

Effect of Bioirrigation on Sediment–Water Exchange of Methylmercury in Boston Harbor, Massachusetts

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Coastal marine sediments are important sites of methylmercury (MMHg) production, and dissolved efflux provides an important source of MMHg to near-shore, and possibly off-shore, water columns and food webs. We measured the flux of MMHg across the sediment–water interface at four stations in Boston Harbor that span a range of infaunal population densities and bioirrigation intensities. At each station we carried out total MMHg flux measurements using core incubations and collected near-surface pore waters to establish MMHg gradients for diffusive flux calculations. The flux cores were also imaged by CT scanning to determine the distribution of infaunal burrows, and pore–water sulfide and ²²²Rn profiles were measured. Total MMHg fluxes, measured using core incubations, ranged from -4 to $191 \text{ pmol m}^{-2} \text{ d}^{-1}$, and total MMHg fluxes were strongly correlated with burrow densities at the stations. Estimated diffusive fluxes, calculated based on MMHg concentration gradients below the sediment–water interface, were much lower than total fluxes at three of the stations, ranging from 2 – $19 \text{ pmol m}^{-2} \text{ d}^{-1}$. These results indicate that MMHg exchange may be significantly enhanced over molecular diffusion in bioturbated sediments. Furthermore, burrow density provides a strong predictor of total MMHg flux. Pore–water exchange of both dissolved MMHg and ²²²Rn, a naturally occurring pore–water tracer, increased across the range of observed burrow densities, suggesting that the presence of burrows enhances both MMHg production and flux.

Introduction

The importance of estuarine and coastal marine sediments as sites of net monomethyl mercury (MMHg) production has been demonstrated in a number of environments including the Patuxent River estuary (1), the Chesapeake Bay (2), the Gulf of Trieste (3), Long Island Sound (4), and the Bay of Fundy (5). Sediment-produced MMHg may be mobilized across the sediment–water interface and become available

for bioaccumulation and biomagnification in pelagic food webs. Although the source of MMHg to deep ocean fish is not currently known, it has been estimated that MMHg diffusion from coastal sediments is large enough to sustain MMHg concentrations in marine fish (4). Therefore, it is essential to adequately quantify MMHg fluxes to properly assess all sources of MMHg to the near-shore, and possibly off-shore, marine environments. Furthermore, a better understanding of the controls on MMHg efflux will allow for more effective management of the coastal zone.

Exchange of MMHg across the sediment–water interface has been quantified from pore-water profiles assuming diffusive transport (4, 6), with in situ benthic flux chambers (7–10), and using sediment-core incubations (11–13). The latter two methods quantify total (or actual) flux of MMHg, whereas diffusion estimates only account for molecular diffusive flux expected due to pore-water MMHg gradients near the sediment–water interface. Total and diffusive fluxes may differ markedly when the two are compared at the same location.

Several studies of MMHg exchange using benthic flux chambers indicate that diffusion-based rates may underestimate the flux of MMHg from estuarine and marine sediments (8–10, 13). For example, Covelli et al. (8) found that benthic fluxes of MMHg were greater than diffusive fluxes in the Gulf of Trieste throughout most of the year. Similarly, Choe et al. (9) found that diffusive flux accounted for only 0.3–65% of the total MMHg flux in the San Francisco Bay-Delta. They attributed this discrepancy to advective processes such as biological irrigation, although they did not explore this possibility explicitly. In Long Island Sound, Hammer-schmidt and Fitzgerald (13) compared diffusive fluxes to total fluxes in core incubations. They found that total flux was up to four times greater than diffusive flux, and that total/diffusive flux ratios were positively correlated with dissolved oxygen (DO) concentrations in bottom waters, suggesting a bioirrigation control. Finally, Point et al. (10) found that the diffusive flux of MMHg represented only 1.5% of the total MMHg flux measured in benthic chambers in Thau Lagoon, and argued that the difference could be attributed to advective flux brought about by bioturbation/bioirrigation processes.

