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Accumulation history of anthropogenic heavy metals (Cu, Zn, and Pb) in Masan Bay sediments, southeastern Korea: A role of chemical front in the water column

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ABSTRACT: In Masan Bay, the drainage basin for the wastewater of heavily-industrialized cities and harbors in the southeastern Korea, a composite analysis of sediment cores reveals that accumulation history and behaviors of heavy metals are distinctive depending on anthropogenic activities and dissolved oxygen in water column. In the inner bay, Cu, Zn, and Pb have been enriched, associated with organic and sulfide matter, over background levels since the mid-1940s. It seems to result from the deposition of stream-disposed sewage under a poor water circulation before most of sewage collected in Masan City has been treated and disposed through an outfall into the outer bay since the late 1993. The outfall disposal contaminated the topmost sediments of the outer bay with the three metals, 2.2 to 3.2 times as much as the background. The three metals are strongly associated with Mn in the bay mouth, probably resulting from their oxidative precipitation beneath a chemical front of water column that forms by expansion and mixing of anoxic bay bottom water with oxygenated coastal water. The bay sediments seem to act as a mobile pool in that Mn and the pollutant metals are often remobilized to the anoxic bottom water in summer.

Key words: Masan Bay, sediment cores, accumulation history, pollutant metals, anthropogenic activities, chemical front

1. INTRODUCTION

Masan Bay is a significantly polluted embayment in the southeastern Korea, around the coast of which population, industrial and shipping activities have rapidly increased for the last six decades (Masan City, 1994). The bay is characterized by the accumulation of fine-grained sediments under a week water circulation (KORDI, 1981; 1999; Park and Lee, 1996). In the bays like Masan Bay, bottom sediments are feasible to pollution due to easy accumulation of fine-grained suspended materials which act as the major carrier of metal pollutants and organic matters due to their negatively-charged large surface area (Olsen et al., 1982; Turner and Millward, 2000). The pollution of coastal sediments with heavy metals has declined after its maximum in the 1970s (e.g., Valette-Silver, 1993). However, this general trend is quite deviated from many countries, depending on development history, pollution control policy, biogeochemical and physical characters of coastal waters (Kersten and Forstner, 1986; Shaw et al., 1990; Grousset et al., 1999).

The sediment contamination results from the supply of pollutants through anthropogenic activities exceeding the removal capacity of early sediment diagenesis which is accompanied essentially with decomposition of organic matter (Ridgeway and Price, 1987; Shaw et al., 1990; Rae and Allen, 1993). It is also dependent on the chemical characters of the overlying water that control the accumulating and remobilizing behaviors as well as existing phases of pollutant metals in the sediments (Elderfield et al., 1981; Kersten and Forstner, 1986; Morse, 1994). The anthropogenic heavy metals tend to be concentrated at various sediment depths comprising the times of industrial and municipal activities, different from the naturally-derived metals which are often enriched in the topmost part of sediments due to co-precipitation with oxyhydroxides of Fe and Mn remobilized diagenetically together from the deeper sediments (Ridgeway and Price, 1987; Calvert and Pederson, 1993; Grousset et al., 1999). Both the cases are always characterized by their concentration larger than the background level of pre-industrial sediments that is controlled mainly by the grain size and composition of sediments (Goldberg et al., 1979; Olsen et al., 1982; Grousset et al., 1999). In oxygen-depleted waters, the anthropogenic metals are less soluble and selectively associated with sulfide and organic matter fractions of sediments (Jacobs et al., 1985; Skei et al., 1988; Macdonald et al., 1991), reversed to the concentration of Mn and Fe through the sediment depth (Hines et al., 1991; Neumann et al., 1997; Sternbeck and Sohlenius, 1997). In this situation, the pollutant metals can be partly remobilized from the sediments to the bottom water and accumulated ultimately back to the sediments where the dissolved oxygen is rich in the water column (Emerson et al., 1979; Hines et al., 1991; Klinkhammer et al., 1997).

This study is aimed to reconstruct the contamination history and to decipher the accumulation behaviors of pollut-

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ant metals in Masan Bay that might be controlled by anthropogenic activities as well as redox conditions of sediments and the overlying bottom water. For this, total concentration of S, Al, Fe, Mn, Co, Ni, Cr, Cu, Zn, Pb, organic C and N, grain size but also ^{210}Pb-derived sedimentation rate was analyzed in three sediment cores. In addition, dissolved oxygen in the water column was measured in summer.

2. MASAN BAY

Masan Bay is a funnel-shaped shallow (less than 20 m in water depth) coastal embayment with long axis of about 15 km and width of less than 6 km, open southward Jinhae Bay (Fig. 1). Water circulation is sluggish with a small tidal range (< 130 cm) and weak current velocity (< 15 cm/s), taking 139 days to refresh the bay with offshore water (KORDI, 1981; 1999). It is also limited by ubiquitous islands, complicated coastline, and a shoaled sill in the bay mouth. Caused by the excess supply of terrestrial nutrients, red-tide outbreak of phytoplankton recurs especially in summer that depletes dissolved oxygen in the bottom water from the bay head (< 1 mg/L), the outer bay (1 to 2 mg/L), to the bay mouth (> 5 mg/L) (Yang & Hong, 1982; Yang et al., 1984; Hong et al., 1991). The inner bay bottom water seems to be permanently in anoxic condition (Hong et al., 1991).

Bottom sediments consist of silty clay deposited at rate less than 0.5 cm/yr (Lee et al., 1988; Yang et al., 1995; Park and Lee, 1996). They are progressively finer toward the bay head from the bay mouth, indicating that the sediments derived from Nakdong River, east of the bay, exceeds those from the streams draining directly into the bay (KORDI, 1999). Park and Lee (1996) estimated, based on clay minerals, ^{210}Pb-derived sedimentation rate, and thickness of Holocene sedimentary layer, that 20% of Nakdong River suspended materials (4.6x10^{6} t/y) has been deposited at a constant rate for the last 5,000 years in Jinhae and Masan bays since the offshore geographic barriers protect the bays from eventual activities such as storm surges. The river sediments are transported into the bays in winter by tide-imposed coastal current which is constrained by the offshore Tshushima Current to flow along the nearshore of southeastern Korea (Yu et al., 1985; Park and Lee, 1996).

