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Significance of submarine groundwater discharge in the coastal fluxes of mercury in Hampyeong Bay, Yellow Sea

MD. Moklesur Rahman [a], Yong-gu Lee [a], Guebuem Kim [b], Kitack Lee [c], Seunghee Han [a,*]

[a] School of Environmental Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju 500-712, Republic of Korea
[b] School of Earth and Environmental Sciences, Research Institute of Oceanography, Seoul National University, Seoul 151-742, Republic of Korea
[c] School of Environmental Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, Republic of Korea

HIGHLIGHTS

- ▸ We estimated mercury mass fluxes in the Hampyeong Bay, Yellow Sea.
- ▸ Submarine groundwater discharge was the major source of mercury.
- ▸ The coastal mercury budget estimation needs to include groundwater discharge.

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ABSTRACT

Submarine groundwater discharge (SGD) and various solutes released with SGD have received particular attention recently; however, understanding of the impact of SGD on trace metal fluxes in the coastal ocean is limited. To understand the contribution of SGD to the coastal Hg input, the Hg mass fluxes associated with SGD were estimated from Hampyeong Bay, a coastal embayment in the Yellow Sea. Hg concentrations in filtered groundwater and seawater ranged from 1.3 to 4.4 pM and from 0.83 to 2.0 pM, respectively, and Hg concentrations in unfiltered seawater ranged from 1.7 to 4.6 pM. The Hg flux estimation showed that SGD was the prime input source of Hg in the bay (18 ± 12 mol yr^{-1}), contributing 65% of the total input. Atmospheric deposition was the second dominant source of Hg (8.5 ± 2.7 mol yr^{-1}), contributing 31% to the total input. The results of the current study suggest that SGD can be a significant source of Hg in estuarine/coastal systems; therefore, estimating the coastal mass budgets of Hg must include SGD as a prime source of Hg.

1. Introduction

Subterranean estuaries are coastal aquifer zones where land-derived freshwater is combined with intruding saltwater. Direct discharge of groundwater from subterranean estuaries into coastal oceans appears to be a common global phenomenon (Moore, 2006, 2010). Based on recent estimates, the average annual fluxes of submarine groundwater discharge (SGD) all along the continental shelf of the South Atlantic Bight were 3 times larger than the river fluxes (Moore, 2010). Local groundwater fluxes contribute a significant portion of the river discharge in many estuaries (Ferrarin et al., 2008; Santos et al., 2008; Peterson et al., 2010). For example, SGD contributed 10–80% of the river discharge in the Indian River Lagoon, Florida (Peterson et al., 2010), and the SGD was 5–30 times the river discharge in the Venice Lagoon, Italy (Ferrarin et al., 2008). Submarine groundwater can enrich coastal waters with nutrients; coastal eutrophication and algal blooms have been related to SGD (Basterretxea et al., 2010; Hwang et al., 2010; Knee et al., 2010).

Large amounts of land-derived pollutants, such as toxic trace metals from agricultural and industrial sites, and atmospheric deposition in the groundwater recharge area can be transported to coastal waters along the groundwater flow path (Dowling et al., 2003; Beck et al., 2009; Ganguli et al., 2012). Submarine groundwater fluxes of Sr and Ba to the ocean were equal to the river fluxes in the Bengal basin (Dowling et al., 2003). In Jamaica Bay, New York, the SGD is an important source of Fe, Zn, Co, and Ni for coastal waters (Beck et al., 2010). The non-conservative mixing behavior of metals has been found in subterranean estuaries, indicating that water–sediment reactions in subterranean estuaries are critical for the mass flux of metals associated with SGD (Slomp and Van Cappellen, 2004; Charette and Sholkovitz, 2006; Beck et al., 2010).

Mercury is a well-documented neurotoxicant that poses a hazard to the environment and public health (Castoldi et al., 2008).

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

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Human exposure to Hg occurs primarily through dietary uptake of Hg-contaminated fish (Campbell et al., 2008; Mahaffey et al., 2008). Once Hg is introduced into a coastal zone, Hg(II)-methylating bacteria (e.g., sulfate-reducing and iron-reducing bacteria) convert inorganic Hg(II) to monomethyl Hg (MMHg) in anoxic and suboxic compartments of the coastal zone (Warner et al., 2003). In general, the MMHg found in the coastal food web is regarded as arising from near-shore sediment (Fitzgerald et al., 2007). Consequently, Hg loading in coastal systems is associated with an elevated MMHg level in fish (King et al., 2002; Warner et al., 2003). In fact, atmospheric deposition of Hg showed a positive correlation with the MMHg concentration in fish in lakes (Hammerschmidt and Fitzgerald, 2006).

Although many studies have reported coastal mass balances of Hg, the studies considered river discharge and atmospheric deposition as the primary input sources of Hg (Mason et al., 1999; Faganeli et al., 2003; Balcom et al., 2004). Recently, the limited literature has suggested that SGD may have a great influence on the coastal mass budget of Hg (Bone et al., 2007; Laurier et al., 2007; Black et al., 2009; Lee et al., 2011; Ganguli et al., 2012). For instance, the total dissolved Hg input through SGD was higher than the inputs received through atmospheric deposition and riverine input on the East Coast of the United States (Bone et al., 2007) and on the central and southern California coasts (Black et al., 2009; Ganguli et al., 2012). Mussels collected near the groundwater discharge zone of the French coast exhibited significantly higher Hg values than those found at the control site, suggesting a considerable amount of bioavailable Hg is discharged from submarine groundwater (Laurier et al., 2007). In general, studies regarding the influence of groundwater discharge on the coastal Hg budget are limited; thus, the role of SGD in Hg transport to the ocean is largely unknown.

