The Behaviors of Trace Metals (Fe, Mn, Co, Cu, Cd, Zn and Pb) in the Han River Estuary, Korea

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In order to investigate the temporal variability of dissolved and particulate trace metals in the Han River, water samples were collected intermittently at two sites for 3 years (August 91 to December 94). Surface seawaters covering the range of salinity were also collected at the estuarine region to evaluate the role of estuary for the riverine fluxes of trace metals within the estuary during October 95 and 96. During the study period, dissolved metal concentrations in riverwaters varied by a factor of 5–10 for Fe, Ni, Co and Cu and 50–100 for Mn, Cd and Pb depending upon the water level; high concentration during the low water and low concentration in high water period except for Fe. The concentration of dissolved Fe increased with increasing water discharge. These concentration-discharge relationships of the studied trace metals are explained by the successive dilution of waters from two different origins, which can be presumably identified as anthropogenic discharges and watershed flushing. Although estuarine waters at early mixing region were not collected due to the difficulty of sampling, mixing behaviors of metals were inferred from the concentration-salinity relationships through the laboratory mixing experiment and field sampling, and distribution coefficients between dissolved and labile particulate phases. It is suggested that the Han River estuary plays a role of accumulating Fe, Mn, Co and Pb from riverine sources due to high turbidity caused by strong tidal current, whereas this system serves as a source of dissolved Cd due to release caused by extended residence time of riverine particles.

INTRODUCTION

Many studies for the geochemistry of trace metals in estuaries have been focused on their behaviors occurring during the mixing of freshwater and seawater within the estuary in order to identify the role of riverine inputs in the global geochemical cycle of trace metals more accurately. There is, however, much variability from one system to another for the estuarine behaviors due to local hydrodynamic, sedimentologic and biological processes. For example, Cu, Ni, Zn and Cd show frequently the mid-salinity maximum resulted by the desorption from suspended matters or bottom sediments (Boyle *et al.*, 1982; Edmond *et al.*, 1985; Windom *et al.*, 1983) or by the regeneration from organic matters (Church, 1986; Windom *et al.*, 1988; 1991). However, the removal process of Cu by the biological uptake (Eaton, 1979) and of Cd by the sulfide formation (Windom *et al.*,

1991) has been also reported. Furthermore, the simple mixing behaviors have been also reported for Cu, Zn and Ni (Edmond *et al.*, 1985; Danielsson *et al.*, 1983; Boyle *et al.*, 1982).

Studies on the mixing behavior of trace metals for the Han River estuary were limited due to difficulties in approaching to the mixing region by the military problem. Jeon *et al.* (1994) reported the mixing behaviors of trace metals in the Han River estuary through five surveys but could not determine the mixing pattern due to the coastal inputs from the Inchon harbor, sludge dumping site and industrial complexes.

The variability of the riverwater concentrations affects the estuarine mixing behaviors (Head, 1985). In the Keum River, the concentrations of dissolved and particulate trace metals are extremely variable according to the water discharge (Choi, 1998), which will be the same case for the Han River.

This study was performed to investigate, firstly, the temporal variability of dissolved and particulate trace metals in the Han River, and secondly, the mixing

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behavior of trace metals in the Han River estuary to determine the estuarine modifications of the river input of trace metals.

MATERIALS AND METHODS

Study area

Draining the granitic basement with a drainage basin area of 26,000 km² with a total length of 488 km, the Han River discharges annually waters of about 25×10^9 m³ and solids of 2×10^6 ton into the Yellow Sea (Shubel et al., 1986). The water discharge varies from 140 m³/s to 20,000 m³/s and the average discharge is 720 m³/s. In the upper reach of this river, several dams have been constructed for the purposes of the generation of electricity and the control of the water levels in the lower reach where a metropolitan city (Seoul) and a wide agricultural field are located (Fig. 1). The annual precipitation is about 1200 mm but more than 50% is concentrated in summer, which results in short-term variations of water discharge in the lower reach despite of active flood control by dams in the upper reach. Due to extensive industrial and agricultural activities, and a high population density, strong anthropogenic influences could be expected.

There are three branches of the Han River estuary in coastal areas (Fig. 1): the western branch, which is the main one, cannot be accessed due to the military problem; the branch near the Kyunggi Bay is

contaminated by the harbor and industrial complexes (Jeon et al., 1994); the middle branch is the waterway between Kangwhado and Sukmodo (Sukmo Waterway). However, both the Imjin River and the Yeasung River flow into the upper estuary although the water discharge of the Han River is the greatest. This study selected the middle branch to infer the mixing behaviors of metals in this estuary although it was very difficult to define the riverwater endmember because there are missing salinities between the riverwater and the first sample collected in the estuary, and other rivers, e.g., the Imjin River and the Yeasung River, are mixed between them. Drainage basins of the Imjin River and the Yeasung River are about one-third and one-sixth of the Han River, respectively, and so, about 70% of water discharge flown into the Han River estuary comes from the Han River although the uneven geographical distribution of rainfall in the case of stormy events, may make the proportion of water discharge different.

The semidiurnal and macrotidal regime (mean tidal range of 6 m) dominate in the Han River estuary. Strong tidal current and shallow water depth derives partially-mixed and/or well-mixed water circulation in the estuary. In addition, the wide tidal flats are formed in the lower estuary and near the river mouth, and bottom resuspension by strong tidal currents are frequently observed (Chang and Oh, 1991).

Sampling and analytical method

In order to determine the temporal variation of trace metals in the Han River, we collected riverwater samples at two sites (Jungjido and Kwangnaru) located in the middle reach of the river near Seoul during 3 years from Aug-91 to Oct-94 (Fig. 1). The intermittent sampling cycle gives some limitations in the determination of temporal variation but widely covered discharges may permit the evaluation of the concentration-discharge relationships. Most samples were collected in the low water period, while fourteen samples were collected at flood. Surface estuarine waters were collected at sites in regular interval along the Sukmo Waterway in the middle branch of the estuary in Oct-95 and Oct-96. The riverine end-members were selected as positions of the limit of salinity intrusion, Haengjudaekyo.

