

Has Submarine Groundwater Discharge Been Overlooked as a Source of Mercury to Coastal Waters?

SHARON E. BONE,^{*,†} MATTHEW A. CHARETTE, CARL H. LAMBORG, AND MEAGAN EAGLE GONNEEA

Woods Hole Oceanographic Institution, Department of Marine Chemistry and Geochemistry, Woods Hole, Massachusetts 02543

We measured the mercury (Hg) in groundwater, aquifer sediments, and surface water in Waquoit Bay (Massachusetts) and found that this toxic metal (range: <3.2–262 pM) was being released within the subterranean estuary, with similarly high levels (range: 18–256 pM) found in the surface waters of the bay. None of the dissolved species (DOC, chloride, and Fe) normally observed to influence Hg partitioning correlated well with the observed Hg concentrations. It was hypothesized that this was in part due to the variable loading in time and space of Hg onto the aquifer sands in combination with the seasonality of groundwater flow through the aquifer. Aquifer sediment samples from the study site ranged from <1 to 12.5 pmol of Hg/g of sediment, suggesting log K_d values on the order of 1. We hypothesize that this was due to the low organic carbon content typical of the aquifer sediments. Last, it was estimated that submarine groundwater discharge supplied 0.47–1.9 nmol of Hg m⁻² day⁻¹ to the bay, which is an order of magnitude higher than the atmospheric deposition rate for the northeastern U.S.

Introduction

Subterranean estuaries are defined as the zone within coastal aquifers where terrestrial-derived freshwater mixes with intruding saltwater. Like their surface, river-fed counterparts, subterranean estuaries can be important geochemical linkages between terrestrial water sources and coastal waters (1). A variety of solutes in terrestrial groundwater can be modified within the saltwater–freshwater mixing zone through complexation with saltwater components, sorption reactions, and precipitation.

The water that discharges from the subterranean estuary into coastal waters, referred to as submarine groundwater discharge (SGD), is chemically distinct from both the fresh groundwater and the saline coastal water endmembers. Additionally, SGD may be comparable in magnitude to river discharge (2). SGD is therefore a potential source of metals and nutrients to the coast. Several studies have demonstrated the role that SGD plays in eutrophication (3), and a few have analyzed the influence of SGD on metal transport into coastal waters (4–7). There are, to our knowledge, very few studies

that attempt to gauge the impact that subterranean estuaries have on mercury geochemical cycling in coastal zones (8).

The goal of this study was to explore the transport of Hg through a subterranean estuary located at the Waquoit Bay National Estuarine Research Reserve in Cape Cod, MA. This was done through analysis of total dissolved Hg in groundwater and surface bay water. Additionally, Hg associated with the sediments in two cores located within the mixing zone was measured.

Materials and Methods

Study Site. The study site is located at the Waquoit Bay National Estuarine Research Reserve along the south shore of Cape Cod, MA. Waquoit Bay is shallow (1 m in most places) and is connected to Vineyard Sound by a narrow channel at its southern end. The bay is well-mixed. Waquoit Bay is fed by the Quashnet and Childs Rivers, which are largely groundwater fed, as well as by direct groundwater discharge along the entire shoreline. The subterranean estuary is located in a sandy permeable aquifer at the north end of the bay (head of the bay; ref 9). Water discharges from the subterranean estuary at the head of the bay in a narrow band (10). This discharge is spatially variable on both large and small scales as a result of shoreline topography and sediment permeability, respectively (10). SGD has both a saline and a fresh component. The saline component is due to recirculation of seawater in the subterranean estuary. Michael et al. (11) showed that saline recirculation and discharge are due to the seasonal movement of the water table. There is a delay of 1–5 months between the time when recharge is highest and the time when the water table height is the highest. This leads to a net outflow of seawater during the summer months and net inflow during the winter months. Because of the high permeability of Cape Cod soils in this region, ~50% of the local precipitation recharges the aquifer. As a result, the residence time is relatively short, on the order of 10–50 years. The rate of groundwater flow between sampling wells (discussed under Sampling Methods) located ~2 m apart is on the order of a few days.

The pycnocline established within the subterranean estuary by the mixing of seaward flowing fresh groundwater with denser intruding seawater constrains the movement of solutes within the aquifer: most movement is lateral (advective), while movement due to upward diffusion is very minor (11). Inflowing saltwater wedges under outflowing fresh groundwater, forcing the freshwater plume to narrow and increase in velocity as it flows toward the bay.

The Waquoit Bay subterranean estuary exhibits an active Fe redox cycle. At the saltwater–freshwater interface, the dissolved Fe is precipitated out as Fe (hydr)oxides, leading to an area of iron-coated sands within the aquifer, which have been observed to act as a geochemical filter for metals and nutrients, preventing their release into the bay (7, 12). A previous study by Charette et al. (5) indicated that the Fe-coated sands contain a variety of Fe (hydr)oxide types including goethite, ferrihydrite, and lepidocrocite, which vary vertically and laterally within the subterranean estuary.

Sampling Methods. Six groundwater profiles were collected along a 20 m transect perpendicular to the shore over an 8 day period in June 2005 (Figure 1). The profiles were obtained using a stainless steel drive point piezometer system (Retract-A-Tip, AMS Inc.) and were all approximately 6–8 m deep. Groundwater samples were pumped through fluorinated polyethylene tubing using a peristaltic pump and were collected every 0.15 m in the mixing zone (transition between

* Corresponding author phone: (510) 643-9951; e-mail: sbone@nature.berkeley.edu.

