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Mercury flux from salt marsh sediments: Insights from a comparison between $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium and core incubation methods

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Abstract

In aquatic environments, sediments are the main location of mercury methylation. Thus, accurate quantification of methylmercury (MeHg) fluxes at the sediment-water interface is vital to understanding the biogeochemical cycling of mercury, especially the toxic MeHg species, and their bioaccumulation. Traditional approaches, such as core incubations, are difficult to maintain at *in-situ* conditions during assays, leading to over/underestimation of benthic fluxes. Alternatively, the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium method for tracing the transfer of dissolved substances across the sediment-water interface, has proven to be a reliable approach for quantifying benthic fluxes. In this study, the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium and core incubation methods were compared to examine the benthic fluxes of both ^{224}Ra and MeHg in salt marsh sediments of Barn Island, Connecticut, USA from May to August, 2016. The two methods were comparable for ^{224}Ra but contradictory for MeHg. The radiotracer approach indicated that sediments were always the dominant source of both total mercury (THg) and MeHg. The core incubation method for MeHg produced similar results in May and August, but an opposite pattern in June and July, which suggested sediments were a sink of MeHg, contrary to the evidence of significant MeHg gradients between overlying water and porewater at the sediment-water interface. The potential reasons for such differences are discussed. Overall, we conclude that the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach is preferred for estimating the benthic flux of MeHg and that sediment is indeed an important MeHg source in this marshland, and likely in other shallow coastal waters.

Keywords

Methylmercury; ^{224}Ra - ^{228}Th disequilibrium; Core incubation; Benthic fluxes

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1. INTRODUCTION

A significant fraction of the mercury (Hg) that enters aquatic systems is deposited in bottom sediments such that sediments are an important reservoir for Hg in the earth system, especially for “legacy Hg” derived from anthropogenic pollution over the past 150 years (Mason et al., 1999; Fitzgerald and Lamborg, 2007). Sediments are also regions where net methylation of inorganic Hg to methylmercury (MeHg) occurs, making them an important reservoir for MeHg in aquatic systems as well. By a variety of processes, such as bioturbation, wave action, physical and bio-irrigation or episodic natural events, the dissolved Hg and MeHg present in sediment porewater may be returned into overlying water by desorption or advection/diffusion. These processes further affect the concentration and bioavailability of dissolved Hg complexes to methylating bacteria, and therefore the formation of MeHg, which is the most bioaccumulative and toxic form of Hg to aquatic organisms (Jensen and Jernelöv, 1969; Gilmour and Henry, 1991). Moreover, sediments are also active places for methylating bacteria. Substantial quantities of MeHg are produced by anaerobic bacteria, e.g. sulfate- and iron-reducing bacteria, given the abundant supply of dissolved Hg in sediments (Compeau and Bartha, 1985; Gilmour et al., 1998; Benoit et al., 2003). The biophysical processes noted above can enhance MeHg transport to the water column. This may lead to more MeHg accumulation in fish by its delivery through the food chain, further aggravating the risk of human exposure. Overall, the quantification of sediment contribution is essential to adequately understanding the Hg (including MeHg) cycle in aquatic ecosystems, and in particular coastal waters.

A variety of approaches have been developed to estimate the dissolved constituent exchange across the sediment-water interface. *In situ* benthic flux chambers, a direct method for flux estimation, have been deployed in a number of Hg and MeHg studies (Covelli et al., 1999; Gill et al., 1999; Choe et al., 2004). But the shortcomings, including the cost, high requirement of operation or the strict deploying environment, limit the implementation of these devices to only some special sites. As an alternative, Hammerschmidt and Fitzgerald (2008) developed a shipboard core incubation method to resolve the limitation of sampling sites and operation, and similar approaches have been used by others (e.g. Mason et al., 2006; Benoit et al., 2009). Both of the direct measurement approaches demonstrated that sediment mostly was a net source of Hg and MeHg to overlying waters, with sediment bioactivity, such as bioturbation and benthic photosynthesis, cited as the potential driving mechanisms (Gill et al., 1999; Choe et al., 2004; Covelli et al., 2008; Hammerschmidt and Fitzgerald, 2008; Benoit et al., 2009). However, consistent redox conditions are difficult to maintain with flux chamber and core incubation assays. Additionally, as the flux calculation depends on measuring changes in the Hg-species water concentration above the sediment over time, estimates can be influenced by particulate removal or various biochemical reactions that may take place in the water column, such as demethylation of MeHg and Hg redox reactions. Therefore, there may be a discrepancy between the change in concentration in the water and the actual flux from the sediment, and this potential error always exists during such incubations, especially for compounds sensitive to redox conditions and other transformations, such as trace metals. In addition, mass balance calculation has also been applied to benthic flux estimates in previous research (Mason et al., 1999; Sellers et al.,

2001; Fitzgerald et al., 2007) but poor knowledge and quantification for each source and sink term has highlighted the difficulty to obtain more accurate results for the relative importance of the sediment flux.

Surface sediment $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium has recently been developed as a robust proxy for quantifying the exchange of dissolved species across the sediment-water interface, especially in locations with high biogeochemical dynamics, such as coastal areas (Cai et al., 2015; Hong et al., 2017). Cai et al. (2014) derived a net efflux estimate based on ^{224}Ra (a half-life of 3.66 d) with an integrated time scale of 1–10 days under sediment-reworking processes such as hydrodynamic turbulence, bioturbation or irrigation. Furthermore, the intricate benthic interface was simplified into a one-dimensional diffusion model with highly irrigated burrows. The model could be applied to most solute flux estimates at the sediment-water interface based on measurements of ^{224}Ra and ^{228}Th in the near surface sediments. This approach can not only quantify the local benthic transfer under field conditions, but is also more accessible because of its ease of operation. In this study, the new isotopic method and the traditional core incubation approach were compared to assess the validation to the local flux estimation for both ^{224}Ra and MeHg. Moreover, we aimed to understand the factors influencing the flux of Hg species (inorganic Hg and MeHg) and evaluate the role of sediments in their cycling at Barn Island, a coastal salt marsh on the shores of Connecticut, USA.

2. FIELD SITE AND METHOD

2.1. Study site and sampling

Barn Island is a pristine and preserved salt marsh between the Wequetequock Cove and the Pawcatuck River, with a marsh area of 1.4 km². The area is influenced by semi-diurnal tides and the average tidal range is 0.8 m (Langer et al., 2001). The sampling site (41°20.39'N, 71°52.47'W) was located off the bank of the tidal creek, uncovered by plants. The surface sediment was composed of sandy mud of high organic matter content derived primarily from surrounding biotic debris. The activity of molluscs and crustaceans could be observed on the sediment surface. The deep sediment was clayey and compact without evidence of bio-burrows or buried rocks or roots. Measurable tidal change occurred at the sampling site with the highest water depth about 0.5 m. The sampling site is generally inundated by seawater except for a ~4-h interval around the lowest tide.