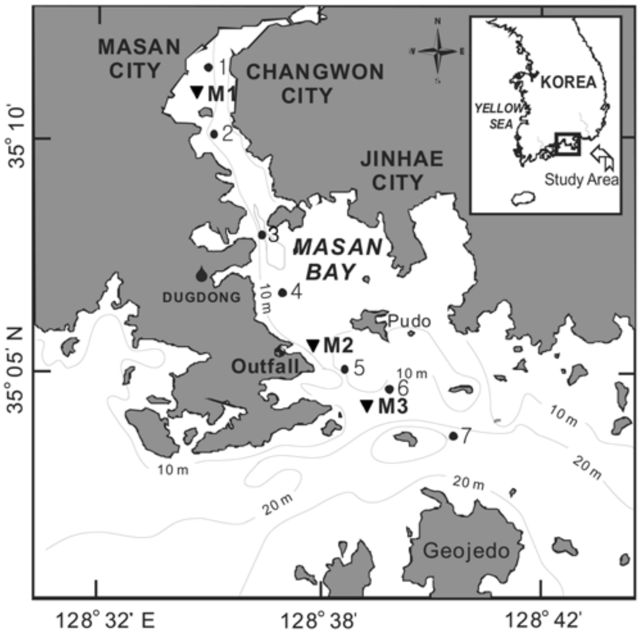

Fig. 1. Physiographic characteristics and location of sediment core sites (solid triangles) and dissolved oxygen survey (solid circles) in Masan Bay. Dukdong sewage treatment plant and its outfall are located on the western side of the bay. Water depth is contoured by thin line in 10 m interval.

Masan Bay is surrounded by Masan, Changwon, and Jinhae cities which contain more than 1 million population and about 1,470 factories, mostly of metal and machine manufacturing, and ship-building established since the early 1960s (Ok, 1982; Masan City, 1994). Masan commercial harbor and Jinhae naval harbor were opened in the northwest, 1889, and in the southeast of the bay, 1912, respectively (Ok, 1982). Since the 1920s, brewery has been thrived with military industry and small-scale smelters, of which about 70% was destroyed in the World War II. According to Masan City (1994), shipping activity in the bay consists of about 13,000 vessels including fishing boats, and coastal and international liners. The bay received directly the terrestrial water of about 650,000 m^{3}/day, including domestic (251,000 m^{3}/day), industrial (about 60,300 m^{3}/day) and livestock wastewater (131 m^{3}/day) from Masan and Changwon cities before the late 1993. About 90% of Masan City sewage has been one-time treated and discharged into the outer bay through an outfall since that time (Kwon and Lee, 1998). In the inner bay, significantly contaminated sediments were partly dredged in 1994 (Masan City, 1994).

3. SAMPLING AND ANALYTICAL METHODS

Sediment cores were collected in pre-cleaned transparent acryl liners up to 50 cm depth by using a gravity corer off Masan Harbor in the inner bay (M1), off the outfall in the outer bay (M2), and on the top sill in the bay mouth (M3) in May, 1998 (Fig. 1). Immediately after retrieving the cores, sediment core was cut into every 2 cm depth interval with a teflon knife by extruding the sediments with a teflon piston through the liner in a glove box filled with nitrogen gas to prevent the sediments from oxidation. During this procedure, visual characters of sediments were observed for color change, traces of benthic animal activity and incorporated erratic materials. The samples were frozen with dry ice and transported to the laboratory. In the water column, the amounts of dissolved oxygen were measured at three to five depths at 7 sites along the long axis of the bay in August, 1998 by using an oxygen sensor attached to current meter (RCM9-MKII, AAnderAA Inst.).

Sediment grain size was analyzed by using an X-ray analyzer (Sedigraph 5005D) after organic and carbonate materials were removed with H_2O_2 and HCl solutions. A part of each dried sediment sample was powdered homogeneously for chemical analysis. Excess ^{210}Pb activity was counted by using an α-spectrometer (Canberra Silicon Surface Barrier Detector) at Korea Basic Science Institute, via its granddaughter nuclide ^{210}Po a year after the collection of cores when the secular equilibrium between ^{210}Pb and ^{210}Po is established (Harada and Tsunogai, 1985). Based on the assumption of constant ^{210}Pb flux to marine sediments, slope gradient (i.e., sedimentation rate) of logarithmic decrease of excess ^{210}Pb activity was determined by best-fitting regression (error <5%) beneath the topmost mixed layer to the depth where the activity is uniform (Woo et al., 2003).

Total organic C (TOC), N (TN), and S (TS) of sediments were analyzed using a Carlo-Erba CHN analyzer after removing inorganic carbon with 10% HCl. For the analysis of metal concentration by using an ICP-MS, sediment samples were fully digested overnight with 5 ml mixed acids (HNO_3:HF:$HClO_4$ = 3:1:1) in teflon bombs on a hot (180 °C) plate. Complete digestion of samples was confirmed by adding 2 mL $HClO_4$ and reheating. The liquefied samples were diluted with 1 N HNO_3 and filtered through 0.45 mm membrane filter paper. Analytical error was less than 5%, checked by analyzing four PACS-1 and three BCSS-1 standards together with the samples. Enrichment factor (EF) of each metal was estimated as the ratio of its concentration to background value after normalizing to Al, i.e., EF=$(Metal/Al)_{sample}/(Metal/Al)_{background}$. The background value of each metal was estimated by averaging the concentrations at four depths of the bottommost part where the concentration is nearly uniform.

4. RESULTS

4.1. Distribution of Dissolved Oxygen in Water Column

In summer, the bottom water is nearly anoxic (<2 mg/L) to the outer bay (M2 site) from the bay head (Fig. 2). The oxygen-depleted bottom water layer is thick (>7 m) in the bay head, but thins abruptly to less than 2 m off Masan Harbor (near M1 site) and extends to the outer bay (M2 site). On the top of sill in the bay mouth (M3 site), the dissolved oxygen is saturated, more than 6 mg/L even in the bottom water layer. This distribution pattern of dissolved oxygen is very similar to those revealed earlier (Yang & Hong, 1982; Yang et al., 1984; Hong et al., 1991).

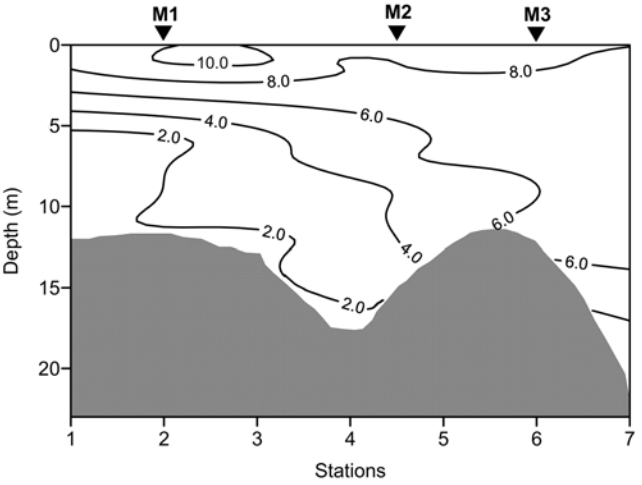

Fig. 2. Vertical distribution of dissolved oxygen (mg/L) in the water column of Masan Bay in August, 1998.

