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 (Elderfield et al., 1981; 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 Söhlénius, 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-
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 Tushima Current to flow along the nearshore of southeastern Korea (Yu et al., 1985; Park and Lee, 1996).

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