

Submarine Groundwater Discharge of Total Mercury and Methylmercury to Central California Coastal Waters

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Fluxes of total mercury (Hg_T) and monomethylmercury (MMHg) associated with submarine groundwater discharge (SGD) at two sites on the central California coast were estimated by combining measurements of Hg_T and MMHg in groundwater with the use of short-lived, naturally occurring radium isotopes as tracers of groundwater inputs. Concentrations of Hg_T were relatively low, ranging from 1.2 to 28.3 pM in filtered groundwater, 0.8 to 11.6 pM in filtered surface waters, and 2.5 to 12.9 pM in unfiltered surface waters. Concentrations of MMHg ranged from <0.04 to 3.1 pM in filtered groundwater, <0.04 to 0.53 pM in filtered surface waters, and 0.07 to 1.2 pM in unfiltered surface waters. Multiple linear regression analysis identified significant ($p < 0.05$) positive correlations between dissolved groundwater concentrations of Hg_T and those of NH_4^+ and SiO_2 , and between dissolved groundwater concentrations of MMHg and those of Hg_T and NH_4^+ . However, such relationships did not account for the majority of the variability in concentration data for either mercury species in groundwater. Fluxes of Hg_T via SGD were estimated to be $250 \pm 160 \text{ nmol day}^{-1} \text{ m}^{-1}$ of shoreline at Stinson Beach and $3.0 \pm 2.0 \text{ nmol m}^{-2} \text{ day}^{-1}$ at Elkhorn Slough. These Hg_T fluxes are substantially greater than net atmospheric inputs of Hg_T reported for waters in nearby San Francisco Bay. Calculated fluxes of MMHg to coastal waters via SGD were $10 \pm 12 \text{ nmol day}^{-1} \text{ m}^{-1}$ of shoreline at Stinson Beach and $0.24 \pm 0.21 \text{ nmol m}^{-2} \text{ day}^{-1}$ at Elkhorn Slough. These MMHg fluxes are similar to benthic fluxes of MMHg out of surface sediments commonly reported for estuarine

and coastal environments. Consequently, this work demonstrates that SGD is an important source of both Hg_T and MMHg to coastal waters along the central California coast.

Introduction

Mercury is a toxic heavy metal found at elevated levels in the environment due to anthropogenic activities (1, 2). Methylated forms of mercury are the most toxic, with monomethylmercury (MMHg) being of most concern for ecological and human health because it is readily biomagnified in aquatic food chains (3, 4). Wildlife are at risk because of environmental mercury exposure (5), and elevated mercury levels have resulted in fish consumption advisories for some freshwater, estuary, and coastal areas in North America and Europe. Although fish represent an important protein source for humans and fisheries form the economic backbone of many coastal areas, the consumption of fish is also the pathway responsible for most human exposure to mercury (3). However, many aspects of mercury's cycling in marine ecosystems remain unknown (6, 7), among them the source of MMHg that is biomagnified to potentially toxic levels.

Although elevated levels of mercury in groundwater and soil pore waters have been reported in coastal plains (8, 9) and the potential importance of groundwater-surface water interactions in the migration of mercury has been suggested (10), groundwater was not previously believed to be an important transport medium for mercury in the environment (11). Recent studies of mercury dynamics in subterranean estuaries in Massachusetts (12) and northern France (13) have suggested that the flux of total mercury (Hg_T) to the ocean via groundwater discharge may be more important than previously believed, and may even be the dominant input of mercury to some coastal systems. These new results corroborate research over the last two decades demonstrating that groundwater inputs of nutrients and pollutants to coastal zones can be substantial and significantly affect coastal ecosystems (14–18). There have been very few studies of MMHg in groundwater, and we are not aware of any reports on MMHg fluxes in submarine groundwater discharge (SGD). Despite this, given concentrations of MMHg in groundwater elsewhere (10, 19) and recent reports of Hg_T in groundwater discharge to coastal ecosystems (12, 13), SGD may represent a previously unidentified source of MMHg to coastal waters.

The potential for subterranean estuaries to be an important source of mercury to marine waters is exceptionally high along the central California coast. The reasons for this are: (1) the area's location within the highly mineralized circum-Pacific mercury belt and the existence of several large economic mercury deposits responsible for the contamination of surface waters in the region (20, 21), (2) the presence of oil-bearing rock formations along the central California coast coupled with the co-occurrence of mercury with hydrocarbon deposits (22, 23), (3) the same geothermal processes responsible for past mercury mineralization and association with metalliferous deposits may result in currently active hydrothermal systems that are prevalent in the region being a source of mercury to groundwater (23, 24), and (4) anthropogenic activities (e.g., mining and industrial processes) have created a large reservoir of contaminant mercury at the land-sea interface in central California (25), much of which exists in soils and unconsolidated sediment where the mercury may be methylated and subsequently advected and discharged to coastal waters via SGD.