† Current address: University of California, Berkeley, Dept. of Civil and Environmental Engineering, Berkeley, CA 94720.

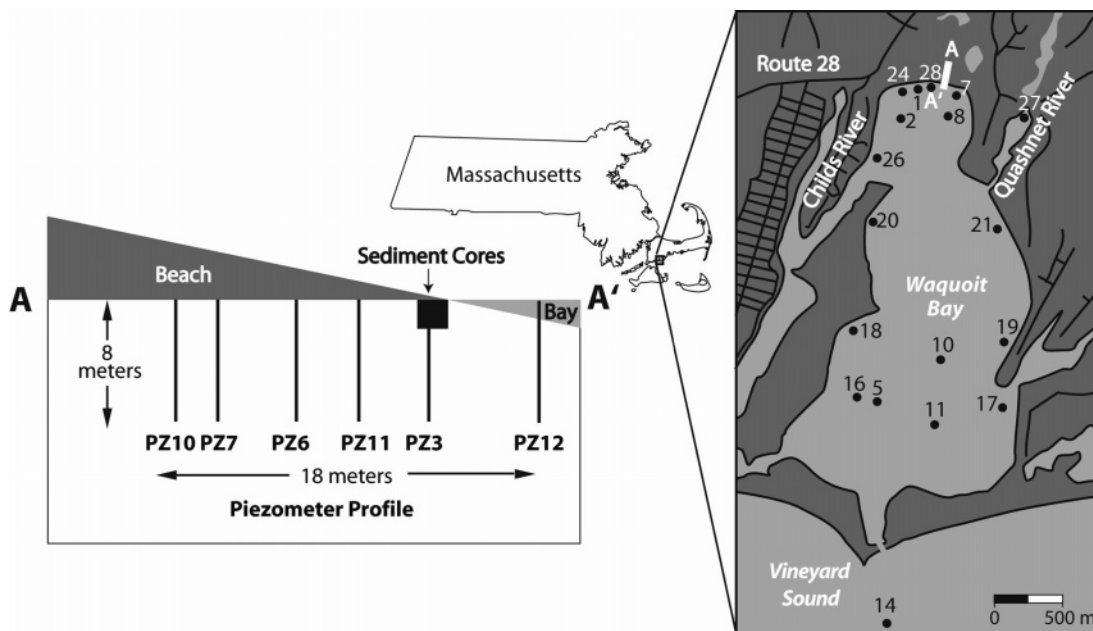


FIGURE 1. Location of the study site including piezometer wells, cores, and surface water sampling locations.

fresh and saline groundwater) and every 0.3–0.6 m elsewhere. Samples were filtered in the field using an inline $0.45\ \mu\text{m}$ Pall AquaPrep 600 filter. Procedural blanks were collected by pumping $18.2\ \text{M}\Omega\ \text{cm}^{-1}$ water through the entire system, including the piezometer head, tubing, and filter. The procedural blank was $3.0\ \text{pM}$ ($n = 2$). The oxidation reduction potential (ORP), pH, dissolved oxygen, and temperature were measured in the field using a YSI 600XLM in a flow through cell (YSI, Inc.).

Surface water samples from Waquoit Bay and Vineyard Sound were collected at the same time as the groundwater samples (June 2005). A PVC extension pole, to which a trace metal clean 60 mL syringe (plunger removed) and a $0.2\ \mu\text{m}$ filter were attached, was used to collect water upstream from the boat. The plunger was reattached to the syringe, and samples were filtered into 15 mL LDPE bottles that had previously been cleaned in 10% HCl (trace metal grade) and MilliQ water. The sample bottles were pre-acidified in the clean room with $50\ \mu\text{L}$ of 8 N HNO_3 (Optima grade).

In addition to the ground and surface water samples, Hg was measured in two cores, collected in the summer of 2002, which were previously characterized by Charette et al. (5). The cores were each $\sim 1.5\ \text{m}$ deep and came from a section of the aquifer that corresponds to piezometer well 3 (Figure 1). Upon collection, the cores were air-dried and hand-sieved with a nominal retention diameter of 1 mm. It was assumed that there was no change in the redox state of the sediments because the color stratigraphy observed initially was maintained. The sedimentary Fe and OC (organic carbon, % OC) concentrations reported here are taken from Charette et al. (5). The sedimentary Fe values used in this study correspond to the values reported in the L3 + L4 leach, which was designed to target both the amorphous and the crystalline Fe (hydr)oxides (5). Sedimentary Hg was measured on the archived sediment samples during the summer of 2005.

Analyses. At least 12 h before analysis, $100\ \mu\text{L}$ of 30% H_2O_2 was added to the 15 mL of Hg groundwater samples (12). This method was originally adapted from Klaue and Blum (13) for treatment of dissolved As samples and was used here to treat Hg samples. Samples from piezometer 11 (PZ11) were treated with $100\ \mu\text{L}$ of BrCl followed by $40\ \mu\text{L}$ of NH_2OH , as per EPA Method 1631, Revision E (14). In all samples, dissolved Hg was then determined using dual gold-

amalgamation cold-vapor atomic fluorescence spectroscopy (15, 16) using a Tekran CVAFS Mercury Detector 2500.