For sampling of riverwaters, we used a pole sampler made with PVC rod, which was pushed to about 1m below the water surface to prevent sampling of surface film waters. Estuarine water samples were
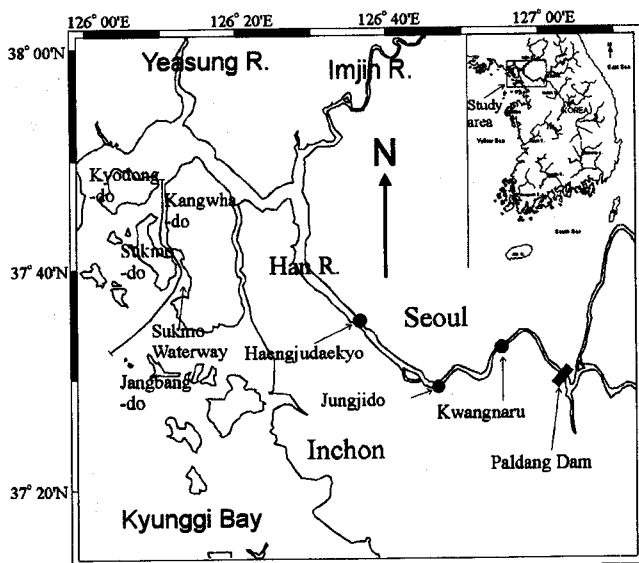

Fig. 1. Sampling stations in the Han River. Estuarine waters were collected in an equal distance along the Sukmo Waterway (solid line).

collected in the front of a small boat by the pole sampler during towing the boat. After capping the bottles with water samples and packing with double vinyl bags, samples were delivered to the laboratory in an ice-box. In the night time, water samples were filtered with vacuum filtration system and 0.45 μm membrane filter paper, which was pre-cleaned and pre-weighed, in a laminar flow clean bench. Sampling bottles were acid-soaked for at least 2 weeks and washed with de-ionized water (18 Mohms). An aliquot of filtrate was acidified with purified conc. HNO_3 to measure cations and trace metals. Another aliquot of filtrate was stored unacidified in a refrigerator for further analysis of pH, Alkalinity, nutrients and anions.

The dissolved trace metals in riverwaters were preconcentrated about 5 times by evaporation on the hot plate in an air-controlled drying box within the clean booth (5 m × 6 m). Several drops of purified conc. HNO_3 were added to the sample at near dryness in order to dissociate the residual organic materials, and then metals were extracted with dilute nitric acid.

The separation and preconcentration method of dissolved trace metals in estuarine waters is followed by Choi (1998) using Chelex-100 resin.

The particles on the filter were digested with mixed acids ($HF + HClO_4 + HNO_3$) by the method of Choi et al. (1995) but the pre-digestion with conc. HNO_3 at room temperature to dissociate filter paper with small quantities of acids and the usage of all purified acids (HF, HNO_3, $HClO_4$) with quartz or teflon subboiling systems to reduce the metal blank level.

In order to extract the labile fraction of particulate trace metals, 1M NH_4OAc (pH = 5) solution was used for extracting ion exchangeable and easily reducible metals. For this purpose, 1M NaOAc (pH = 5) solution is usually used. However, high Na content of the matrix make the measurement using ICP/MS difficult due to the blockage of cone by high dissolved solids or signal suppression by matrix effect. Ammonium ion has nearly similar ion exchange capability to Na ion and has little effects to the measurement. Metals in this fraction will be designated as labile metals in this document.

The dissolved and particulate trace metals (Mn, Co, Ni, Cu, Zn, Cd, Pb) were measured with standard techniques by ICP/MS (PQ3 models; VG Elemental Ltd.). Signal drift and matrix effects were overcome by internal standard techniques using 5 ppb solution of [115]In and [205]Tl. The dissolved (Mg, Ca, Sr, B, S) and particulate (Fe, Mn) major elements, and dis-

solved Fe were measured with pneumatic or ultrasonic nebulization techniques by ICP/AES, respectively (ICPS-1000III model; SHIMADZU).

The laboratory mixing experiments with riverwater and seawater were conducted on each survey to evaluate the roles of flocculation and river particles in the mixing behaviors of trace metals. Riverwater (Haengjudaekyo) and seawater (the highest salinity station determined by hand refractormeter in the field) were collected into 4 L bottles and kept in an ice box. In the night time, half of riverwater and all seawaters were filtered with several membrane filter papers. Two sets of samples were prepared to cover the whole salinity range: one was with filtered riverwaters and seawater, and the other with unfiltered riverwater and filtered seawater. After the waters were mixed, the bottles packed with vinyl bags were mixed with the horizontal shaker for 3 hrs, and then the solution was filtered with membrane filter paper and the filtrates were reserved for the analysis of trace metals after acidification.

Analytical precision and accuracy for dissolved trace metals were checked for every batch of analysis through the analysis of trace metals with SLRS-2 and CASS-2 (Canadian reference materials; NRCC) and total analytical errors were ±15%. For the labile particulate metals, duplicate or triplicate samples were extracted for the measurement of metals and their variability was within ±20% of the mean value.

The concentrations of SPM, nutrients, salinity and pH were also measured with standard techniques.

Results and Discussion

Temporal variability of trace metals in the river

Dissolved metals: Fig. 2 shows the variations of dissolved trace metals for the instantaneous discharge at two sampling stations (Jungjido and Kwangnaru in Fig. 1) in the middle reach of the Han River. The outflow discharge of the Paldang-dam (Discharge annual report in Korea; Ministry of Construction & Transportation) was used because there were no data for the water discharge near the sampling sites. The concentration ranges of dissolved trace metals measured in this study were 0.28–64.9 μg/kg for Mn, 3.7–54.4 μg/kg for Fe, 0.05–0.45 μg/kg for Co, 0.3 –5.5 μg/kg for Ni, 0.58–3.74 μg/kg for Cu, 0.06– 19.0 μg/kg for Zn, 0.001–0.11 μg/kg for Cd, and 0.05–1.08 μg/kg for Pb (Table 1). These large variations would be primarily caused by the large flow
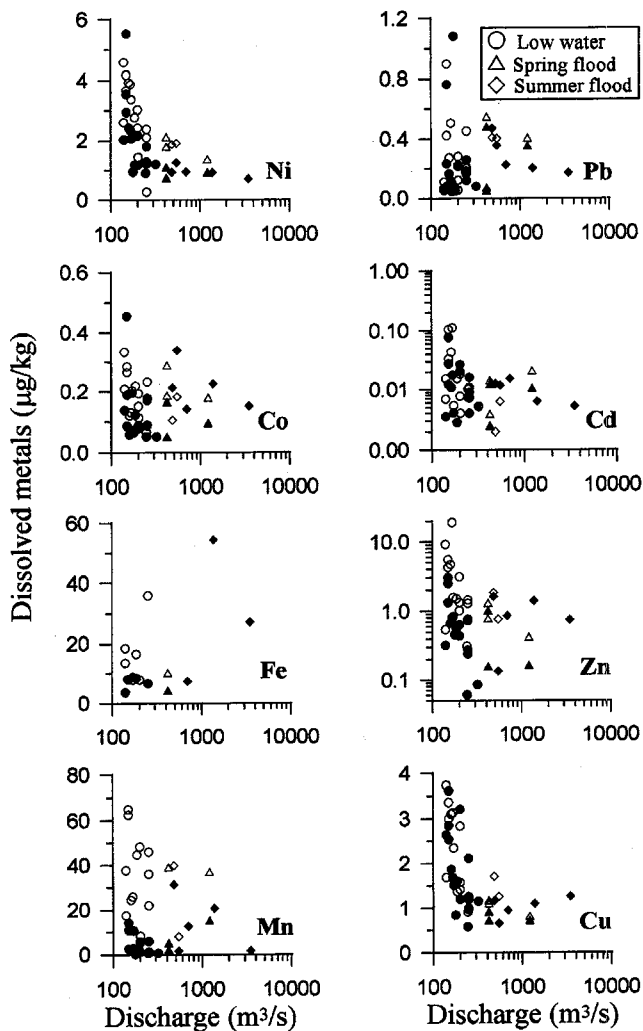
Fig. 2. Concentrations of dissolved trace metals *vs.* discharge in the Han River. Solid symbols indicate upstream site (Kwangnaru) and open symbols downstream site (Jungjido). Data are presented with respect to both water level and season; circle is low water, triangle is flood in spring, and diamond is flood in summer.