Sampling was conducted twice a month from May to August, 2016. One collection per month was for samples for flux estimation based on $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium and the other in the following week was for core incubation flux experiments. The benthic flux based on $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium represents an integrated sediment contribution on a time scale of ~10 days, covering the contiguous week when core incubation was deployed. So we can assume that any temporal deviation was incorporated into the disequilibrium estimation because of the timeframe. During sampling, the overlying water had a salinity >15, pH 6.5–7.0 and was unsaturated with dissolved oxygen. All water samples and sediment cores were transported to the lab within 2 h after sampling and Hg sampling was strictly carried out using trace-metal clean techniques.

2.1.1. Overlying water—Overlying water was sampled directly using an acid-cleaned plastic beaker, stored in clean cubitainers and preserved in a cooler (keep dark and at *in-situ* temperature) before being taken back to the laboratory. Water samples, except for ^{224}Ra , were filtered through 47-mm quartz microfiber filters (combusted) using acid-cleaned Nalgene vacuum filter units immediately after returning to the lab. Filtrates were acidified to 0.2% with 9N H_2SO_4 (trace metal grade) and preserved in amber bottles in a refrigerator prior to mercury analysis; for DOC, filtrates were collected in combusted borosilicate glass bottles and stored frozen until analysis. Filters with suspended particles were transferred to clean petri-dishes, and frozen. One or two procedural blanks of Milli-Q water were collected with each sampling. For ^{224}Ra , ~10 l overlying water was filtered through a 142-mm GF/F filter and the ^{224}Ra in the filtrate was pre-concentrated onto MnO_2 -coated acrylic fibers (Mn-fiber) for measurement (Moore and Reid, 1973).

2.1.2. Sediment core and porewater—The first week of sampling was generally carried out during a flooding tide when the water began to inundate the sampling site so sediment cores could be easily obtained by hand using 30-cm-long clean polycarbonate tubes (6.35 cm i.d.). Once retrieved from the sediment, the cores were capped and kept upright during transport to the lab. One of the intact cores was used for ^{224}Ra and ^{228}Th analysis, processed as described by Cai et al. (2012). Briefly, the sediment core was sliced every 1 or 2 cm and each 1-cm-thick slice was placed in a glass beaker. One third was removed to a clean petri dish for water content determination and the remainder was added to a beaker with 250 ml Milli-Q water and mixed well. Subsequently, concentrated $\text{NH}_3\cdot\text{H}_2\text{O}$, KMnO_4 (3.0 g l^{-1}) and MnCl_2 (8.0 g l^{-1}) solutions were added to produce MnO_2 to co-precipitate all the dissolved ^{224}Ra . Lastly, the sediment slurry was evenly filtered onto a 142-mm GF/F filter by a special filtering device for ^{224}Ra and ^{228}Th measurements. A separate intact core for bulk Hg and ancillary parameters was sectioned and frozen prior to freeze drying.

Porewater was collected from 8 to 10 sediment cores within 2 h after returning to the lab. Cores greater than 10 cm in length were sectioned at 1–2 cm intervals and each subsection at the same depth was pooled together and centrifuged to extract porewater. The centrifuged porewater was then filtered through a quartz filter using an acid-cleaned Nalgene filter unit. All extractions were processed in glove bags under a flowing N_2 atmosphere. Aliquots of porewater (5 ml) were immediately preserved in sulfide antioxidant buffer (SAOB) in glove bags for sulfide measurement; 10 ml was transferred to an acid-cleaned centrifuge tube containing 0.5 ml BrCl for total mercury (THg) analysis and preserved in a refrigerator; The remaining porewater was preserved frozen in a combusted-cleaned amber bottle for MeHg and DOC. Additionally, surface sediment was sampled in the field and kept in a clean jar so that the surficial porewater could be obtained by centrifugation for dissolved ^{224}Ra .

2.1.3. Core incubation—Nine sediment cores were collected using acid-cleaned polycarbonate tubes (inner diameter, 6.35 cm; height, 30 cm) for core incubation with triplicates for each incubation time. In order to obtain sufficient overlying water to fill the tubes, core collection was generally deployed during a falling tide. The tubes were specially marked to control the length of sediment to 10 cm. The remaining space was filled with *in-*

situ overlying water. The incubation setup in the lab followed the methods described in Hammerschmidt and Fitzgerald (2008). During the incubation experiments, the core overlying water was stirred continuously by a Teflon bar. Meanwhile, the dissolved oxygen (DO) concentration was monitored and the changes were found to be within $\pm 10\%$. Sampling was carried out after three time durations of ~6 h, 12 h and 20 h. At the end of each period, core water (overlying water in the tube) was withdrawn via clean silicon tubing into a clean Teflon bottle and filtered through quartz filters. About 250 ml of filtrate was subsampled into clean amber bottles for MeHg and stored acidified to 0.2% with 9N H₂SO₄ in a fridge, as was done with the overlying water samples; the remaining of filtrate was combined (~1.1 l) and processed through Mn fibers as with the overlying water ²²⁴Ra. A control incubation, which consisted of a tube without sediment and only overlying water, was included together with the sediment incubation experiments under the same conditions. At the end of 20 h, the core water, as well as the control, was subsampled and filtered in the same way as described above. In addition, the *in-situ* overlying water was collected and processed along with the incubation sediment cores as the initial condition (t = 0) of MeHg and ²²⁴Ra.

2.2. Analysis

2.2.1. Measurements of ²²⁴Ra and ²²⁸Th—Both dissolved ²²⁴Ra and sediment ²²⁴Ra were determined in a radium decayed coincidence counting system (the RaDeCC system) (Moore and Arnold, 1996) at Woods Hole Oceanographic Institution (WHOI) within 24 h after sampling, following the protocol described by Cai et al. (2012). After an additional 8 days, when ²²⁴Ra had ingrown to a level close to its parent, the sediment plates were remeasured in the same systems, then both ²²⁴Ra and ²²⁸Th activities in the sediment can be calculated from the two measurements (details are shown in Appendix 2). All final data for ²²⁴Ra and ²²⁸Th were corrected for the decay since sampling, the chance coincidence signals and background signal. The RaDeCC system efficiency was calibrated with a purified ²³²Th standard solution (daughters in secular equilibrium) and the overall efficiency for sediment measurements was determined from the spiked standard addition (Cai et al., 2012). The ²²⁴Ra and ²²⁸Th errors are $\pm 1\sigma$ uncertainty derived from counting statistics as well as propagation from all the above corrections. It should be clarified that the sediment ²²⁴Ra and ²²⁸Th here represent the fraction that was absorbed on sediment particles and potentially exchangeable with porewater.

2.2.2. Measurements of mercury species—MeHg was determined using a Tekran 2700 purge and trap gas chromatographic cold vapor atomic fluorescence spectrometry (CVAFS) automated instrument, following derivatization with sodium tetraethylborate (NaTEB) in the pH range of 4.6–4.9 (Tseng et al., 2004). For filtered seawater, the samples were acidified to 0.2% using 9N H₂SO₄ overnight and 2.5% ascorbic acid was added before MeHg analysis. For suspended particles, MeHg was extracted first with 4.5N HNO₃ in a 60 °C water bath and analyzed as with filtered seawater. For porewater and sediment, MeHg was extracted from the matrix by distillation with 50% H₂SO₄ and 20% KCl (Hammerschmidt and Fitzgerald, 2001; Balcom et al., 2015). All acids or reagents for analysis were trace metal grade or pretreated to remove Hg. The MeHg data were calibrated by generating MeHg standard curves (Alfa Aesar, NIST) and the results were corrected

based on the field blank samples that ranged from 0.05 pmol l⁻¹ to 0.13 pmol l⁻¹. The relative standard deviations (RSD) of duplicates for aqueous samples and distilled samples were under 10% and the recoveries of standard spike ranged from 60% to 115%. The detection limit (DL) of the method is 0.05 pmol l⁻¹ for water and 0.02 pmol g⁻¹ for sediment.