4.2. Description and Sedimentation Rate of Sediment Cores

M1 sediment core is characterized by grayish dark color without any signal of bioturbation through the depth of 50 cm, but by abundant black speckles in the upper part. On the other hand, M2 core is grayish green with some burrows to the bottom, except for the grayish topmost sediment layer (5 cm in thickness) with no trace of benthic animal activity. M3 core is colored also in grayish green and bioturbated down to 7 cm depth but less below that depth. The core sediments are dominantly of clay (>60%) and silt with a trace (<2%) amount of sand through the depth. The grain size of M2 core sediments is very uniform and finer (10.0 to 10.2ϕ) than that (9.4 to 9.9ϕ) of M1 and M3 (Table 1 and Fig. 3).

In the M1 core, excess ^{210}Pb activity decreases linearly from the top to the bottom, indicating no sediment mixing by either biological or physical activities (Fig. 3a). However, it is constant from the top to 5 and 7 cm depths of M2 and M3 cores, respectively (Fig. 3b, c). The former is ascribed to rapid accumulation of sludge disposed together with treated wastewater from the outfall, whereas the latter to active biomixing of sediments. Based on the excellently fitted (R^2, 0.95 to 0.98) regression of excess ^{210}Pb activity beneath the topmost mixed sediment layer, sedimentation rates are estimated 0.33, 0.22, and 0.33 cm/yr, respectively, in the M1, M2, and M3 cores (Woo et al., 2003). The rates are similar to those (0.31 to 0.48 cm/yr) at the other sites in the bay (Lee et al., 1988; Yang et al., 1995; Park and Lee, 1996). The lower rate of M2 core comprises the deposition of finer sediments (Table 1).

4.3. Total Organic C, N, S, and Metal Concentrations

Through the cores, TOC ranges from 1.3 to 2.1%, except for the large values (>2.5%) in the topmost (5 cm) sediment layer of M2 core (Table 1 and Fig. 4). It generally increases toward the top from 15, 10, and 20 cm depths of M1, M2, and M3 cores, respectively, although it is variable below those depths. TN is less than one tenth of TOC and is dis-

Table 1. Summary for sedimentation rate, grain size, and concentration of geochemical components in three sediment cores of Masan Bay, southeastern Korea.

	M1 Core (inner bay)			M2 Core (outer bay)			M3 Core (bay mouth)		
	Range	BG	EF	Range	BG	EF	Range	BG	EF
Sedimentation Rate (cm/yr)	0.33			0.22			0.33		
Grain Size (ϕ)	9.4-9.8			10.0-10.2			9.5-9.9		
Total Organic C (%)	1.3-2.0			1.4-2.8			1.5-2.1		
Total N (%)	0.11-0.16			0.14-0.27			0.10-0.19		
Total S (%)	0.39-1.24			0.38-0.68			0.01-0.45		
C/N ratio	10.4-14.2			9.3-12.9			10.2-19.8		
C/S ratio	1.6-4.2			2.2-5.2			3.8-129.0		
Al (%)	9.9-12.4			8.9-10.9			9.5-10.2		
Fe (%)	3.8-5.1	4.9	0.9-1.0	3.9-5.0	4.9	0.9-1.0	4.6-4.9	4.8	1.0-1.1
Mn (mg/kg)	650-879	849	0.8-1.1	555-887	849	0.9-1.2	715-1165	739	0.9-1.6
Cr (mg/kg)	35-43	41	0.7-1.1	45-62	54	0.8-1.2	43-62	55	0.8-1.2
Co (mg/kg)	14-17	16	0.8-1.1	13-16	16	0.9-1.0	15-16	16	0.9-1.0
Ni (mg/kg)	15-18	18	0.8-1.1	23-27	26	0.9-1.1	24-26	25	1.0-1.1
Cu (mg/kg)	27-71	27	0.9-2.6	13-38	14	0.9-3.2	13-23	13	1.0-1.8
Zn (mg/kg)	97-192	97	0.9-2.0	85-178	89	1.0-2.3	83-112	84	1.0-1.4
Pb (mg/kg)	24-53	27	0.9-1.9	14-31	16	0.9-2.2	14-23	15	0.9-1.5

BG and EF represent background level and enrichment factor, respectively.

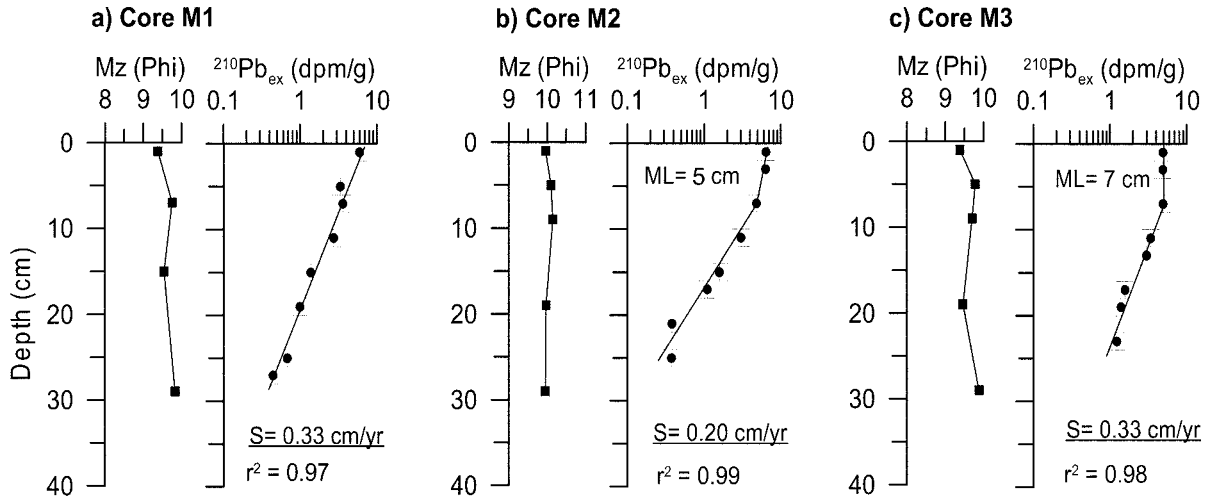

Fig. 3. Mean sediment grain size (Mz (ϕ)) and sedimentation rate (S) in M1 (a), M2 (b), and M3 core (c). ML represents the topmost mixed sediment layer.

