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, Dept. of Marine Chemistry and Geochemistry, Woods Hole, MA 02543 USA
[§]now at: University of California, Berkeley, Dept. of Civil and Environmental Engineering, Berkeley, CA 94720 USA
sbone@nature.berkeley.edu
(510) 643-9951

Abstract:

Total dissolved Hg (Hg_{TD}) was measured in groundwater, aquifer sediments, and surface water in Waquoit Bay (Massachusetts, USA). It was found that the total dissolved Hg (range: <3.2-262 pM) was being released within the subterranean estuary, with similarly high levels (range: 18-256 pM) of total dissolved Hg found in the surface waters of the bay. None of the dissolved species (DOC, chloride, Fe) normally observed to influence Hg partitioning correlated well with the observed Hg_{TD} 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. A subset of the core sediments was subjected to batch equilibria experiments in which the sediment was incubated in a synthetic DOC or NaCl solution, or groundwater from the study site. These experiments and the sediment data revealed that the solid-solution Hg partitioning (K_d) was controlled by the organic carbon content of the sediments; the K_d for total Hg ranged from 20-91 L/Kg, far lower than partition coefficients normally observed in estuarine systems. It was hypothesized that this was due to the extremely low organic carbon content that are typical of the aquifer sediments. Lastly, it was estimated that submarine groundwater discharge supplied 0.47-1.9 nmol Hg m^{-2} d^{-1} to the bay, which is an order of magnitude higher than the atmospheric deposition rate for the northeastern USA.

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. Hydraulic gradients force water from the subterranean estuary into adjacent marine waters.

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 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.

Changing redox conditions and salinity gradients present in surface estuaries are observed to influence the partition coefficient of Hg, thereby dictating its release into the water column (*8,9*). The redox and salinity gradients that regulate Hg release in surface estuaries are also present in subterranean estuaries. The goal of this study is to outline the transport of Hg through a subterranean estuary located at the Waquoit Bay National Estuarine Research Reserve in Cape Cod, MA. This is done by 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. Furthermore, select samples from these cores were incubated in natural groundwater as well as synthetic NaCl and DOC solutions to obtain partition coefficients under a variety of potential environmental conditions present within the aquifer.

Methods

Study Site. The study site is located at the Waquoit Bay National Estuarine Research Reserve along the south shore of Cape Cod, Massachusetts. The subterranean estuary is located in a sandy, permeable aquifer that discharges along a narrow band at the head of Waquoit Bay (*5*). Because of the high permeability of Cape Cod soils in this region, a large percentage of the local precipitation recharges the aquifer, as opposed to becoming surface water runoff. As a result, the residence time for water in the aquifer is relatively short, on the order of 10-50 years (*10*). The rate of groundwater flow between sampling wells (discussed under sampling methods) located ~2 m apart is on the order of a few days (*11*). Waquoit Bay is shallow (1 m in most places), and is connected to Vineyard Sound by a narrow channel 3.6 km from where the subterranean estuary discharges into the bay. In addition to the coastal aquifer, Waquoit Bay is fed by the Quashnet and Childs Rivers, which are largely groundwater fed.

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, while movement due to upward diffusion is very minor (*11*). It is important to note that the location of the mixing zone within the Waquoit Bay coastal aquifer varies seasonally (*12*). During the winter when freshwater recharge is highest, this interface moves seaward; during the summer when the water table drops the interface moves landward. As noted by Michael et al. (12), this seasonality may influence the chemistry of the sediments.

The Waquoit Bay subterranean estuary exhibits an active Fe redox cycle. Previous studies have observed a large Fe plume that enters the subterranean estuary with the terrestrially derived groundwater (*13*). 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 (*7,14*). It has been hypothesized that the Fe precipitation results from the mixing of low pH fresh groundwater with recirculated alkaline baywater (*15*). Fe is remobilized under reducing conditions within the saline portion of the aquifer. 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 spatially, both 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 eight-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 fresh and saline groundwater), and every 0.3-0.6 m elsewhere. Samples were filtered in the field using an inline 0.45 μm Pall AquaPrep 600 filter. Procedural blanks were collected by pumping MilliQ (18.2 MΩ) water through the entire system. 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-μm 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 μL of 8N 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 ~1.5 m deep and came from a section of the aquifer that corresponds to piezometer well 3 (Figure 1). 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 crystalline Fe (hydr)oxides (*5*).