THg in aqueous samples was measured with a Tekran Series 2600 automated system including the dual gold pre-concentration/CVAFS detection method as described in Bloom and Fitzgerald (1988). Briefly, samples were digested with BrCl overnight (for porewater, in a 60 °C water bath) to convert all mercury to Hg^{II} and then pre-reduced with addition of 12% NH₂OH·HCl to consume any remaining BrCl. Saturated SnCl₂ was added to convert all Hg^{II} to Hg⁰ before purging samples into the instrument. For suspended particle samples, digestion was deployed with both 4.5N HNO₃ and BrCl in a 60 °C water bath. Results were calibrated by standard curves using certified standards (Alfa Aesar, NIST) and corrected based on field blanks which were in the range of 0.5–0.8 pmol l⁻¹ in overlying water and 3–7 pmol l⁻¹ in porewater. The RSD of duplicates was <5%. The DL of the method is 0.25 pmol l⁻¹ for water. THg in sediment was measured using a Milestone direct mercury analyzer (DMA-80) after sediment freeze-drying and homogenization. The DL for this analysis is 0.1 nmol g⁻¹.

2.2.3. Ancillary parameters—Sulfide in porewater was determined with an ion-selective electrode (Orion) (Brouwer and Murphy, 1994). Total suspended solids (TSS) were measured following the standard methods of APHA (American Public Health Association, 1995). Sediment loss-on-ignition (LOI) was obtained from the weight difference after combustion at 550 °C for 6 h. Dissolved organic carbon (DOC) in aqueous samples was diluted and analyzed in a Shimadzu TOC analyzer (TOC-VCPN).

3. RESULTS

All results for each parameter in both the solid and aqueous phases are presented in tables in Appendix 1. Specifically, the activities of ²²⁴Ra and ²²⁸Th in the sediment are shown in Table S1 while Table S2 shows concentrations of MeHg, THg, DOC and sulfide in both overlying water and porewater, and the results of the core incubations are listed in Table S3. We first present the results of the field measurements and incubation experiments before describing the model approaches used to estimate fluxes based on the ²²⁴Ra/²²⁸Th disequilibrium and from the core incubations.

3.1. Ancillary parameters

As the sampling site was a salt marsh, it was organic-rich with a sediment LOI range of 6–15%. The highest organic contents were in May with generally lower values in summer. Dissolved organic carbon (DOC) in porewater increased with depth and sulfide distributions followed the same pattern (Fig. 1). Except in May, the sediment was oxic at the surface, leading to the low sulfide content in porewater; sulfide increased significantly with depth, up to 40–200 μmol l⁻¹.

3.2. ^{224}Ra and ^{228}Th distributions

Due to sampling artifacts, the isotopic data in May is not reported. The profiles of ^{224}Ra and ^{228}Th activities for June, July and August are presented in Fig. 2. The activity of ^{228}Th ranged from $0.325 \pm 0.017 \text{ dpm g}^{-1}$ to $0.911 \pm 0.037 \text{ dpm g}^{-1}$, without significant variations over the summer. In June and July, ^{228}Th had a higher activity at the surficial sediment, with a minimum at mid-depth, suggesting a source from sinking particles at the surface and *in-situ* production from its grandparent ^{228}Ra in the deeper sediments. The results for August imply weaker particulate deposition in late summer. As the daughter of ^{228}Th , ^{224}Ra followed a similar distribution, with activities in the range of $0.319 \pm 0.017 \text{ dpm g}^{-1}$ to $0.908 \pm 0.042 \text{ dpm g}^{-1}$. It is, however, worthwhile to note that ^{224}Ra was in substantial deficit relative to ^{228}Th in the upper 0–3 cm sediment, indicating a loss of ^{224}Ra from the sediment. In contrast, ^{224}Ra and its parent were at or close to secular equilibrium below 4 cm (the average activity ratio of $^{224}\text{Ra}/^{228}\text{Th}$ is 0.96 ± 0.06 , 1SD, $n = 16$), suggesting that no external water movement or convection occurred within the deeper sediments. For dissolved ^{224}Ra , the activity in overlying water was relatively constant during the study period, between 1.21 ± 0.05 – $2.29 \pm 0.10 \text{ dpm l}^{-1}$, slightly lower than the surficial porewater, which ranged from $3.68 \pm 0.72 \text{ dpm l}^{-1}$ to $7.81 \pm 1.33 \text{ dpm l}^{-1}$ (Table 1).

3.3. MeHg concentrations

MeHg had similar distributions in the aqueous phase in each month (Fig. 3). Namely, a maximum appeared in the near surface porewater and concentrations declined with depth until depletion, which may be ascribed to sulfide inhibition of Hg methylation (Compeau and Bartha, 1983; Winfrey and Rudd, 1990). In May, the surficial porewater had the highest concentration of 8.10 pmol l^{-1} , much higher than overlying water and other layers; in June, July and August, concentrations ranged from 0.16 pmol l^{-1} to 1.59 pmol l^{-1} , 0.32 pmol l^{-1} to 2.87 pmol l^{-1} , 0.03 pmol l^{-1} to 1.44 pmol l^{-1} , respectively. Sediment-phase MeHg was in a range of 0.02 – 2.17 pmol g^{-1} with high concentrations near the surface followed by a decrease with depth. Notably, the surface sediment in May had a concentration as high as the suspended particles. This feature is consistent with the anomalously high concentrations of porewater MeHg and sulfide in the same layer, implying that strong methylation had taken place in surface sediment compared to that in the deeper sediments. The distribution of MeHg in the overlying water column showed a different pattern. The suspended particles (SPM) had much higher MeHg, ranging from 6.97 pmol g^{-1} to $55.12 \text{ pmol g}^{-1}$, one order of magnitude higher than sediments. The partition coefficients of SPM (K_D , Table S2) was extremely high (over 10^5 l kg^{-1}) compared to the sediments or previous research in Long Island Sound (Hammerschmidt et al., 2004; Balcom et al., 2015), suggesting a strong particulate adsorption for MeHg at this site.

3.4. Total Hg (THg) concentrations

Compared with MeHg, concentrations of dissolved THg were 1–2 orders of magnitude higher and showed an increasing trend with depth (Fig. 3). The overlying water had the lowest concentrations of 6.42 – 9.14 pmol l^{-1} without significant temporal distinction. The May profile was different from other months but correlated well with the high MeHg in surficial porewater and the solid phase. The concentrations of THg in sediment particles

(151–361 pmol g⁻¹) were comparable to the previous studies in Eastern Long Island Sound (ELIS) (<500 pmol g⁻¹), but relatively low compared to Western Long Island Sound (WLIS) (>1000 pmol g⁻¹) (Hammerschmidt et al., 2004; Balcom et al., 2015), suggesting relatively minor anthropogenic influence in the research area.