Other flux chamber studies have measured MMHg fluxes that are lower than estimated diffusive fluxes of pore-water MMHg (7, 9). Suppressed MMHg flux may result from trapping of MMHg within an oxidized surface layer, as has been observed in the Saguenay Fjord (14, 15). A geochemical box model in this Fjord suggests that oxic sediments provide an adsorptive barrier to exchange of dissolved MMHg across the sediment–water interface. A redox control on MMHg exchange is consistent with the diurnal variation in benthic MMHg flux observed in Lavaca Bay (7) where benthic chamber flux exceeded diffusive flux by a factor of 6 during a 9-h dark period, but became negative during a 22-h light period. The large flux in the dark was attributed to the onset of anoxic conditions at the sediment–water interface when oxygen production by photosynthetic organisms declined. Work by Mason et al. (11) in Baltimore Harbor provides an alternative explanation for enhanced MMHg flux under anoxic conditions. In long-term (5-day) sediment-core incubations they found that the flux of MMHg was unrelated to the flux of Fe or Mn, and they suggested that enhanced MMHg flux occurs due to direct release of MMHg produced at the sediment–water interface, rather than release during dissolution of Fe and Mn oxohydroxides. Covelli, et al. (12) also observed increases in MMHg flux in core incubations from Grado Lagoon after 10 days, when sulfide began to

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build up in the overlying water, and they attributed this increase to enhanced net methylation under anoxic conditions and/or increased mobilization.

Since bioirrigation tends to enhance both penetration of oxygen into the sediment pore water and exchange of dissolved constituents out of the sediment, benthic macrofauna might influence MMHg efflux in two distinctly different ways. First, bioirrigation could decrease MMHg efflux due to increased oxidation of the sediment–water interface. On the other hand, ventilation of deep burrows could facilitate transport of MMHg from where it is produced below the sediment–water interface into the overlying water column. Therefore, when predicting the relationship between burrow density and MMHg flux it is reasonable to posit two alternative hypotheses: (1) MMHg efflux will be negatively correlated with burrow density, or (2) MMHg efflux will be positively correlated with burrow density. In previous studies in Boston Harbor, we established that increasing burrow densities lead to an increase in the depth of the oxic and suboxic zones, as indicated by pore water oxygen and sulfide profiles (16), and an increase in radon flux due to bioirrigation (17). Therefore, the Harbor provides an ideal environment to test these alternative hypotheses. In this study, we compared diffusive and total fluxes of MMHg from Boston Harbor sediments and related total MMHg fluxes to infaunal burrow densities. We also compared the flux of a tracer of pore water transport, ^{222}Rn , to MMHg flux to gain insight about the impact of bioirrigation on MMHg production.

Experimental Section

Stations in Boston Harbor (Figure S1) were chosen to span a range of infaunal population densities, based on our previous investigation (16). The stations included BH04 (42°18.60' N, 71°2.49' W), QB01 (42°17.61' N, 70°59.27' W), and BH08A (42°17.12' N, 70°54.75' W), all of which had been sampled in summer 2003. For our current investigation a fourth station, BH02 (42°20.63' N, 71°00.12' W), was sampled to represent sediments with very dense infaunal populations. Cores were collected from Boston Harbor sediments in July 2007 into acid-cleaned 12.7-cm diameter by 32-cm long polycarbonate tubes by divers or by use of a HAPS bottom corer. At each station four sets of triplicate cores were collected for the following purposes: (1) total MMHg fluxes and burrow densities, (2) surface bulk-sediment total mercury (HgT) and MMHg and pore-water MMHg for diffusive flux estimates, (3) down-core pore-water ^{222}Rn profiles, and (4) down-core bulk-sediment HgT/MMHg and pore-water sulfide profiles.