variation (140–3500 m³/sec), but other controlling factors, such as the nature of source and the dissolved-particulate interactions, would be superimposed.

The relationships between concentration and instantaneous discharge can be used in discriminating the source types (Shiller and Boyle, 1987; Chilton, 1989; Probst *et al.*, 1992; Neal *et al.*, 1996; Elbaz-Poulichet *et al.*, 1996). The positive slope of discharge and concentration can be made when the near-surface water (soil-water and overland flow) has higher concentration than in water at baseflow or when the flow mobilizes sediments and sediment-attached metals. Both cases are all diffusive in the source type, which closely related to the catchment nature and land-use.

The negative slope means the dilution of concentrated water body by surface run-off with low concentration. The concentrated water bodies may be industrial or sewage wastewater for both dissolved and particulate metals. Moreover, the groundwater may be a point source for dissolved species and in the rivers through the mineralized area, major elements usually show the negative flow concentration relationships (Gordeev and Sidorov, 1993; Cameron, 1996).

The water levels are divided as follows; low water, summer flood and spring flood. In the Keum River, flushing of dissolved Mn, Co, Cu and Zn by floods in spring has been observed, which would increase metal fluxes during this season (Choi, 1998). This flushing effect may occur by the leaching from riparian and from organic debris that accumulates in parts of the channel that are dry during low flow or by the flushing of solutes concentrated in soil water in the riparian zone (Hart and Hines, 1995).

In the low water period (discharge less than 300 m³/s), the concentrations of dissolved metals are variable and generally decrease with increasing of discharge (negative slope type) except for Fe. The discharge data in the low water period would not be representative at the sampling positions because the water discharge used in this study was that of outflow from Paldang-dam, and hence this fact may increase scattering in the concentration-discharge relationships. The concentrations of Cu and Ni, however, show relatively smooth relationships, which indicate the direct inputs of other metals or the release of metals by some biogeochemical reactions, *e.g.*, degradation of organic matters. In flood events, Mn, Co, Zn, Cd and Pb show flushing and dilution effects regardless of season. Although there is small data set for dissolved Fe, it is evident for Fe to increase with flow (positive slope type), which suggests that dissolved Fe may be largely colloidal form because it behaves like particles, and be discharged from soil-water or leached from soil particles. The concentrations of dissolved metals in the downstream (Jungjido) are generally higher than those in the upstream (Kwangnaru), especially in the low water period due to the input from the domestic and industrial wastewater. Thus, there seems to be a significant pollution build-up of dissolved trace metals in the river water when the river flow decreases down to very small values.

In summary, the large concentration variations of trace metals are a characteristic feature in the Han River and may occur from the successive dilution

Table 1. Concentrations of dissolved trace metals in riverwaters (μg/kg).

Rivers	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb	References
Han (Kwangnaru)	7.43	25.3	1.10	0.15	1.20	0.73	0.009	0.23	this work*
Han (Jungjido)	28.3	15.8	2.14	0.18	1.53	2.02	0.018	0.32	this work*
Han (Range)	0.28–64.9	3.7–54.4	0.3–5.5	0.05–0.45	0.58–3.74	0.06–19	<0.001–0.11	0.05–1.08	this work**
Han	10.7–128				0.63–6.2	0.55–12.3	0.004–0.041	0.11–2.3	1
Keum	49.4	50.7	2.0	0.26	2.05	2.18	0.008	0.23	2
Changjiang	0.5–1.5		0.117–0.294	0.1	1.14–1.33	0.04–0.08	0.001–0.002	0.052	3, 4, 5
Huanghe	0.55–2.20		0.29–0.59	0.006–0.03	0.95–1.53	0.065–0.33	0.001–0.006	0.01–0.04	9
Mississippi	2.63		1.35		1.46	0.196	0.014	0.11	6, 7
Amazon		9.9–70.9	0.3		1.52	0.02–0.25	0.007		6
Lena		22.9	0.3		0.6	0.35	0.003–0.008	0.017	10
World average	8.2	40	0.5	0.2	1.59	0.6	0.023	0.104	8

(1) Lee et al. (1989); (2) Choi (1998); (3) Edmond et al. (1985); (4) Wang et al. (1990); (5) Elbaz-Poulichet et al. (1990); (6) (6) Shiller and Boyle (1987); (7) Trefry et al. (1986); (8) Martin and Windom (1991); (9) Zhang and Huang (1993); (10) Martin et al. (1993).
*discharge weighted concentration
**range of concentration

of two different origins, which can be presumably identified as anthropogenic discharges and watershed flushing. The former would predominate during the low water period and the latter during the flood.

The concentrations of dissolved trace metals in the Han River are compared with the previous studies and other rivers (Table 1). The concentration ranges of dissolved trace metals obtained in this study are generally similar to those of the previous study (Lee et al., 1989), but are wider due to the wider range of water discharge. The discharge-weighted concentrations at Jungjido are similar to those of the Keum River, while concentrations at Kwangnaru are comparable with the world average (Martin and Windom, 1991). Compared to Chinese rivers, e.g., Changjiang and Huanghe, the concentrations of trace metals are generally higher except for Cu, which show similar concentration range of 1–2 μg/kg for all of rivers around the Yellow Sea.

Particulate metals: Metal contents of suspended particulate matters in riverwaters vary depending upon the composition of SPMs such as organic materials, clay mineral, metal oxide etc (Horowitz, 1991). Since the composition of SPMs varies with SPM concentrations or water discharge, metal contents in SPM may vary with SPM concentrations or water discharge. This was documented in the Keum River (Choi et al., 1995).