To establish the equivalence between total dissolved Hg samples treated with BrCl/ NH_2OH and H_2O_2 , 22 samples from two profiles that covered a wide range of water chemistries (and Hg concentrations) were separated into two different 15 mL LDPE vials and treated with an aliquot of either the halogen or the peroxide. The samples were taken from either PZ12, which is the most bayward profile and is saline at all depths, or PZ7, which is located inland and is predominantly fresh with the mixing zone occurring at depth. The Hg_{TD} concentrations determined using these treatments were comparable, with the peroxide treatment resulting in slightly higher values on average ($110 \pm 11\%$; see Supporting Information).

Dissolved Fe and Mn were determined as per Charette et al. (5). Briefly, a 1:20 dilution of each sample, to which an indium standard had been added to control for instrument drift, was measured using ICP-MS on a Finnegan Element 2. Dissolved organic carbon (DOC) was determined with an OI TOC/TIC analyzer interfaced to a PDZ Europa 20–20 IR-MS at the UC–Davis Stable Isotope Facility. The sample inorganic carbon was converted to CO_2 with phosphoric acid, and sodium persulfate was used to oxidize the organic carbon to CO_2 .

The digestion method used to determine sedimentary Hg content corresponds to the L3 + L4 leach used in Charette et al. (5), which was adapted from Hall et al. (17). Briefly, 15 mL of 1 M hydroxylamine-hydrochloride in 25% acetic acid was added to approximately 0.4 g of sediment and then heated in an oven at $90\ ^\circ\text{C}$ for 3 h. After this time, the aqueous phase was removed and saved. This process was repeated and combined with the existing solution. Samples were analyzed by CVAFS, as before. A subset of three sediment samples (3_1, 3_17, and 2_41) was also subjected to a concentrated acid leach, in which the sediments were heated to $90\ ^\circ\text{C}$ for 16 h in 16 N HNO_3 in Teflon bombs. This was performed to ascertain whether there was an organic Hg fraction present in the sediments that was not being targeted by the acetic acid leach, which was developed to target Hg associated with Fe/Mn (hydr)oxides. Hg concentrations were comparable between the two leaches (range 64–96%). Some of this variation may be due to the variable size of the sand grains. Sediment standard MESS-3 was subjected to the same

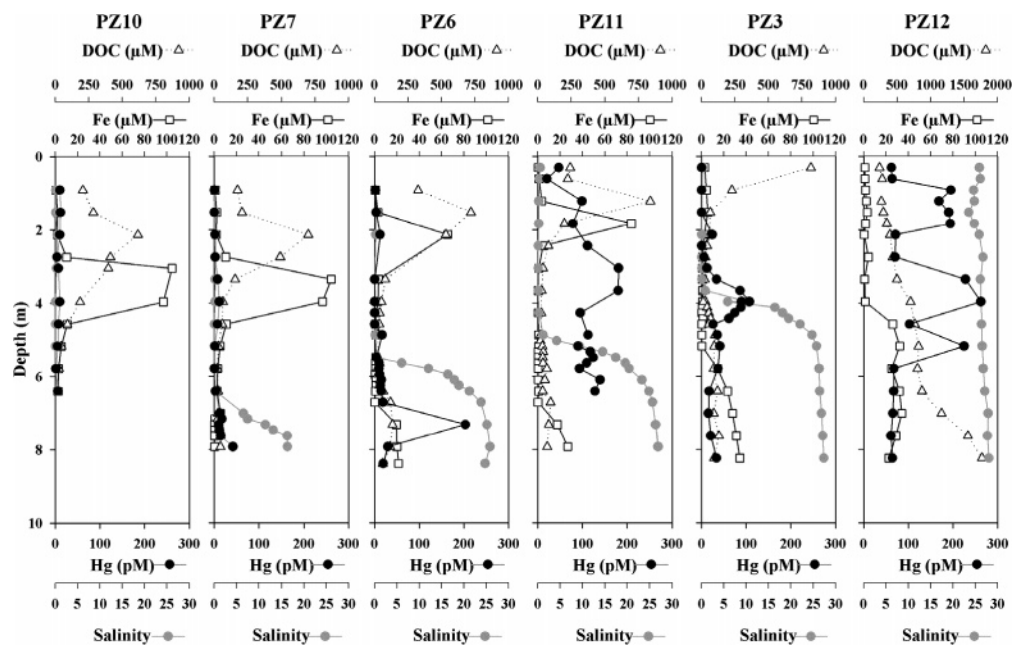


FIGURE 2. Groundwater profiles showing total dissolved Hg (black circles), salinity (gray circles), dissolved Fe (open squares), and DOC (open triangles).

concentrated acid leach. We found the mean Hg concentration for MESS-3 ($n = 3$) to be $98 \pm 7 \mu\text{g kg}^{-1}$, which compared well with the certified value of $91 \pm 9 \mu\text{g kg}^{-1}$.

Results and Discussion

Description of Hg in the Groundwater Profiles. The total dissolved Hg (Hg_{TD}) in the groundwater ranged from below detection limit (3.2 pM) to 262 pM . Figure 2 presents depth profiles for Hg_{TD} in the six groundwater profiles. Included in this figure are the dissolved Fe and DOC concentrations in the groundwater, as well as salinity. The data presented in Figure 2 are also presented in table format in the Supporting Information, along with DO, although there was no obvious correlation between Hg concentrations in the groundwater and dissolved oxygen.