Total and Diffusive Fluxes. For the measurement of total sediment–water exchange of MMHg, we used incubations in core chambers similar in design to those described by Giblin et al. (18) to measure nutrient exchange in Boston Harbor and Hammerschmidt and Fitzgerald (13) to measure Hg flux in New York/New Jersey Harbor. Our chambers consisted of 12.7-cm (ID) by 32 cm long polycarbonate tubes fitted with leak-proof bottoms and caps and equipped with stirring motors and sampling ports. After cores were collected in the chamber tubes, the chambers were sealed and maintained at ambient temperature. In the laboratory, the overlying water was replaced with bottom water from the station, and chambers were incubated with gentle stirring at ambient bottom-water temperatures. Overlying water was collected periodically using peristaltic pumping and in-line filtration through 0.2 μm polysulfone membranes in Teflon filter units. Procedural blanks were determined using chambers filled with bottom water, but without sediment. All equipment was rigorously acid-cleaned and trace-metal-free protocols were followed throughout the procedure. MMHg exchange was calculated using the following equation:

$$F = (C_f - C_0)(V/A)/(t_f - t_0)$$

where C_f and C_0 are the final and initial concentrations, t_f and t_0 are the final and initial sampling times, V is the volume of water overlying the core, and A is the surface area of the core. Corrections were made for dilution by bottom water, which was used to replace overlying water during sampling. Bottom-water dissolved MMHg concentrations were below the detection limit (<0.05 pmol/L) at all stations.

At the end of the incubation period, the flux cores were imaged using a General Electric Lightspeed QX/i CT scanner, and the density of burrows was determined by image analysis (19, 20). This approach provides measurements of both flux and burrow density in each of two cores at four stations, and prevents the need to take averages for these two parameters within stations.

Surface sediment porosity and pore-water concentrations were used to calculate diffusive fluxes based on an approximation of Fick's First Law. Diffusive flux of a dissolved pore-water constituent is described as follows: $F = -\varphi D_s dC/dz$, where F is the flux of a solute with concentration C and depth z , φ is the sediment porosity, and D_s is the tortuosity-corrected molecular diffusion coefficient. Porosity determination is described below. The tortuosity-corrected molecular diffusion coefficient was estimated as $D_s = D_w/\theta^2$, where D_w is the molecular diffusion coefficient for CH_3HgSH^0 in water at 25 °C, 1.2×10^{-5} $\text{cm}^2 \text{s}^{-1}$ (4), and θ is tortuosity calculated using the relationship $\theta = 1 - \ln(\varphi^2)$ (21). The value of dC/dz at the sediment–water interface was approximated as $\Delta C/\Delta z$, the MMHg concentration gradient between overlying water and pore water at 2 cm depth in the sediment. This general approach has been used widely to estimate diffusive fluxes in coastal sediments (e.g., 4, 7, 22), although the gradient depth and choice of diffusing species varies somewhat among investigators.

Ambient and Supported ^{222}Rn . Additional cores were collected for ^{222}Rn analysis. These cores were sectioned into 2-cm increments immediately upon returning to shore. Sections were transferred to glass jars containing 100 mL of harbor water, and then the jars were sealed with airtight lids. Rn-222 was sparged from samples and collected by cold trapping following the methods of Mathieu et al. (23), and ^{222}Rn activities were measured using a DRC-MK10-2 scintillation counter (Applied Techniques, Co., Hendersonville, NC). After the samples were purged of radon, ^{222}Rn was allowed to grow in to reach secular equilibrium with its parent ^{226}Ra . ^{222}Rn was measured again to determine supported activity due to decay of ambient ^{226}Ra . The ^{222}Rn system was calibrated with standards made from NIST traceable ^{226}Ra .

Mercury Determination. Cores were also collected for down-core solid-phase MMHg measurements. These cores were extruded and cut into 2-cm sections in an oxygen-free glovebox. Pore waters were separated from these sections for sulfide analysis (see below) using vacuum filtration in disposable filter units with 0.2- μm polysulfone membranes. The top 0–4 cm sections of three additional cores were used for collection of pore waters for dissolved MMHg and solid-phase HgT and MMHg determinations. In this case, acid-cleaned filter units were used and blanks were produced by filtering purified laboratory water through the acid-cleaned filter units.