Here we describe measurements of Hg_T , MMHg, and nutrients (NH_4^+ , NO_3^- , PO_4^{3-} , and SiO_2) in groundwater and

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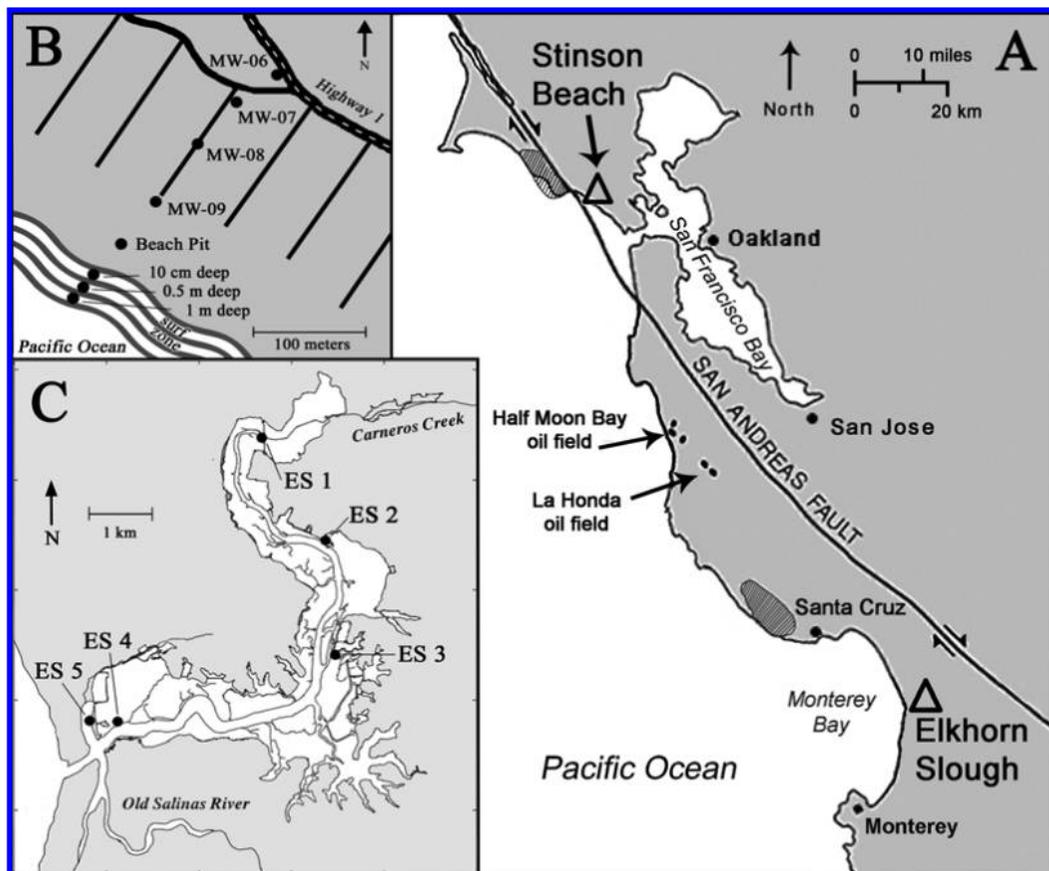


FIGURE 1. (A) Location of the study sites, Stinson Beach and Elkhorn Slough, on the central California coast. Cross-hatched areas in A denote location of oil-bearing sandstone intrusions. (B) Location of sampling wells and surface water sites at Stinson Beach. (C) Sites of groundwater and surface water sample collection at Elkhorn Slough.

adjacent surface waters at two locations along the central California coast. These data were combined with measurements of naturally occurring radium (Ra) isotopes and other hydrological parameters to calculate SGD related fluxes of mercury species and elucidate the role of other variables controlling these fluxes. We present the first reported estimates of MMHg fluxes to coastal waters via SGD, and discuss the importance of SGD as a source of Hg_r and MMHg to coastal ecosystems relative to other sources.

Materials and Methods

Study Sites. Stinson Beach (Figure 1) is an open-ocean, southwest-facing, reflective beach composed principally of medium grain sand with mixed semidiurnal tides and a high energy surf zone. The central California coast is characterized by a Mediterranean climate, with rainfall occurring predominately during the winter between November and April. Land cover in the area is primarily forested, but a small coastal town using individual septic systems for wastewater disposal is located along the beach. Microbial pollution and elevated nutrient levels have been documented in the subsurface, as has groundwater discharge to the Pacific Ocean (26). The unconfined aquifer is composed primarily of beach and dune sands underlain by lacustrine clay, which in turn is underlain by an assemblage of highly fractured sandstone, limestone, and shale (26).

Stinson Beach is located near the San Andreas Fault system (Figure 1), which is associated with mercury mineralization in the region (23). Groundwater movement along faults might therefore encounter naturally occurring mercury in the subsurface before discharging to the ocean. Stinson Beach is also located near oil-bearing sandstone units, the weathering of which may release mercury into local groundwater.

Discharge of nutrient-rich septic effluent to shallow groundwater results in reducing conditions within a few meters of the water table, which could increase microbial MMHg production and export from the surficial aquifer.

