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ORIGINAL PAPER

Seasonal Cycling and Transport of Mercury and Methylmercury in the Turbidity Maximum of the Delaware Estuary

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Abstract The Delaware River Estuary (DRE) is a cornerstone of industrialization, shipping, and urban usage, and has a long history of human impact on pollution and recovery. Mercury (Hg) is a contaminant of concern in the DRE based upon concentrations in some fish samples that were found to exceed State and Federal fish tissue criteria. Methylation of Hg often follows a seasonal pattern as its production is biologically mediated. Surveys were conducted in November 2011, April 2012, and July 2012 to assess this effect. We sampled surface and bottom water at six sites spanning the estuarine turbidity maximum (ETM) in the main channel of the river, plus three sediment sites at shallow, subtidal locations. Our results indicate there is a clear seasonal increase in both water column and sediment methylmercury (MeHg) and %MeHg concentrations in the ETM during July. Water-column-filtered total mercury (HgT), suspended particle HgT, and MeHg concentrations were found to fluctuate little with location or season in the ETM. In contrast, sediment MeHg, water-column-filtered MeHg, and pore water HgT varied seasonally. Furthermore, pore water MeHg levels were elevated in concert with increased k_{meth} rates in July. Estimated river input and sediment and atmospheric depositional MeHg flux were compared seasonally. River flux was more than an order of magnitude higher than sediment flux in April, coinciding with higher fluvial transport. However, during July, river flux decreases and sediment flux becomes a larger relative source. This trend has potential implications for fish and other biota residing in the DRE during summer.

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1 Introduction

Methylmercury (MeHg) is a biomagnifying neurotoxin, which is ubiquitously produced within aquatic systems throughout the world (Ullrich et al. 2001; Driscoll et al. 2013; Pucko et al. 2014; Merritt and Amirbahman 2009; Schäfer et al. 2010). Consumption of fish containing elevated concentrations of MeHg is associated with adverse health effects in humans and other wildlife (Chen et al. 2008; Clarkson 2009; Oken et al. 2005). As seafood from marine and estuarine systems account for nearly 90 % of fish consumed in the USA (Sunderland 2007) and elsewhere, it is important to assess the potential environmental health impacts from elevated MeHg in the numerous estuaries for both commercial and recreational fishing, given that many coastal ecosystems have been impacted by anthropogenic mercury (Hg) inputs.

The Delaware Estuary is an urban and industrialized region that encompasses all tidally inundated regions from Trenton, New Jersey, to the mouth of Delaware Bay (Hall and Burton 2005). Like most estuaries, the salinity is variable (0–18 ppt) and affected by seasonal freshwater output. Prior sampling indicated that concentrations of total mercury (HgT) was elevated in striped bass arriving to spawn in the upper estuarine turbidity maximum (ETM), with a mean concentration in excess of 500 ng g^{-1} wet weight (Greene 2011). Recent testing confirmed that adult striped bass collected from the less contaminated Delaware Bay have lower HgT levels than those residing in the more contaminated ETM (Greene 2013), suggesting potential contamination with MeHg from the estuary. The DRE has a long history of heavy industrial activity with a variety of substantial past and present sources of Hg, including a local chloralkali plant, several coal-fired power plants, petroleum refineries, steel mills, chemical manufacturing, wastewater treatment, and medical and dental practices. However, as a result of Federal and State regulations and increased environmental awareness, the release of Hg from these sources has been greatly reduced, or even eliminated (Reinfelder and Totten 2006; Hartwell et al. 2001). Accordingly, most of the current impacts associated with Hg in the system are thought to be a result of seasonal exchanges with 'legacy' pollution residing in the sediments, and inputs to the water column from local and watershed sources. Though Hg input into the DRE has been decreasing, the current Hg levels could still provide a sufficient foundation for profuse Hg methylation within the sediments and contamination of the food chain (Hartwell et al. 2001; Kim et al. 2006; Merritt and Amirbahman 2009). As MeHg is the dominant species in biota, in situ Hg methylation within the estuary could contribute to the elevated MeHg levels in biota and be a concern for local consumers of DRE fish and other aquatic biota.

