribution of the salinity (S‰), the pH and the suspended load (mg/l) at individual sampling Station.

Sample No.	S‰	pH	S.S(mg/l)		S‰	pH	S.S(mg/l)
M 2	25.61	8.0	303	K 1	4.29	7.5	180
M 3	26.65	8.35	200	K 2	5.89	7.4	543
M 3.5	26.78	7.8	102	K 3	6.16	7.5	ND
M 4	28.29	8.3	85	K 4	9.95	7.6	82
M 5 A	26.67	8.1	33	K 5	11.92	7.4	53
M 5	28.0	8.15	25	K 6	12.81	7.6	80
M 5 B	ND	ND	ND	K 7	14.96	7.6	151
M 6	28.04	7.9	59	K 8	19.73	7.7	301
M 6 A	27.46	7.5	30	K 9	20.87	7.7	235
M 7	28.40	8.0	96	K 9 A	21.06	7.7	340
M 7 A	28.29	8.3	105	K10	23.82	7.9	230
M 8	28.76	7.7	71	K11	26.60	8.0	158
M 8 B	28.08	8.2	30				
M 9	28.19	7.9	35				
M 9 A	29.17	8.1	60				
M10	ND	ND	ND				
M10 A	28.35	7.9	139				
M11	ND	ND	ND				

ND: not determined S.S: suspended substance weight.

Table. 2. Size analysis data and size distribution parameters values of the sendiments at the individual sampling station.

Sample No.	Sand (%)	Silt (%)	Clay (%)	Mz(ϕ)	σI	SK	KG		Sand	Silt	Clay	Mz(ϕ)	σI	SK	KG
M 2	ND	ND	ND	ND	ND	ND	ND	K 1	91.0	4.4	4.5	1.90	1.16	1.14	1.27
M 3	31.3	57.3	4.0	4.37	1.79	0.59	2.27	K 2	84.4	11.9	2.8	2.53	1.82	−0.26	0.96
M 3.5	ND	ND	ND	ND	ND	ND	ND	K 3	ND	ND	ND	ND	ND	ND	ND
M 4	34.3	64.3	1.4	3.80	0.60	0.05	1.02	K 4	64.4	25.9	9.6	3.47	1.45	0.60	3.79
M 5 A	2.8	89.5	3.8	4.67	1.40	0.74	1.49	K 5	20.8	65.2	12.0	5.0	2.23	0.14	0.72
M 5	ND	ND	ND	ND	ND	ND	ND	K 6	ND	ND	ND	ND	ND	ND	ND
M 5 B	78.21	18.6	3.2	3.30	0.56	0.44	2.25	K 7	32.7	45.5	17.8	4.93	3.19	0.08	0.86
M 6	16.6	80	3.4	4.43	1.11	0.35	1.90	K 8	6.9	84.2	7.5	5.6	1.69	0.35	1.05
M 6 A	ND	ND	ND	ND	ND	ND	ND	K 9	ND	ND	ND	ND	ND	ND	ND
M 7	69.3	24.9	5.8	3.90	1.40	0.67	0.69	K 9 A	24.7	55.2	19.6	5.47	2.25	0.13	0.80
M 7 A	ND	ND	ND	ND	ND	ND	ND	K 10	ND	ND	ND	ND	ND	ND	ND
M 8	57.7	41.4	0.8	3.40	0.41	0.07	1.15	K 11	ND	ND	ND	ND	ND	ND	ND
M 8 B	73.8	22.4	3.1	3.33	0.56	0.10	1.00								
M 9	ND	ND	ND	ND	ND	ND	ND								
M 9 A	56.6	42.9	0.4	3.40	0.59	−0.03	0.97								
M10	ND	ND	ND	ND	ND	ND	ND								
M10 A	91.60	4.2	4.1	3.03	0.56	0.17	1.70								
M11	ND	ND	ND	ND	ND	ND	ND								

at northern part(3.30∼4.67ϕ).

The sediments in the Kum estuary are poorly sorted and very poorly sorted according to scheme of Folk and Ward. Sorting values are ranged from 1.16 to 3.19. The sample in the Mankyung estuary are well sorted(0.16-1.79).