Elkhorn Slough is a small, shallow (mean depth ~2.5 m), tidally flushed estuary that empties into Monterey Bay (Figure 1). The estuary is comprised of a main channel that reaches approximately 11 km inland and numerous tidal creeks and wetlands that surround the main channel. Mudflats comprise ~59% of Elkhorn Slough's area, and intertidal salt marshes an additional ~29% (27). Freshwater inputs are minimal, and in the winter rainy season are limited to Carneros Creek at the head of the slough, and in the summer dry season to the Old Salinas River channel near the mouth of the slough via Moss Landing Harbor. The estuary's tidal prism accounts for 60–75% of the mean estuary volume (28). Estimates of mean water residence time in Elkhorn Slough's main channel are on the order of ~1 day, but can be substantially greater in the tidal flats and upper reaches of the slough during the dry season (28).

The regional water table near Elkhorn Slough has experienced substantial overdraft because of intensive agricultural practices, and saltwater intrusion has become increasingly common (27). As a result, advective inputs of fresh groundwater represent only a minor source of freshwater to the slough. Nevertheless, recent work suggests that tidally controlled recirculated seawater through wetland sediments is significant and can account for 12% of the water volume of the slough daily (29). Elkhorn Slough is surrounded by large tracts of wetlands, which are hotspots for the production of MMHg (30–32). We hypothesized that the tidally driven seawater recirculation through surficial marsh sediments that

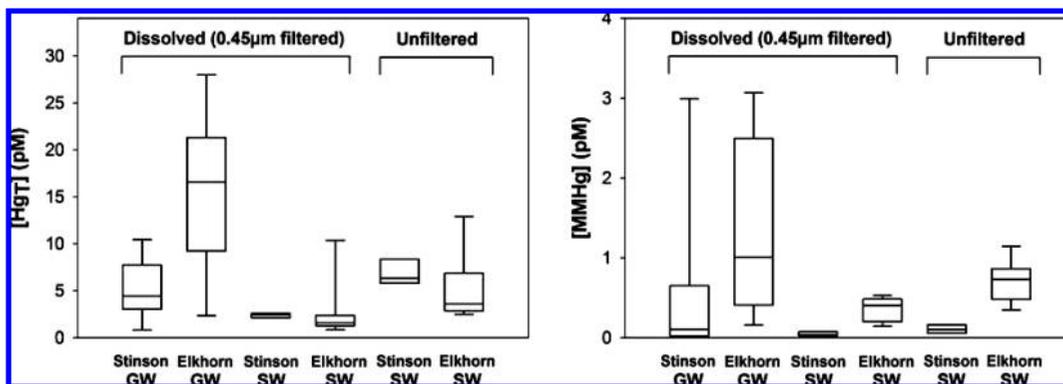


FIGURE 2. Box plots of Hg_T and MMHg concentrations in 0.45 μm filtered and unfiltered groundwater (GW) and surface waters (SW) at Elkhorn Slough and Stinson Beach. The median is represented by the middle line of each box, hinges represent the 25% quartiles, and whiskers represent the 5 and 95 percentiles.

results in substantial transfer of nutrients to the slough and adjacent coastal waters (29) would also transport MMHg.

Sample Collection. Groundwater and surface seawater samples were collected along ~ 300 m cross-shore transects at Stinson Beach (Figure 1) on October 31, 2007 (one transect at high tide) and July 7, 2008 (one transect at low tide, a second transect at high tide). Filtered (0.45 μm) groundwater samples were collected from one hand-dug pit in the beach zone and four inland wells with PVC casings installed to depths of 3–6 m such that they intersect the unconfined coastal aquifer within 250 m inland of the high tide line (see de Sieyes et al. (26)). Filtered and unfiltered surf zone seawater was collected along cross-shore transects (3 sample points per transect) extending ~ 20 m out into the surf zone, where water depths were approximately 10 cm, 0.5 m, and 1 m.

Filtered and unfiltered surface waters and filtered groundwater were collected at Elkhorn Slough along an ~ 10 km transect (Figure 1) on June 18, 2008, from the head of the slough to its mouth. On June 19, 2008, multiple samples were collected at a single point (ES 2) as part of a seven hour time series. At each sampling site or time in Elkhorn Slough, a groundwater sample (from a 1–2 m deep hand-dug pit employed to retrieve groundwater from the surficial unconfined aquifer) and adjacent surface water samples were collected as close together temporally and spatially as possible.

Both groundwater and surface water samples were collected using trace metal clean techniques with the use of a peristaltic pump using Teflon sampling lines with C-Flex tubing in the pump head. Methods for acid cleaning sample bottles, filters, and tubing are in the Supporting Information. Filtered water samples were collected using an acid cleaned 0.45 μm polypropylene cartridge filter (Osmonics) fitted to the end of the sample line. Because the advection of sediment- or particle-associated nutrients or mercury species is unlikely in the subsurface on time scales of interest to our study, filtered (0.45 μm) groundwater samples were collected at all sites, but only limited sampling of unfiltered groundwater was undertaken. Samples for Hg_T and MMHg were collected in acid-cleaned Teflon bottles, placed on ice in the field, and kept cold and dark until transported back to the laboratory where they were preserved the same evening. Samples for Hg_T were preserved by amendment to 1% BrCl, except for organic rich unfiltered groundwater, which was amended to 2% BrCl. MMHg samples were preserved by amendment to either 18 mM H_2SO_4 (saline and brackish samples) or 30 mM HCl (low salinity samples). Samples were stored in the dark at either 4 $^{\circ}C$ (MMHg samples) or room temperature (Hg_T samples) and were analyzed within 2 months of collection.