Mercury analyses were carried out as previously described in Benoit et al. (16). Containers were rigorously acid cleaned, and trace-metal-free protocols (e.g., (24)) were used during all phases of sample handling, storage, and analysis. MMHg concentrations in waters and sediments were determined by distillation (25), aqueous-phase ethylation, purge and trap, gas chromatographic separation of ethylated species, pyrolytic decomposition, and cold-vapor atomic fluorescence (CVAFS) detection (26). HgT concentrations in sediments

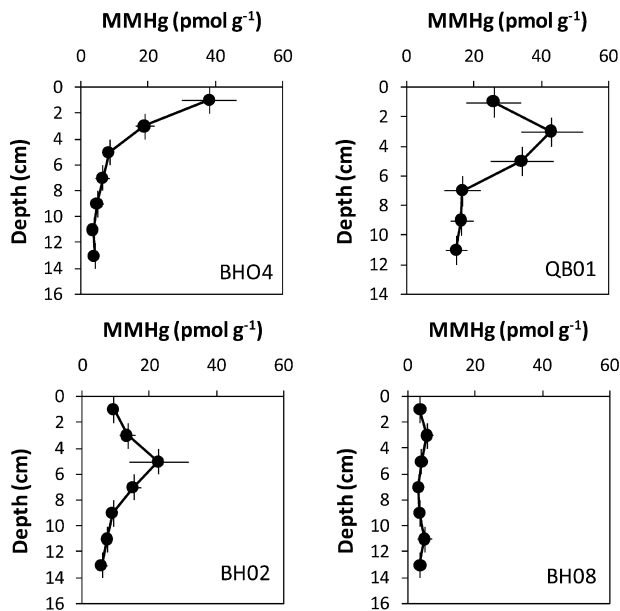


FIGURE 1. Solid-phase sediment MMHg distributions at four stations in Boston Harbor. Concentrations are expressed on a dry weight basis.

were determined by acid digestion, SnCl_2 reduction, purge and trap on gold, thermal desorption, and CVAFS detection (27, 28). Accuracy of the methods was determined by analysis of certified reference materials, PACS-2 (National Research Council of Canada) for HgT and IAEA-405 (International Atomic Energy Agency) for MMHg. We measured an average ($n = 6$) concentration of $3.16 \pm 0.23 \mu\text{g Hg g}^{-1}$ in PACS-2, which is within the reported range of $3.04 \pm 0.20 \mu\text{g Hg g}^{-1}$. For IAEA-405, our measured average ($n = 9$) concentration of $5.73 \pm 0.48 \text{ ng Hg g}^{-1}$ (as MMHg) also fell within the certified range of $4.96\text{--}6.02 \text{ ng g}^{-1}$. Sediments from these stations were previously used in a side-by-side comparison of distillation and nitric acid leaching as sample pretreatment methods prior to MMHg analysis. Results showed insignificant artifactual MMHg production in these sediments during distillation (16). Analytical uncertainties, determined using triplicate sample measurements and expressed as % relative standard deviation were as follows: 8.9% ($n = 5$ triplicates) for HgT and 8.7% ($n = 7$ triplicates) for MMHg. Spike recoveries for pore waters and flux samples were $100 \pm 10\%$ ($n = 4$). Detection limits for 2 g of wet sediment were 0.02 nmol g^{-1} for HgT and 0.05 pmol g^{-1} for MMHg. For 50 mL of pore water or flux sample the MMHg detection limit was 0.05 pmol L^{-1} .

Ancillary Measurements. The pore waters collected for sulfide determination were preserved in sulfide antioxidant buffer (SAOB) and analyzed for total dissolved sulfide using an ion-selective electrode. For our diffusion estimates, porosity was determined from known masses of sediment dried to constant weight in a 70°C oven, using the following equation:

$$\phi = (\text{g water}/1.02 \text{ g mL}^{-1}) / [(\text{g water}/1.02 \text{ g mL}^{-1}) + (\text{g dry sediment}/2.6 \text{ g mL}^{-1})]$$

Percent organic matter (%OM) was determined by measuring the loss on ignition in dried samples combusted at 600°C for 8 h.

