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# Historical trend in heavy metal pollution in core sediments from the Masan Bay, Korea

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### ABSTRACT

The spatiotemporal distribution and their mass accumulation rate (MAR) of heavy metals were investigated to evaluate the time-dependent historical trends of heavy metal concentration. The three short cores used for this study were collected from the catchment area (MS-PC5, 60 cm length), the central part (MS-PC4, 40 cm length) and the offshore (MS-PC2, 60 cm length) of the Masan Bay, Korea. The concentration of heavy metals (Co, Ni, Cu, Zn, Cr and Pb) in catchment area is as much as 1.5–2 times higher than central part of the Bay, and about 2 times higher than offshore area approximately. In particular, MAR of metals (Cu, Zn and Pb) show clear spatiotemporal variation, so that MAR's of heavy metal may provide more accurate information in evaluating the degree of pollution. Temporally, the heavy metal concentration had been increased since the late 1970s, but it seems to decrease again since the 2004 yr in catchment area. This may came from concentrated efforts for the government to reduce industrial waste release.

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A large amount of industrial effluents usually had been brought significant and rapid environmental degradation, in particular in coastal and bay environments. Consequently, ecosystem surrounded in these circumstances might be destroyed and threaten all kind of living things including human being (Forstner and Wittman, 1981). These sever circumstances, therefore led to concentrated effort to lessen the pollution degree. Within this point of view, it is necessary to evaluate exact tendency of pollution and/or natural background of heavy metal concentration. Numerous studies concerning the heavy metal pollution and its related environmental changes have been conducted in coastal and bay environments in various regions (Feng et al., 2004; Hyun et al., 2007; Niencheski et al., 2014; Wu et al., 2014).

Masan Bay shows one of typical bay system, reserve various characteristics such as high influx of organic matters and metals (Hong et al., 2003; Hyun et al., 2007; Lim et al., 2012), and very sluggish ventilation compared to off shore and seasonal variations of oceanographic environments (Choi, 1993). Also, as most of other bays, environmental deterioration of Masan Bay was strongly associated with benthic environment, benthic animals' habitation (Choi

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http://dx.doi.org/10.1016/j.marpolbul.2015.03.034 0025-326X/© 2015 Elsevier Ltd. All rights reserved. et al., 2005). Masan Bay borders one of the most concentrated industrial areas of Korea and surrounded by the cities of Masan and Changwon, where large industrial complexes have been built since 1960 (Fig. 1). Therefore, serious environmental pollution by heavy metal and organic pollutant in Masan Bay has been reported previously (e.g., Hong et al., 2003; Jeong et al., 2006; Hyun et al., 2007; Lim et al., 2012). However, it has not been attention to lessen the influx of pollutant materials until the 1990s in Korea. This is due to the government policy that industry priority rather than environmental protection.

Large amounts of discharge in industrial waste may cause significant and rapid environmental changes results in environmental deterioration in this bay (Jeong et al., 2006; Hyun et al., 2007; Lim et al., 2012). However, synthesized studies in terms of spatiotemporal variations of heavy metal pollution are not enough to future expectation and prevention. In particular, previous studies had been accomplished only by metal concentration, not by time-dependent metal mass accumulation rate (MAR). The aim of this research is to evaluate the time-dependent spatiotemporal changes of heavy metals, and also investigate historical records from three sedimentary core sediments.

Masan Bay, located at the southern coast of Korea, is characterized by its semi-enclosed, elongated geographic surroundings. The cities of Masan and Changwon are nearby, representative

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J. Cho et al./Marine Pollution Bulletin xxx (2015) xxx-xxx



Fig. 1. Sampling locations of gravity core sediments from the Masan Bay, Korea. Note that those of Masan, Jinhae and Changwon cities surround the Masan Bay. DST is Dukdong Sewage treatment plant.

industrial complex in Korea (Fig. 1). Masan Bay has been used important sea port since the 1930s, and elongate tidal flats had already been converted into artificial container, industrial complexes, and development is still ongoing.

Sediment core samples were collected in Masan Bay using a potable gravity piston core in 2006 yr (Fig. 1; Table 1). After collection, the core samples were split into two parts, and the sampling was conducted from the archived half. All the samples for grainsize, organic matter and metal concentration were dried at 60 °C for overnight and crashed by agate mortar in laboratory condition. About 10 g sediment was run for grain size at the Korea Institute of Ocean Science and Technology (KIOST). For the metal analysis, powdered samples were digested by a mixture of HNO<sub>3</sub>, HF, and HClO<sub>4</sub> using Atomic Absorption Spectrometer (AAS) at the KIOST. Also, total carbon content was determined by the direct measurement by CHNS analyzer (EA 1112). The organic carbon was determined by the subtraction of inorganic carbon from total carbon (TC). Duplicate analysis showed that all analytical errors were less than 5% for each element.

In particular, the <sup>210</sup>Pb sediment accumulation rates were determined by an independent method for calculating sedimentation rates and <sup>137</sup>Cs chronology. Dry sediment samples (15–20 g) were loaded into a cylindrical vial (5 cm i.d.), sealed

and counted over 24 h. <sup>137</sup>Cs and <sup>210</sup>Pb were determined using the 661.6 and 46.5 keV photopeaks, respectively. The samples were counted again at least 30 days after sealing and the <sup>226</sup>Ra content was estimated from the <sup>214</sup>Bi (609.3 keV) and <sup>214</sup>Pb (352.0 keV) photopeaks (Gilmore and Hemingway, 1995). The excess <sup>210</sup>Pb were determined as the difference between total <sup>210</sup>Pb and <sup>226</sup>Ra activities (Radakovitch et al., 1999). Also, <sup>137</sup>Cs were measured by its emission at 662 keV. The absolute efficiencies of the detectors were determined using calibrated sources and sediment samples of known activity. The mass accumulation rate (MAR) of any metals was calculated as follows; some element concentration (µg/g) × dry bulk density (cm<sup>2</sup>) × linear sedimentation rate (cm/ year).

As each coring places are thought to have different oceanographic conditions such as productivity changes through the seasonal variation, different current and circulation systems, sedimentary environment of the each place might be expected different. Also, because of the accumulation rate of heavy metal is strongly associated not only with the influx of metal but also benthic environment such as sedimentation rate and sediment grain size, the metal concentration of three sites may be different each other. This oceanographic difference among site may provide valuable insight into concentrations of heavy metal accumulation.

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