Dissolved radium was extracted from ~ 100 L water samples in the field by filtering through columns of MnO_2 -impregnated acrylic fiber at a flow rate not exceeding 1 L

min^{-1} (33, 34). Untreated acrylic fiber plugs were used to prevent the contamination of the MnO_2 fiber with particulate matter. The fibers were removed from the columns and stored in plastic bags until processing and analysis. The collection and analysis of nutrient samples and suspended particulate matter samples using established techniques are described in the Supporting Information.

Sample Analysis. Total mercury concentrations were determined by oxidation with BrCl, reduction with $SnCl_2$, gold trap amalgamation, and quantification by cold vapor atomic fluorescence spectrometry (CVAFS) using established methods (35). The average daily Hg_T detection limit, calculated as $3 \times$ the standard deviation of Milli-Q water blanks amended to 1% BrCl, was 0.5 pM. The relative standard deviation of samples ($n = 3$) collected and analyzed for Hg_T in triplicate averaged (mean \pm s.d.) $6 \pm 7\%$, whereas field blanks (Milli-Q water pumped in the field through sample tubing and filter) averaged 1.2 ± 0.4 pM Hg_T ($n = 3$).

MMHg concentration measurements were made on 45 mL aliquots by distillation, aqueous phase ethylation, separation by gas chromatography, thermal decomposition, and quantification by CVAFS (36). Each set of up to 20 MMHg samples distilled was accompanied by at least two distillation blanks (Milli-Q water amended to either 30 mM HCl or 0.1 M KCl and 18 mM H_2SO_4) and two MMHg matrix spikes. MMHg matrix spike recoveries ($n = 11$) averaged $93 \pm 10\%$. The MMHg detection limit, calculated as $3 \times$ the standard deviation of distillation blanks ($n = 10$), was 0.04 pM MMHg. The relative standard deviation of samples ($n = 3$) collected and analyzed for MMHg in triplicate averaged $8 \pm 6\%$, and MMHg field blanks ($n = 3$) averaged 0.02 ± 0.02 pM. Tests for artifactual formation of MMHg and methods for its correction are described in the Supporting Information.

MnO_2 fibers used for collecting Ra isotopes were rinsed with Ra-free water to remove salts and particles, then hand-squeezed to remove excess water. Activities of the short-lived isotopes ^{223}Ra and ^{224}Ra were measured within 2 days of collection using a delayed coincidence counter (33, 37). Samples were rerun 3–6 weeks after collection to account for ^{228}Th -supported ^{224}Ra activity, which accounted for $\sim 3\%$ of the original ^{224}Ra activity. Uncertainties associated with Ra isotope activities were calculated using the method of Garcia-Solsona et al. (38) and averaged 34 and 3% for ^{223}Ra and ^{224}Ra , respectively.

Results and Discussion

Hg_T Concentrations in Groundwater and Surface Waters.

Concentrations of Hg_T in groundwater were greater than those in adjacent surface waters (Figure 2). However, Hg_T levels were relatively low (< 29 pM) in all samples and displayed only modest spatial and temporal variability (Figures 3 and 4, and Figure 2 in the Supporting Information).

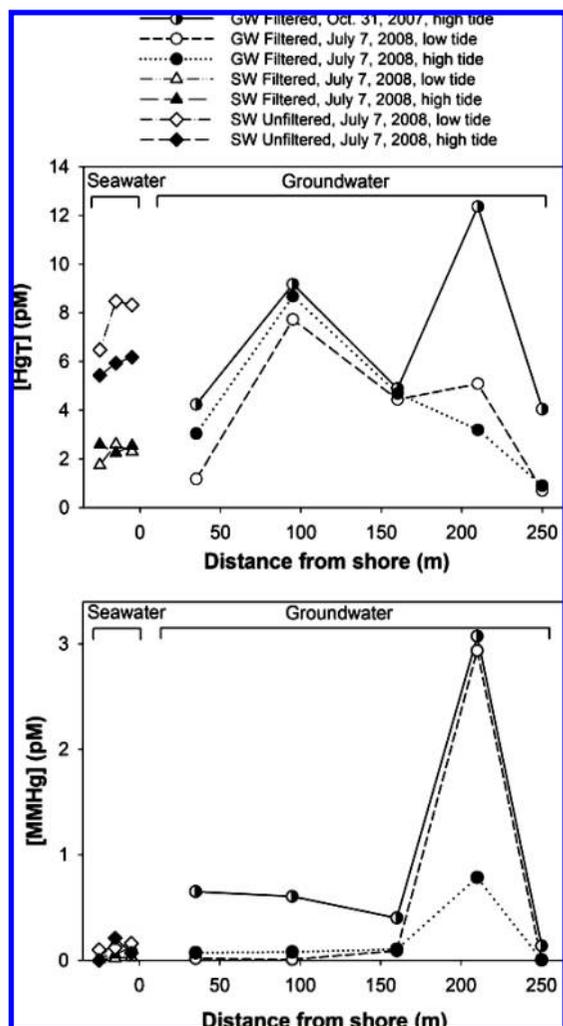


FIGURE 3. Concentrations of Hg_T (top plot) and $MMHg$ (bottom plot) in filtered and unfiltered groundwater (GW) and surface seawater (SW) measured at Stinson Beach.