All the samples in these two estuaries except for the K2 and M9A show positive skewness values. Skewness values are ranged from −0.26 to 1.14 in the Kum estuary and ranged from −0.07 to 0.74 in the Mankyung estuary.

Kurtosis values are ranged from 0.80 to 3.79 in the Kum estuary and ranged 0.69 to 2.25 in the Mankyung estuary.

3. Suspended matter and suspended trace metals

The dispersal of sediment is of great importance to chemical processes in an estuary(Aston 1973). Drake(1976) has discussed the nature of the solid fraction enclosed within a fluid medium. The colloidal particles involved are small enough to be subjected to the forces producing Browninan motion and collombic repulsion by settling of grains in polydisperse systems, and by fluid shearing(Krone 1972). 40-60% of the total suspended material is inorganic(Parson 1961).

Much of the river borne suspended solids entering a estuary never reaches the sea, so the estuarine environment is a sink for sediment (Drake 1976).

The technique for removing supended samples from the water using centrifuges(Spencer et al. 1970) or membrane filtration(Banse *et al.* 1973) is subject to some question. Some of trace metal particles pass the millipore filter, because the particles are smaller than 0.5μm(Shigematus et al. 1970). However, membrane filtration is preferred for subsequent laboratory work(Drake 1976).

The variability of the amount of suspended matter in the Kum estuary water is very high

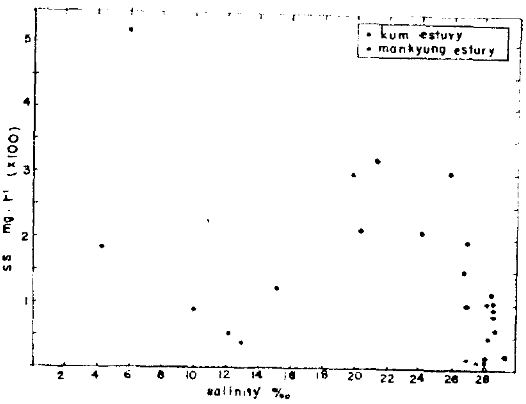

Fig. 3. Relation between salinity and suspended particulate matter.

compared to that of Mankyung. It is may be explained by the type of sediments prevalent and esturine mixing which is more vigorous in the Kum estuary.

The occurrence of a maximum content of particulate matter within a eddy area K2 in Kum river(Fig. 1) supports the idea that turbidity mixing increases particulate matter content. Minimum amounts of suspended matter(25-96 mg/*l*) was found in the open part of the Mankyung estuary in a area of maximum salinity (Fig. 3). The suspended particulate matter content in these estuaries shows high correlation to the type of sediment due to the strong interaction between suspended sediment and the bottom silt or sand.

With the exception of copper the amount from particulate matter leachable trace metal in these two areas show a similar pattern to the suspended matter content(Fig. 4-9). Irrespective of high concentration of suspended matter and trace metals in surface sediment, the leachable trace metals were low in the particulate carbonate rich station K9A. These mimimum values may be due to biochemical processes which can increase settling rates by several orders of magnitude. These metals are associated with organic or sulfide solids of the carbonate.

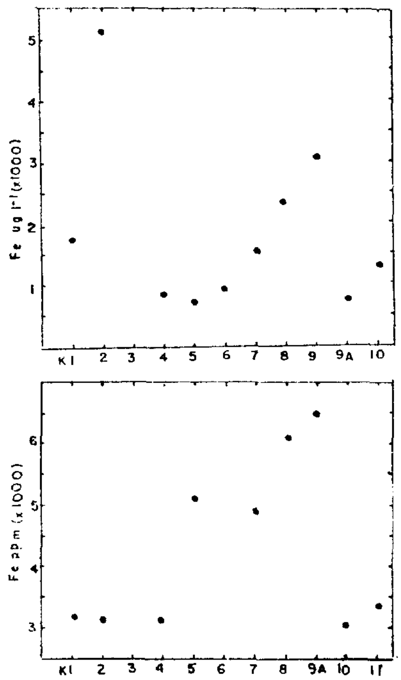

Fig. 4. Distribution of leacheable Fe content in suspended particulated matter(above) and distribution of Fe content in bottom sediment(below) at individual sampling station in the Kum estuary.