DOC is generally higher in the upper 1.5 m of the groundwater profiles, decreases toward the freshwater–saline interface, and finally increases again at the lowest depths where salinity begins to increase. Generally, Hg_{TD} is low or at background levels ($<15 \text{ pM}$) in the entirely freshwater portion of the aquifer (PZ10) and elevated in the entirely saltwater portion of the aquifer (PZ12). PZ7 and PZ6 are mostly freshwater profiles; salinity begins to increase at depth within these two wells. Hg_{TD} is at relatively low levels throughout these two profiles, exhibiting slightly higher values at depth. In PZ11 and PZ3, the mixing zone is well-represented. In PZ11, Hg_{TD} is above background levels throughout the entire profile; however, it shows a minor peak in the region where the dissolved Fe is low ($\sim 2.5\text{--}4.5 \text{ m}$). In PZ3, this effect is more dramatic; Hg_{TD} has a well-defined peak that occurs concurrent with the dissolved Fe minimum, although salinity also begins to increase around this depth. Although the porewater Hg concentrations in some of the samples are significantly elevated above typical fresh and salt surface waters, they are similar in magnitude to those found in coastal sediment porewaters (18) and also within the range of concentrations observed in fresh groundwaters (19–21).

The Hg_{TD} versus salinity piezometer plots show a pattern that is consistent with the release of Hg that occurs within the subterranean estuary (Figure 3). PZ10 shows a distribution that is similar to the value measured in the Childs River (surface water site #26). PZ7 and PZ6, which represent mostly

freshwater, show a small but linear increase in Hg. There is one large peak in Hg_{TD} in PZ6; however, this peak is only supported by one point. In PZ11 and PZ3, which represent the mixing zone, Hg increases at zero salinity, peaks around mid-salinity, and declines slightly toward higher salinities, thus representing the area of the aquifer in which Hg is being released from the solid phase.

Hg Mobilization within the Subterranean Estuary. These groundwater profiles suggest that Hg is partitioning into the aqueous phase within the subterranean estuary; however, it is not clear by what mechanism this is taking place. Thermodynamic considerations indicate that Hg will desorb off of metal (hydr)oxides at increasing concentrations of chloride through the formation of soluble Hg–Cl complexes (22), and studies have demonstrated desorption of Hg from sandy, low organic matter aquifer sediments with the addition of NaCl (23). However, a plot of Hg versus salinity for all the groundwater profiles shows that Hg_{TD} increases where salinity remains close to zero, indicating that increasing chlorinity is not the only variable driving Hg mobilization (Figure 3).

Work done by Lamborg et al. (24) indicates that within the range of DOC and chloride concentrations observed for most estuarine systems, DOC is predicted to exert a greater influence on Hg speciation than chloride. Other studies have indicated that concentrations of labile Hg complexes do not necessarily increase with increasing salinity (25). Our groundwater data, however, do not show an obvious correlation between total dissolved Hg and DOC. Indeed, the highest dissolved Hg concentrations are observed under some of the lowest DOC concentrations in the dataset. Ravichandran (26), however, notes that because Hg is usually associated with a small fraction of DOC, and because these sites are usually in excess of Hg, it can be difficult to discern a correlation between DOC and Hg in natural systems, even when a relationship between the two solutes does exist.

Furthermore, dissolved Hg concentrations in the subterranean estuary do not appear to be controlled by precipitation/dissolution dynamics of Fe. As noted, Hg concentrations in solution are low in the freshwater plume carrying dissolved Fe at PZ10, PZ7, and PZ6 and show only a weak relation to Fe in PZ11, PZ3, and PZ12 at depth. If Hg were coprecipitating with Fe as the freshwater plume mixes with seawater, the profiles of these two metals would appear similar. This is in