Concentrations of Hg_T in filtered groundwater ranged from 1.2 to 12.4 pM at Stinson Beach and 1.8–28.3 pM at Elkhorn Slough (Figure 2). These Hg_T concentrations are similar to those reported for groundwater studies in some areas (11, 13, 19), but somewhat lower than those in others (8, 9, 12). Concentrations of Hg_T in filtered surface water samples ranged from 1.7 to 2.6 pM at Stinson Beach and 0.8–11.6 pM at Elkhorn Slough, while Hg_T concentrations in unfiltered surface water samples ranged from 5.4 to 8.5 pM at Stinson Beach and 2.5–12.9 pM at Elkhorn Slough (Figure 2). These Hg_T concentrations are typical of uncontaminated coastal and estuarine surface waters (39–44), but are higher than in continental shelf and open ocean waters (<3 pM) (6).

Dissolved Hg_T levels were generally only slightly higher in groundwater compared to adjacent surface waters (Figures 3 and 4 and Figure 2 in the Supporting Information). Exceptions to this trend were near the head of Elkhorn Slough, where concentrations of dissolved Hg_T were substantially higher in groundwater than surface water. The similarity between dissolved concentrations of Hg_T in groundwater and surface waters is attributed to mercury being very particle reactive. Values of $\log K_d$ (partition coefficient) for Hg_T in surface seawater at Stinson Beach were in the range 5.0–5.6, which is typical of values reported for coastal and estuarine waters elsewhere (39–44). $\log K_d$ values for Hg_T in Elkhorn Slough surface waters were noticeably lower, with a range of 3.3–4.0. Sampling of unfiltered groundwater for both mercury and suspended solids was only conducted at Elkhorn

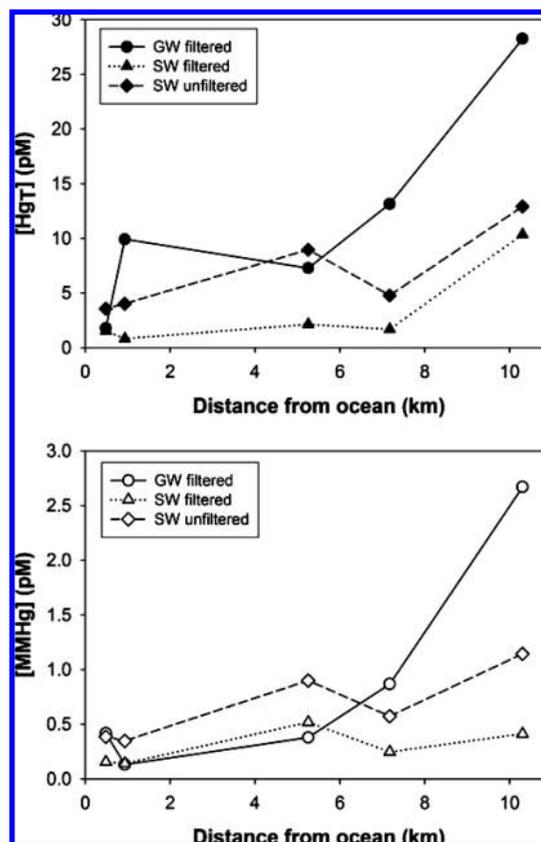


FIGURE 4. Concentrations of Hg_T (top plot) and $MMHg$ (bottom plot) in filtered and unfiltered groundwater (GW) and adjacent surface waters (SW) along transect of Elkhorn Slough sampled June 18, 2008.

Slough, where $\log K_d$ values for Hg_T in groundwater were ~ 1.5 in the harbor at the mouth of the slough and 4.2–5.8 near the head of the slough. The lower degree of partitioning of Hg_T onto the solid phase in groundwater in the harbor was likely due to the unconfined aquifer material here being composed of coarse quartz sands with low organic matter content, compared to the much smaller particle sizes and higher organic matter content characterizing the aquifer moving toward the head of the slough. Similar reasoning was invoked by Bone et al. (12) to explain the low K_d values for Hg_T in groundwater measured in that study.