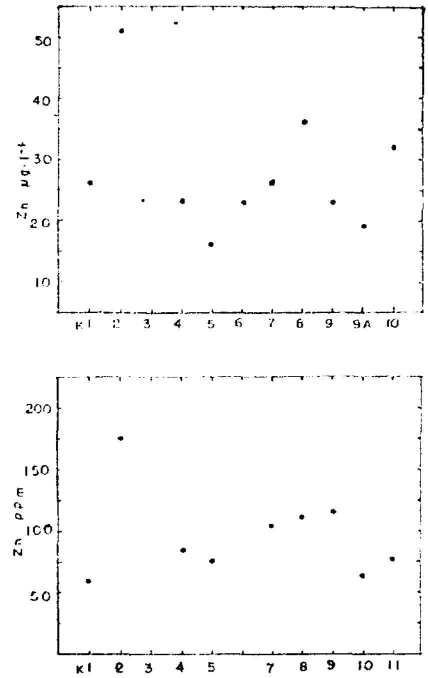

Fig. 6. Distribution of leacheable Zn in suspended particulate matter(above) and distribution of Zn content in botton sediment(below) at individual sampling station in the Kum estuary.

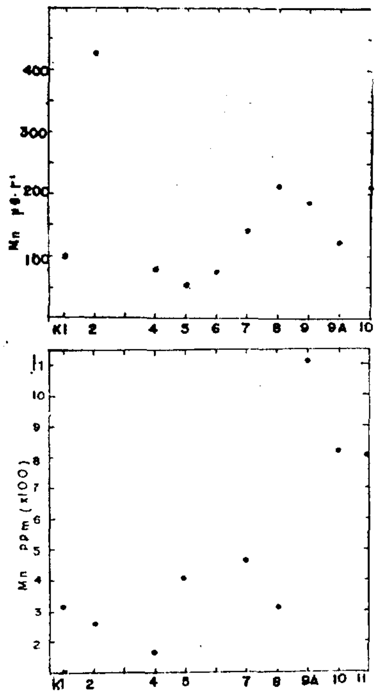

Fig. 5. Distribution of leacheable Mn content in suspended particulated matter(above) and distribution of Mn content in bottom sediment(below) at individual sampling station in the Kum estuary.

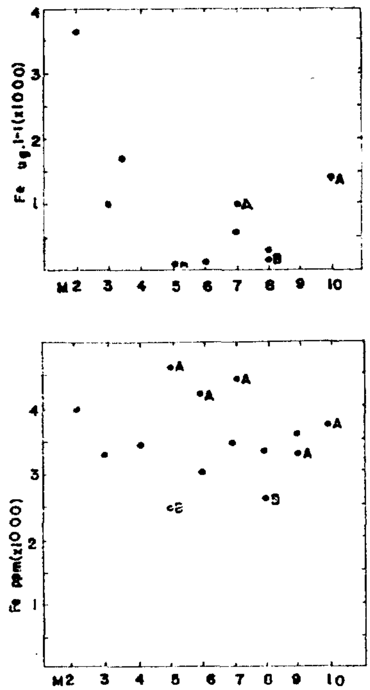

Fig. 7. Distribution of leacheable Fe content in the suspended matter (above) and distribution of Fe content in bottom sediment (below) at individual sampling station in the Mankyung estuary.

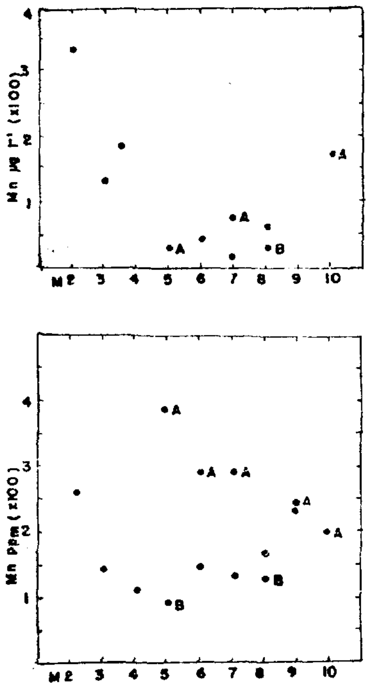

Fig. 8. Distribution of leacheable Mn in suspended matter(above) and distribution of Mn content in bottom sediment (below) at individual sampling station in the Mankyung estuary.