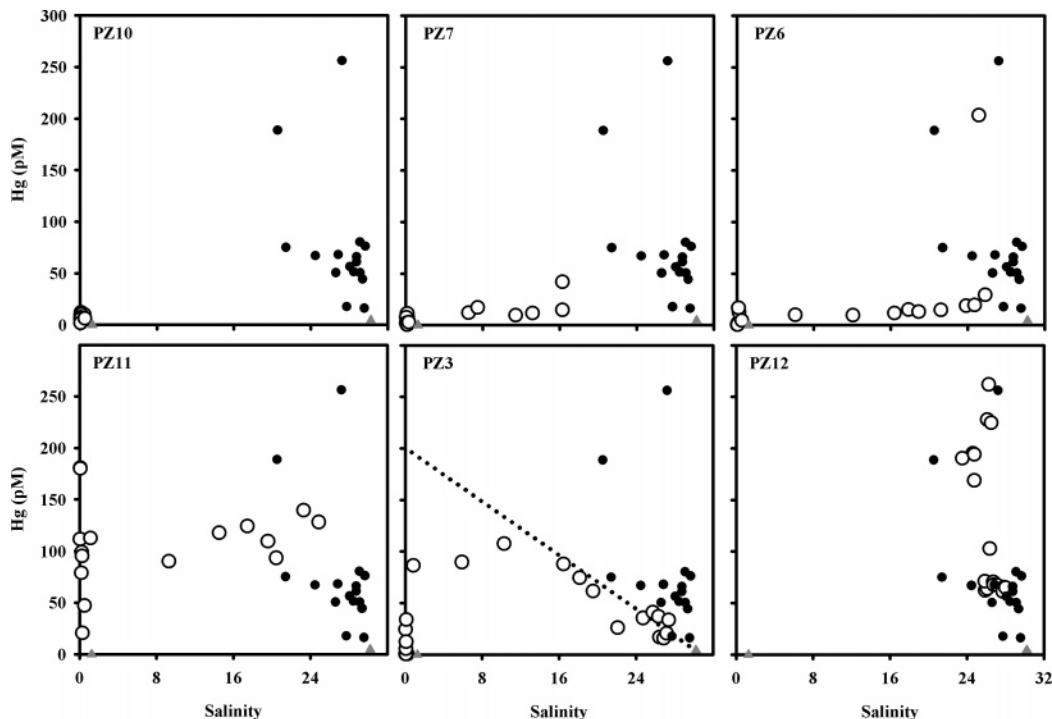


FIGURE 3. Hg in groundwater and surface water vs salinity. Surface water Hg is shown in all plots as black circles. Groundwater Hg is shown as empty circles. The gray triangles designate fresh and saltwater endmembers. The dashed line on the PZ3 plot indicates the approximate effective groundwater endmember concentration, which assumes that groundwater is the primary source of Hg to Waquoit Bay surface waters.

contrast to work suggesting just such a removal mechanism for Hg (27).

The observation that three leading geochemical candidates (chloride, DOC, and Fe) do not satisfactorily explain Hg partitioning in the subterranean estuary of Waquoit Bay suggests that other mechanisms or processes drive the distribution of this metal at this site. We propose that variable Hg loadings to the solid phase have occurred over time and space in accordance with seasonal variation in the mixing zone. These loadings provide the material that is then partitioned according to the presence or absence of the agents listed previously. Seasonal variation in the freshwater–saltwater interface necessarily changes the vertical location of the pycnocline and, subsequently, the flow paths for different solutes. Additionally, this variation may change the solution chemistry to which sediments at a particular location are exposed. At our study site, Hg could be accumulated on the sands when these sands are in the freshwater zone and then released when these sands are inundated with salt water.

Sedimentary Hg Concentrations and Partition Coefficients. Sedimentary Hg was seen to vary with sedimentary OC content ($r^2 = 0.82$, $n = 9$, Supporting Information). This and the weaker correlation between sedimentary Hg and sedimentary Fe ($r^2 = 0.40$, $n = 10$) indicate that Hg is more sensitive to changes in the OC content of the sediments than to changes in the Fe (hydr)oxide type or content. Changes in sediment organic carbon content may influence dissolved Hg concentrations. Sedimentary OC content has previously been shown to strongly influence Hg partitioning in natural systems (28). Hammerschmidt and Fitzgerald (18) showed that, for both inorganic Hg and monomethylmercury (MMHg), $\log K_D$ was strongly and positively correlated with % LOI (% loss upon ignition, a measure of OC) in sediments taken from Long Island Sound, the continental shelf of New England (29), and several Alaskan lakes (30).

$\log K_D$ values observed in natural systems are usually between 3 and 6 (18). Because the core samples and

groundwater samples do not directly correspond to each other (they were not taken at the same time or exact same location), it is not possible to determine partition coefficients for the field data. However, we can establish a range for the partition coefficient by comparing the highest and lowest Hg_{TD} concentrations to the highest and lowest sedimentary Hg concentrations. This results in a large range ($\log K_D$ ranges from <1 to ~ 4). A $\log K_D$ of 4 is within the range typically observed in natural systems. However, as sedimentary OC attenuates quickly with depth (5) and the highest Hg concentrations are found at intermediate depths, most of the field samples will exhibit a $\log K_D$ that is closer to 1.

One possible explanation for the low partition coefficients is that the organic carbon content (% OC) of our sediment samples was very low as compared to many lake and estuarine sediments ($<0.1\%$ OC, as compared to $>5\%$ LOI) (18, 29), which would decrease the affinity of Hg for the sediment. However, if we extrapolate back to the % LOI = 0 intercept on the plots of $\log K_D$ (for Hg(II)) versus % LOI, comparable to our % OC; OC is approximately equal to half LOI) provided by Hammerschmidt et al. (18, 29, 30), K_D is >1 order of magnitude larger than our partition coefficient values. The relationship between $\log K_D$ and % LOI is linear over a wide range of Hg concentrations, as is indicated by Hammerschmidt et al. (18, 29, 30); thus, the range of Hg concentrations measured in our system is not expected to be responsible for the discrepancy between our measured K_D values and those of Hammerschmidt and colleagues.

It is possible that the slope of the $\log K_D$ versus % LOI plot changes as the % LOI approaches zero. Additionally, the equilibrium constant for mercury–organic complexes is dependent on the source of the organic matter (24, 31, 32). Therefore, differences in OM type and age between the Waquoit Bay study site and those studied by Hammerschmidt and co-workers could result in differences in the partition coefficients. Indeed, using the DOC from these surveys and the OC from the sediment samples suggests that the K_D for OC in these locations is of the same order as Hg (range in

$\log K_{\text{DOC}} = \sim 0.89-3.3$), suggesting that the OC in the system is of a kind that is not sorbing well to the solid phase or that these sands are not effective at hosting this organic material. Additionally, previous studies have demonstrated that partition coefficients appear to be low due to the fact that a large percentage of dissolved Hg exists largely in the colloidal fraction (28, 33).