Analyses. At least 12 hours before analysis, 100 μL 30% H_2O_2 was added to the 15 mL Hg groundwater samples (*14*). This method was originally adapted from Klaue and Blum (*16,14*) for treatment of dissolved As samples, but was used here to treat Hg samples. Samples from piezometer 11 (PZ11) were treated with 100 μL BrCl followed by 40 μL NH_2OH, as per EPA Method 1631, Revision E (*17*). In all samples, dissolved Hg was then determined using dual gold-amalgamation cold-vapor atomic fluorescence spectroscopy (*18,19*) using a Tekran CVAFS Mercury Detector 2500.

In order to establish the equivalence between total dissolved Hg samples treated with BrCl/NH_2OH and H_2O_2, 22 samples from 2 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 farther up the beach and is predominantly fresh, with the mixing zone occurring at depth. All samples were equivalent to within 11% (see Supplemental 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 IRMS at the UC-Davis Stable Isotope Facility. The sample inorganic carbon is converted to CO_2 with phosphoric acid, and sodium persulfate is 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. (*20*). Briefly, 15 mL of 1M-hydroxylamine hydrochloride in 25% acetic acid was added to approximately 0.4 g sediment and then heated in an oven at 90°C for three hours. 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.Sediment standard MESS-3 was subjected to a concentrated acid leach, in which the sediments were heated to 90°C for 16 hours in 16N HNO_3 in Teflon bombs. The mean sedimentary Hg concentration determined for MESS-3 (n=3) was 98 μg/Kg +/- 7 ug/Kg. The standard value is 91 μg/Kg +/- 9ug/Kg.

Sediments from three depths were used in Hg leaching experiments designed to simulate field conditions in the laboratory. Two sediment samples were taken from core 3; 3-1 was Fe-rich/OC-poor (6020 mg/kg Fe and 0.008% OC) and 3-17 was Fe-poor/OC-rich (906 mg/kg Fe and 0.030% OC) (5). One sediment sample was taken form core 2 (2-41), and was Fe-rich/OC-poor (2800 mg/kg Fe and 0.014% OC). Twenty mL of leaching solution (see below) was added to 3.5 g of sediment in a 60-mL centrifuge tube and allowed to shake for 24 hours. The samples were then centrifuged at 2000 rpm for 15 minutes and filtered using 0.2 μm Whatman nylon filters that had been washed in 1 M NaOH and MilliQ water. After filtration into 60-mL HDPE or 15-mL LDPE vials, 100 μL of BrCl was added to the solution followed by 40 μL NH_2OH, and the samples were analyzed via CVAFS, as before. The pH of the solution was measured before addition to the sediment as well as after removal from the sediment (but before filtration).

The leaching solutions consisted of MilliQ water, 0.0015 M Cl^-, 0.4 M Cl^-, 40 μM DOC and 800 μM DOC. The DOC solutions were made by adding IHSS Suwannee River Natural Organic Matter (#1R101N) to MilliQ water. Chloride and DOC concentrations were chosen to bracket the range of values observed at the study site. The pH of these solutions was adjusted to between 6.5 and 7.0 before addition to the sediments with a phosphate buffer solution. Additionally, the sediments were exposed to four groundwater samples taken from the sampling site (which correspond to groundwater from PZ3). No attempt was made to maintain the original redox potential of the groundwater, although ORP values were measured during sampling. The groundwater samples were chosen to cover a range of salinities from <1 to >24 (see Supplemental Information for chemical parameters of groundwater). The partition coefficient ($K_D = [Hg]_{sediment, exchangeable}/[Hg]_{dissolved}$ in L/Kg) was determined for each leaching solution-sediment sample pair by dividing the Hg concentration in the sediment sample, as determined by the acetic acid leach ("L3+L4" leach), by the dissolved concentration of Hg left in the leaching solution after equilibration.

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 is also presented in table format in the Supplemental Information.