Trace metal contents in the Han River also vary with the concentration of SPM or water discharge (Fig. 3; Appendix 4-2a, b of Choi, 1998). In spite of much scattering, metal contents are generally higher

at low SPM concentrations rather than at high SPM concentrations. However, metal contents at the low SPM concentration (<10 mg/l) are highly variable and show two groups of samples except Mn, Co and Pb; one is a group with high contents and the other with low contents. Samples applicable to the former group are collected almost in the low water period but samples for the latter group are waters collected during the low water followed after spring or summer flood. The contents of Mn, Co and Pb in low SPM are the highest regardless of sampling period, which indicates the different input sources of these metals from others. One possible explanation is that major source of the particulate Mn, Co and Pb is located in the upper reach in particulate form, but major source of other metals is near sampling position in dissolved form. Then the contents of Mn, Co and Pb are controlled by the composition of SPM even after flood event but other metals are low untill the dissolved metals are in equilibrium with SPM. If samples with low contents at the low SPM concentrations are excluded, contents of all metals decrease with increasing SPM, which can be interpreted by the addition of detrital materials or coarse particles. There is little difference of metal contents between two sampling sites unlike dissolved metals. Sometimes extraordinary values for Cu, Zn, Cd and Pb were shown at both sites due to nearby anthropogenic sources (circles in Fig. 3).

The contents of particulate metals are calculated as SPM-weighted contents because the metal contents vary depending upon the concentrations of SPM, and compared with those of other rivers (Table 2). Com-
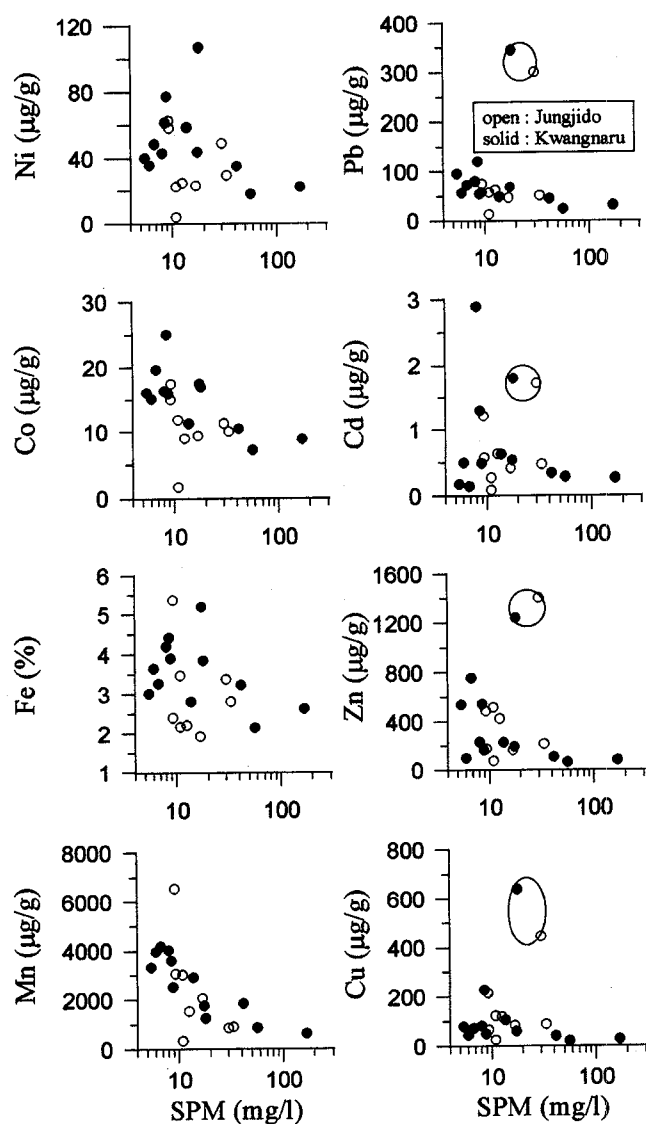
Fig. 3. Plots of metal contents with the concentrations of SPM in the Han River. Samples within circles seem to be affected by local anthropogenic source.

pared to the Keum River, Cu and Zn are higher in this river but Mn is lower. Other metals show similar levels of contents. The concentrations of Mn, Cu, Zn, Cd and Pb are generally higher and the concentrations of Fe, Co and Ni are lower than those of Chinese rivers (Huanghe and Chanjiang). Like the dissolved metals, the metal compositions of SPM in the Han River are similar to those of world average except for Fe.

Mixing behaviors of trace metals in the estuary

To determine the processes involved in the estuarine mixing of dissolved trace metals, observed distributions are evaluated with regard to those predicted from the theoretical dilution line of river water with seawater, where salinity is considered as a conservative index of mixing (Liss, 1976). Deviations from the ideal mixing are compared with the results of the mixing experiments and the variations of other parameters.

As stated above, there were no samples in low salinity region for both cruises (Appendix 4-3a, b, c, d of Choi, 1998). Due to the inflow of other rivers in this region, it was difficult to define the riverwater end-member but might be assumed that the concentration of metals in the Han River be similar level to that of the freshwater flowing into the estuary because about 70% of total water discharge in three rivers were from the Han River and the possible input sources of trace metals were abundant in this river. We checked the mixing profiles of major elements in estuarine waters in order to confirm that all the samples in both mixing experiment and field sampling were underlain on the same mixing lines. This

Table 2. Contents of trace metals in suspended matters of the Han River and other rivers (Fe %, others μg/g).

	Fe	Mn	Co	Ni	Cu	Zn	Cd	Pb	References
Han River	3.0	1453	11	34	100	281	0.6	71	*this work*
Keum River	3.3	2324	12	32	66	185	0.6	86	1
Changjiang	5.2		19	124	62	120	0.3	50	2, 3
Huanghe	4.4	885	15	52	23	53	0.4	14	2, 3
Mississippi	4.4	1260	21	51	39	193	1.0	39	4, 5
Amazon	5.6	1033	41	105	266				6
Gironde	4.3	1100	15			550		72	7
Rhone				51	46		1.1	44	8
Lena				31	28	143		23	9
World average	4.8	1050	20	90	100	250	1.0	100	10

