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## Baseline Toxicological impact assessment of heavy metal contamination on macrobenthic communities in southern coastal sediments of Korea

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#### ABSTRACT

In the heavily industrialized Masan Bay of southern coast, Korea, the potential harmful effects of heavy metals (Cd, Co, Cu, Ni, Pb, Sn, Zn, and Hg) were evaluated in terms of the pollution load index (PLI) and ecological risk assessment index (ERI) methods, and the results obtained were considered alongside the health of the macrobenthic fauna communities. The results revealed that the bay sediments, especially in the inner bay and the outfall area of a sewage treatment plant, are exposed to moderate to serious levels of metal pollution. Hg and Cd contributed the most to the potential toxicity response indices in sediments recently deposited in the bay. The potential ecological risk assessment of heavy metals in the bay was highlighted by the use of the benthic biological pollution index (BPI), suggesting that the ERI is a useful toxicity response index, which can quantify the overall ecological risk level to a target environment.

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With the rapid industrialization and economic development experienced in coastal regions over the past century, sediment pollution by heavy metals has become a serious environmental problem due to toxicity, persistence, non-biodegradability, and bioaccumulation (Chapman et al., 1998; Klavins et al., 2000; Tam and Wong, 2000; Todd et al., 2010). In addition, heavy metals can be biomagnified through food chains, resulting in potentially serious consequences for both the sensitive lowest levels of the food chain and ultimately to human health (Schafer et al., 1981; Croteau et al., 2005; Hammerschmidt and Fitzgerald, 2006). Heavy metals in sediments can be released and transferred to aquatic and benthic biological communities via sediment porewater and seawater (Luoma, 1983, 1989). However, there are numerous uncertainties when evaluating the effects of heavy metals on the health of biological communities, including the ionization efficiency of solid heavy metals in a dissolved form in diverse pore and aquatic water conditions, the toxicity of each metal species, and the uptake rate and biological tolerance of each biological species for each heavy metal species (Luoma, 1989; Bryan and Langston, 1992; Zabetoglou et al., 2002; Yi et al., 2011). Therefore, it can be very difficult to assay the overall effect of sediment heavy metal concentrations on benthic biological communities. Despite these difficulties, Haksan (1980) suggested an ecological risk index (ERI) that can be used to estimate the effect of heavy metals in sediments on ecological communities, and many scientists have adopted this index when evaluating environmental conditions (e.g., He et al., 2009; Zhang et al., 2012; Zhu et al., 2012; Suresh et al., 2012). However, a basic question regarding the effect of heavy metals on biological communities under different aquatic sedimentary environments still remains. Determination of the biological pollution index (BPI) is difficult and can be subjective. Despite these constraints in BPI results, it is still regarded as the ultimate end point when evaluating the potential health impact of specific environmental conditions. Here, we attempted to connect the ERI directly with the BPI, which was evaluated using the diversity and species composition of benthic biology in the coastal environment of Masan Bay, Korea; this location has a long recorded status of being heavily polluted (Lee and Min, 1990; Kang, 1991; Chang et al., 2012). Although numerous investigations have been conducted in the bay regarding heavy metal contamination and organic pollutants (Yim et al., 2005; Jeong et al., 2006; Hong et al., 2010: Lim et al., 2012), there is almost no information available in the published literature with regard to the potentially harmful effects of heavy metals in the bay sediments on the benthic community.

A total of 42 surface sediment samples were collected from Masan Bay on the southern coast of Korea in August 2010 and 2011 (Fig. 1). Grain-size analysis was undertaken using a standard sieving technique for the sand fractions (>4  $\phi$ ) and a pipette method for the mud fractions (<4  $\phi$ ). Total carbon and inorganic carbon contents were measured using a Carlo Erba Elemental Analyzer 1108 (CE Instruments, Wigan, UK) and a CO<sub>2</sub> coulometer (model CM5014; UIC Inc., Joliet, IL, USA), respectively. Analyses were accurate to within a 5% analytical error. For concentrations of metals (Cd, Co, Cu, Ni, Pb, Sn, and Zn), the powdered sediments were