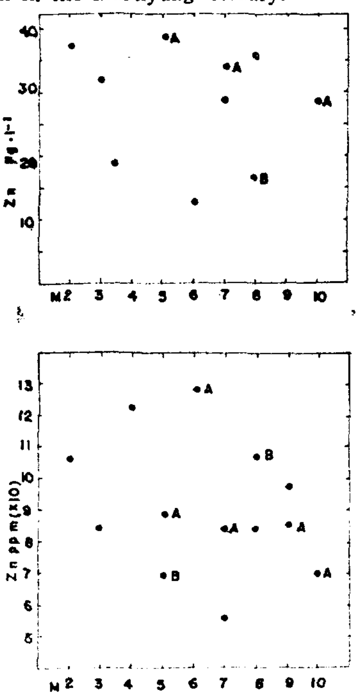

Fig. 9. Distribution of leacheable Zn in suspended matter (above) and distribution of Zn content in bottom sediment (below) at individual sampling station in the Mankyung estuary.

4. Dissolved metal content

Mobility of trace metal in the esturay may be determined by presence of hydroxide floccule (Eisma 1975), dissolved organic component (Boxma 1976) and released from surface sediment. To obtain information on the mobilization processes the dissolved metal contents were also investigated. The concentration in the Kum estuary were Fe: <0.2ppm, Mn: 0.037 to 0.043 ppm, Cu: <0.05ppm, Zn: <0.1ppm. In the Mankyung estuary concentrations for Fe: 0.21 to 0.33ppm, Mn: 0.043 to 0.058ppm, Cu: <0.05ppm to 0.081ppm, Zn: <0.1ppm were found, showing a dissolved metal concentrations slightly lower than in the Kum estuary. Any relation between salinity and dissolved metal content and noticeable increase in trace metal concentration in solution due to cation exchange in the brackish parts (Boyle *et al.* 1974) of these estuaries were not found.

5. Trace metals in surface sediments

In estuaries a processes for transferring trace metals from solution to the surface sediment during their way to the sea are: peptization with hydrated oxide at low *p*H values (Degen 1974), adsorption by organisms (Foster 1975) and precipitation in excess of permitted solubility by presence of CuO, ZnO.

The range of metal concentrations in surface sediment of these two estuaries (Fig 4-9) suggests that the variation in the Kum estuary is larger and more or less systematic within the position series due to sedimentation and resuspension of sediment in different phases of the tidal cycle as associated with bottom topography. On the other hand, values increase in the direction of the open sea for these metals.

The distibution pattern of zinc particularly pronounced as compared with suspended matter.

The variations in the Mankyung estuary are smaller and considerably more homogenous than the Kum estuary and values are higher in northernsilt rich part than the southern sand part. Greater velocity of the ebb tide may cause the accumulation of fine sand particles in southern regions of the Mankyung estuary.

The metal concentrations in the surface sediments increase with increases of the clay and silt contents (K5, K7, M5A, M7A, M10A). These increase in both estuaries may be due to the ion-exchange with clay minerals and the great surface of area for adsorption presented by small particles (Carrol 1959). The distribution pattern of leachable particulate metals and surface sediment metals shows a similar relation in the Kum estuary are interpreted as being caused by reworking and resuspension of bottom sediment caused by tidal turbidity.

6. Correlation coefficient between trace metals

To know the correlation relationships between the metal concentrations the pair diagram of these elements are plotted in Fig 10, 11, 12. The

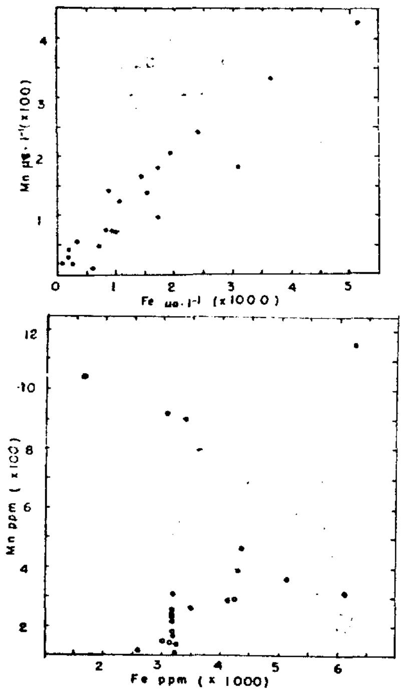

Fig. 10. Correlation of Manganese with Iron in particulate leacheable matter (above) and in bottom sediment (below). ○ : Mankyung estuary ● : Kum estuary