(1) Choi (1998); (2) Zhang *et al.* (1990); (3) Huang *et al.* (1992); (4) Presley *et al.* (1980); (5) Trefry *et al.* (1986); (6) Gibbs (1977); (7) Elbaz-Poulichet *et al.*(1982); (8) Elibaz-Poulichet *et al.* (1996); (9) Martin *et al.* (1993); (10) Martin and Whitfield (1983)
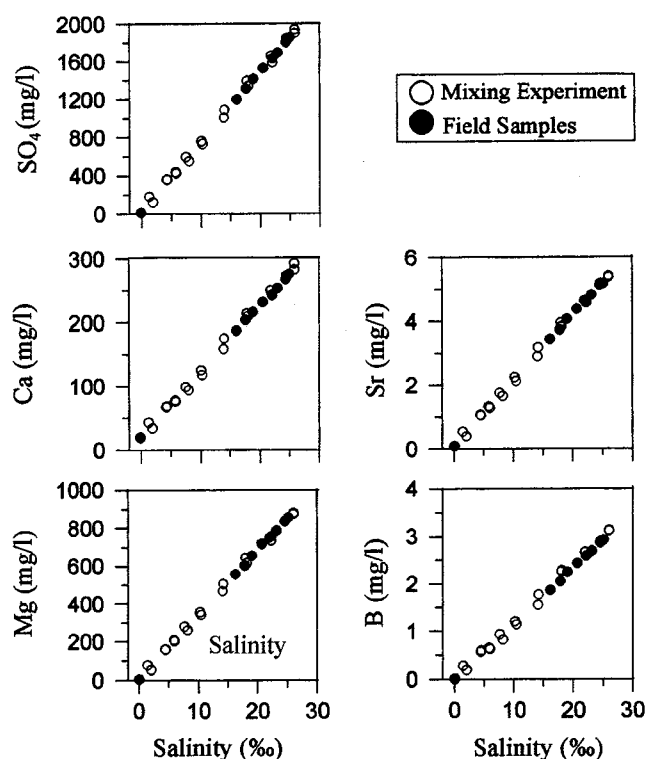
Fig. 4. The mixing profiles of major ions (Mg, Ca, SO₄, B and Sr) in the mixing experiment (open) and in the field (closed) for Oct-95 survey.

Fig. 5. The mixing profiles of SPM and nutrients in Oct-95 (open) and Oct-96 (solid) surveys.

indicates that the riverwater sample collected in this study can be regarded as a river end-member although major element compositions in other rivers are not quite different from those of the Han River. In Fig. 4, all of major elements were on the same mixing lines for the samples of both the mixing experiments and field sampling.

In order to compare the river end-members in estuarine transactions with the above riverwater data, the dissolved trace metals of riverwaters collected in Oct-91, Oct-94, Oct-95 and Oct-96 at three riverine sampling sites are listed in Table 3. If annual variation may be less than seasonal variation like in the Keum River (Choi, 1998), this comparison can be used for
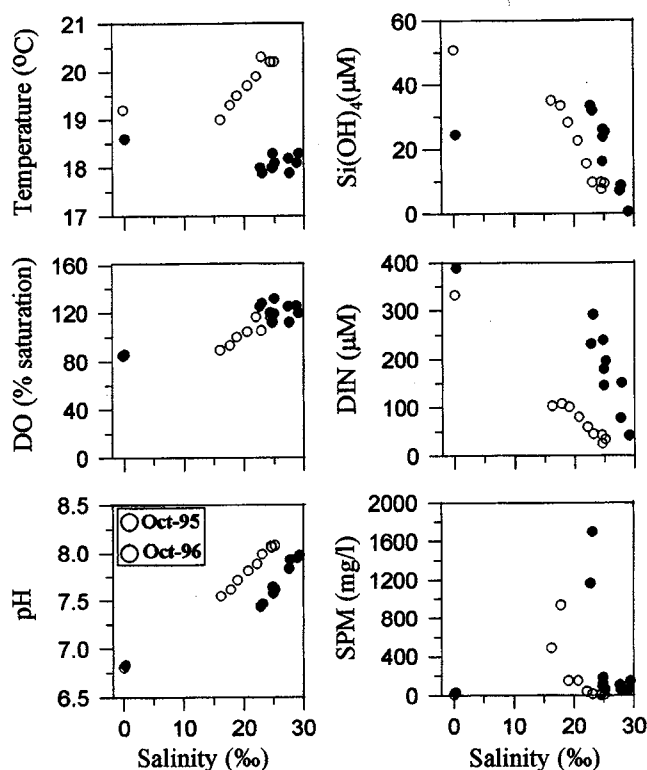
the identification of riverine processes during transport. The concentrations of Cu, Cd, and Pb decrease downstream but those of Mn and Zn increase (Table 3). There seems to be some input sources at Jungjido for Fe, Ni and Co. However, the concentrations of the metals vary downstream less than their temporal variations in riverwater endmember except for Mn. Therefore, the riverwater in Hangjudaekyo may represent the freshwater end-member for the low water period. There may be an input source of Mn in lower reach of the river, where there are wide agricultural fields.

Fig. 5 shows the variations of dissolved oxygen saturation, pH, nutrients and SPM concentrations with salinity in the Han River estuary. The distribution of

Table 3. Comparison of dissolved trace metals in three sites of the Han River (μg/kg).

Sites	Sampling Date	Mn	Fe	Ni	Co	Cu	Zn	Cd	Pb
Hangjudaekyo	Oct-95	35.9	12.9	1.18	0.10	1.15	1.01	0.005	0.069
	Oct-96	49.9	6.02			1.47	1.95	0.006	0.077
Jungjido	Oct-91	5.50		2.42	0.15	1.58	1.32	0.008	0.120
	Oct-94	17.6	18.5	2.61	0.21	1.69	0.54	0.007	0.067
Kwangnaru	Oct-91	1.23		1.17	0.08	1.20	0.44	0.021	0.220
	Oct-94	0.81	6.60	1.80	0.18	2.12	0.76	0.004	0.120

SPM concentrations shows a turbidity maximum at the low and/or middle salinity, which was observed even in high river water season due to strong tidal current and shallow water depth (Chang and Oh, 1991). The non-conservative releases of silicate are observed in both surveys. The distributions of dissolved inorganic nitrogen show a conservative behavior in Oct-95 but release in the middle salinity in Oct-96.

Silicate may be released from porewaters enriched by the degradation of diatomaceous tissues in sediments or by the dissolution of alumino-silicate minerals discharged from the river (Mackenzie *et al.*,

1967) or by secondary weathering of clay minerals during transport (Windom *et al.*, 1991). The release of dissolved nitrogen would be related to the decomposition of organic matters.

