

Mercury and methylmercury flux estimation and sediment distribution in an industrialized urban bay



Eunhee Kim^{a,b}, Seam Noh^a, Yong-gu Lee^a, Sampa Rani Kundu^b, Byeong-Gweon Lee^b, Kihong Park^a, Seunghee Han^{a,*}

^a School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, 500-712, Republic of Korea

^b Department of Oceanography, Chonnam National University, Gwangju, 500-757, Republic of Korea

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ABSTRACT

Our objectives of this study were to estimate mercury (Hg) flux to Masan Bay, an industrialized urban bay in Korea, and to examine important factors influencing the Hg distribution and transformation in Masan Bay sediment. As the first attempt to estimate Hg flux for Masan Bay, we found out that stream water discharge was the prime source of Hg, contributing 76% of the total input. Estimating the methyl Hg (MeHg) flux showed that groundwater discharge is the major source, contributing 53% of the total input. The large MeHg input through groundwater discharge emphasizes the importance of the in-situ sediment production of MeHg. The fraction of MeHg over total Hg (%MeHg) in the bay sediment, ranging from 0.10% to 1.5%, showed a strong negative correlation with the sediment organic matter content (2.8–14% as a loss on ignition). However, when different urban and industrialized estuarine sediments were compared, sediment organic matter either promoted or constrained %MeHg in sediment, suggesting that the role of sediment organic matter for the net Hg methylation varies, relying on the biogeochemical conditions of estuarine sediments. Despite the large variations in Hg and MeHg concentrations among different urban and industrialized estuarine sediments, relatively small variations were determined for the %MeHg, i.e., 0.52% on average.

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1. Introduction

Mercury (Hg) is a persistent global pollutant that undergoes various biogeochemical processes (e.g., oxidation, reduction, methylation, and demethylation) in the aquatic environment. A key biogeochemical process is Hg methylation, which forms methylmercury (MeHg) by a diverse range of microorganisms including sulfate-reducing bacteria, iron-reducing bacteria, methanogens, and *Firmicutes* (Gilmour et al., 1992; Benoit et al., 1999; Kerin et al., 2006; Han et al., 2010; Gilmour et al., in press). Recently, the gene orthologs of *hgcAB* were found to be present in confirmed methylators, suggesting that possessing *hgcAB* may predict Hg methylating capability of microorganisms (Gilmour et al., 2013; Parks et al., 2013). MeHg, a major form of organic Hg, is more toxic and biomagnifies more efficiently than inorganic Hg within aquatic food chains. Coastal and estuarine sediments are major MeHg repositories and may act as either a sink or a potential source of MeHg for the overlying water (Benoit et al., 1998; Mason et al., 1999; Sunderland et al., 2004; Kim et al., 2006; Hollweg et al., 2009).

Previous studies showed that the Hg methylation potential in coastal/marine sediments was closely related to sediment organic matter (OM) and sulfide concentrations, which influences Hg partitioning

and bioavailability to methylating bacteria (Sunderland et al., 2004; 2006; Han et al., 2007, 2011; Hammerschmidt et al., 2008; Hollweg et al., 2009; Hsu-Kim et al., 2013). Sediment OM content appeared to be more important in controlling Hg methylation potential at low-sulfide conditions (<10 μM) than at high-sulfide conditions (Sunderland et al., 2006; Hammerschmidt et al., 2008; Hollweg et al., 2009). In high-sulfide sediment (>10 μM), MeHg production was associated with the dissolved Hg speciation (Benoit et al., 2001, 2003; Drott et al., 2007; Hollweg et al., 2009; Han et al., 2011). Cell culture, chemical equilibrium models, and field data have suggested that high levels of dissolved sulfide decrease Hg bioavailability to Hg-methylating bacteria due to the formation of hydrophilic Hg-sulfide species (Benoit et al., 2001; Drott et al., 2007). A recent review by Hsu-Kim et al. (2013) emphasizes the role of Hg-sulfide nanoparticles in Hg methylation, suggesting that Hg methylation cannot be sufficiently explained with conventional chemical equilibrium models.