DOC is generally higher in the upper 1.5 m of the groundwater profiles, decreases toward the fresh-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 pM), in the entirely freshwater portion of the aquifer (PZ10), and elevated in the entirely saltwater portion of the aquifer (PZ12). PZ7 and 6 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, as the freshwater-saltwater interface occurs at an intermediate depth. 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 (~2.5-4.5 m). In PZ3 this effect is more dramatic; Hg_{TD} has a well-defined peak that occurs concurrent with the dissolved Fe minimum. Though 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 (*21*).

Examination of the Hg_{TD} vs. salinity piezometer plots demonstrates 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. PZ7 and 6, 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 3, which represent the mixing zone, Hg increases at zero salinity, peaks around mid salinity, and declines slightly toward higher salinities, especially in PZ3. PZ11 and 3 thus represent the area of the aquifer in which Hg is being released from the solid phase.

Hg mobilization within the subterranean estuary. It is apparent from these groundwater profiles 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 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 is chloride. Additionally, in a study of the Seine estuary, Laurier et al. (*25*) found that the easily reducible fraction, the fraction that contains inorganic-Hg complexes and labile organic-Hg complexes, did not vary with salinity, supporting the hypothesis that Hg speciation is still largely governed by the formation of non-labile Hg-organic matter complexes, even at high salinities. 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, especially those where Hg is introduced to the system through precipitation (as opposed to introduction via wetlands), even when a relationship between the two solutes does, in fact, exist.

Furthermore, dissolved Hg concentrations in the subterranean estuary do not appear to be controlled by precipitation/dissolution dynamics of Fe in the way that As is for this system (*14*). As noted, Hg concentrations in solution are low in the freshwater plume carrying dissolved Fe at PZ10, 7 and 6, and only vaguely correlative with Fe in PZ11, 3 and 12 at depth. Were Hg co-precipitating with Fe as the freshwater plume mixes with seawater, the profiles of these two metals should look more alike. This is in contrast to work suggesting just such a removal mechanism for Hg (*8*).

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 location. These loadings provide the material that is then partitioned according to the presence or absence of the agents listed above. Seasonal variation in the fresh-saltwater interface necessarily changes the vertical location of the pycnocline, and thus 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 during the wet season (late-winter/early spring) when these sands are in the freshwater zone, and then be released when these sands are inundated with salt water during the dry season (summer).

Hg Batch Equilibria. In order to elucidate the mechanism by which Hg is released into the aqueous phase within the subterranean estuary, a series of batch equilibria experiments were performed. The results are summarized in the Supplemental Information. It appears that neither of the salt solutions (0.0015 M Cl^- or 0.4 M Cl^-) decreased the partition coefficient below that observed for sediment treated with MilliQ water. For all three sediment samples, the partition coefficient decreased with increasing DOC concentration. Hence, our results corroborate the conclusion that the DOC concentration is a far more important factor than the salinity in regulating the partition coefficient.

The groundwater chosen for these experiments was chosen because it covered the mixing zone in a profile equivalent to PZ3, and exhibited a range of salinities with relatively similar DOC concentrations (25-90 μM). However, there was no significant difference observed between treatments for any of the sediment samples, although sample 3-17 (high OC, low Fe) showed much higher partition coefficients across all groundwater types compared to either 3-1 or 2-41 (low OC, high Fe). The average partition coefficient values were also higher for 3-17 sediments treated with MilliQ water, 40 μM DOC, and 800 μM DOC. This is in agreement with the fact that high Hg_{TD} concentrations were observed for groundwater in the region of the iron curtain.

Sedimentary Hg, as determined by the L3+L4 leach, was seen to vary with sedimentary OC content (r^2=0.82, n=9, Supplementary Information). This, in conjunction with the results from the batch equilibria experiments, indicates that Hg is far more sensitive to changes in the OC content of the sediments than to changes in the Fe (hydr)oxide type or content. Sedimentary OC content has previously been shown to strongly influence Hg partitioning in natural systems (*27*). Hammerschmidt et al. (*21*) showed that, for both inorganic Hg and monomethylmercury (MMHg), the 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 (*28*), and several Alaskan lakes (*29*).