tributed, similar to TOC in the upper part, but largely deviated from TOC in the lower part of cores. In the M1 and M2 cores, C/N ratio ranges in 10.4 to 14.2, similar to that (8.4 to 14.0) determined earlier in Masan and Jinhae bays (Park and Lee, 1996). It is notable in the M3 core that the ratio is large (15.0 to 19.8) in the lower part of 25 cm depth. In the M1 core, TS ranges from 0.4 to 1.2%, decreasing downcore the minimum value at 30 cm depth, whereas it is rather constant (0.4 to 0.7%) in the M2. In the M3 core, it is less than 0.1% in the lower part of 17 cm depth but abundant up to 0.5% in the upper part. The C/S ratio is relatively small (<2.0) to 17 cm depth from the top and progressively increases to the bottom of the M1, whereas it is largely variable in the M2 core (2.2 to 5.2). In the M3 core, the ratio ranges from 3.8 to 10.4 in the upper part of 17 cm, but exceptionally large (11.5 to 129.4) in the lower part.

Metal concentrations in the sediments (Table 1) are similar to those reported earlier in Masan Bay (Lee et al., 1988; Yang et al., 1995). However, Cu, Zn, Pb, and Mn are much more concentrated than those in the world average shale (Turekian and Wedepohl, 1961) and more or less than those in the coastal sediments of heavily industrialized countries

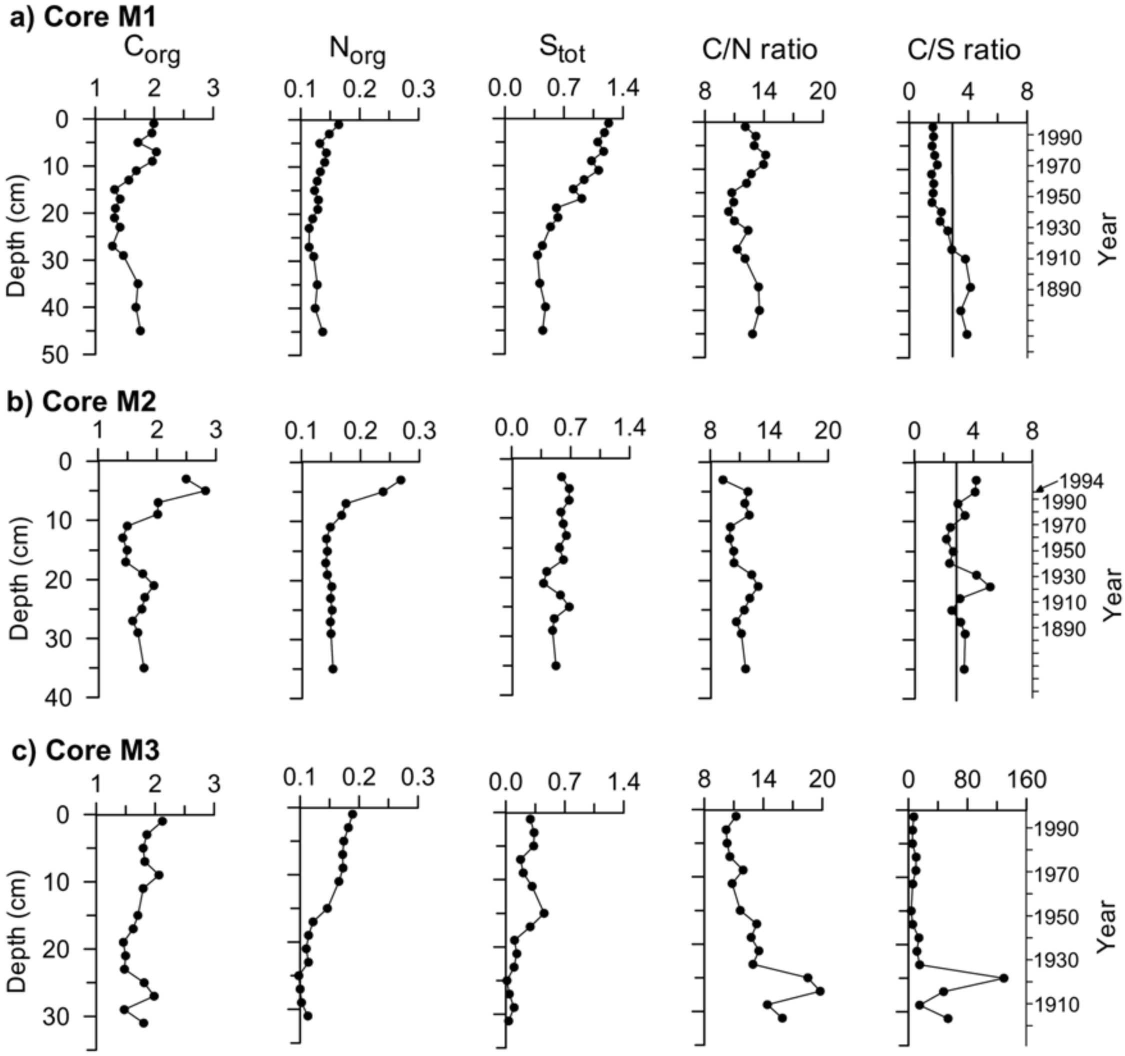

Fig. 4. Distribution of total organic C, N, total S, C/N and C/S ratio in M1 (a), M2 (b), and M3 core (c). Sediment dates are also presented along the core depth.

(Goldberg et al., 1977; Vallette-Silver, 1993; Grousset et al., 1999). The former three metals are prominently abundant in the M1 core, up to twice higher than those in the other two cores (Fig. 5). They increase simultaneously toward the top from 20 cm depth (chronologically, mid-1940s) of M1 and 12 cm (1970s) of M2 core, below those depths they are quite constant. It is characteristic that the concentration of all the metals analyzed is less than the background value at 23 cm depth (late 1920s) of M1, but four metals, Mn, Cu, Zn, and Pb at 17 cm (mid-1940s) of M3 core. In these two cores, Cu, Zn, and Pb decrease slightly at the depth of 5 cm (early 1980s). The distribution pattern of three metals shows a close affinity to TOC, TN, and TS especially in the younger sediments (Figs. 4 and 5), suggesting that they are largely associated in organic matter and sulfide in the M1 and organic matter in the M2 core (Goldberg et al., 1977; Kitano et al., 1980; Ridgeway and Price, 1987). This enrichment is comparable to that found earlier near the site of M1 core (Lee et al., 1988). In the M3 core, the three metals and Mn increase together with TS rather than TOC, like those reported near its site (Hong et al., 1983; Yang et al., 1995; Cho, 2000). The maximum EFs in the three cores are 1.8 to 3.2 for Cu; 1.4 to 2.3 for Zn; and 1.5 to 2.2 for Pb. The largest EFs are always encountered at the top of M2 core.