Results and Discussion

Sediment Profiles. Solid-phase MMHg (Figure 1) and pore-water sulfide (Figure 2) concentration profiles follow a pattern we have observed in previous years (16). In our prior

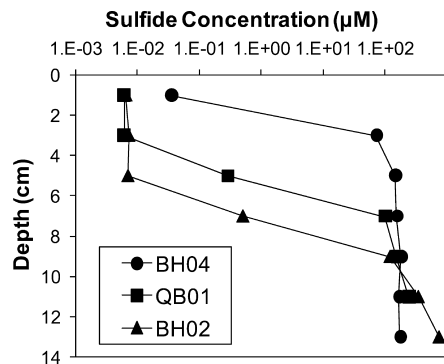


FIGURE 2. Pore-water dissolved total sulfide profiles at three stations in Boston Harbor. Undetectable concentrations are plotted at the method detection limit, $0.005 \mu\text{M}$.

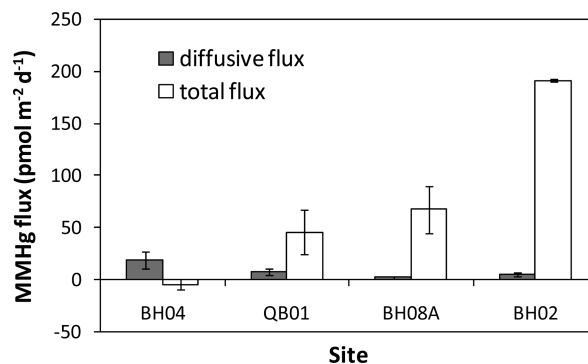


FIGURE 3. Total and diffusive fluxes measured at four stations in Boston Harbor. Averages from duplicate cores from each site are shown, and error bars represent one standard deviation.

investigation in Boston Harbor MMHg peaks occurred just above the depth where dissolved sulfide reached ca. $10 \mu\text{M}$. We proposed a descriptive model in which MMHg peaks occur in a zone of optimal MMHg production that is delimited at the top by the depth where sulfate reduction becomes dominant and at the bottom by the depth where high sulfide concentration becomes limiting to methylation (29, 30). We found that the depths of peak MMHg concentration increased with increasing burrow densities, and we concluded that bioirrigation influences the down-core accumulation of MMHg by changing the three-dimensional geometry of sediment redox conditions and/or by increasing MMHg efflux (16). The solid-phase MMHg profiles at BH04, QB01, and BH02, which had 300, 800 and 12,000 burrows m^{-2} , respectively, are consistent with our previous results and support our model. We were unable to obtain sufficient pore water from BH08A cores for sulfide analysis, because the sediments at this station were very sandy and had much lower porosity than the other stations (Table S1). The low organic matter content limits the retention of MMHg, resulting in relatively constant and low MMHg concentrations with depth.

MMHg Fluxes. The main goals of this investigation were to compare diffusive and total fluxes of MMHg and to determine the relationship between total MMHg fluxes and burrow densities. The magnitudes of these two types of fluxes varied widely among the four stations (Figure 3). Diffusive fluxes of MMHg ranged from 2 ± 1 to $19 \pm 8 \text{ pmol m}^{-2} \text{ day}^{-1}$. These fluxes are within the range of -10 to $440 \text{ pmol m}^{-2} \text{ d}^{-1}$ observed in a number of other estuarine and coastal environments, as summarized in Table 1. Differences largely reflect different pore-water gradients at the various study locations, but may also be influenced by the choice of the diffusing species, and hence, the molecular diffusion coefficient used in the calculations. For example, Gill et al. (7) estimated diffusive fluxes for MMHgCl to be about 6 times

TABLE 1. Summary of MMHg Diffusive (Fdiff) and Total (Ftotal) Sediment Flux Measurements in Estuarine and Coastal Marine Environments (NA Means Not Available)

study area	Fdiff (pmol m ² d ⁻¹)	Ftotal method	Ftotal (pmol m ² d ⁻¹)	source
Gulf of Trieste, Italy	-9-26	flux chambers	-520-11,800	8
Lavaca Bay, TX	50-80 (open water)	flux chamber	770/-1650 (light)/4150 (dark)	7
San Francisco Bay-Delta, CA	-4-440	flux chambers	-92-850	9
Long Island Sound, USA	24-174	NA	NA	4
Baltimore Harbor, MD	NA	core incubations	<24-1440 after 16 h	11
Thau Lagoon, France	4	NA	NA	32
Thau Lagoon, France	NA	flux chambers	94-300/-147 (light)/315 (dark)	10
Grado Lagoon	-10-84	flux chambers	1050 7430	12
NY/NJ Harbor, USA	13-17 (Feb) 54-86 (Aug)	core incubations	170 (oxic)/2480 (anoxic)	13
Mugu Lagoon, CA	0.7-26	NA	NA	33
Boston Harbor, MA	2-19	core incubations	-4-191	this study

higher than fluxes for MMHg associated with macromolecular organic matter.