3.5. Changes of ²²⁴Ra and MeHg during the core incubations

For ²²⁴Ra, the core incubations for the four months yielded similar trends over time (Fig. 4). At the beginning of the core incubations (t = 0), the activities of *in situ* ²²⁴Ra ranged from 0.64 ± 0.08 to 0.99 ± 0.05 dpm l⁻¹ (Table S3). As the incubations proceeded, ²²⁴Ra activities in core overlying water increased from t = 0 to t = 6 h and reached a plateau after the 12-h incubation duration. The container of overlying water for ²²⁴Ra in July was damaged during transportation so the average of May and June was assumed to be the initial ²²⁴Ra activity for July given that the initial ²²⁴Ra activity for each incubation was comparable.

In-situ MeHg in the overlying water, MeHg in the filtered core water during the incubations and MeHg in the non-sediment control core are all shown in Fig. 5. Core incubation MeHg concentrations were highest in May and increased from 0.23 pmol l⁻¹ to 5.37 ± 2.01 pmol l⁻¹ (average of triplicates, the same below) during the 20-h incubation. In June and July, incubation results exhibited a contrary trend of declining MeHg concentrations time, from 0.77 pmol l⁻¹ to 0.08 ± 0.03 pmol l⁻¹, and from 1.37 pmol l⁻¹ to 0.59 ± 0.39 pmol l⁻¹, respectively. Finally, the August MeHg concentrations increased in the core water from 0.17 pmol l⁻¹ to 0.41 ± 0.09 pmol l⁻¹ within the first 12 h of incubation, then decreased to near the t = 0 value. As to the non-sediment control cores, only in August was there no significant variation in concentration between the beginning and the end of the incubation (0.17 pmol l⁻¹ vs. 0.18 pmol l⁻¹). A drop from 0.77 pmol l⁻¹ to 0.13 pmol l⁻¹ was evident in June, and a decrease from 1.37 pmol l⁻¹ to 1.07 pmol l⁻¹ was observed in July. This observation suggests that processes independent of sediment biogeochemistry, such as adsorption or demethylation, were responsible for the loss of dissolved MeHg in the sediment core incubations.

4. DISCUSSION

4.1. Benthic flux estimation of total ²²⁴Ra

4.1.1. Fluxes based on ²²⁴Ra/²²⁸Th disequilibrium—With respect to the timeframe of the method, it is equivalent to several times the ²²⁴Ra half-life, and additionally, the distribution of ²²⁴Ra and ²²⁸Th in the sediments can be considered to be at steady state. Invoking this assumption, ²²⁴Ra flux across the sediment-water interface can be estimated from its deficit relative to ²²⁸Th (Cai et al., 2012), by:

$$F_{\text{Ra}} = \int_0^Z \lambda (A_{\text{Th}} - A_{\text{Ra}}) dz \quad (1)$$

where A_{Th} and A_{Ra} are the activities of ²²⁸Th and ²²⁴Ra per unit volume of bulk sediments (dpm cm⁻³) that is estimated by $A_{\text{bulk}} = A_s \frac{\rho\phi}{(1-\phi)}$, wherein A_s is the activity of dry

sediment (dpm g^{-1}) shown in Table S1; ϕ is sediment porosity and ρ is sediment density of 2.6 g cm^{-3} . The flux is estimated from trapezoidal integration of ^{224}Ra deficit relative to ^{228}Th from the surface until the depth of equilibrium between the two radionuclides. The results are presented in Table 2. The depth of ^{224}Ra deficiency (up to 3 cm) followed a declining trend from June to August, which translated to a decrease in the total ^{224}Ra flux (from 0.088 ± 0.026 to $0.031 \pm 0.026 \text{ dpm cm}^{-2} \text{ d}^{-1}$) with time (Fig. 2). This reduction was consistent with the sediment becoming more anoxic and temperatures increasing from June to August, and was potentially a result of changing microbial activities and/or distributions over this period (Pierce et al., 2016). Notably, the sediment at the sampling site is under periodic tidal flushing (16 h d^{-1}) so the benthic ^{224}Ra flux calculated by this approach reflects an average exchange on a timescale of several days.

Generally, molecular diffusion is a rate-limiting step when it comes to the aqueous diffusive transport between sediment and overlying water (Berner, 1980). Burrows introduced by infauna can expand the effective sediment-water interface area (Aller, 1977; Aller et al., 1980) and physical (e.g. tidal flow) and biological processes (bioturbation/bio-irrigation) can further enhance the flux. These factors can be accounted for via application of an adjusted Fick's First Law (Cai et al., 2014):

$$F_{\text{Ra}} = \xi \phi D_s^{\text{Ra}} \cdot \frac{\partial A_{\text{Ra-dis}}}{\partial z} \quad (2)$$

where ξ is an area enhancement factor representing the extended embedded interface and advective influences on the diffusive flux; ϕ is the porosity of sediment; D_s^{Ra} is the molecular diffusion coefficient of dissolved Ra, corrected for tortuosity (Θ) as $D_s = D_w/\Theta^2$ where D_w is diffusion coefficient in free solution and Θ can be calculated from sediment porosity as $\Theta^2 =$

$1 - \ln \phi^2$; and $\frac{\partial A_{\text{Ra-dis}}}{\partial z}$ is the ^{224}Ra activity gradient at the sediment-water interface and can be estimated from the difference in ^{224}Ra activity between the overlying water and the surficial porewater. With knowledge of F_{Ra} derived from ^{224}Ra and ^{228}Th measurements in the sediment, Eq. (2) was solved for ξ at each sampling time using a literature value of D_w^{Ra} which was temperature corrected (Schulz, 2006). Our results showed that ξ ranged from 33 ± 23 to 590 ± 330 (Table 2), indicating that the effective area of the sediment-water interface was significantly larger than the traditionally-defined boundary, and that physical and biological advection were important components of the flux. Hence, methods only based on Fick's First Law, or molecular diffusion, would greatly underestimate the actual flux. As ξ is a function of bioturbation, irrigation, and shear flow, the variation of ξ indicates that biophysical exchange processes were strongest in June and July but much weaker in August.