In the M1 and M2 cores, Fe decreases slightly toward the top in the upper part, and Mn does prominently from the maximum value at the bottom bottom (Fig. 5a, b). These distribution patterns of Fe and Mn resemble those reported in anoxic sediments (Hines et al., 1991; Macdonald et al., 1991; Neumann et al., 1997). However, in the M3 core, the EF of Fe increases toward the top, although Fe tends to decrease, due to the decrease of Al (Fig. 5c). On the other hand, Mn is enriched 1.4 to 1.7 times as much as the background value in the upper part of 23 cm (mid-1920s) with a significant decrease at 17 cm (mid-1940s). Characteristically, Co is concentrated in similar range (13-17 mg/kg) over the background value in the three cores, whereas Ni is less concentrated in the M1 with the smaller background than in the M2 and M3 cores. These two metals generally decrease upward to the concentration less than the background, similar to Fe. Chromium is also much less in the M1 than in the M2 and M3 cores, and is variable in distribution through the cores.

5. DISCUSSION

5.1. Accumulation History of Anthropogenic Heavy Metals

It is well known that Cu, Zn, and Pb are supplied by anthropogenic activities such as of fossil fuel burning, metal manufacturing, and ship building etc. (Goldberg et al., 1977; Kitano et al., 1980; Valette-Silver, 1993). In Masan Bay, the simultaneous enrichment of the three metals is prominent in the younger part of sediments which consist of nearly uniform-sized grains with similar concentration of Fe through the cores (Table 1, Figs. 3 and 5). This character indicates that the three metals have accumulated in a very stable sedimentary environment (Park and Lee, 1996). In this case, the pollution history of sediments can be successfully reconstructed by using ^{210}Pb-radiometric dating alone without normalizing the concentration of pollutant metals and referring to other time markers (Kitano et al., 1980; Grousset et al., 1999).

In the inner bay (M1 core), Cu, Zn, and Pb have initiated to be enriched in the sediments over the background level since the mid-1940s (Fig. 5a) when the population increased rapidly from about 30,000 to 200,000 in Masan City (Ok,

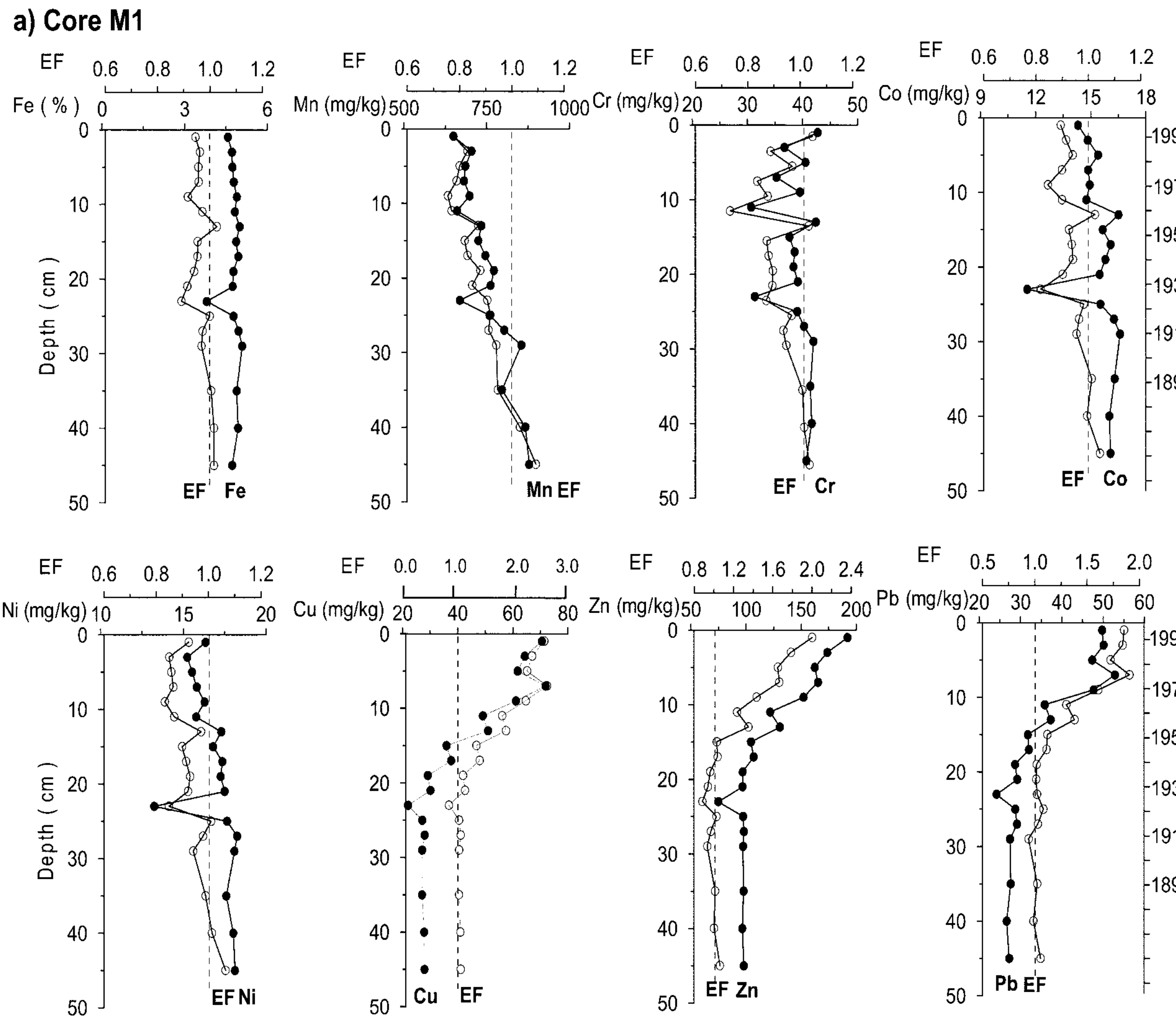

Fig. 5. Distribution of concentration (solid circle) and enrichment factor (EF, open circle) of Fe, Mn, Cr, Co, Ni, Cu, Zn, and Pb in M1 (a), M2 (b), and M3 core (c). Dashed line is the unit of enrichment factor for each metal.