MMHg Concentrations in Groundwater and Surface Waters. Concentrations of filtered $MMHg$ in groundwater varied more than those in surface waters (Figure 2), ranging from below the limit of detection (0.04 pM) to 3.1 pM at Stinson Beach and 0.13–3.1 pM at Elkhorn Slough (see Figures 3 and 4 and Figure 2 in the Supporting Information). Previous studies reported that $MMHg$ was not detectable (<0.04 pM) in groundwater of a subterranean estuary (13), but that $MMHg$ ranged from <0.04 to 2.9 pM in groundwater of a wetland-forested watershed (19) and 0.6–35 pM in near surface groundwater from a peatland (10). $MMHg$ concentrations measured in coastal groundwater in our study were intermediate of these and within the range generally reported for estuarine and coastal sediment porewaters (31, 32, 45–51).

$MMHg$ concentrations in filtered surface water samples ranged from below the detection limit to 0.13 pM at Stinson Beach and from 0.14 to 0.53 pM at Elkhorn Slough, whereas $MMHg$ concentrations in unfiltered surface water samples ranged from 0.07 to 0.25 pM at Stinson Beach and from 0.35 to 1.2 pM at Elkhorn Slough (Figures 3 and 4 and Figure 2 in the Supporting Information). $MMHg$ levels in surface seawater are within the range typically reported for coastal and estuary waters elsewhere (39–44).

Values of $\log K_d$ for MMHg were in the range 5.1–6.2 for surface seawater at Stinson Beach and 4.5–5.1 for surface waters of Elkhorn Slough. These values of K_d for MMHg are higher than those for Hg_T in the same waters, which is unusual, although the reason for this is unclear. $\log K_d$ values for MMHg in groundwater were ~ 1.9 at Moss Landing Harbor at the mouth of the slough and 3.0–3.3 near the head of the slough. The lower K_d values for MMHg in groundwater measured at the mouth of the slough compared to further inland was similar to the trend described for Hg_T above, and likely controlled by the same differences in aquifer material.

Large variations in the percentage of Hg_T as MMHg in groundwater were measured, indicating that conditions in some regions of these subterranean estuaries are more conducive than others to the net production of MMHg and/or its partitioning into the dissolved phase relative to Hg_T . The percentage of Hg_T present as MMHg in groundwater tended to be relatively high at Elkhorn Slough (3–23%), but was low at Stinson Beach (<16%), with the exception of groundwater from well MW-07 (25–58%). This particular well also had consistently higher MMHg concentrations than elsewhere at Stinson Beach (Figure 3) and high concentrations of dissolved NH_4^+ (57–510 μM) that were $3\times$ greater than those at any other Stinson Beach well sampled during the study. Perennially high fecal indicator bacteria and nitrogen concentrations measured at MW-07 in 2005–2007 indicate septic effluent contamination at that location (N. R. de Siewes, unpublished data), implying a possible connection between this MMHg hotspot and groundwater contamination by sewage. The lack of a decreasing seaward trend in groundwater MMHg concentration at wells between MW-07 and the ocean (Figure 2), as would be expected because of the seaward direction of groundwater flow (26) and dilution in the brackish mixing zone, is likely the result of nonconservative behavior of MMHg in this region of the subterranean estuary.

The high percentage of Hg_T as MMHg in unfiltered surface waters at Elkhorn Slough (9–33%) is in contrast to both surface waters at Stinson Beach (<4%) and coastal and estuary surface waters elsewhere, where MMHg generally constitutes <4% of the total mercury pool (39–44). This difference is likely because wetlands (such as those surrounding Elkhorn Slough) are hotspots for the production of MMHg (30–32) that can subsequently be advected to adjacent surface waters.

In contrast to surface waters, sediment porewaters typically have a high ratio of MMHg to Hg_T because surficial sediments are important sites of microbial production of MMHg (39, 52–54). Thus, the high percentage of Hg_T as MMHg measured in groundwater in this study (up to 58%) is typical of surficial sediment porewaters. However, previous studies of MMHg in sediment porewaters have typically focused on the upper 10–15 cm of sediments and have shown that MMHg concentrations and net mercury methylation potentials are often greatest near the oxic/suboxic interface and decrease above and below this depth (31, 45, 50, 54, 55).

The groundwater collected in this study was from wells with screen intervals of 1.5–3 m at Stinson Beach and from 1–2 m deep pits at Elkhorn Slough. Our groundwater samples essentially represent a composite of groundwater collected across a large vertical depth interval far greater than 10 cm, which in the case of Elkhorn Slough spanned the oxic/suboxic interface. Given the previously reported low concentration of MMHg in many sediment porewaters on either side of the oxic/suboxic interface, one would therefore have expected the MMHg concentrations in these composite samples to be low. But instead, the MMHg concentrations and the %MMHg measured were relatively high in a number of samples from both Stinson Beach and Elkhorn Slough. This observation may indicate that the production and/or transport of MMHg

occur over a wider depth interval in coastal groundwater systems compared to nontidally flushed estuary and coastal sediments.

Temporal variability and the effect of daily tidal cycle on concentrations of Hg_T and MMHg in groundwater and surface waters (of which there was relatively little and no consistent patterns discernible) are discussed in the Supporting Information.