If the total Hg measured at our study site existed largely as MMHg or Hg^0 , then the partition coefficients would be lower than those expected for total Hg that contained a greater amount of Hg(II). MMHg exhibits lower partition coefficients than Hg(II) (18, 29, 30). It is expected that Hg^0 would have a very low partition coefficient due to its lack of charge. Because the aquifer is a semi-enclosed system and the water residence time is $\sim 10-50$ years, Hg^0 may be able to accumulate through, for instance, the reduction of Hg(II) by bacteria (34). As we did not determine Hg^0 in our samples, and no previous studies have attempted to determine this species in groundwater, we currently have no way of predicting how important the reduction of Hg in the system would be in affecting Hg partitioning.

Hg_{TD} in the Surface Water of Waquoit Bay. The Hg_{TD} concentration was determined for Vineyard Sound (the salt water endmember of the bay), as well as for several locations within Waquoit Bay (Figure 1). Hg_{TD} is 4.4 pM in the Sound, which is comparable to values observed in Long Island Sound (35). Hg_{TD} increases to a maximum at the head of the bay adjacent to the groundwater sampling site. Hg was also measured in the zero salinity region of the Childs River at the point where the river empties into the bay and was determined to be less than the detection limit (3.2 pM). The Waquoit Bay surface water Hg concentrations do not fall along a conservative mixing line for these two endmembers (Figure 3, surface water Hg_{TD} and salinity also available in the Supporting Information). This supports the idea that Hg is being leached from the sediments within the subterranean estuary and that SGD is delivering Hg to the surface waters of the bay. Furthermore, the distribution of Hg_{TD} versus salinity in PZ12 (Figure 3), which represents an entirely saline portion of the aquifer, is highly similar to the distribution of Hg_{TD} versus salinity in the surface waters (Figure 3), excepting the fresh and saltwater endmembers. This demonstrates continuity between groundwater and surface water Hg chemistry.

Submarine groundwater discharge contains both fresh and saltwater components, which are characterized by different Hg concentrations. Although a previous study (10) has been able to resolve the saline and fresh fluxes at the head of the bay, the spatial variability of SGD makes it difficult to extend these fluxes to the entire bay. However, we are able to determine a first-order estimate of the SGD-derived Hg_{TD} flux to the bay using a recent estimate of total (saline + fresh) SGD to the entire bay ($37\,000\text{ m}^3\text{ day}^{-1}$; ref 36) and an average groundwater Hg concentration of 50 pM or an effective groundwater endmember concentration of ~ 200 pM (Figure 3; ref 7). This gives a range of 1.9–7.4 mmol of Hg day^{-1} . When normalized to the entire area of Waquoit Bay, the Hg–SGD flux becomes 0.47–1.9 nmol of Hg $\text{m}^{-2}\text{ day}^{-1}$. Because a groundwater endmember concentration <200 pM would dilute the bay, recirculated saline SGD, as opposed to fresh SGD, is the likely source of Hg to the bay. The atmospheric Hg wet deposition flux for Cape Cod is estimated to be 92 ± 11 pmol of Hg $\text{m}^{-2}\text{ day}^{-1}$ from the Mercury Deposition Network site at the Cape Cod National Seashore (MA01; <http://nadp.sws.uiuc.edu/mdn/>). Thus, as a first approximation, SGD–Hg flux appears to be an order of magnitude greater than direct atmospheric Hg wet deposition. The SGD flux reported here was determined during the summer. Michael et al. (11) report that saline discharge is controlled largely by seasonal variation in the water table and that there

is net inflow of seawater during the winter months, potentially decreasing winter SGD and the associated Hg flux.

Because there is likely a net saline inflow to the aquifer during the winter months, it is conceivable that any Hg associated with the bottom sediments of Waquoit Bay could be transported back into the aquifer, thus creating a mercury loop wherein Hg is transported across this high organic matter boundary. Hence, recirculated saline SGD would contain a fraction of Hg that originated from fresh SGD (originally from precipitation to the Waquoit Bay watershed) and a fraction that was recycled from surface bay water. These combined fractions would then account for the large Hg concentrations we observed in mixed groundwater.

We hypothesized that Hg was being deposited onto the aquifer sands, which then acted as a source of Hg to Waquoit Bay. To constrain the amount of Hg that could be discharged into Waquoit Bay, we multiplied the precipitation rate on Cape Cod by the Waquoit Bay watershed area ($5645 \times 10^4\text{ m}^2$; ref 9), which gives a rough estimate of the maximum amount of Hg that can be delivered to the bay annually. This generated a value of 1900 mmol of Hg year^{-1} , which is on the same order of magnitude as values obtained for Hg–SGD flux per year (690–2700 mmol of Hg year^{-1}). This is consistent with the hypothesis that Hg derived from SGD can be supported by atmospheric deposition to the Waquoit Bay watershed. Since potential sinks within the watershed/aquifer have not yet been identified, we cannot fully test this hypothesis.

Given the Waquoit Bay average concentration of ~ 60 pM and a bay volume of $6.3 \times 10^6\text{ m}^3$, the bay inventory is 0.4 mol of Hg. When divided by the upper limit SGD-derived flux, we estimate a residence time for Hg in the bay of ~ 54 days, significantly longer than the ~ 10 day water residence time (36). This disagreement may be that (i) our flux estimates are too low (SGD was not directly quantified during this study), (ii) we may be missing additional sources of new Hg to the bay, or (iii) Hg is being recycled within the bay. We did not measure particulate Hg in the rivers; hence, we are unable to report whether this is a significant source of new Hg. Once Hg enters the bay, a number of processes may influence its flux into and out of the water column. Most notably, Waquoit Bay water column particles and bottom sediments are enriched in organic matter relative to the aquifer materials. These differences will likely cause increased partitioning of Hg onto the solid phase, which would increase the residence time of Hg within the bay.