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digested with a mixture of hydrofluoric and perchloric acids and analyzed using inductively coupled plasma mass spectrometry. Total Hg was determined using an analyzer with a cold vapor atomic absorption spectrometry (CVAAS) module (Hydra-C; detection limit, 0.005 ng Hg; Teledyne Leeman Labs, Hudson, NH, USA) based on USEPA method 7473. The accuracy of the data was determined to be less than 10% by the repeated analysis of standard reference materials (MAG-1 for trace metals; MESS-2 for Hg) together with a batch of sediment samples. To determine historical variations in potential ecological risk, heavy metal data from two cores (see Fig. 1 for sampling sites), reported by Lim et al. (2012), were used. The macrobenthic organisms used to determine the BPI were collected from 11 same sampling sites of the bay (see Fig. 1 for sampling sites) in February and August 2011. Routine analytical processes were undertaken for the taxonomic sorting and species identification of organisms, and the BPI calculation used in the assessment of macrobenthic fauna health has been described in detail previously (Choi and Seo, 2007; Seo et al., 2012).

Statistical summary of analytical data in surface sediments from the study area and their spatial distributions are shown in Table 1 and Fig. 2, respectively. The mean grain-size of the surface sediments ranged from approximately 7 to 9  $\phi$  and mostly comprised silt (average 40 ± 8%) and clay (average 54 ± 13%), except for some samples with a high sand content in the innermost bay (Fig. 2). The total organic carbon (TOC) content of bulk sediment samples varied between 1.1% and 3.7% (average 2.1 ± 0.6%), and the highest contents (>2.0%) tended to occur in the inner part of the bay and

the outfall area of a sewage treatment plant (STP) (Fig. 2). Overall, TOC content was not correlated well with sediment grain-size in their relative analysis (Table 2). Masan Bay is rated good (<2%) or fair (2-5%) for organic carbon content in terms of EPA criteria (USEPA, 2008). Metal concentrations displayed the following ranges: Cd =  $0.01-2.15 \ \mu g/g$  (average  $0.66 \pm 0.45 \ \mu g/g$ ), Co = 12.9-16.0  $\mu$ g/g (average 14.8 ± 0.6  $\mu$ g/g), Cu = 21.6–113.9  $\mu$ g/g (average  $53.3 \pm 23.1 \,\mu g/g$ ), Ni = 15.5–46.6  $\mu g/g$  (average  $32.4 \pm 5.4 \,\mu g/g$ ), Pb = 29.0–82.5  $\mu$ g/g (average 48.4 ± 15.6  $\mu$ g/g), Sn = 1.3–11.9  $\mu$ g/g (average  $3.2 \pm 1.8 \,\mu g/g$ ), Zn = 95.2–443.4  $\mu g/g$  (average 218.3  $\pm$  79.4 µg/g), and Hg = 17.1–375.8 ng/g (average 109.1  $\pm$  67.5 ng/ g). For the organic carbon contents, most metals (except Co) were also present in higher concentrations in the inner bay and STP outfall area (Fig. 2), suggesting an association with anthropogenic effluents. Overall, the spatial distributions of heavy metals (except for Ni and Co) and TOC in the study area exhibited similar patterns and TOC content correlated well with heavy metals (Table 2), indicating their association with anthropogenic origin. It is well established that organic matter has a high affinity through adsorption or complexation for heavy metals in the aquatic environment of the study area. Therefore, it affects the eco-toxicity, environmental transfer and geochemical behavior of heavy metals in the aquatic environment. In contrast, Ni and Co are well correlated with sediment grain-size, but not with TOC, indicating that they were not influenced by anthropogenic activity.

The degree of anthropogenic metal contamination in surface and core sediments from the study area was assessed using the



**Fig. 1.** Map of the study area indicating surface sediment (SS), core sediments (CS), and macrobenthic organism (MO) sampling sites. Note that the semi-enclosed Masan Bay is surrounded by several big cities (Masan-Changwon-Jinhae) and a large industrial complex. The total amount of sewage effluent from the sewage treatment plant (STP) is  $63 \times 10^6 \text{ m}^3/\text{yr}$  (Kwon and Lee, 1998).

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