4.1.2. Fluxes based on core incubation experiments—For the core incubations, it is generally assumed that there are no sources or sinks to the core overlying water besides the sediment-water exchange. Therefore, only two terms, sediment input and decay, may affect the ^{224}Ra activities in core water above the sediment. Given these assumptions, the flux can be described as:

$$\frac{\partial A_{Ra-I}}{\partial t} = \frac{F_{Ra-I}}{H} - \lambda A_{Ra-I} \quad (3)$$

where A_{Ra-I} is the ^{224}Ra activity of incubation core water, F_{Ra-I} is the sediment ^{224}Ra flux and H is the height of core water above the sediment interface. As noted above, if solute transfer across the sediment-water interface is mainly by way of diffusion, the sediment flux in core incubation can be expressed with a constant K as

$$F_{Ra-I} = K \cdot (A_{p-I} - A_{Ra-I}), \quad (4)$$

then Eq. (3) can be transformed by re-arranging Eq. (2), such that:

$$\frac{\partial A_{Ra-I}}{\partial t} = \frac{K(A_{p-I} - A_{Ra-I})}{H} - \lambda A_{Ra-I} \quad (5)$$

where A_{p-I} is the ^{224}Ra activity of surficial sediment pore-water in the incubation cores. With a boundary condition $A_{Ra-I} = A_0$ at the beginning of incubation ($t = 0$), the general solution of Eq. (5) is

$$A_{Ra-I} = \frac{K}{K + \lambda H} A_{p-I} + \left(A_0 - \frac{K}{K + \lambda H} A_{p-I} \right) \cdot e^{-\left(\frac{K}{H} + \lambda\right)t} \quad (6)$$

Owing to the increase of core water activity (A_{Ra-I}) with time, the benthic flux (F_{Ra-I}) is expected to decrease with time based on Eq. (4). If such, the initial stage ($t = 0$) of the incubation should be closer to the *in-situ* situation, namely, $F_{Ra-I} = K(A_{p-I} - A_0)$. The variation of ^{224}Ra activity with time in the core water of each set of incubations is depicted in Fig. 4; these data can be fitted with a regression $y = y_0 + a \cdot e^{-bx}$ as Eq. (6), then the parameters K and A_{p-I} in Eq. (6) can be deduced from the regression coefficients. However, the regressions in May and June failed to provide consistent coefficients. Under these circumstances, the sediment fluxes could be approximately estimated based on the results for the initial time points. Practically, with the assumption of constant flux (F_{Ra-I}) and the same boundary conditions ($A_{Ra-I} = A_0$ when $t = 0$) as noted above, the general solution of Eq. (3) can be expressed as

$$F_{Ra-I} = \frac{\lambda H (A_{Ra-I} - A_0 e^{-\lambda t})}{1 - e^{-\lambda t}} \quad (7)$$

and F_{Ra-I} could be calculated by substituting the ^{224}Ra activity at $t = \sim 6$ h in the equation. Given the concerns expressed in this study about maintaining environmental conditions in the core incubations, calculating fluxes using the initial measurements is a valid approach. All coefficients and the calculation results are listed in Table 3. In this approach, the benthic

fluxes reflected a short-term continuous release from sediment, ranging from 0.055 dpm cm⁻² d⁻¹ to 0.172 dpm cm⁻² d⁻¹. The estimates are comparable with the results obtained from the ²²⁴Ra/²²⁸Th disequilibrium method, in particular when considering the errors associated with these measurements and the different time scales to which the two methods applied. Both methods present a similar trend that sediment fluxes in June and July were higher than August. The average ratio of the flux (hourly) from June to August (the last column of Table 3) is 0.98, indicating the ²²⁴Ra fluxes obtained by the two methods are quite consistent. Therefore, we will use the incubation result of May for the missing result of ²²⁴Ra flux in Table 2 for the following calculations.

4.2. Benthic flux estimation of Hg species

4.2.1. Fluxes based on ²²⁴Ra/²²⁸Th disequilibrium—As shown as Eq. (2), molecular diffusion is a rate-limiting step for the aqueous ²²⁴Ra transport across the interface between sediment and overlying water. Thus, we assume that all dissolved substances (c) have similar

transport mechanisms with the same n in the research area as ²²⁴Ra, namely, $F_c = \xi \phi D_s^c \cdot \frac{\partial c}{\partial z}$. Combining Eq. (2) and the concentration gradients of various mercury species, the sediment-water exchange of dissolved MeHg & THg can be calculated (Cai et al., 2014) as:

$$F_{Hg} = \frac{D_s^{Hg} \cdot (\partial c_{Hg} / \partial z)}{D_s^{Ra} \cdot (\partial A_{Ra-dis} / \partial z)} \cdot F_{Ra} \quad (8)$$

where F_{Hg} and F_{Ra} are the Hg and ²²⁴Ra fluxes from the sediment, respectively; D_s^{Hg} and D_s^{Ra} are the *in-situ* molecular diffusion coefficients of Hg species and Ra corrected for tortuosity (h) and temperature using the relationship of $D_{s(T)} = D_{s(25)} (1 + 0.048T)/2.2$, where T is the temperature in degrees Centigrade (Lerman, 1979). The concentration gradients of Hg species and Ra are c_{Hg}/z and A_{Ra-dis}/z , respectively. All Hg species are particle reactive and the largest gradient in the sediment may have a length scale of a few mm across the interface. Given the measurements made and their vertical resolution, the gradients are calculated as the difference between overlying water sampled above the sediment and the average surficial (0–1 cm) porewater concentration (note, however, that for July, the ²²⁴Ra sample referred to a 0–2 cm porewater sample). While Ra and Hg species have different geochemical behaviors, this has been taken into account in Eq. (8) by the various terms: the diffusion coefficients for the various species and the corresponding gradients, which for ²²⁴Ra had a smaller varying range than the Hg species during the research period. Here, the diffusion coefficients at 25 °C ($D_{s(25)}$) for MeHg and THg are adopted from the literature with values of 1.2×10^{-5} cm² s⁻¹ and 9.5×10^{-6} cm² s⁻¹, respectively, assuming that both forms are mostly present as inorganic sulfide complexes in the sediment porewater under the conditions of the sediments studied (Hollweg et al., 2010 and references therein). The benthic fluxes of Hg species based on ²²⁴Ra/²²⁸Th disequilibrium are shown in Table 2. The error, ranging from ~37% to 60%, was mainly derived from the ²²⁴Ra flux model error.

MeHg fluxes varied significantly between the different months. July had the highest flux of $2470 \pm 1360 \text{ pmol m}^{-2} \text{ d}^{-1}$ during the research period, followed by May ($690 \pm 260 \text{ pmol m}^{-2} \text{ d}^{-1}$); June and August were one order of magnitude lower, at $92 \pm 47 \text{ pmol m}^{-2} \text{ d}^{-1}$ and $40 \pm 29 \text{ pmol m}^{-2} \text{ d}^{-1}$, respectively. These differences are mainly the result of the substantial differences in the sediment-water MeHg concentration gradients. In comparison, the benthic flux of THg displayed no significant temporal variability from May ($3570 \pm 1340 \text{ pmol m}^{-2} \text{ d}^{-1}$) to July ($5620 \pm 3100 \text{ pmol m}^{-2} \text{ d}^{-1}$) but decreased substantially in August ($830 \pm 590 \text{ pmol m}^{-2} \text{ d}^{-1}$). Simultaneously, August had the lowest MeHg flux, suggesting that the activities of the benthos in enhancing benthic flux were comparable from May to July but weaker in August.