1982). It is ascribed to the stream disposal of industrial and municipal wastewater prior to the outfall disposal since the late 1993, as shown by the abundance of three metals in the sediments dredged near the streams in 1994, up to four times higher than those in the M1 core (Masan City, 1994). Their rapid enrichment during the mid-1960s to mid-1970s is coupled with the establishment of large-scale industrial zones in Masan and Changwon cities as well as the increase of shipping activity in the bay. The increased Cu and Zn concentration in the topmost sediments suggests that the outfall disposal of one-time treated sewage of Masan except Changwon City into the outer bay is not effective enough to reduce the pollution of inner bay sediments (Fig. 5a). Characteristically, the significant decrease of all the metals analyzed to less than the background level in the late-1920s is regarded to reflect the deposition of fresh terrestrial soils leaked by the reclamation to enlarge Masan Harbor in 1927 (Ok, 1982). The slight decrease of three metals in the 1980s sediments of both the inner bay and the bay mouth (Fig. 5a, c) probably reflects the short-term effect of environment preservation regulations such as phasing out of anti-knocking Pb additive in gasoline since 1981 (Lee et al., 1988).

In the outer bay, the outfall disposal of treated sewage is apparent to have contaminated the sediments with the three metals, as distinguished by the characters of topmost sediment layer, such as constant excess ^{210}Pb activity, no trace of benthic animal activity, and their largest EFs in the three sites (Table 1, Figs. 3b, 4b, and 5b). The outfluent contains the three metals in similar concentration to the influent (Kwon and Lee, 1998). The contamination appears to extend to the depth of 1970s sediments, probably resulting from downward mixing of waste sludge by benthic animal activities at the early stage of outfall disposal. This postulation is supported by upward increase of the three metals through the early 1980s sediments, different from the decreased pattern in the inner bay and bay mouth (Fig. 5).

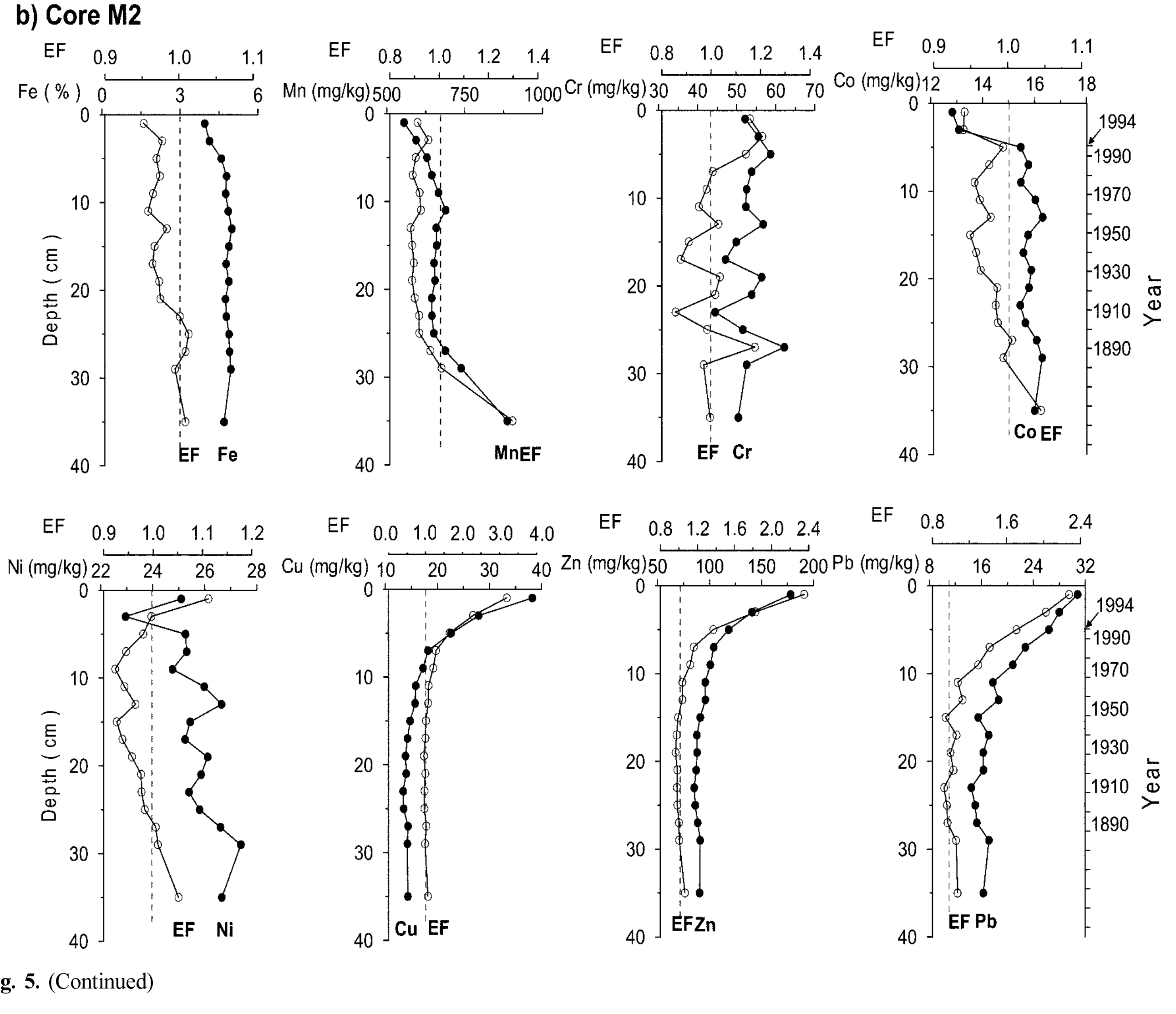
b) Core M2

Fig. 5. (Continued)

No contamination of outer bay sediments before the outfall disposal is attributed to the deposition of stream-disposed metals mainly as particulate form confined to the inner bay due to the poor water circulation (Yu *et al*., 1985; Park and Lee, 1996; KORDI, 1999). It is also recognized by the largest abundance in the M1 and constant distribution of the three metals below the 1970s sediments of the M2 core (Table 1, Fig. 5a, b). Presently, the sludge derived from the outfall seems to prevail the outer bay over the Nakdong River sediments which are characterized by the lower background values of Cu, Zn, and Pb, but the larger abundance of Ni and Cr than in the inner bay (Lee et al., 1988; Yang et al., 1995; Kim et al., 2001).