The magnitude of the measured partition coefficients is low. The partition coefficients obtained during our batch equilibria experiments were far lower than expected. The log K_D values observed in natural systems are usually between 3 and 6 (*21*), while those we observed were often less than 1 (range in K_D= 20-91 L/Kg). Because the core samples and groundwater samples do not directly correspond to each other (they were not taken at the same time, or the exact same location), it is not possible to determine partition coefficients for the field data. However, we can get a range for the partition coefficient by comparing the highest and lowest Hg_{TD} concentrations to the highest and lowest sedimentary Hg concentrations. This gives a large range (logK_D ranges from <1 to ~4). A logK_D of 4 is within the range typically observed in natural systems, however, it is far greater than any of the partition coefficients measured during the incubation experiments. 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 logK_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 compared to many lake and estuarine sediments (<0.1% OC, as compared to >5% LOI) (*21,28*), 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)) v. %LOI (comparable to our %OC; OC is approximately equal to half LOI) provided in Hammerschmidt et al. (*21,28,29*), the 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 in Hammerschmidt et al (*21,28,29*), thus the range of Hg concentrations measured in our system are 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 v. %LOI plot changes as the %LOI approaches zero. Additionally, the equilibrium constant for Hg-organic complexes is dependent on the source of the organic matter (*24,30,31*), and thus differences in OM type and age between the Waquoit Bay study site and those studied by Hammerschmidt and colleagues 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 $\log K_{D,OC}$~0.89-3.3), suggesting the OC in the system is of a kind that is not sorbing well to the solid phase, or that these sands are not good at hosting this organic material.

Additionally, it should be noted that we are comparing partition coefficients derived for total mercury to partition coefficients determined for Hg(II) in Hammerschmidt et al. (*21,28,29*). If the total Hg measured at our study site existed largely as MMHg or Hg^0, the partition coefficients would be lower than those expected for total Hg that contained a greater amount of Hg(II). MMHg is observed to exhibit lower partition coefficients than Hg(II) (*21,28,29*), and it is expected that Hg^0 would have a very low partition coefficient due to its volatility.

In addition to the effects that Hg speciation and sedimentary OC type and concentration may have on the partition coefficient, it is also possible that the measured partition coefficients could appear to be low due to a colloidal effect, i.e. it is possible that the dissolved Hg measured here is in fact composed of both truly dissolved and colloidal Hg. If a large portion of the dissolved Hg is in fact colloidal then the partition coefficients we obtained would be biased towards smaller values. Stordal et al. (*32*) concluded that a large fraction of Hg existed in the colloidal form, and that variation in the partition coefficient was actually caused by variation in colloidal Hg. Based on this study, Sunderland et al. (*27*) speculated that low partition coefficients obtained for coastal sediments in the Bay of Fundy could be due to the prevalence of colloidal Hg complexes in the "dissolved" fraction.

Hg_{TD} in the Surface Water of Waquoit Bay. The Hg_{TD} concentration was determined for Vineyard Sound (the salt water end member for 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 (*33*). 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 Supplemental Information), which 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, it can be seen that the distribution of Hg_{TD} vs. salinity in PZ12 (Figure 3), which represents an entirely saline portion of the aquifer, is highly similar to the distribution of Hg_{TD} vs. salinity in the surface waters (Figure 3), excepting the fresh and saltwater endmembers. This demonstrates continuity between groundwater and surface water Hg chemistry.

Using a recent estimate of total SGD to the bay (37,000 m^3 d^{-1}; *34*) and an average groundwater Hg concentration of 50 pM or an effective groundwater endmember concentration of ~200 pM (Figure 3; *7*), the SGD-derived flux of Hg_{TD} is between 1.9-7.4 mmol Hg d^{-1}. When normalized to the entire area of Waquoit Bay, this flux becomes 0.47-1.9 nmol Hg m^{-2} d^{-1}, which is an order of magnitude higher than the atmospheric deposition rate for Hg for nearby Long Island Sound (110 ± 27 pmol Hg m^{-2} d^{-1}; *35*). Given the Waquoit Bay Hg average concentration of ~60 pM and a bay volume of 6.3 x 10^6 m^3, the bay inventory is 0.4 mol Hg. When divided by the upper limit SGD-derived Hg flux, we estimate a residence time for Hg in the bay of ~54 days, significantly longer than the ~10 day water residence time (*34*). This disagreement may be that (1) our flux estimates are too low (SGD was not directly quantified during this study), (2) we may be missing additional sources of "new" Hg to the bay, or (3) that Hg is being recycled 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, and far greater than the 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 do either precipitation or direct groundwater discharge (*10*). 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 (*36,37,12*). Thus we predict that SGD may be an important source of Hg to coastal systems, with potential impacts for MMHg production and bioaccumulation in the productive coastal zone.