In the present study, we aimed to estimate the significance of Hg input flux through SGD in Hampyeong Bay, a semi-enclosed embayment in the eastern Yellow Sea. We estimated the percent contributions of Hg input through SGD as well as atmospheric deposition and benthic diffusion, based on the measurements of Hg from these sources.

2. Methods and materials

2.1. Study site

Hampyeong Bay, on the southwest of Korean peninsula, is elongated northwest–southeast with a maximum width of 8.5 km and a length of 17 km (Fig. 1). The bay is situated in a pristine area devoid of large cities and industrial areas. Land use is dominated by fisheries, aquaculture, and agriculture (Waska and Kim, 2010). The bay has a total water area of 85 km^2 and a mean water depth of 4 m (Waska and Kim, 2011). The surroundings of the northeast side of the bay are characterized by low mountains 100–400 m high, whereas the gently sloping Imsu Peninsula restricts the southwest side of the bay (Ryu, 2003). The mouth of the bay is deep and narrow, with a maximum water depth of about 23 m and a width of 1.5 km (Ryu, 2003). A large area of tidal flats has developed along the side of the bay, characterized by small sand bars and cheniers (Ryu, 2003). Tides in this region are semidiurnal, and the mean tidal range is 3.46 m, with mean neap and spring tidal ranges of 2.37 m and 4.55 m, respectively (Waska and Kim, 2011). No rivers flow into the bay, and the groundwater discharge runoff in the intertidal area is large enough to form small streams, which causes thriving microphytobenthos (Waska and Kim, 2010). The tidal ranges on the sampling dates in 2010 were 5.09 m on January 18 and 4.97 m on January 19, 5.32 m on May 1 and 4.26 m on May 20, and 2.51 m on August 5 (Korea Hydrographic and Oceanographic Administration, KHOA, http://www.khoa.go.kr/). The seasonal precipitation pattern is characterized by heavy rainfall in summer, as Korea is situated in the Asian monsoon climate region. The monthly precipitation amounts in 2010 were 37 mm in January, 99 mm in May, and 338 mm in August (Korea Meteorological Administration, KMA, http://www.kma.go.kr/). Hampyeong Bay has a considerable intertidal zone (>50% of the total bay area), and the SGD magnitudes, calculated based on a mass balance model of ^{226}Ra, were 0.14–0.35 m^3 m^{-2} d^{-1} in the literature (Waska and Kim, 2011).

2.2. Sampling methods

Groundwater samples from shallow wells of different depths, ranging from 30 cm to 1 m, were collected from Woldu, Dolmori, and Songseokri on January 18 and 19, May 1 and 20, and August 5, 2010. All the groundwater samples were collected in active seepage runoff areas in the intertidal zone. Zero salinity groundwater samples after heavy rain events were collected from Songseokri on May 20, 2010. At low tide, a well was excavated to a depth of 30–100 cm. After the dirty water was discarded, clear groundwater samples were collected using a peristaltic pump along with Teflon tubing connected to a Millipore groundwater filter capsule (0.45 μm pore size) in 500 mL pre-acid-cleaned Teflon bottles. Using recorded GPS points, pH, salinity, and temperature were measured in situ using the Orion 5 Star™ Series Meters.

Surface seawater samples were collected on May 17 and August 3, 2010. Samples were collected in a similar way as the groundwater, using the peristaltic pump and the same filter attached to the Teflon tubing at a depth of approximately 20 cm from the surface water. Filtered and unfiltered samples were collected in 500 mL Teflon bottles that had previously been treated by soaking them in an HCl solution (30% v/v) to make them Hg free. Returning to the laboratory, the groundwater samples were acidified with approximately 0.4% 12 N HCl (trace metal grade), while the seawater samples were acidified with 0.2% 9 N H_2SO_4 (trace metal grade), and kept at 4 °C in a dark environment (Lee et al., 2011). To measure dissolved gaseous mercury (DGM), filtered seawater samples from the same depth (20–30 cm from the surface) were collected in 1 L glass bottles and 500 mL Teflon bottles on January 2 and February 13, 2012. The glass and Teflon bottles provided almost the same result for the DGM. No free space was allowed at the top of the sampling bottle to prevent even a subtle loss of DGM through evasion to the headspace before analysis.

Seawater samples for ancillary measurements of dissolved organic carbon (DOC), particulate organic carbon (POC), suspended particulate matter (SPM), and chlorophyll-a (Chl-a) content were collected along with Hg samples. DOC and POC samples were collected in precombusted (450 °C for 10 h) 40 mL glass vials and 500 mL acid-cleaned, low-density polyethylene (LDPE) bottles, respectively. Unfiltered seawater samples for SPM and Chl-a analysis were collected in 2 L LDPE bottles.

Sediment samples were collected in acrylic cores 30 cm deep with a 12 cm diameter on September 9, 2010, and February 14, 2011. The total Hg concentrations in the sediments and pore waters were determined with concomitant measurements of organic carbon content and sediment density. Sediment cores for chemical analysis were sectioned within 5 h of collection. Cores were placed inside a N_2-filled glove box before the overlying water was removed, after which the cores were sectioned up to 4 cm down the core. Pore waters were extracted from the sediments with centrifugation, and the supernatant was filtered through 0.45 μm syringe filters (Mason et al., 1998). The filtered pore waters were acidified to about 0.4% final concentration with 12 N HCl (trace metal grade) and stored at 4 °C in a dark environment until analysis. After being removed from the glove box, the