It is characteristic in the bay mouth sediments that the three metals are enriched together with Mn and subordinately sulfide component since the mid-1920s with the significant decrease in the mid-1940s (Figs. 4c and 5c). Their enrichment before the mid-1940s is suspected to had been caused by dumping of coal ashes from steam-powered vessels (Masan City, 1994), based on the anomalously high C/N and C/S ratios as commonly found in marine (Stein et al., 1994) and terrestrial dumping sites of coal ashes (Rumpel et al., 2000). The contribution of Nakdong River sediments to this earlier contamination is excluded, although it passes Busan City, the oldest and largest harbor in Korea, because the onset of sediment pollution is dated to the post-1930s in the Nakdong Estuary (Kim et al., 2001) and a bay adjacent to Busan (Yang and Kim, 1994). The mid-1940s gap of sediment contamination reflects the mass destruction of industrial facilities around Masan Bay in the World War II (Ok, 1982), as found in the Nakdong Estuary (Kim et al., 2001).

5.2. Accumulation Behaviors of Pollutant Metals

In Masan Bay, the concentration patterns of Cu, Zn, and Pb in the sediments are largely different between the parts

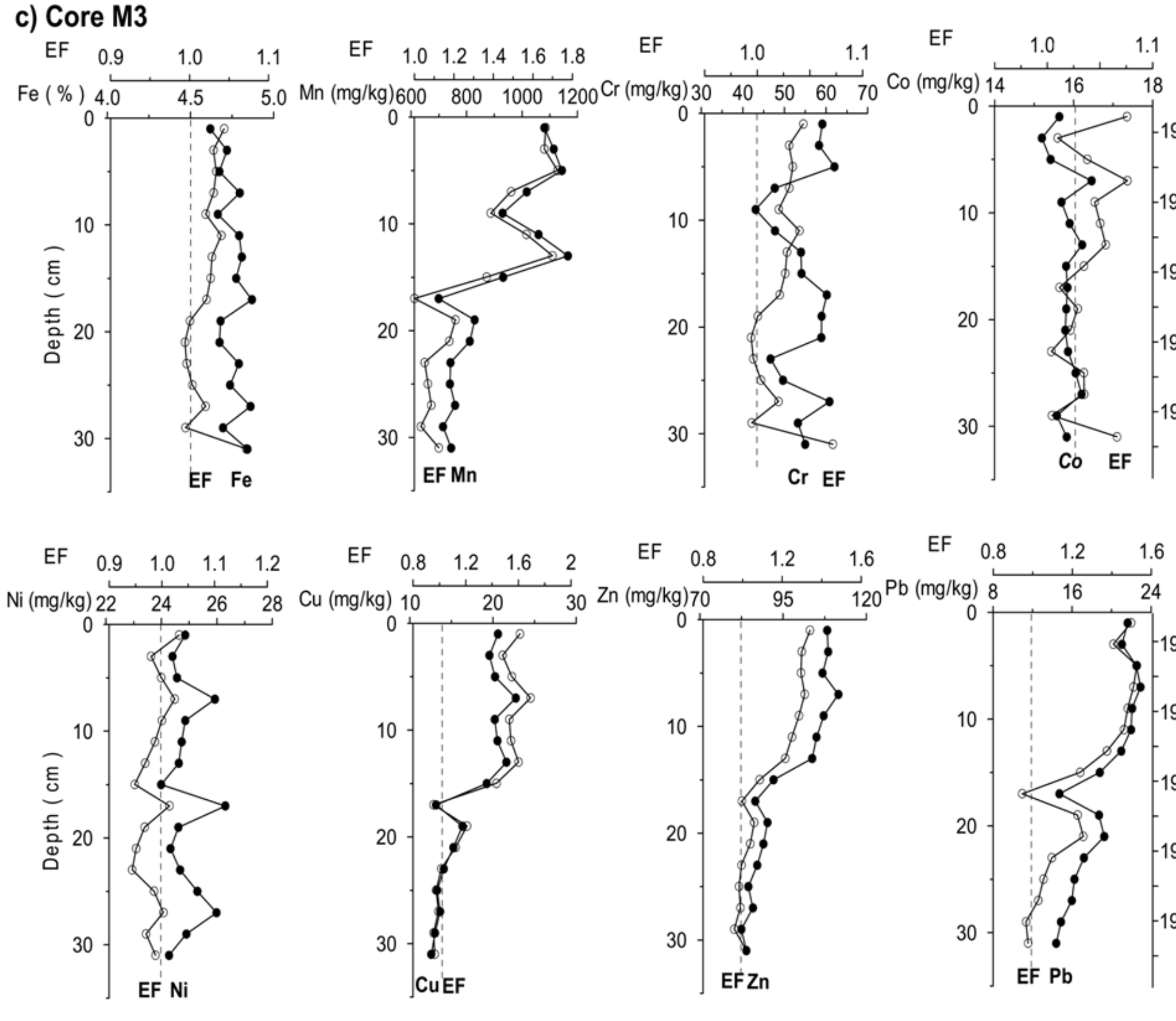

Fig. 5. (Continued)

of bay, depending on the distribution of dissolved oxygen in the bottom water and the sediment geochemical components (Figs. 2 to 5). In the inner bay, the three metals are strongly associated with both sulfide and organic matter, showing the typical existing phase of anthropogenic metals in anoxic sediments (Jacobs et al., 1985; Hines et al., 1991; Macdonald et al., 1991). Based on the ratio (<2.8) of sedimentary C to S (Fig. 4a), the criteria for the anoxic state (Berner and Raiswell, 1983), the bottom water of the inner bay is regarded to have been dominantly anoxic since the 1920s, probably caused by the stream dumping of brewery sludge and municipal wastewater (Ok, 1982). It is postulated to have been similar to that of the present summer season (Fig. 2) that is caused by red tides of phytoplankton bloom, which, in turn, is due to the excessive supply of terrestrial nutrients (Yang and Hong, 1982; Yang et al., 1984; Hong et al., 1991). In this condition, labile fraction of organic matter is dissociated by sequentially utilizing other oxidants such as nitrate, Fe-Mn oxyhydroxide, and sulfate in the sediments (Jacobs et al., 1985; Skei et al., 1988; Sternbeck and Sohlenius, 1997), resulting in the similar distribution of TOC, TN, TS and upward decrease of Fe and Mn through the sediment depth (Figs. 4a and 5a). The prominent upward decrease of Mn is ascribed to its higher mobility than Fe and S to redox change during the anoxic sediment diagenesis (Emerson et al., 1979; Kersten and Forstner, 1986; Calvert and Pederson, 1993). The three metals are more closely related to TS than TOC and TN, suggesting together with ubiquitous sulfide speckles that they have been redistributed from their fractions associated in organic matter and Fe-Mn oxyhydroxide into sulfide compounds in the bottom water and at the sediment surface (Elderfield et al., 1981; Morse, 1994; Sorensen and Jorgensen, 1987). The larger background levels of the three metals than those in the outer bay and bay mouth (Table 1) support for the prolonged sulfide formation in anoxic state (Jean and Bancroft, 1986; Shaw et al., 1990) of the inner Masan Bay. The metal concentrations largely deviated from the C/N ratio in the deeper sediments indicates that the older refractory fraction of organic matter is unfavorable to concentrate the metals (Gaillard et al., 1986; Skei et al., 1988).