Previous research has indicated that sediments can play a key role in Hg cycling in coastal and estuarine regions (Chen et al. 2014; Schäfer et al. 2010; Hammerschmidt et al. 2008; Kim et al. 2006; Conaway et al.,2003). Sediment can be a significant source of MeHg into the overlying water column through various processes, including resuspension, pore water advection and diffusion, and bioturbation (Bloom et al. 1999; Mason et al. 1999; Kim et al. 2006; Lambertsson and Nilsson 2006; Hollweg et al. 2009). A crucial point of interest in MeHg transfer is the ETM, where intense mixing of fresh and saline generates waters laden with suspended particulate matter and enhances benthic–pelagic coupling. Particle exchange in the ETM can be intense and tidally controlled. Also,

seasonal flow volumes could possibly impact the overall influence of ETM cycling by providing a shallower interface between the sediment and the overall water column. Low oxygen concentrations can form in surface waters in estuarine ETM regions (Parker et al. 1994), further exposing particulate material to anoxic conditions at neap tides, and oxic conditions at spring tide, which could potentially impact chemical speciation and net Hg methylation. Moreover, sediment resuspension in the ETM could amplify Hg methylation rates and transfer of MeHg into the overlying water column (Heyes et al. 2004; Kim et al. 2004). Thus, this region was specifically examined to determine its importance and impact on the Hg and MeHg cycling and flux in the Delaware estuary.

Some fish only have a seasonal presence in the DRE; therefore, it is important to assess seasonal changes in Hg inputs and methylation, especially the impact during the summertime to properly assess exposure. This is also important for the fish which continuously inhabit the region. We undertook a seasonal investigation of the DRE in order to assess the seasonal impacts of on Hg and MeHg sources and cycling into this important commercial and residential region. Our results indicate that seasonal methylation and sediment MeHg flux could be a significant source of MeHg into the DRE during the summertime, potentially impacting the health and vitality of commercial fisheries in the region. Furthermore, water column turbulence, in addition to enhanced diffusion from sediment and groundwater flow, is likely to increase and influence MeHg transfer and bioaccumulation within the ETM. Sediment MeHg flux could be especially critical during the low-flow summer period, when the region provides a nursery habitat for many fish. Our results suggest that the impact of sediment MeHg source is less important during the higher-flow months of the year.

2 Methods

Sampling was conducted in the DRE in November 2011, April 2012 and July 2012. The three sediment core sampling locations in the ETM and are noted on Fig. 1: Evraz/Gen Chem Cove (EGC), Lukens Marsh (LM), and Hamburg Cove (HC). Surface and bottom water column samples were collected concurrently at six sites in the deep-water channel of the ETM (Fig. 1). Water sample sites from north to south were: Marcus Hook (MH), Oldmans Point (OP), Cherry Island (CI), New Castle (NC), Pea Patch (PP), and Reedy Island (RI). Total distance covered by this study was roughly 20 river miles.

Sediment was collected in acid-cleaned polycarbonate coring tubes using a stainless steel gravity corer attached to a steel pole. Coring tubes with overlying water were capped and sealed immediately after sediment collection to preserve ambient oxygen conditions, and were stored upright on ice (out of direct sunlight) until processed. Sediments were processed the day of collection at the Delaware DNREC, Division of Water Environmental Laboratory (Dover, DE). Subsections (2 cm) were frozen in acid-washed, screw cap plastic cups. Core sectioning for pore water collection was done inside a nitrogen-filled glove bag to maintain low-oxygen conditions. Sediment core pore water was extracted from each 2-cm sediment subsection using direct vacuum filtration with pre-rinsed Nalgene plastic filter units and 0.22-μm cellulose acetate filters, and was centrifuged prior to filtration. Pore water collection required pooling water from $\sim$4 separate cores for each depth. Aliquots of pore water were stored frozen in Teflon bottles. Pore water samples for sulfide analysis were preserved with sulfide antioxidant buffer (SAOB) and held inside the glove bag for no more than 24 h prior to analysis using a sulfide electrode (method detection limit 0.17 μM; Bouwer and Murphy 1994; Hollweg et al. 2009).