The relative differences between the monthly flux estimates for MeHg and THg suggest that there are other local sources or sinks (e.g. methylation/demethylation, biotic uptake) for porewater MeHg besides dissolved-particulate partitioning, which contributes to the concentration gradient in the porewater. The significant decrease of MeHg flux in June could likely be ascribed to the role of net methylation in the MeHg concentration. Methylation is a vital process producing MeHg in sediment, mediated by sulfate reducing bacteria (SRB) which are mainly active within the suboxic layer in the sediment (Compeau and Bartha, 1985). Additionally, demethylation of MeHg can also occur in sediments (Hintelmann et al., 2000; Benoit et al., 2003), so the net production is a complex function of these two biologically mediated processes. Thus, the seasonal variability in the activities of SRB and other bacteria, as well as the abundance of bioavailable organic materials in the surface sediment may result in variability in the net methylation rate, further leading to changes in the MeHg distributions. The relatively low sulfide concentration in sediment porewater observed in June may imply weaker SRB activities than May and July. Furthermore, at the same site as this study, Langer et al. (2001) found high MeHg accumulation in surficial porewater in May because of a high methylation rate. The highest concentration gradient of MeHg was also observed in May in this study, and was associated with anomalously high sulfide and THg in surficial porewater, suggesting that the extent of methylation is likely the dominant factor influencing the magnitude of the benthic MeHg flux.

4.2.2. Fluxes based on core incubation experiments—Fig. 5 depicts changes in the average MeHg concentration in core overlying water with incubation time. Within the 12-h duration, a linear correlation between the average MeHg concentration vs. incubation time was evident. Consequently, on the basis of the traditional approach, the MeHg benthic flux can be solved from the slope of the linear equation with the assumption that sediment flux was the sole MeHg source and negligible MeHg removal processes occurred in the core overlying water during the incubation time (Hammerschmidt and Fitzgerald, 2008):

$$c_t = \frac{F_{\text{MeHg-I}}}{H} t + c_0 \quad (9)$$

where $F_{\text{MeHg-I}}$ is the benthic flux from core sediment, H is the height of water in the core tubing ($\sim 20 \text{ cm}$), and c_0 is the initial MeHg concentration at the start of the incubation ($t = 0$). The benthic flux can be estimated from the slope of the best fit of the data to Eq. (9).

Here the averages of triplicate cores and initial MeHg concentrations were employed in the regression analysis. The parameters and results are presented in Table 4.

The incubation results for MeHg seem to point to a discrepant conclusion when compared to the flux estimates calculated from the ^{224}Ra disequilibrium data. In May and August, the incubation-derived MeHg sediment fluxes to the core overlying water were $1280 \pm 96 \text{ pmol m}^{-2} \text{ d}^{-1}$ and $98 \pm 14 \text{ pmol m}^{-2} \text{ d}^{-1}$, respectively, in accordance with the calculations based on the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium method. Conversely, the incubation data suggest sediments were a sink for MeHg in June and July: $-197 \pm 53 \text{ pmol m}^{-2} \text{ d}^{-1}$ and $-383 \pm 86 \text{ pmol m}^{-2} \text{ d}^{-1}$, respectively. The estimates of May and August are comparable to previous chamber/core incubation experiments in other coastal ecosystems (Gill et al., 1999; Choe et al., 2004; Point et al., 2007; Covelli et al., 2008; Hammerschmidt and Fitzgerald, 2008; Benoit et al., 2009). While most studies have reported sediments as a source of MeHg, there are examples where they have been shown to be a sink (e.g. Mason et al., 2006; Point et al., 2007; Choe et al., 2004). Regardless, given the vertical distributions of dissolved MeHg in porewater (Fig. 3), which showed obviously higher concentrations than the overlying water in all cases, MeHg should be transported from sediments to the water column by molecular diffusion and/or advection.

Moreover, the non-sediment MeHg control experiment (Fig. 5; Table S3) exhibited a decreased MeHg concentration during the incubation in June and July, suggesting that dissolved MeHg in core overlying water was influenced by processes unrelated to sediment-water exchange. These could include processes such as MeHg demethylation by bacteria, photochemical degradation, non-reversible adsorption by suspended particulates/plankton or changes in the speciation of Hg complexes, or other possible processes (Seller et al., 1996; Benoit et al., 1999, 2003; Fitzgerald et al., 2007). Unfortunately, as we only measured dissolved MeHg in the overlying waters, we do not have enough information to confirm or refute any of these specific processes. However, as the changes of MeHg concentration in non-sediment control cores ranged from little to an 83% decrease over the 18 h incubation in this study, two processes are likely accounting for most of the changes: net demethylation of MeHg and changes in dissolved-particulate partitioning.

As the core incubations were done in the lab without natural sunlight, and no UV, which are the dominant wavelengths for photodemethylation, the impact of photodemethylation was likely small but biotic demethylation can also occur (Oremland et al., 1991). However, based on “dark” demethylation rates ($\sim 10^{-6} \text{ s}^{-1}$) measured by Whalin et al. (2007) in coastal waters, the expected change would be <10% over the 18 h, so we conclude that demethylation is not the major factor involved in the changes in MeHg seen in the non-sediment control cores.

Changes in partitioning could occur if there was a particulate-dissolved MeHg disequilibrium at the beginning of the experiments, and/or changes in the suspended particulate load (e.g. microbial growth) could lead to changes in the dissolved MeHg that would be unrelated to any flux from the sediment. June and July were the two occasions when the dissolved MeHg concentration in the core incubations decreased over time. In June, TSS was low but K_D was the highest among all of the sampling periods (2–5 times

higher; Table S2). An inverse relationship between K_D and TSS has been found for MeHg (e.g. Balcom et al., 2015), as is found for other metals (Benoit et al., 1994). The high K_D coincides with the largest decrease in water column dissolved MeHg concentration in the non-sediment control incubations, which suggests that scavenging removal of MeHg from the dissolved phase was the major reason for the changes observed in the core incubations rather than the uptake into the sediments. Potentially, given the relatively high particulate loading in the shallow, dynamic ecosystem, it is possible that the dissolved and particulate phases were not at equilibrium at the time of sampling and the changes in the core water reflected the slow exchange dynamics for MeHg in natural systems, where equilibrium between dissolved and particulate phases can take up to 24 h, with K_D 's changing by up to an order of magnitude (Hintelmann and Harris, 2004; Kim et al., 2008). Additionally, June was the occasion when the gradient between the overlying water and porewater was smallest and the estimated fluxes derived from Ra/Th was lower, suggesting that the removal was more apparent given the low sediment flux. The drop after the peak concentration at 12 h in the August incubation further highlights the removal influence with a longer incubation time. Regardless, we conclude that the different source-sink patterns for dissolved MeHg in the core incubation are not likely due to differences in the fluxes from the sediment, but are more likely attributable to changes occurring within the water column above the sediment during the incubations.

It is worth noting that many prior studies of MeHg flux from sediments using sediment core incubations have not performed adequate controls to determine the changes in MeHg concentration over time due to factors besides fluxes at the sediment-water interface. Overall, the assumption that there is no dissolved MeHg removal or addition to core overlying water during the incubation from processes besides sediment-water exchange is obviously not valid based on the comparison of the Ra (considered an unreactive species) and MeHg fluxes for the core incubations.