The concentrations of dissolved trace metals are plotted against salinity with the results of two-kinds of mixing experiments in Oct-95 and Oct-96 surveys (Fig. 6a and 6b). Result for the mixing experiment is depicted only for the survey of Oct-95 because both surveys show the same results. From the mixing experiment with filtered waters, the flocculation process can be confirmed. The role of river particles may be evaluated by the mixing experiments with unfil-
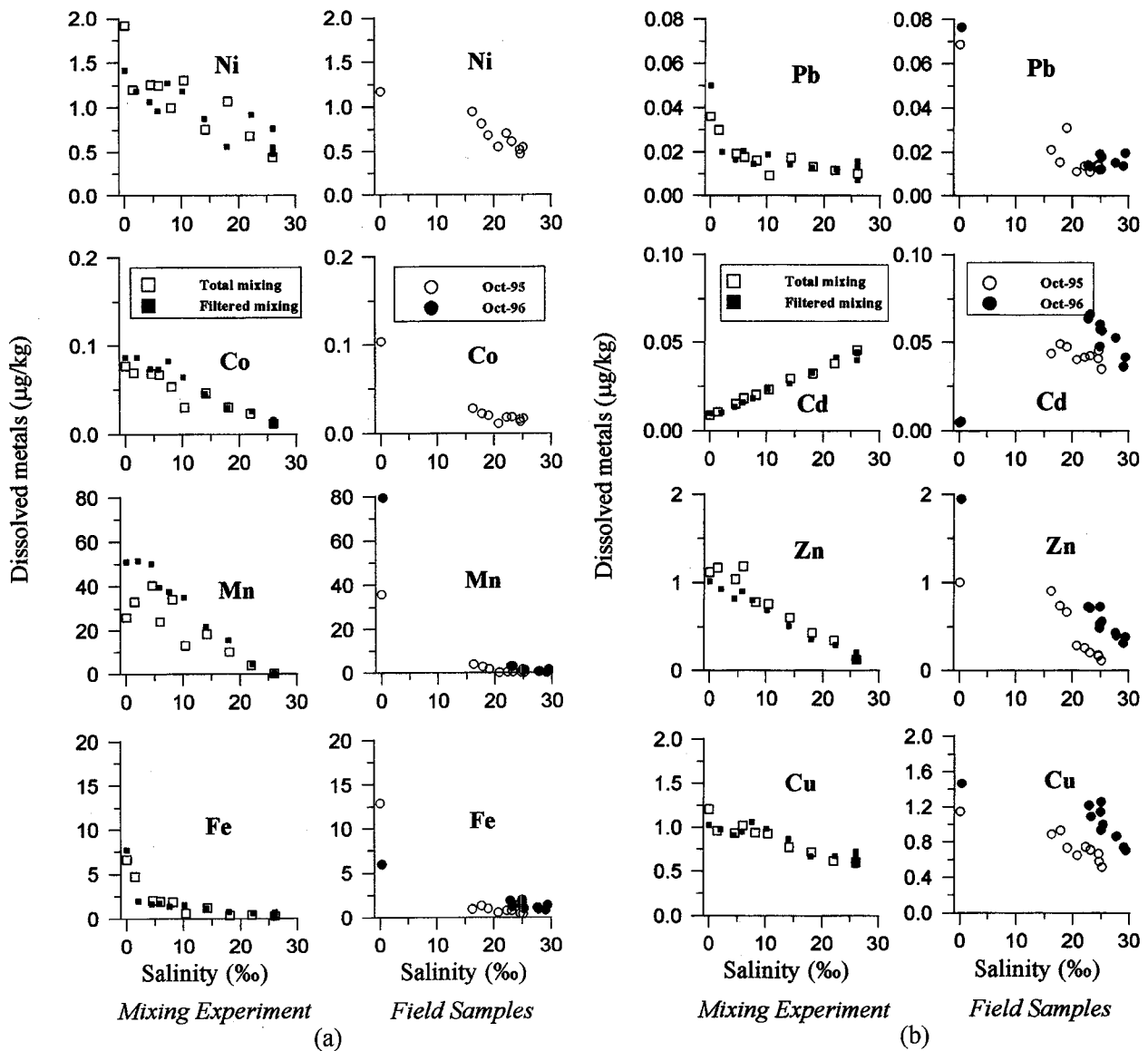

Fig. 6. (a) Dissolved trace metals (Fe, Mn, Co and Ni) *vs.* salinity in the Han River estuary. The results of laboratory mixing experiments (Oct-95) are depicted in the left column and field results are in the right column (Oct-95 and Oct-96). (b) Continued except for Cu, Zn, Cd and Pb.

tered samples. Other processes also may be elucidated from the comparison of field sampling with mixing experiment.

Dissolved Fe and Pb are removed in both mixing experiments and field samples at both surveys. The removal of dissolved Fe at the low salinity (<5‰) region is accepted as the general phenomena occurred in the estuary and is related to the formation of iron oxy-hydroxide or the flocculation process from the destabilization of colloidal humic-iron compounds abundant in river waters by seawater cations, e.g., Ca, Mg (Sholkovitz and Copland, 1981). The position and removal rate of dissolved Pb is similar to the dissolved Fe, which imply that the same mechanism with dissolved Fe can be applied to the behavior of dissolved Pb. The removal of dissolved Pb by the flocculation processes has been also reported in the Savannah Estuary (Windom et al., 1988) and Gota River (Danielsson, 1983). However, the concentrations of seawater end-member are slightly higher than those at 20‰, which means no net flux out of the estuary (Officer, 1979). Because Pb has the strong affinity to particles, especially to inorganic particles, the removal of Pb in this estuary or at least in high salinity region of this estuary may be related to the adsorption of dissolved Pb in wide turbidity maximum zone.

Of the metals interested, some differences between the mixing experiments using filtered and unfiltered samples are found only for Mn and Co. The concentrations of dissolved Mn and Co in the mixing of filtered waters change conservatively against salinity, which means that there are no removal by flocculation process, on the other hand, those in the mixing of unfiltered waters show the removal at low salinity region. In the field data, the concentrations of dissolved Mn and Co show a curvature. The removal of dissolved Mn may occur by the flocculation of colloids like dissolved Fe (Boyle et al., 1982; Sholkovitz and Copland, 1981), or by the oxidative precipitation of Mn(II) ions into insoluble Mn(IV) in low-salinity high turbidity area (Morris, 1986). Furthermore, there can be removal of dissolved Mn even in river water by the oxidative precipitation catalyzed by bacteria (Ponter et al., 1992). In this estuary, the precipitation of dissolved Mn onto particles may be the main removal mechanism. The mid-salinity maximum of dissolved Mn has been frequently observed (Evans et al., 1977; Salomons and Kerdijk, 1986; Byrd et al., 1989) but there seems to be no mid-salinity maximum in this estuary. The

removal of dissolved Co has been explained as the flocculations of colloids (Sholkovitz and Copland, 1981) or the adsorptive precipitation related to the turbidity maximum (Byrd et al., 1989). Based on the removal of dissolved Co by riverine particles at low-salinity in the mixing experiment with unfiltered waters and the removal in the mid-salinity zone with high turbidity in field samples, an adsorptive removal related to turbidity maximum can be a mechanism plausible for the behavior of dissolved Co in this estuary.