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Figure Captions

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

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

Figure 3. Hg in groundwater and surface water versus salinity. Surface water Hg is shown in all plots as black circles. Groundwater Hg is shown as empty circles. The grey 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.

Figure 1

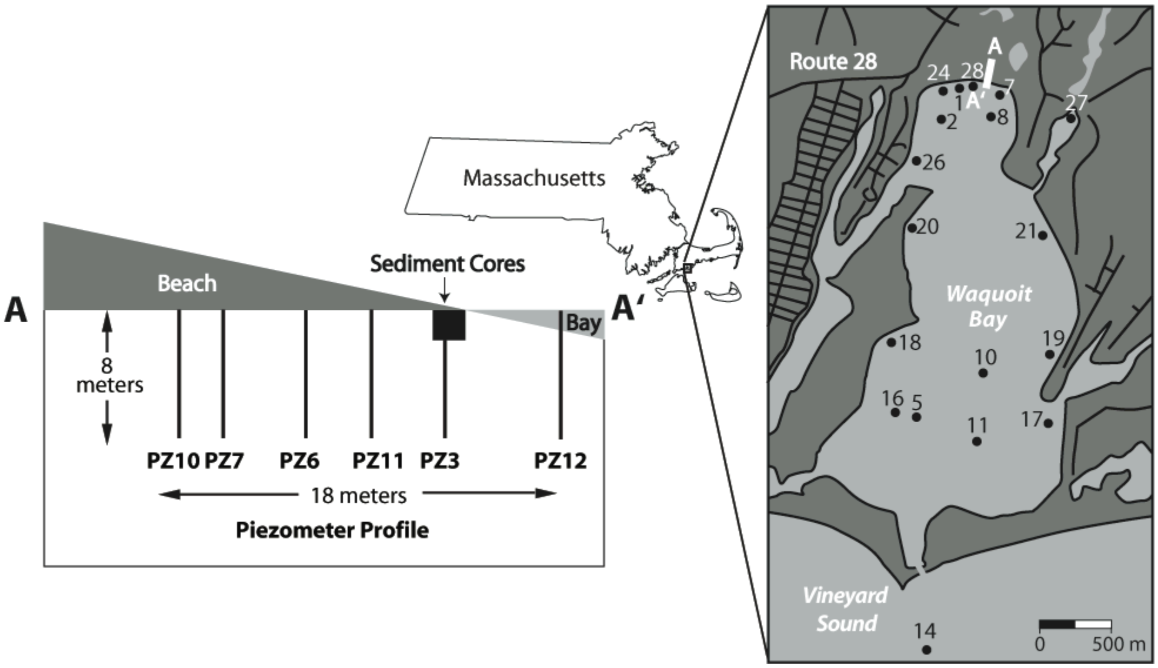

A
Beach
Sediment Cores
Bay
A′
8 meters
PZ10
PZ7
PZ6
PZ11
PZ3
PZ12
18 meters
Piezometer Profile
Massachusetts
Route 28
A
A′
24
28
1
7
2
8
27
26
20
21
Waquoit Bay
18
10
19
16
5
11
17
Vineyard Sound
14
0
500 m