This study demonstrates the potential importance of SGD for mercury budgets in coastal systems. Total dissolved Hg introduced to the bay through SGD is higher than the flux through atmospheric deposition during the summer months and far greater than the dissolved Hg introduced through riverine input. This is despite the fact that rivers account for a larger percentage of the water budget to Waquoit Bay than precipitation or direct groundwater discharge (9). The main driver of this flux appears to be the low organic carbon content of the aquifer sediments, a characteristic that is common to subterranean estuaries in general (11, 37, 38). This study also demonstrates the complexity of Hg transport within groundwater systems. More research is needed to constrain SGD–Hg flux, elucidate the role of the organic matter-rich bottom sediments, as well as to explore the seasonality of SGD–Hg flux. We predict that SGD may also be an important source of Hg to many other coastal systems, with potential impacts for MMHg production and bioaccumulation in the productive coastal zone.

Acknowledgments

The authors thank Paul Henderson, Adam Rago, and Prae Supcharoen for assistance with sample collection and

analysis. We extend our continued appreciation to the director and staff of the Waquoit Bay National Estuarine Research Reserve for their assistance with logistics during field sampling. S.E.B. was supported through a National Science Foundation (NSF) REU grant to WHOI. This research was supported by a National Science Foundation grant (OCE-0425061) to M.A.C.