In Boston Harbor, average total fluxes ranged from -4 ± 5 to 191 ± 1 pmol m⁻² d⁻¹, and they were much greater than estimated diffusive fluxes at three of the four stations (Figure 3). A wide range of total fluxes have been measured in coastal marine sediments (Table 1), and greater total flux has generally been observed when both diffusive and total fluxes have been measured. At BH04, the station with the highest organic matter content and pore-water sulfide concentrations and the lowest burrow densities, the total flux was not significantly different from zero although the estimated diffusive flux was relatively large. The lack of a significant total flux at this site suggests that over the time period of the incubation (16 h) oxygen did not become sufficiently depleted at the sediment-water interface for enhanced flux to occur, as has been observed in other coastal marine sediments (7, 10-12). It appears that direct release of MMHg from the sediment-water interface was not significant, even at our most eutrophic station (BH04).

Our sampling stations included a range of infaunal burrow densities, from 300-12,000 burrows m⁻² at the sediment surface (Table S1), enabling us to test our alternative hypotheses about the effect of bioirrigation on MMHg flux. There is a significant positive, linear correlation between total MMHg fluxes and infaunal burrow densities (Figure 4). This relationship supports the second alternative hypothesis, and is consistent with the idea that burrows stimulate the exchange of dissolved MMHg. This study underscores the importance of measuring total fluxes in bioturbated sediments. The strong linear relationship between MMHg fluxes and burrow densities indicates that sediments with dense infaunal populations export MMHg more efficiently than sediments with lower infaunal densities. This trend is consistent with observations in Long Island Sound, where

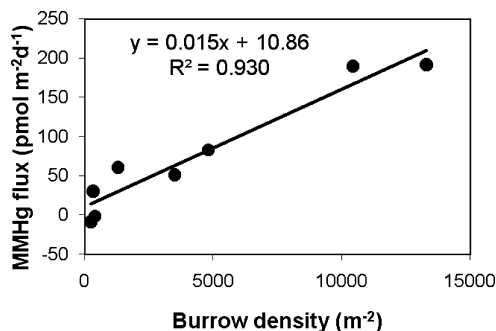


FIGURE 4. Relationship between total dissolved MMHg flux and burrow density in Boston Harbor flux cores. The eight points represent four stations with duplicate cores, each of which provided measurements of both infaunal density and MeHg flux.

flux enhancements (total:diffusive flux ratios) were positively related to bottom-water dissolved oxygen concentrations, and presumably to infaunal population densities (13). Similarly, Point et al. (10) compared MMHg flux in benthic chambers at stations in Thau Lagoon with 0 and 510 macrofaunal individuals m⁻², and found a 3-fold greater total flux at the latter station. In Boston Harbor, average macrofaunal population densities were also linearly related to average MMHg fluxes across the stations (results not shown, $r^2 = 0.94$), confirming the relationship between burrow densities and MMHg fluxes observed in individual cores (Figure 4).

Examination of the flux of ²²²Rn can provide further insight into the effect of burrows on pore-water transport. Dissolved gaseous ²²²Rn is continuously produced in sediments from the radiodecay of solid-phase ²²⁶Ra and lost via radiodecay to ²¹⁸Po. Since pore-water ²²²Rn has no other significant sources or sinks, deficits in measured pore-water ²²²Rn activity, relative to its supported activity from ²²⁶Ra, can be used to determine the ²²²Rn flux. We measured ambient and supported ²²²Rn activity profiles at each of the stations (17) and used the observed deficits to calculate average ²²²Rn fluxes (Figure 5). The flux of radon increases with increasing burrow densities, indicating that sites with higher densities of burrows have higher rates of bioirrigation. Observed ²²²Rn profiles can be explained with a transport control that depends on diffusive exchange of dissolved pore-water constituents across burrow walls and periodic flushing of burrows (17). According to this model, as the number of burrows increases, the surface area for exchange also increases until a point is reached where the burrows are so close together that the ²²²Rn deficit zones around the burrows fuse together. At this point, additional burrows fail to increase

