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Baseline

Sedimentary records of metal contamination and eutrophication in Jinhae-Masan Bay, Korea

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ABSTRACT

Historical environmental pollution in a semi-enclosed coastal bay was investigated using high-resolution sedimentary records for C_{org}, N_{tot}, $CaCO_3$, $\delta^{13}C$, and $\delta^{15}N$ signatures, and trace metals. A temporal increase in organic matter might have been attributable to enhanced primary marine productivity, presumably caused by increased anthropogenic nutrient inputs in the semi-enclosed, eutrophic system. Metal accumulation occurred in three stages: a preindustrial stage before the 1930s with natural concentrations of metals, an industrialization stage (1940s–1970s) with the highest concentrations, and a postindustrial stage (post 1970s) with stable or decreasing concentrations. However, Hg exhibited a different accumulation history, with concentrations increasing in the early 1900s and accelerating after the 1920s, probably in response to coal burning.

Following urbanization and industrialization, coastal areas can become significant sinks for anthropogenic pollutants, leading to abrupt environmental changes and threats to ecosystem sustainability. Urbanization of the semi-enclosed Jinhae-Masan Bay of Korea began to supplant rural communities approximately one hundred years ago. Accelerated urbanization corresponded to the Japanese colonial period (around 1920) and was associated with enhanced fossil fuel consumption, including coal and wood. After an interval of slow economic growth following World War II, the area became densely industrialized, particularly by the chemical sector (Ok, 1982; Masan City, 1994; http://www.happobay.org, 2011). Since 1990s, the Korean government has attempted to improve water and sediment quality in Masan Bay through a "Total Pollutant Load Management System (TPLMS)" (http://www.happobay.org, 2011). As a result, such a pollution history of Jinhae-Masan Bay, including the urbanization and industrialization stages as well as the effects of the recent TPLMS policy, should be recorded in local sediment. Although metal contamination has been reported in Jinhae-Masan Bay sediments (Jeong et al., 2006); (Hyun et al., 2007), the possible sources and transport pathways of toxic metals (particularly Cd and Hg) and organic matter, and previous variations in eutrophication and bottom-water oxygenation in the bay, remain poorly understood.

Four sediment cores (length, 90 cm) were collected from Jinhae-Masan Bay in 2009, using a gravity corer (Fig. 1). Each core was sampled at intervals of 2–5 cm, yielding 92 samples, which were oven-dried at 60 °C and powdered in an agate mortar. For ^{210}Pb geochronology, ^{210}Pb activities were determined at the Korea Basic Science Institute by counting the alpha decay of its granddaughter, ^{210}Po. The ^{210}Pb-derived linear sedimentation rates were estimated to be 0.32, 0.22, and 0.20 cm/y in cores JM1, 4, and 13, respectively (Fig. 2). Core JM7 showed a very high sedimentation rate (1.69 cm/yr). Stable carbon and nitrogen isotopic compositions of sediments were determined using a Delta plus Finnigan MAT isotope mass spectrometer (Thermo Scientific, San Jose, CA) after combustion in a Carlo Erba NA-1500 Elemental Analyzer (CE Instruments, Milan, Italy). Analytical precisions for standard preparation and mass spectrometric analysis were ±0.25‰ and ±0.20‰ for carbon and nitrogen isotope ratios, respectively. For trace metals, samples were digested with a mixture of hydrofluoric and perchloric acids, and analyzed using inductively coupled plasma mass spectroscopy. Total Hg was determined using a analyzer with CVAAS module (Hydra-C; detection limit, 0.005 ng Hg; Teledyne Leeman Labs, Hudson, NH) based on USEPA method 7473. Accuracy of data determined by repeated analysis of standard reference materials (MAG-1 for trace elements; MESS-2 for Hg) together with a batch of sediment samples was less than 10%. Total carbon and nitrogen (N_{tot}) contents were measured using a Carlo Erba Elemental Analyzer 1108 (CE Instruments). Total inorganic carbon (TIC) was measured using a CO_2 coulometer (model CM5014; UIC Inc., Joliet, IL). Analyses were accurate to within a 5% analytical error. Calcium carbonate ($CaCO_3$) contents were calculated as weight percentage from the TIC content, using a conversion factor of 8.33 g $CaCO_3$ gC^{-1}.

In all cores, C_{org} and N_{tot} content increased from a sediment depth of ~10–30 cm, with the largest increases in cores JM1 and