Masan Bay, a semi-enclosed bay located on the southeastern coast of Korea (Fig. 1), is surrounded by highly populated cities (Masan, Changwon, and Jinhae) and large industrial complexes, including petrochemical, electrical, plastic, and metal industries (Moon et al., 2009). Large inputs from these industrial and municipal effluents cause environmental problems due to high nutrient loadings as well as organic and metal contamination (Hyun et al., 2007; Moon et al., 2008; Hong et al., 2010; Jang et al., 2011). Additionally, sluggish water circulation, ascribed to weak currents (2–3 cm s⁻¹), results in high accumulation

* Corresponding author. Tel.: +82 62 715 2438; fax: +82 62 715 2434.
E-mail address: shan@gist.ac.kr (S. Han).

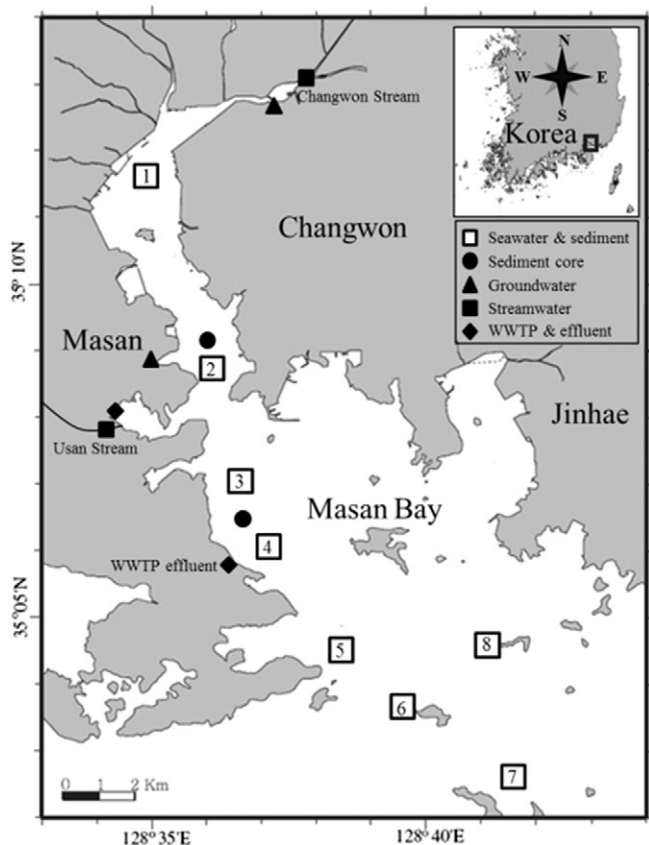


Fig. 1. A map of the study area and sampling locations.

of contaminants especially in the upper bay (Hyun et al., 2007; Hong et al., 2009). A wastewater treatment plant (WWTP) was constructed to mitigate the environmental problems in Masan Bay and has been in operation since 1994 (Fig. 1; Moon et al., 2009). The WWTP treats 2.6×10^5 tons of wastewater; mostly domestic, daily, and effluents are discharged through an underwater outfall pipe (Moon et al., 2009, Fig. 1).

A recent study showed a fairly high concentrations of total Hg (THg) and MeHg in some benthic fish and invertebrate species collected from Masan Bay (Kim et al., 2012). Submarine groundwater discharge (SGD) ranged from 4.8×10^6 to 5.7×10^6 $\text{m}^3 \text{day}^{-1}$ in Masan Bay, or approximately 540% to 840% of the surface water discharge (Lee et al., 2009). Owing to this high SGD rate, the inorganic phosphorus and silicate flux was approximately 2–3 fold higher through the SGD than through river water discharge (Lee et al., 2009). Previous studies have shown that Hg flux by SGD in several estuarine/coastal environments is significant, exceeding river discharge and atmospheric inputs (Bone et al., 2007; Laurier et al., 2007; Black et al., 2009). Lee et al. (2011) found that the THg and MeHg flux through SGD for Hwasun and Bangdu Bay located on Jeju Island, Korea, was substantially higher than that through atmospheric deposition and sediment diffusion. Given this, Hg inputs via SGD to Masan Bay, which may be larger than industrial/river discharge and atmospheric deposition, can be important. To date, however, no information is available for estimating the distribution and sources of THg and MeHg in Masan Bay.