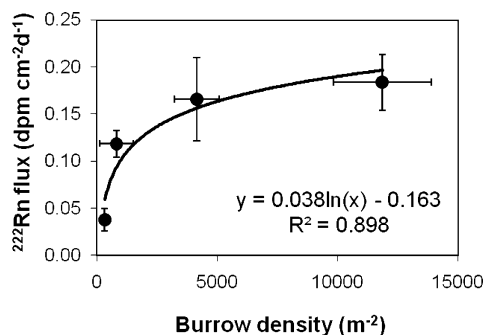


FIGURE 5. Relationship between average dissolved gaseous ²²²Rn flux and average burrow density in Boston Harbor. Averages from triplicate cores for radon and duplicate cores for burrow density are shown, and error bars represent one standard deviation.

the ^{222}Rn flux, which approaches the depth-integrated rate of ^{222}Rn production by its parent ^{226}Ra within the bioturbated zone.

Mass balance considerations require that in the steady state, net production of MMHg (the balance of methylation and demethylation) must equal the total flux. The observed increase in MMHg flux across the stations indicates that greater net methylation must occur at the stations with higher burrow densities. Enhanced fluxes could be driven by greater net production with similar rates of bioirrigation, if more concentrated pore water were exchanged at the more densely populated stations. However, our results do not support this possibility because pore-water MMHg concentrations do not increase with increasing burrow densities (Table S1). Also, since ^{222}Rn is a tracer of pore-water transport, the positive relationship between ^{222}Rn flux and burrow density indicates enhanced pore-water exchange at stations with higher MMHg flux. Therefore, it is likely that the observed relationship between MMHg flux and burrow density occurs due to a combination of increased net MMHg production and enhanced bioirrigation.

There are several possible mechanisms for the observed enhancement of net MMHg production at higher burrow densities. Rapid bioirrigation may remove MMHg more rapidly than it can be demethylated so that a greater proportion of MMHg produced in the sediment is transferred to the water column. Alternatively, burrow irrigation might indirectly augment net MMHg production through the stimulation of Hg-methylation. Bioirrigation can enhance rates of microbial activity, sediment respiration, and organic matter degradation (31) or increase the bioavailability of Hg(II) by lowering pore water sulfide concentrations (29, 30), and thus might boost rates of Hg methylation carried out by sulfate-reducing bacteria. Further, sediments that support high infaunal densities may also be favorable for large populations of methylating bacteria. A third possible mechanism is a reduction in the density or activity of demethylating organisms due to changes in sediment characteristics caused by bioirrigation. Our data do not enable us to differentiate among the possibilities, and these mechanisms warrant further investigation.

Implications. This study is the first to explicitly relate a direct measure of bioirrigation intensity with MMHg efflux from coastal marine sediments across a broad range of benthic population densities. The results demonstrate that MMHg flux from the subsurface can be stimulated by macrofauna, which have a 2-fold effect on MMHg cycling. First, the presence of burrows influences the redox geometry of the sediments and expands the zone of optimal Hg methylation (16), thereby increasing net MMHg production. Second, the penetration of burrows into the sediment allows for efficient transport of MMHg from the regions where maximum production occurs. The overall result is a significant increase in total MMHg flux relative to molecular diffusion in bioirrigated sediments. These results indicate that diffusive flux is not a good measure of sediment-water exchange of MMHg in sediments inhabited by benthic macrofauna. Finally, the observed relationship between burrow density and flux suggests that remediation efforts in impacted estuaries that result in recolonization of previously defaunated sediments may increase MMHg export to the water column as sediments are recolonized.

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Supporting Information Available

A figure indicating the locations of the sampling stations in Boston Harbor and a table of surface sediment and pore water characteristics at the stations. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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