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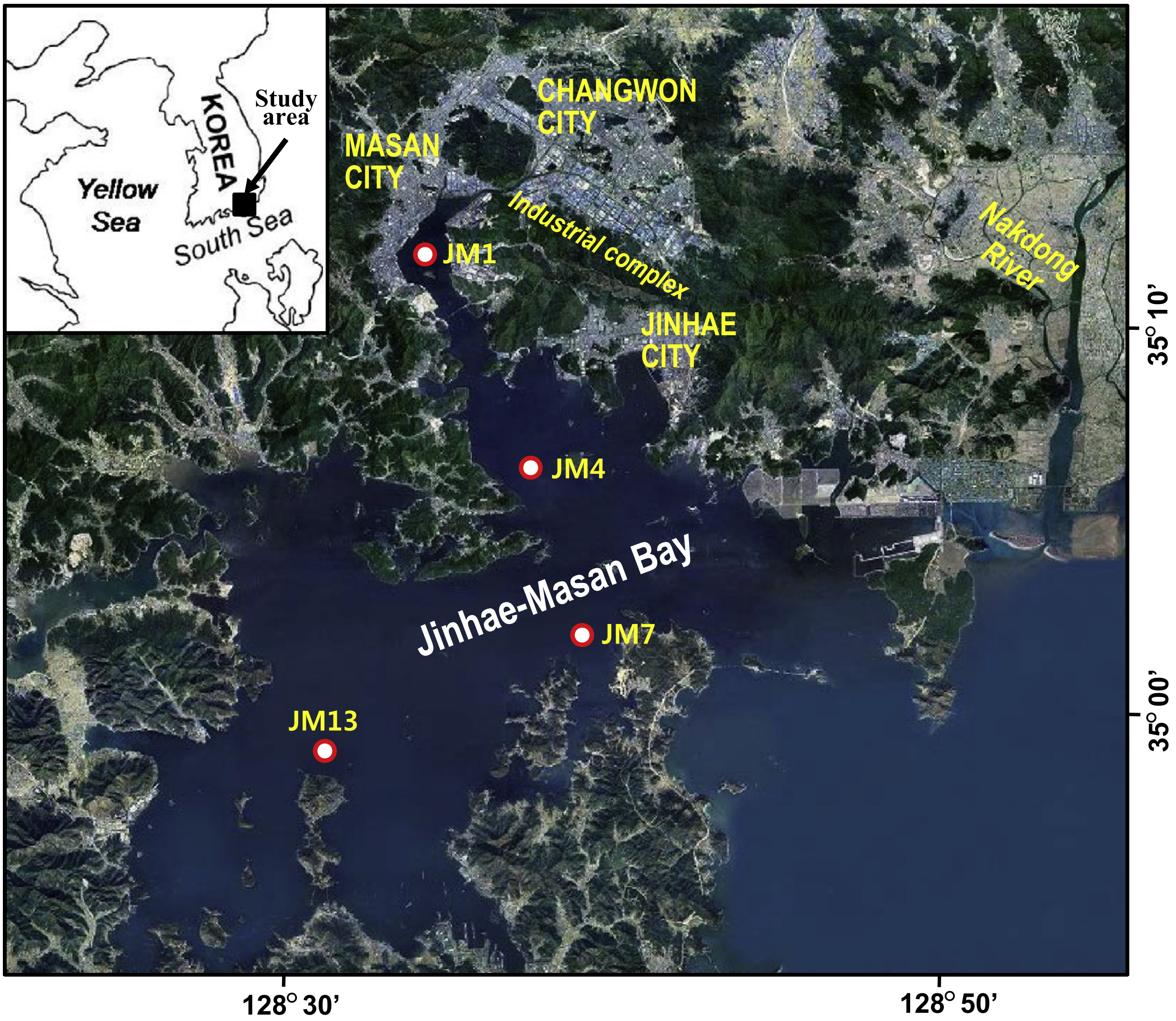

Fig. 1. Location map of the study area with four core sampling sites. Note that the Jinhae-Masan Bay of southeastern Korean coast is characterized by semi-enclosed geographical features, resulting in a restricted water circulation, and surrounded by several big Masan-Changwon-Jinhae cities together with big industrial complex.

4 (the inner bay) (Fig. 3). In contrast, carbonates were rare or absent in the uppermost sediment of cores JM1 and 4, corresponding to an interval of pronounced increase in C_{org} content (Fig. 3). N_{tot} contents in all cores correlated well with C_{org} contents (Fig. 4a), with a best-fit line that passes very close to the origin, suggesting that most nitrogen is probably in the organic form. The C/N ratios were mostly below 10 and exhibited a decreasing pattern in the uppermost part of the cores (except for JM1), representing approximately the last 50–60 years (Figs.3 and 4a). In the uppermost core sediment (except for JM1), the C/N ratio was similar to the Redfield value for unicellular algae (~7; Redfield et al., 1963; Anderson and Sarmiento, 1994) and was lower than the Atkinson ratio for benthic plants (~18; Atkinson and Smith, 1983). This suggests that marine organic matter made a larger contribution to the sediment (Meyers, 1994; Schubert and Calvert, 2001; Smith et al., 2012). Terrestrial organic matter remained an important component, as emphasized by the high C/N ratio (>12) in the uppermost sediment from JM1.

Overall, the δ^{13}C values for core sediments are ranging from -20 to -18‰, except for the uppermost part of JM1 (-22 to -21‰). These values are higher than those for particulate organic matter (POM) in streams flowing into the inner part of the bay (-26.0‰; Kim et al., 1994), suggesting a dominant marine organic source relative to terrestrial sources. However, they are similar to published values for surface sediment in the bay (range, -19.9 to -22.7‰; average, -20.7‰; Hyun et al., 2011) and for POM in the water column of the study area (range, -15.4 to -21.4‰; average, -17.8‰; Kim et al., 1994). Accordingly, the δ^{13}C values for most core sediment samples were within a range typical for marine plankton (-16 to -23‰; Gearing et al., 1984; Meyers, 1994; Smith et al., 2012). Figs. 4b and c, furthermore, organic matter deposited in the bay was derived predominantly from marine phytoplankton, and terrestrial contributions were less than 20%. The uppermost sediment of JM1 (inner part of bay) revealed an increase of terrigenous organic matter, although δ^{15}N values suggested that it was not associated with anthropogenic nitrate (10–20‰; Aravena et al., 1993). The large increase in organic content in recent core sediments was probably caused by eutrophication, leading to a marked increase in primary productivity.

Generally, correlation value between geochemical compositions gives some light on the identification of the factors controlling their contents and temporal-spatial distributions in polluted coastal area. Pearson's correlation matrix for the metals in the uppermost sediments of JM1 and 4, having anthropogenic metal accumulation (Table 1) demonstrated that C_{org} correlated inversely with both Al and metals. This result suggested that organic matter