Correlations between Groundwater Concentrations of Mercury Species and Nutrients. Concentration data for mercury species (Hg_T and MMHg), dissolved nutrients (NH_4^+ , NO_3^- , PO_4^{3-} , SiO_2), and ancillary parameters (pH, salinity, temperature, total suspended solids, distance from shore) were analyzed by multiple linear regression to identify correlations between mercury species and other variables. When treating dissolved Hg_T in groundwater as the dependent variable the only factors contributing to the model at the $p = 0.05$ level were dissolved concentrations of NH_4^+ and SiO_2 . The multiple linear regression analysis for dissolved MMHg in groundwater revealed that only dissolved concentrations of Hg_T and NH_4^+ contributed to the model at the $p = 0.05$ level. This is in contrast to concentrations of filtered or unfiltered MMHg in surface waters, which did not correlate with any of the variables measured ($p > 0.1$, multiple linear regression). Thus, a weak positive relationship ($r^2 = 0.31$, $p = 0.003$) was found to exist between dissolved MMHg and Hg_T in groundwater, but not in adjacent surface waters (see Figure 1 in the Supporting Information).

Bone et al. (12) found no discernible relationship between concentrations of Hg_T in coastal groundwater and those of iron, dissolved organic matter, or chloride, despite their ability to influence the transport and fate of Hg_T . Our results suggest that the transport and partitioning of Hg_T between the solid phase and dissolved phase in the groundwater systems we studied are controlled by similar mechanisms to those of NH_4^+ and SiO_2 , but differ from those controlling NO_3^- and PO_4^{3-} . The positive correlation between dissolved NH_4^+ and both Hg_T and MMHg in groundwater may be related to the remineralization of organic matter, which would release NH_4^+ and organic matter-bound mercury species into solution. Another possibility is that reducing conditions in the subsurface would favor the presence of NH_4^+ (mean NH_4^+ concentration in Elkhorn Slough groundwater was $460 \pm 390 \mu M$ compared to $47 \pm 90 \mu M$ for NO_3^-), the microbial production of MMHg, and the release of sorbed Hg_T and MMHg due to the reductive dissolution of manganese and iron oxyhydroxides.

The production, decomposition, and export of MMHg from sediments are controlled by the complex interplay of various geochemical, biological, and physical factors (39, 49, 50, 52, 54, 55). These include parameters measured in this study (pH, temperature, salinity, and nutrients) that influence sorption as well as microbial community diversity and respiration rates. However, the multiple linear regression model could account for only 36% of the variance in groundwater MMHg concentrations ($r^2 = 0.36$, $p < 0.001$), so the two variables found to have significant correlations with MMHg (dissolved Hg_T and NH_4^+) were apparently not the only factors controlling concentrations of MMHg in the two groundwater systems studied.

Fluxes of Hg_T and MMHg to Coastal Waters via Submarine Groundwater Discharge. Hg_T and MMHg concentration data were used to calculate fluxes by combining them with estimates of SGD, which were in turn based on excess radium activities and a simple mass balance model (17, 18, 37). A SGD flux at Stinson Beach of $30 \pm 11 L min^{-1} m^{-1}$ of shoreline was calculated from the average excess ^{224}Ra activity of $24 \pm 4 dpm (100 L)^{-1}$ at the surf zone (within 20 m from the shoreline), a residence time of water at this site of 6 h (based on estimates of littoral drift, rip cell spacing, and

dilution length scales), and unconfined coastal aquifer groundwater ^{224}Ra levels of 81 ± 27 dpm (100 L^{-1}). Uncertainties associated with the SGD fluxes are based on uncertainty in ^{224}Ra activities, whereas uncertainties reported for fluxes of Hg_T and MMHg in SGD presented below are reported with respect to both the variability in the groundwater concentration of mercury species and uncertainties in the SGD flux. At Stinson Beach, the average concentration of dissolved Hg_T in groundwater from the beach pits and well MW-09 was 5.7 ± 3.2 pM (groundwater composition at these locations nearest the beach best represents the discharging mixture of fresh and saline groundwater). This corresponds to a dissolved Hg_T flux of 170 ± 110 pmol $\text{min}^{-1} \text{ m}^{-1}$ of shoreline (250 ± 160 nmol $\text{m}^{-1} \text{ day}^{-1}$). The average concentration of MMHg in groundwater at Stinson Beach (beach pits and well MW-09 only) was 0.24 ± 0.26 pM, corresponding to a MMHg flux in SGD of 7.2 ± 8.2 pmol $\text{min}^{-1} \text{ m}^{-1}$ of shoreline (10 ± 12 nmol $\text{m}^{-1} \text{ day}^{-1}$). SGD fluxes at Stinson Beach were normalized to shoreline length (m^{-1}) rather than area (m^{-2}) because there were insufficient data to accurately define the area of the seepage face at this coastal ocean beach site.