The distribution of dissolved Cd shows the broad maximum in the estuary compared to the theoretical mixing line at both surveys. The concentrations of Cd in river waters are nearly the same at both surveys but the maximum concentration in the mixing zone is higher in Oct-96 survey. The mixing experiments for dissolved Cd show simple mixing lines regardless of sample types. The release of dissolved Cd in the mid-salinity zone is a common feature in the estuary although the removal by sulfide formation in the upper estuary has been reported in the Rhine estuary (Duinker and Nolting, 1978). The adsorption and desorption reaction of dissolved Cd with suspended matters occur reversibly in riverwater, and the decrease of free Cd with the increasing ionic strength promotes the desorption reaction in estuarine mixing zone (Comans and van Dijk, 1988). The increased chloro-complexes increase the stabilization of dissolved phase, which results in the addition of dissolved Cd to the mid-salinity zone (Elibaz-Poulichet et al., 1987). This release of dissolved Cd is well explained by the analytical or mathematical model (Kraepiel et al., 1997; Thouvenin et al., 1997; Pham et al., 1997). The broad maximum of dissolved Cd concentrations at high salinity zone has been observed in Amazon, Gironde, Orinoco, Changjiang, Hunaghe and Keum rivers (Boyle et al., 1982; Edmond et al., 1985; Elibaz-Poulichet et al., 1987; Byrd et al., 1989). In the Bohai Sea near the river mouth of the Huanghe, the broad maximum of dissolved Cd occurs near 30‰ (Elibaz-Poulichet et al., 1987). In order to explain the broad maximum at high salinity zone, other hypotheses in addition to the desorption from river particles have been proposed, which include: (a) desorption of Cd from resuspended bottom materials in shallow water region; (b) release of Cd at the sediment-water interfaces caused by the changes in the redox condition in bottom sediments; and (c) regeneration of Cd along with the decomposition/mineralization of organic materials by bacteria

(Zhang, 1995). The position and magnitude of the maximum concentrations of dissolved Cd can be related to the salt dispersion of the estuary (Thouvenin et al., 1997). If so, the higher concentration and higher salinity of maximum Cd in Oct-96 than those of Oct-95 can be explained by the difference of tidal regime because the river discharge is the same in both surveys. That is, seawater at the spring tide can meet with more river particles or resuspended particles than at the neap tide and the possibilities of Cd release increase in the spring tide.

In the mixing experiments with both sample types, the concentrations of dissolved Cu, Ni and Zn follow the simple mixing lines. However, there are differences in the mixing behaviors in the field depending upon the type of metals and the survey period. The dissolved Cu, Ni, and Zn are released in the low to mid-salinity zone in Oct-95, while the concentrations of dissolved Zn in Oct-96 shows a conservative behavior similar to the results of mixing experiments. The distributions of Cu, Ni and Zn have been reported much variable depending upon the system, and therefore, all of conservative, removal and release mixing behaviors were observed. In the Han River estuary, the metals seems to be released in the low-salinity zone although it is not definitive due to the lack of field samples at low salinity. Their releases may be related to biological mineralization, desorptions from river particles or resuspended particles, and/or secondary weathering of alumino-silicate clay minerals in turbidity maximum zone coupled to the release of silicate.

The contents of labile metals in SPMs show large variations over the range of salinity having similar variation pattern for all the metals (Fig. 7): mid-salinity minimum. From the view of metal behaviors during estuarine mixing, all the metals have to release at early mixing and adsorb to SPMs in seawaters. However, the release of metals from particulate forms is not reflected in the dissolved metal profile. Furthermore, in the high salinity region, any dissolved metals did not show the removal during mixing (Fig. 6a, 6b). The variation of particulate metals would be explained by the mixing of particles with different composition, e.g., mixing of detrital and organic matters or riverine particles and metal-impoverished bed materials (Jouanneau et al., 1983) rather than dissolved-particulate interaction. The variation of SPMs concentration over salinity shows the mirrored shape of all labile metal contents. That is, high-suspended solids resuspended from bottom sediments due to
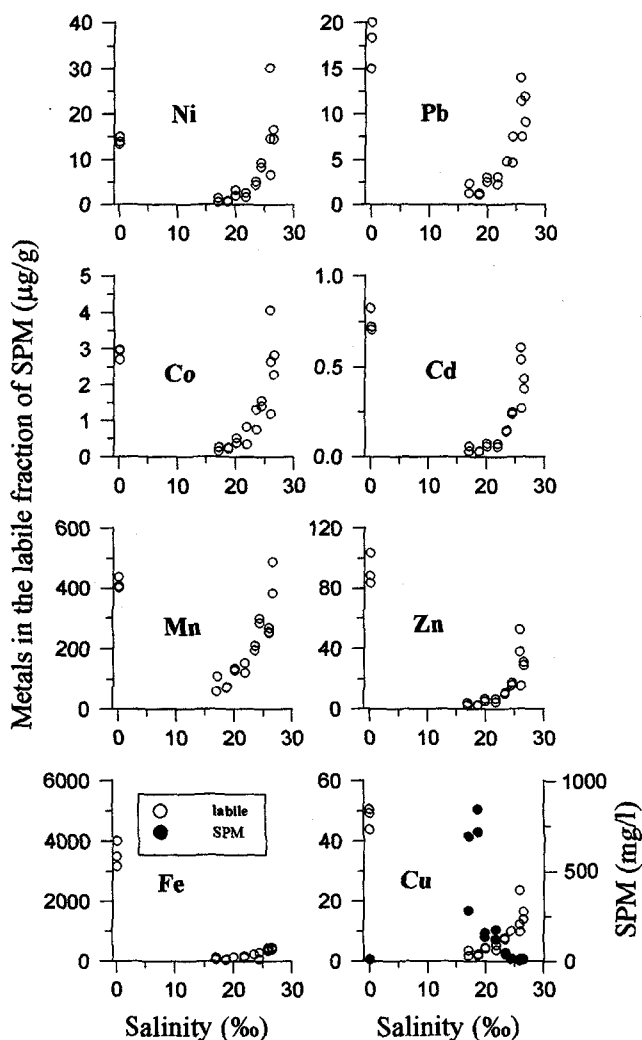

Fig. 7. Metal contents in the labile fraction of SPMs vs. salinity for Oct-95 survey.

strong tidal currents dilute high contents of metals in both riverine particles and marine particles (Fig. 7).