Figure 2

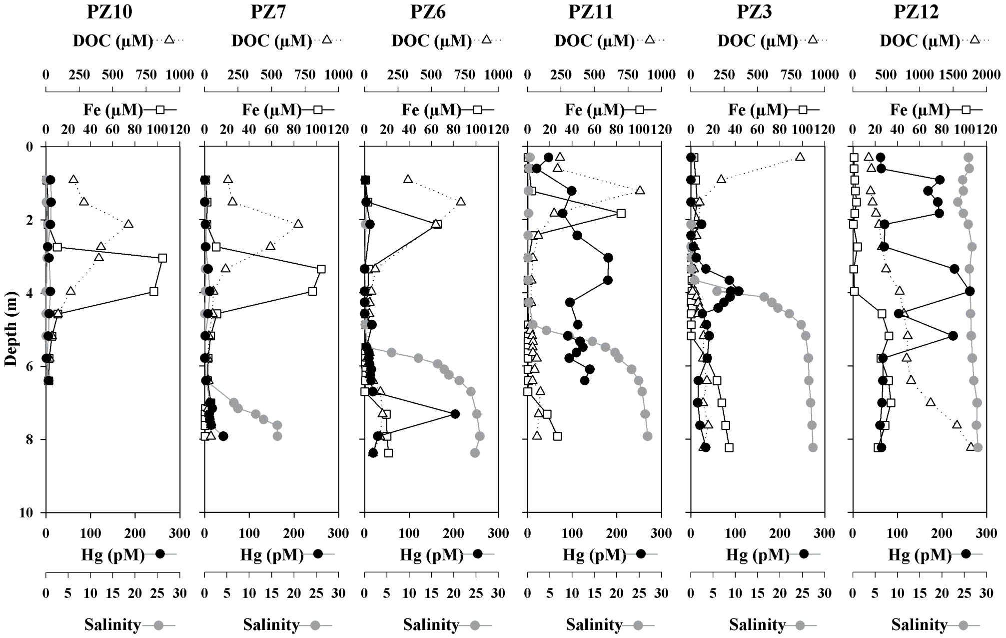
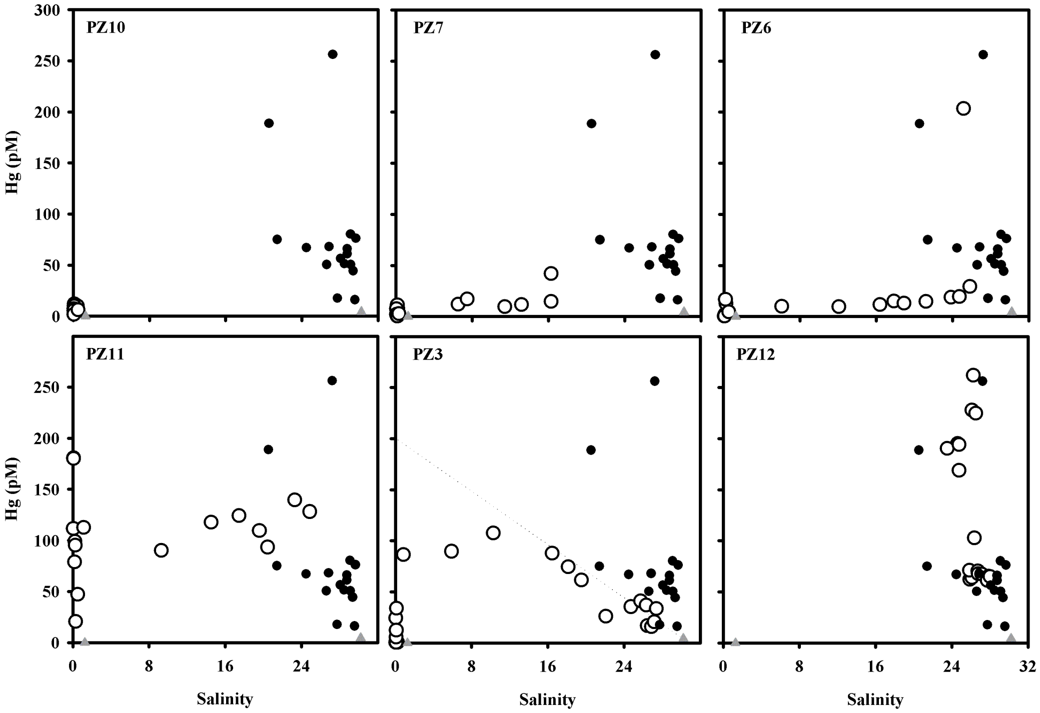

PZ10
PZ7
PZ6
PZ11
PZ3
PZ12
DOC (µM)
0 250 500 750 1000
0 500 1000 1500 2000
Fe (µM)
0 20 40 60 80 100 120
Depth (m)
0 2 4 6 8 10
Hg (pM)
0 100 200 300
Salinity
0 5 10 15 20 25 30

Figure 3


PZ10
PZ7
PZ6
PZ11
PZ3
PZ12
Hg (pM)
Hg (pM)
300
250
200
150
100
50
0
0
8
16
24
32
Salinity
Salinity
Salinity