Supporting Information Available

Table containing dissolved Hg and Fe data, as well as DOC concentrations, salinity, and dissolved oxygen for the groundwater and surface water. Plot of sedimentary mercury vs sedimentary organic carbon content. Table showing the results from the comparison of two different treatments used to determine dissolved mercury concentrations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- (1) Moore, W. S. The subterranean estuary: A reaction zone of ground water and sea water. *Mar. Chem.* **1999**, *65*, 111–125.
- (2) Moore, W. S. Large groundwater inputs to coastal waters revealed by Ra-226 enrichments. *Nature* **1996**, *380*, 612–614.
- (3) Slomp, C. P.; van Cappellen, P. Nutrient inputs to the coastal ocean through submarine groundwater discharge: Controls and potential impact. *J. Hydrol.* **2004**, *295*, 64–86.
- (4) Montlucon, D.; Sanudo-Wilhelmy, S. A. Influence of net groundwater discharge on the chemical composition of a coastal environment: Flanders Bay, Long Island, New York. *Environ. Sci. Technol.* **2001**, *35*, 480–486.
- (5) Charette, M. A.; Sholkovitz, E. R.; Hansel, C. M. Trace element cycling in a subterranean estuary: Part 1. Geochemistry of the permeable sediments. *Geochim. Cosmochim. Acta* **2005**, *69*, 2095–2109.
- (6) Shaw, T. J.; Moore, W. S.; Kloepfer, J. Sochaski, M. A. The flux of barium to the coastal waters of the southeastern U.S.: The importance of submarine groundwater discharge. *Geochim. Cosmochim. Acta* **1998**, *62*, 3047–3054.
- (7) Charette, M. A.; Sholkovitz, E. R. Trace element cycling in a subterranean estuary: Part 2. Geochemistry of the pore water. *Geochim. Cosmochim. Acta* **2006**, *70*, 811–826.
- (8) Laurier, F. J. G.; Cossa, D.; Beucher, C.; Breviere, E. The impact of groundwater discharges on mercury partitioning, speciation, and bioavailability to mussels in a coastal zone. *Mar. Chem.* **2006**, in press.
- (9) Cambarer, T. C.; Eichner, E. M. Watershed delineation and ground water discharge to a coastal embayment. *Ground Water* **1998**, *36*, 626–634.
- (10) Mulligan, A. E.; Charette, M. A. Intercomparison of submarine groundwater discharge from a sandy unconfined aquifer. *J. Hydrol.* **2006**, *327*, 411–425.
- (11) Michael, H. A.; Mulligan, A. E.; Harvey, C. F. Seasonal oscillations in water exchange between aquifers and coastal ocean. *Nature* **2005**, *436*, 1145–1148.
- (12) Bone, S. E.; Gonnee, M. E. Charette, M. A. Geochemical cycling of arsenic in a coastal aquifer. *Environ. Sci. Technol.* **2006**, *40*, 3273–3278.
- (13) Klaue, B.; Blum, J. D. Trace analyses of arsenic in drinking water by inductively coupled plasma mass spectrometry: High-resolution versus hydride generation. *Anal. Chem.* **1999**, *71*, 1408–1414.
- (14) U.S. EPA. *Method 1631, Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*; U.S. EPA Office of Science and Technology: Washington, DC, 2002; EPA-821-R-02-019.
- (15) Fitzgerald, W. F.; Gill, G. A. Subnanogram determination of mercury by two-stage gold amalgamation applied to atmospheric analysis. *Anal. Chem.* **1979**, *51*, 1714–1720.
- (16) Bloom, N.; Fitzgerald, W. F. Determination of volatile mercury species at the picogram level by low-temperature gas chromatography with cold-vapor atomic fluorescence detection. *Anal. Chim. Acta* **1988**, *208*, 151–161.
- (17) Hall, G. E. M.; Vaive, J. E.; Beer, R.; Hoashi, M. Selective leaches revisited with emphasis on the amorphous Fe oxyhydroxide phase extraction. *J. Geochem. Explor.* **1996**, *56*, 59–78.
- (18) Hammerschmidt, C. R.; Fitzgerald, W. F. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* **2004**, *38*, 1487–1495.
- (19) Zelewski, L. M.; Krabbenhoft, D. P.; Armstrong, D. E. Trace metal concentrations in shallow groundwater. *Ground Water* **2001**, *39*, 485–491.
- (20) Krabbenhoft, D. P.; Gilmour, C. C.; Benoit, J. M.; Babiary, C. L.; Andren, A. W.; Hurley, J. P. Methyl mercury dynamics in littoral sediments of the temperate seepage lake. *Can. J. Fish. Aquat. Sci.* **1998**, *55*, 835–844.
- (21) Barringer, J. L.; Szabo, Z.; Schneider, D.; Atkinson, W. D.; Gallagher, R. A. Mercury in groundwater, seepage, leach-field effluent, and soils in residential areas, New Jersey coastal plain. *Sci. Total Environ.* **2006**, *361*, 144–162.
- (22) Tiffreau, C.; Kutzenkirchen, J.; Behra, P. Modeling the adsorption of mercury(II) on (hydr)oxides. *J. Colloid Interface Sci.* **1995**, *172*, 82–93.
- (23) MacLeod, C. L.; Borcsik, M. P.; Jaffe, P. R. Effect of infiltrating solutions on the desorption of mercury from aquifer sediments. *Environ. Technol.* **1996**, *17*, 465–475.
- (24) Lamborg, C. H.; Fitzgerald, W. F.; Skoog, A.; Visscher, P. T. The abundance and source of mercury-binding organic ligands in Long Island Sound. *Mar. Chem.* **2004**, *90*, 151–163.
- (25) Laurier, F. J. G.; Cossa, D.; Gonzalez, J. L.; Breviere, E.; Sarazin, G. Mercury transformations and exchanges in a high turbidity estuary: The role of organic matter and amorphous oxyhydroxides. *Geochim. Cosmochim. Acta* **2003**, *67*, 3329–3345.
- (26) Ravichandran, M. Interactions between mercury and dissolved organic matter—A review. *Chemosphere* **2004**, *55*, 319–331.
- (27) Tseng, C. M.; Amouroux, D.; Abril, G.; Tessier, E.; Etcheber, H.; Donard, O. F. X. Speciation of mercury in a fluid mud profile of a highly turbid macrotidal estuary (Gironde, France). *Environ. Sci. Technol.* **2001**, *35*, 2627–2633.
- (28) Sunderland, E. M.; Gobas, F. A. P. C.; Branfireun, B. A.; Heyes, A. Environmental controls on the speciation and distribution of mercury in coastal sediments. *Mar. Chem.* **2006**, *102*, 111–123.
- (29) Hammerschmidt, C. R.; Fitzgerald, W. F. Methylmercury cycling in sediments on the continental shelf of southern New England. *Geochim. Cosmochim. Acta* **2006**, *70*, 918–930.
- (30) Hammerschmidt, C. R.; Fitzgerald, W. F.; Lamborg, C. H.; Balcom, P. H.; Tseng, C. M. Biogeochemical cycling of methylmercury in lakes and tundra watersheds of Arctic Alaska. *Environ. Sci. Technol.* **2006**, *40*, 1204–1211.
- (31) Han, S.; Gill, G. A.; Lehman, R. D.; Choe, K.-Y. Complexation of mercury by dissolved organic matter in surface waters of Galveston Bay, Texas. *Mar. Chem.* **2006**, *98*, 156–166.
- (32) Hsu, S.; Sedlak, D. L. Strong Hg(II) complexation in municipal wastewater effluent and surface waters. *Environ. Sci. Technol.* **2003**, *37*, 2743–2749.
- (33) Stordal, M. C.; Gill, G. A.; Wen, L. S.; Santschi, P. H. Mercury phase speciation in the surface waters of three Texas estuaries: Importance of colloidal forms. *Limnol. Oceanogr.* **1996**, *41*, 52–61.
- (34) Barkay, T.; Miller, S. M.; Summers, A. O. Bacterial mercury resistance from atoms to ecosystems. *FEMS Microbiol. Rev.* **2003**, *27*, 355–384.
- (35) Rolfhus, K. R.; Fitzgerald, W. F. The evasion and spatial/temporal distribution of mercury species in Long Island Sound, CT-NY. *Geochim. Cosmochim. Acta* **2001**, *65*, 407–418.
- (36) Charette, M. A.; Buesseler, K. O.; Andrews, J. E. Utility of radium isotopes for evaluating the input and transport of groundwater-derived nitrogen to a Cape Cod estuary. *Limnol. Oceanogr.* **2001**, *46*, 465–470.
- (37) Windom, H.; Niencheski, F. Biogeochemical processes in a freshwater–seawater mixing zone in permeable sediments along the coast of Southern Brazil. *Mar. Chem.* **2003**, *83*, 121–130.
- (38) Duncan, T.; Shaw, T. J. The mobility of rare earth elements and redox sensitive elements in the groundwater–seawater mixing zone of a coastal shallow aquifer. *Aquat. Geochem.* **2003**, *9*, 233–255.

Received for review September 20, 2006. Revised manuscript received January 26, 2007. Accepted February 7, 2007.

ES0622453