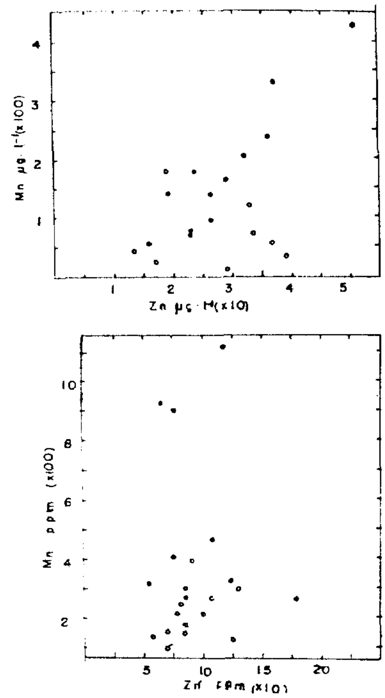

Fig. 11. Correlation of Manganese with Zinc in particulate leacheable matter (above) and in bottom sediment (below) ○ : Mankyung estuary ● : Kum estuary

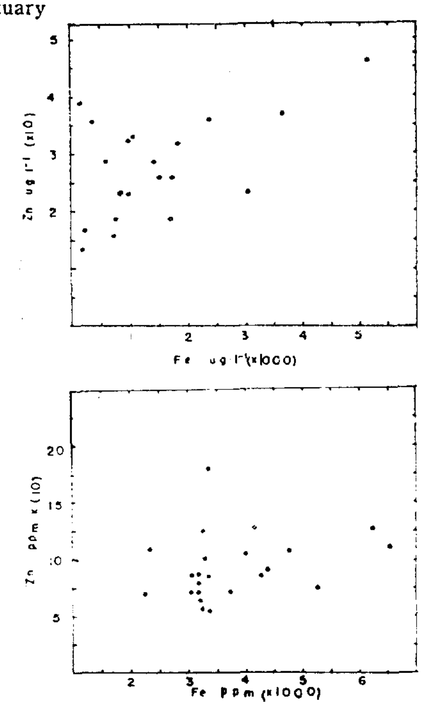

Fig. 12. Correlation of Zinc with Iron in particulate leacheable matter (above) and in bottom sediment (below) ○ : Mankyung estuary ● : Kum estuary

correlation coefficients between the elements are 0.918, 0.924, 0,863 for Fe-Mn, Zn-Zn respectively in the particulte leachable matter in the Kum estuary. Accordingly, it seems that these pairs of elements are in strong liner relationship.

In the Mankyung estuary the values of each of the same pairs as above in the leachable particulate fraction are 0,968, −0.230, −0.235. These data showed significantly weak relationships except iron-manganese pair. These findings are supported by the estuarine mixing. The continuous gradient of *p*H and salinity results in ion-exchange reactions especially on the suspended particles.

The correlation coefficients between single pair of Fe-Mn, Zn-Mn, Fe-Zn in surface sediment are 0.061, −0.236, 0.318 in the Kum estuary and 0.881, 0.223, 0.249 in the Mankyung estuary. At both estuaries there appeared no such relationships as shown above in the case of suspended materials except the Fe-Mn pair.

CONCLUSIONS

1. The *p*H and salinity data for the Mankyung area are suggestive of a bay rather than an estuary.

2. The metal concentrations in the surface sediments increase with increasing clay and silt contents. The variations of this phenomenom in the Mankyung estuary are less than those in the Kum estuary. A similar relation between leachable particulate metals and surface sediments in the Kum estuary is regarded as resulting from sediment resuspension.

3. The correlation coefficients of the metal pairs in the particulate leachable matter of the Kum estuary show a strong relationship presumably caused by the fact that the behavior of metal ions result from estuarine processes.

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