4.3. Mass balance of Hg species based on benthic flux

We developed a mass balance model for THg and MeHg in the salt marsh water column in order to quantify the relative importance of sediment fluxes in the Hg species biogeochemical cycles. In addition to the benthic contribution detailed above, Hg species concentrations in the overlying water can be impacted by: (1) exchange with seawater by tidal fluctuations; (2) scavenging removal on sinking particles; (3) biochemical transfer between Hg species (e.g. demethylation); and (4) other external inputs such as atmospheric deposition and contributions from the watershed/drainage. Given that the sampling site is inundated daily by the tides, and the sediments are covered for 8 h (Δt) during one tidal cycle, thus, the change of inventory (ΔI_{Hg}) during this period should be

$$\Delta I_{Hg} = F_{Hg} \Delta t + F_{atm} \Delta t + c_{sea} h - c_{Hg-p} \omega \Delta t + R \quad (10)$$

where the following terms refer to the Hg species including: I_{Hg} , the inventory per unit area during water inundation; F_{Hg} , the benthic flux; F_{atm} , the atmospheric deposition flux; c_{sea} , the concentration in the seawater surrounding the marshland, including both the dissolved

and particulate phases; ω , the sedimentation rate; and $c_{\text{Hg-p}}$, the concentration on suspended particles. The sampling site is located in an inlet and the watershed or drainage in and around the marshland can converge or diverge from the site with tide, resulting in net transport of Hg species into or away from the site. These terms vary with tide and time, and are affected by quite a few factors (e.g. storms). Therefore, we use a parameter R to represent the sum of all unidentified and unquantified terms, including biochemical transformations in the water column and the local watershed/drainage contribution. Overall, each term in Eq. (10) represents a source or sink of Hg species and their relative importance can be assessed by comparing these terms.

Despite no short-term time-series measurements deployed in this research, we can simplify the model by considering a fixed-volume box with an average water depth of $h = 0.3$ m. The initial inventory is assumed to be zero and the change within an inundation period (8 h) is $I_{\text{Hg}} = -c_{\text{Hg}} \cdot h$, where c_{Hg} refers to the average change of Hg species concentration in overlying water, including both dissolved ($c_{\text{Hg-d}}$) and particulates ($c_{\text{Hg-p}}$). Here we use the measured concentrations to calculate the average change of inventory. The benthic fluxes used in the model are those estimated by the radionuclide approach with an effective exchange time of 16 h per day. An atmospheric deposition of THg of $8.9 \mu\text{g m}^{-2} \text{y}^{-1}$ ($122 \text{ pmol m}^{-2} \text{d}^{-1}$) is used based on Gichuki and Mason (2014) for Avery Point (Connecticut). Nadim et al. (2001) estimated the wet deposition flux of MeHg as $0.06 \mu\text{g m}^{-2} \text{y}^{-1}$ ($0.78 \text{ pmol m}^{-2} \text{d}^{-1}$). For the inflowing seawater, we use the field measurements of Chen et al. (2014) offshore of Barn Island. A ^{210}Pb -dated ω value of 3 cm yr^{-1} (0.008 cm d^{-1}) is adopted from a prior study of Van Metre (2012). Therefore, the factors affecting Hg species can be quantified separately. All parameters used in this model are listed in Table 5 and the contribution pattern of the major terms is depicted in Fig. 6.

Our results reveal that particle scavenging ($<0.1\%$) and atmospheric deposition ($<0.1\%$ for MeHg and $<1.5\%$ for THg) were negligible contributors to the Hg species mass balance in the system. In most cases, sediments were the dominant source of THg to the water column followed by the inflowing seawater. In May–July, the residual term R is entirely attributed to the error of the benthic flux estimates. In August, however, the sediment appeared to contribute a minor fraction to the THg budget. A heavy rain shower occurred before the August sampling, which coincided with the highest observed TSS. Thus, the high R value for August might be explained by a significant, but episodic, terrestrial input of THg to the site.

The pattern for MeHg shows a negative R in May and July that can also be ascribed to the errors involved in the calculations. But in May, both inflowing seawater and sediments input were significant contributors to the water column MeHg inventory. The opposite pattern was observed in June and August: sediments contributed minor amounts to the MeHg budget while other sources (the R term) were more important. Because the sampling site is located at the ocean inlet to the Barn Island salt marsh, it is affected by not only the inflowing seawater, but also the brackish water exported from the marshland watershed. In particular, MeHg from sediment exchange may accumulate in the creek water (Langer et al., 2001) and this elevated MeHg, a term not explicitly considered in this model, may contribute to the sampling site during ebb tide. For example, a rainstorm prior to sampling, as was observed

in August, could enhance the contribution of the watershed. In June, unidentified sources were again a substantial source of MeHg, but less so for THg, suggesting that while external terrestrial inputs could have contributed MeHg, other processes such as methylation in the water column could be another additional source of MeHg (Ortiz et al., 2015; Schartup et al., 2015), or else there was substantial methylation of Hg and subsequent transport from the upper marsh to the sampling site.

5. CONCLUSION

Benthic fluxes of ^{224}Ra estimated using the $^{224}\text{Ra}/^{228}\text{Th}$ disequilibrium approach and sediment core incubations are generally comparable. However, discrepant results are obtained when applying these two methods to estimate MeHg fluxes at the sediment-water interface. The radionuclide approach indicated that the sediments were a source for both MeHg and THg. On the contrary, the core incubation experiments in June and July revealed a loss of dissolved MeHg with time in the core overlying water, indicating active removal of dissolved MeHg from the water column. Based on the concentration gradients between overlying water and the surficial porewater, it is unlikely that interactions between sediment and water, primarily dissolved MeHg flux, accounted for the observed MeHg removal. Changes in the core overlying water, such as partitioning to suspended particles, are considered the factors most likely responsible for the decline of MeHg. We thus conclude that the core incubation approach is not likely to be valid for the flux estimation of MeHg unless all potential processes that can change water column concentrations with time are measured. Similarly, for other non-conservative substances, such a redox sensitive elements like Fe, the problem will always exist if benthic fluxes are estimated based on the change in core overlying water concentration with time. Consequently, any previous benthic fluxes estimate from core incubations should be reevaluated for the potential impact of the artifact found in this study.

In addition, this study indicates that sediment is an important source of MeHg and THg to overlying water column even in a pristine environment like Barn Island, although the site being shallow likely maximizes the potential importance of sediment inputs. The temporal variation of benthic fluxes may be ascribed to changes in biological activities (bioturbation/bio-irrigation), and the significant fluctuation of sediment MeHg fluxes may reflect a temporal variability of the net methylation within sediment. Finally, the contribution pattern from the budgets of Hg species in the study area indicates the importance of other processes such as watershed inputs and water column methylation under conditions when the sediment contribution is low.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.gca.2017.10.033>.

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Fig. 1. Vertical distributions of dissolved DOC ($\mu\text{mol l}^{-1}$) and sulfide ($\mu\text{mol l}^{-1}$) in overlying water and porewater at each sampling time. The dashed line represents the sediment-water interface and the symbols above the line refer to samples in overlying water. Points are plotted at the average depth of the sampled sediment depth interval.

Fig. 2. Vertical distributions of ^{224}Ra and ^{228}Th activities (dpm g^{-1}) in bulk sediment at the different sampling times. Points are plotted at the average depth of the sampled sediment depth interval.

Fig. 3.

(upper panels) Vertical distributions of MeHg in aqueous phase (pmol l^{-1}) and solid phase (pmol g^{-1}) within the sediment at each sampling time; and vertical distribution of THg in aqueous phase and solid phase (lower panels). The dashed line represents the sediment-water interface and the symbols above the line refer to samples in the overlying water. Points are plotted at the average depth of the sampled sediment depth interval.