For these reasons, the objectives of this study were as follows: 1) to examine the spatial and temporal distribution of THg and MeHg in Masan Bay water and sediment, 2) to identify major sources of THg and MeHg in the bay water, and 3) to investigate correlations between biogeochemical factors in sediments, i.e., THg, acid volatile sulfide (AVS) and OM, and the sediment %MeHg (the fraction of MeHg over THg) to

understand the environmental factors that govern Hg methylation potential in urban bays.

2. Materials and methods

2.1. Sample collection

2.1.1. Surface seawater and sediment collection

Surface water samples were collected from eight stations (Fig. 1) on five occasions in 2009 and 2010 (March, May, and August in 2009 and January and May in 2010). Water samples were collected using a Go-Flo bottle (General Oceanics, USA) from about 0.5 m below the water surface. The Go-Flo bottle was filled with trace-metal grade 12 M hydrochloric acid (5% v/v) overnight, rinsed with high purity (18.2 $\text{M}\Omega \cdot \text{cm}$) Milli-Q water several times, and then kept in a plastic bag before use. Water samples from the Go-Flo bottles were transferred to Teflon bottles for the THg and MeHg analyses and polypropylene (PP) bottles to determine the total suspended solids (TSS) and particulate organic matter (POM). Ancillary parameters (temperature, dissolved oxygen [DO], and salinity) were measured with a handheld multimeter (YSI Incorporated, USA) on-site. The pH was measured either on-site or immediately after returning to the laboratory using a pH meter (Thermo Scientific) after calibration. All water samples transferred to the Teflon and PP bottles were kept in coolers with ice until they were transported to the laboratory. Samples were acidified with trace-metal grade 12 M hydrochloric acid (0.5% v/v) and stored at 4 °C until the THg and MeHg analyses. The unfiltered water samples collected for THg in August (2009) and May (2010) were analyzed for MeHg as well. To determine the TSS and POM, the water samples were filtered through pre-weighed 0.4 μm glass fiber filters (Advantec), and the filters were dried at 60 °C overnight. POM was calculated from the difference between the dry weight and loss on ignition (at 550 °C for 4 h, Kim et al., 2004).

Surface sediments (about 15 cm) were collected using a Ponar grab sampler, on five occasions previously mentioned (Fig. 1). Samples were mixed homogeneously on board and transferred to acid-cleaned polypropylene containers. Sediments were stored frozen until the THg and MeHg analyses were conducted. In addition to the THg and MeHg analyses, the sediments collected in May 2010 were analyzed for AVS. The Hg benthic flux was calculated in sediment samples collected in acrylic cores with a 12-cm diameter from inner and outer bay sites (Fig. 1) in May 2011. The cores were placed inside a nitrogen-filled glove box before the overlying water was removed. After the overlying water was removed, the cores were sectioned to 2 cm down the core. Pore waters were extracted from sediments by centrifugation, and the supernatant was filtered through 0.45- μm syringe filters in a nitrogen-filled glove box (Mason et al., 1998). Bottom seawater samples were collected, together with sediment cores from the same sites. The filtered pore waters and seawaters were acidified to a 0.4% (v/v) final concentration with 12 M hydrochloric acid (trace-metal grade) and stored at 4 °C in a dark environment until the analysis was conducted. All analyses of the water for THg and MeHg were performed within a month after the sample was collected.

2.1.2. Collection of inflowing water

In order to estimate the wet atmospheric deposition of Hg, four rainwater samples were collected in May and August 2011 from Gwangju, located in southwestern Korea (about 200 km from Masan Bay). The rainwater was collected using acid-cleaned glass funnels (15 cm diameter) connected to a 2 L acid-cleaned Teflon bottle. The rainwater samples were immediately preserved after collection by adding trace-metal grade 12 M hydrochloric acid (0.4% v/v). Before each sampling, the Teflon bottles and glass funnels were soaked in a hot 4 M hydrochloric acid bath (trace-metal grade) overnight and rinsed with Milli-Q water. The Teflon bottles were filled with trace-metal grade 12 M hydrochloric acid (0.4% v/v) and double-bagged. The glass funnels were kept in a plastic bag until use.

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