In the outer bay, the three metals are predominantly associated with organic matter, as shown by their comparable distributions to TOC and TN through the core depth (Figs. 4b and 5b). The distribution of C/S ratio (<2.8, Berner and Raiswell, 1983) is indicative of two major anoxic periods of bottom water. The small variation in TS with depth and upward decrease of Mn suggest that sediment porewater has been depleted in oxygen enough to reduce Mn-oxyhydroxide but sulfate during the decomposition of organic matter (Jacobs et al., 1985; Kersten and Forstner, 1986; Sternbeck and Sohlenius, 1997). This situation might have occurred intermittently by the summer expansion of anoxic inner bay water, as like the present (Fig. 2). The outfall disposal seems to have caused the upward decrease of Fe and Mn from the sediments dated up to the 1970s by forming an anoxic condition during the incorporated organic matter is mixed into and decomposed in the older sediments.

In the bay mouth, the enrichment of Cu, Zn, and Pb is accompanied with Mn and subsequently S to the 1920s sediments, largely different from those in the other parts of bay (Figs. 4c and 5c). Here, the oxic condition of sediments is confirmed by the high C/S ratio, upward increase of Mn (Figs. 4c and 5c), and ubiquitous traces of benthic animal activity through the core depth but also the saturation of dissolved oxygen in the bottom water (Fig. 2). However, the enrichment pattern of the three metals is distinguished from that resulted from oxic sediment diagenesis which concentrates other metals together toward the sediment top (Gaillard et al., 1986; Ridgeway and Price, 1987; Shaw et al., 1990). This is regarded to result from the oxidative reprecipitation of Mn and the three metals beneath a chemical front formed in the water column by mixing of anoxic inner bay bottom water with the oxygen-rich coastal water on the bay mouth sill (Fig. 2). In this case, the anoxic bottom water appears to carry Mn and pollutant metals supplied excessively from the cities and remobilized partly from the sediments under its pathway to the bay mouth (Fig. 5). Different from Fe, Mn is generally believed as an important carrier of pollutant metals through undergoing several cycles between the water and the underlying sediments (Emerson et al., 1979; Hines et al., 1991; Klinkhammer et al., 1997). The role of chemical front on the oxidative accumulation of metals is also confirmed by decreasing concentration of Mn and the three metals in the surface sediments toward both directions from the bay mouth (Hong et al., 1983; Lee and Lee, 1983; KORDI, 1999). The earlier anoxic condition of bottom water since the 1920s in the inner bay is attributable to the stream dumping of municipal and brewery sludge and wastewater (Ok, 1982), as indicated by the increase of TS and decrease of C/S ratio since that time (Fig. 4a). However, the abrupt decrease of Mn and the three metals in the mid-1940s sediments may indicate that most part of bay water was oxygenated during the World War II when anthropogenic activity has been significantly reduced around the bay (Ok, 1982). The accumulation of Mn-oxyhydroxide to the sediments beneath the chemical front occurs commonly by either the outflow of estuarine water plume into the oxygenated coastal water (Klinkhammer et al., 1997; Turner and Millward, 2000) or the invasion of oxygenated coastal water into the anoxic basins (Neumann et al., 1997; Sternbeck and Sohlenius, 1997).

6. CONCLUSIONS

In Masan Bay, Cu, Zn, and Pb are selectively and simultaneously enriched in the younger part of three sediment cores. The pollution history of the three metals is revealed by dating the cores with ^{210}Pb-derived sedimentation rates of 0.22 to 0.32 cm/yr. In the inner bay, they have been enriched since the mid-1940s, twice as much as those in the other parts of bay, due to their accumulation in particulate form confined by the poor water circulation. Here, the sediment pollution has not reduced even by the treatment and disposal of sewage derived from Masan except Changwon City into the outer bay through an outfall since the late 1993. Instead, the outfall disposal has significantly contaminated the topmost sediments of the outer bay with the three metals up to the EFs of 2.2 to 3.2. The bay mouth sediments have been enriched in the three metals and Mn since the mid-1920s, earlier than in the bay, with a gap in the mid-1940s, reflecting to the accumulation behaviors of the metals in a specific environment and the abrupt reduction of anthropogenic activities during the World War II.

The accumulation behaviors of Cu, Zn, and Pb are different, depending on the proximity to disposal sites and the redox conditions of sediments and the overlying water. In the inner bay, they are associated with both organic and sulfide materials, showing the typical existing phase in anoxic sediments. This is regarded to occur by redistribution of their fractions of organic materials and Fe-Mn oxyhydroxide into sulfide compounds. However, they are incorporated dominantly in the organic matter in the outer bay sediments where Mn is largely depleted upwardly. Based on the depth distributions of TOC, TN, and TS together Mn and C/S ratio, the anoxic state is postulated to have been maintained in the inner bay since the 1920s, whereas in the outer bay it has occasionally formed not much strong to cause sulfate reduction. On the other hand, in the bay mouth, the sediments have been in oxic state, as shown by the saturated dissolved oxygen in the bottom water layer even in summer. The pollutant metals supplied from the anthropogenic activities together with Mn and the metals remobilized partly from the bay sediments appear to have been transported and accumulated back to the bay mouth sediments. Here, their accumulation appears to occur through the oxidative reprecipitation as Mn-oxyhydroxide beneath the chemical front of water column when the anoxic bay bottom water encounters the oxygenated coastal water. These findings suggest that Masan Bay sediments act as a mobile pool especially in summer for pollutant metals to be partly removed and transported to accumulate toward the bay mouth.

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