Fig. 4. Variations of dissolved ^{224}Ra activity (dpm l^{-1}) in filtered core overlying water with incubation duration time in different months.

Fig. 5. Variations of MeHg concentration (both individual cores and the average for the three cores) (pmol l⁻¹) in filtered core overlying water with incubation duration time in different months. The concentration in the control incubation core tubes is also plotted.

Fig. 6. Contribution pattern, as a percentage of the total, of various sources for Hg species (left panel: MeHg; right panel: THg) to the study site. R represents the sum of all unidentified terms.

Table 1

Activity of dissolved ^{224}Ra and the concentrations of Hg species in overlying water and surficial (0–1 cm) porewater.

Month	Overlying water		Surficial porewater			
	^{224}Ra (dpm l ⁻¹)	MeHg (pmol l ⁻¹)	THg (pmol l ⁻¹)	^{224}Ra (dpm l ⁻¹)	MeHg (pmol l ⁻¹)	THg (pmol l ⁻¹)
May	1.88 ± 0.22	0.44	6.42	7.81 ± 1.33	8.10	56.3
June	1.21 ± 0.05	0.93	9.14	3.83 ± 1.08	1.13	26.1
July	2.29 ± 0.10	1.34	6.96	3.68 ± 0.72 ^a	2.87	11.4
August	1.67 ± 0.06	1.08	8.33	5.69 ± 0.92	1.44	17.5

^a 0–2 cm porewater.

Benthic fluxes of ^{224}Ra , MeHg and Hg species based on ^{224}Ra - ^{228}Th disequilibrium as well as related parameters.

Table 2

Month	^{224}Ra flux ($\text{dpm cm}^{-2} \text{ d}^{-1}$) ^a	ξ	D_s^{Ra} ($\text{cm}^2 \text{ d}^{-1}$)	D_s^{MeHg} ($\text{cm}^2 \text{ d}^{-1}$)	D_s^{THg} ($\text{cm}^2 \text{ d}^{-1}$)	MeHg flux ($\text{pmol m}^{-2} \text{ d}^{-1}$) ^b	Total Hg flux ($\text{pmol m}^{-2} \text{ d}^{-1}$) ^b
May	0.037 ± 0.01	–	0.414	0.601	0.475	690 ± 260	3570 ± 1340
June	0.088 ± 0.026	180 ± 92	0.382	0.553	0.438	92 ± 47	6490 ± 3290
July	0.080 ± 0.018	590 ± 330	0.406	0.588	0.465	2470 ± 1360	5620 ± 3100
August	0.031 ± 0.021	33 ± 23	0.466	0.673	0.533	40 ± 29	830 ± 590

^aResult from core incubation experiment.

^b16 h per day.

²²⁴Ra benthic flux based on core incubation experiment as well as the relevant coefficients for calculation.

Table 3

Month	λ (h ⁻¹)	H (cm)	A ₀ (dpm l ⁻¹)	A _{Ra-I} @ ~6 h (dpm l ⁻¹)	F _{Ra-I} (dpm cm ⁻² d ⁻¹)	$\frac{{}^{224}\text{Ra flux}}{F_{\text{Ra-I}}}$
May	0.0079	20	0.95 ± 0.11	1.58 ± 0.17	0.055 ± 0.016	–
June	0.0079	22	0.64 ± 0.08	1.88 ± 0.19	0.124 ± 0.020	0.94
July	0.0079	20	0.80 ± 0.14 ^a	1.87 ± 0.18	0.091 ± 0.019	0.76
August	0.0079	20	0.99 ± 0.05	1.44 ± 0.10	0.058 ± 0.013	1.25

– No data.

^a Average of May & June (t = 0).

Table 4

Parameters relative to MeHg flux estimation based on core incubation.

Time	Incubation time (h)	Average ^a (pmol l ⁻¹)	Slope (pmol l ⁻¹ h ⁻¹)	F _{MeHg-I} (pmol m ⁻² d ⁻¹)
May	0	0.23	0.27 ± 0.02	1280 ± 96
	6	1.42 ± 0.81		
	12	3.60 ± 1.13		
	20	5.37 ± 2.01		
June	0	0.77	-0.04 ± 0.01	-197 ± 53
	5.5	0.32 ± 0.07		
	11.5	0.19 ± 0.00		
	17.5	0.08 ± 0.03		
July	0	1.37	-0.08 ± 0.02	-383 ± 86
	6	0.67 ± 0.04		
	12	0.41 ± 0.11		
	20	0.59 ± 0.39 ^b		
August	0	0.17	0.02 ± 0.00	98 ± 14
	4.3	0.28 ± 0.12		
	11.5	0.41 ± 0.09		
	20.5	0.23 ± 0.06 ^b		

^a Mean ± 1SD of triplicates over the same duration.^b Values exclusive of regression.

Table 5

Summary of parameters in mass balance model.

Symbol	Value	Description
${}^aF_{\text{Hg}}$ (pmol m ⁻² d ⁻¹)		Benthic MeHg flux Benthic THg flux
h (m)	0.3	The average height of overlying water in one tidal cycle
t (h)	8	Total resident time of overlying water in one tidal cycle
${}^b\omega$ (cm d ⁻¹)	0.008	Precipitation rate of suspended particles
$c_{\text{Hg-d}}$ (pmol l ⁻¹)		Dissolved MeHg in overlying water Dissolved THg in overlying water
$c_{\text{Hg-p}}$ (pmol g ⁻¹)		Particulate MeHg in overlying water Particulate THg in overlying water
c_{Hg} (pmol l ⁻¹)		Sum of particulate Hg and dissolved Hg in overlying water ($c_{\text{Hg}} = \text{TSS} \cdot c_{\text{Hg-p}} + c_{\text{Hg-d}}$) ${}^c\text{TSS} = 32.3 \text{ mg l}^{-1}$
$c_{\text{sea-d}}$ (pmol l ⁻¹)	0.02 ^d 2.14 ^d	Dissolved MeHg in invasion seawater Dissolved THg in invasion seawater
$c_{\text{sea-p}}$ (pmol g ⁻¹)	10.6 ^d 47.0 ^d	Particulate MeHg in invasion seawater Particulate THg in invasion seawater
c_{sea} (pmol l ⁻¹)		$c_{\text{sea}} = \text{TSS}_{\text{sea}} \cdot c_{\text{sea-p}} + c_{\text{sea-d}}$ ${}^d\text{TSS}_{\text{sea}} = 29.7 \text{ mg l}^{-1}$
F_{atm} (pmol m ⁻² d ⁻¹)	0.79 ^e 122 ^f	Atmospheric deposition flux for MeHg Atmospheric deposition flux for THg

^aEstimated fluxes in Table 2, based on ²²⁴Ra/²²⁸Th disequilibrium in this study. A factor of 16 h per day is applied.^bAdopted from Van Metre (2012).^cMeasured values in this study.^dAdopted from Chen et al. (2014).^eAdopted from Nadim et al. (2001).^fAdopted from Gichuki and Mason (2014).