Therefore, overall role of this estuary during transport of metals from riverwaters has to be evaluated by considering both dissolved and particulate metals. If the reaction between dissolved and particulate metals during estuarine mixing is quasi-equilibrium, distribution coefficients can be described as followings;

$$K_D = 10^3\, C_p/C_d$$

,where C_p is the content of metals in the labile fraction of SPMs (µg/g) and C_d is the concentration of dissolved metals (µg/l). This coefficient has been applied carefully to evaluate the behaviors of metals during estuarine mixing because several factors including the concentration of SPMs, pH, adsorption site (e.g., Fe) can affect the variation of coefficient
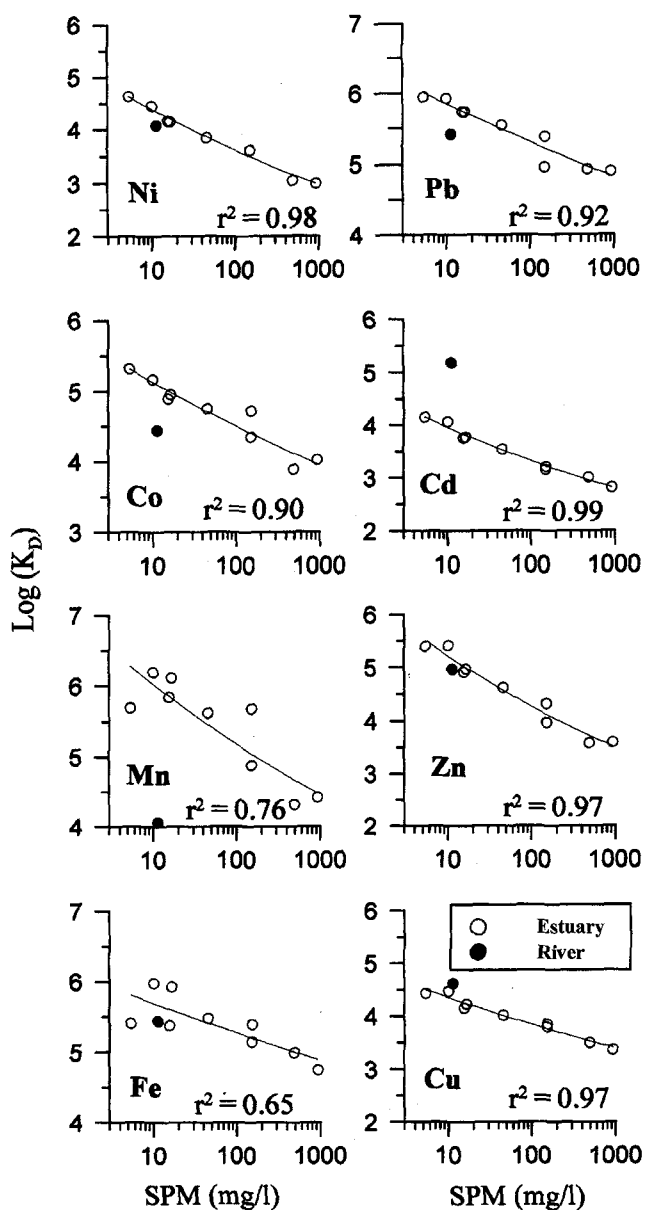
Fig. 8. Distribution coefficient (K_D) vs. SPM. Best fitted lines are also presented.

(Turner *et al.*, 1993; Sung, 1995).

Fig. 8 shows log (K_D) with SPM concentration. The K_Ds of all the metals decrease with the increase of SPM, which has been considered as a general phenomena in marine environments (Balls, 1989) caused by the effect of colloidal metals in the dissolved fraction (Morel and Gschwend, 1987). In order to evaluate the role of this estuary for the behaviors of metals during estuarine mixing, K_Ds in riverwater and seawater end member chosen at the same SPM concentration with riverwater from best-fitted lines are compared. If K_D in seawater is higher than that in riverwater, removal process is dominated, whereas the release of metal is dominated if it is lower than that in riverwater. Fe, Mn, Co, and Pb are removed from dissolved phase and adsorbed to particulate phase. Cd shows the release evidently, but Ni, Zn and Cu show little variation of distribution coefficients between riverine and marine particles. These results give the conflict conclusion for Ni, Zn and Cu in the mixing profiles of dissolved metals. The short-term variability of dissolved and particulate metals in riverwaters may be one reason for this conflict conclusion.

CONCLUSION

In this study we tried to understand the temporal variability of dissolved and particulate metals in riverwaters and to determine estuarine mixing behaviors to evaluate the role of estuary for the riverine fluxes of trace metals.

During the study period, dissolved metal concentrations in riverwaters vary as much as from 5–10 times (Fe, Ni, Co and Cu) to 50–100 times (Mn, Cd and Pb) depending upon the water level; high concentration during low water but low concentration during high water except for Fe. The concentration of dissolved Fe increases with water discharge. These concentration-discharge relationships of studied trace metals may be explained by the successive dilution of two metal sources of different origin, which can be presumably identified as anthropogenic discharges and watershed flushing. The former would predominate during the low water period, and the latter during flooding. Compared to Chinese rivers, *e.g.*, Changjiang and Huanghe, the concentrations of dissolved trace metals in the Han River are generally higher except for Cu, which shows similar concentration range of 1–2 µg/kg for all of rivers around the Yellow Sea.

In the estuary, dissolved Fe and Pb are removed at early mixing by the flocculation of colloids but the additional removal of dissolved Pb by turbidity maximum makes no net flux of dissolved Pb out of the estuary. Dissolved Cu, Ni and Cd are desorbed from riverine particles but the mixing behaviors of dissolved Cu and Zn are variable. In addition to the desorption, dissolved Cd shows always the broad maximum at mid to high salinity zone related to the additional release by desorption from resuspended particles or by remineralization of organic matters in the wide tidal flat. Dissolved Mn and Co in the Han

River estuary show only removal process.

From the comparison of distribution coefficients between riverwater and seawaters, Fe, Mn, Co and Pb show the removal from dissolved phase and the adsorption to particulate phase. Cd shows the release evidently.

Therefore, the Han River estuary serves as a site of accumulating Fe, Mn, Co and Pb from riverine source due to high turbidity caused by strong tidal current, while this system becomes a source of dissolved Cd due to the release caused by extended residence time of riverine particles. Quantitative determination for estuarine modification was impossible in this study due to the absence of low salinity samples.

In the future, we will be able to confirm the results for estuarine behaviors of trace metals when we can approach to upper estuary region by the collaboration among scientists between North Korea and South Korea.

ACKNOWLEDGEMENT

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