At Elkhorn Slough, excess ^{224}Ra in the main channel averaged 42 ± 8 dpm (100 L^{-1}) and the average groundwater (pits) ^{224}Ra was 450 ± 130 dpm (100 L^{-1}). Using channel volume and a water residence time of 1 day for the main channel (28), SGD flux to the slough was estimated at $5.3 \pm 1.8 \times 10^5$ $\text{m}^3 \text{ day}^{-1}$. Using the average dissolved Hg_T concentration in Elkhorn Slough groundwater of 15 ± 9 pM (15 ± 9 nmol m^{-3}), this corresponds to a dissolved Hg_T flux of 8.0 ± 5.5 mmol day^{-1} to the tidal estuary. The area of the slough is 2.7×10^6 m^2 , giving a Hg_T flux via SGD of 3.0 ± 2.0 nmol $\text{m}^{-2} \text{ day}^{-1}$ when normalized to area. This flux is greater than that reported by Bone et al. (12) for Waquoit Bay, MA ($0.47\text{--}1.9$ nmol $\text{m}^{-2} \text{ day}^{-1}$). The average dissolved MMHg concentration in groundwater at Elkhorn Slough (1.2 ± 1.0 pM) was similarly used to estimate a dissolved MMHg flux of 0.65 ± 0.58 mmol day^{-1} to the tidal estuary, giving an area-normalized MMHg flux via SGD of 0.24 ± 0.21 nmol $\text{m}^{-2} \text{ day}^{-1}$.

Although our SGD fluxes are based on data collected over only a few sampling events, they are consistent with previous estimates based on more extensive Ra data sets and/or hydraulic gradients and Darcy–Dupuit estimates in these same systems (26, 29). Using previously published SGD fluxes for Stinson Beach ($17\text{--}23$ L $\text{min}^{-1} \text{ m}^{-1}$ (26)), we calculate a dissolved Hg_T flux of 160 ± 95 nmol $\text{day}^{-1} \text{ m}^{-1}$ of shoreline, and a MMHg flux in SGD of 6.9 ± 7.5 nmol $\text{day}^{-1} \text{ m}^{-1}$ of shoreline. At Elkhorn Slough, tidally driven seawater recirculation through the surficial marsh sediments was previously reported to be 6.8×10^5 $\text{m}^3 \text{ day}^{-1}$ (29). Using this SGD flux, we calculate a dissolved Hg_T flux at Elkhorn Slough of 3.9 ± 2.2 nmol $\text{m}^{-2} \text{ day}^{-1}$ when normalized to area. Similarly, we calculate a dissolved MMHg flux of 0.31 ± 0.33 nmol $\text{m}^{-2} \text{ day}^{-1}$ at Elkhorn Slough when normalized to area.

Comparison of Fluxes of Mercury Species via SGD to Other Sources. The importance of the fluxes of Hg_T and MMHg via SGD to coastal waters estimated above can be evaluated by comparing them to other sources (see Table 1 in the Supporting Information). In marine environments that do not receive substantial fluvial inputs and are not directly affected by local sources of mercury pollution, inputs of Hg_T are generally dominated by atmospheric deposition (1, 2). Net Hg_T atmospheric deposition to surface waters of nearby San Francisco Bay have been estimated to be roughly 0.19 nmol $\text{m}^{-2} \text{ day}^{-1}$ (56, 57). The Hg_T fluxes in SGD we calculated (3.0 ± 2.0 nmol $\text{m}^{-2} \text{ day}^{-1}$ at Elkhorn Slough) are an order of magnitude greater than that atmospheric deposition rate.

The MMHg fluxes in SGD calculated in this study (0.24 ± 0.21 nmol $\text{m}^{-2} \text{ day}^{-1}$ for Elkhorn Slough) are greater than

previously reported MMHg benthic fluxes out of surficial estuary and coastal sediments due to diffusion and bioirrigation ($0\text{--}0.16$ nmol $\text{m}^{-2} \text{ day}^{-1}$) estimated from concentration gradients between pore waters and overlying waters or using laboratory based flux chambers employing sediment cores (31, 45, 46, 48–51). MMHg fluxes to overlying waters measured using in situ benthic flux chambers, which will capture inputs from SGD and other advective processes, are considerably greater and range from -1.5 to 10.9 nmol $\text{m}^{-2} \text{ day}^{-1}$ (31, 45–47). Although it is difficult to distinguish between different components contributing to these fluxes, our results suggest that the higher in situ measured MMHg benthic fluxes are likely in part due to the role of SGD as a source and means of transporting MMHg to overlying waters both from and through surficial and deep sediments.

Surficial sediments are widely held to be the dominant source of MMHg to estuary and coastal waters (31, 45, 46, 50). Thus, the observation that SGD inputs of MMHg are greater than fluxes out of surficial coastal sediments due to diffusion and bioirrigation indicates that benthic inputs of MMHg may be controlled to a greater degree by the flux of submarine groundwater into the system and the parameters impacting this flux. Such a comparison also suggests that estimates of MMHg benthic fluxes derived from laboratory based (rather than in situ) flux chambers or calculated from MMHg concentration gradients are likely to substantially underestimate in situ MMHg fluxes as they do not capture MMHg fluxes from SGD and other advective processes. This in turn suggests that inputs of MMHg, the form of mercury of most concern for marine ecosystems, to some coastal waters may be considerably greater than previously thought.

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Supporting Information Available

Analytical details and data related to ancillary parameters and temporal variability in Hg_T and MMHg concentrations (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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