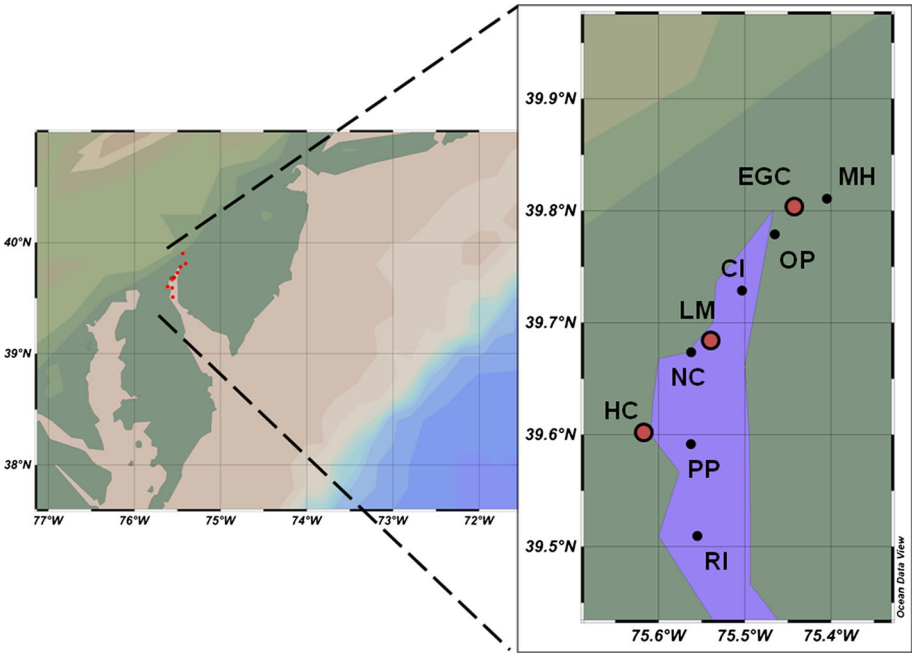

Fig. 1 Delaware River Estuary stations and location of the estuarine turbidity maximum (ETM). Sediment stations are labeled as Evraz/Gen Chem Cove (EGC), Lukens Marsh (LM), and Hamburg Cove (HC). Water stations sampled are noted as Marcus Hook (MH), Oldmans Point (OP), Cherry Island (CI), New Castle (NC), Pea Patch (PP), and Reedy Island (RI)

Water samples were collected during the monthly DRBC survey operations using trace-metal clean techniques. Water samples were transferred from Teflon-coated Niskin bottles to glass holding bottles, and stored in double zip bags inside iced coolers. Field duplicate surface samples were collected at MH in April and at NC in July. Water for Hg speciation was filtered within 24 h of collection using acid-washed Nalgene plastic vacuum filtration units inside a nitrogen-filled glove bag. Filtrates were acidified (0.5 % trace-metal-grade HCl) and refrigerated, and the quartz fiber particulate filters (QF/F; 0.45 μm) were frozen inside acid-washed plastic dishes. Additional ancillary parameter filtrations were done using clean glass or plastic filtration units and QF/F or glass fiber filters (GF/F; 0.7 μm).

Sediment mercury methylation rates (k_{meth}) were estimated using the methylation rate of an enriched stable isotope spike of ^{200}Hg (purity of 96.41 % obtained from Oak Ridge National Laboratory; Gilmour and Riedel 1995; Hintelmann et al. 2000; Heyes et al. 2006). Stock isotope solutions were diluted with filtered bottom water (0.22 μm) and equilibrated for an hour before injection into intact duplicate sediment cores. Injections were done at 1-cm intervals for 12 cm down the core, as well as 2 cm above the sediment into the overlying water. Capped sediment cores were then incubated for 2 h at ambient laboratory temperature. Detection limits (DL) for k_{meth} were estimated to be 0.0006 day^{-1} (Mitchell and Gilmour 2008), and methylation rates were above the DL for all samples. Mercury isotopes were measured using a PerkinElmer ELAN DRCII ICP-MS with an attached flow injection auto sampler (FIAS) for HgT analysis and a Tekran 2700 auto-analyzer for MeHg analysis (Hintelmann et al. 2000; Heyes et al. 2006).

Sediment analyses included HgT and MeHg in sediment and pore water, free sulfide in pore water, and bulk organic content as loss on ignition (LOI). Water analyses included filtered and particulate HgT and MeHg, total suspended solids (TSS), chlorophyll a (chl a), salinity, nitrate, and dissolved organic carbon (DOC). All samples were kept cold or frozen until analyses were conducted at the University of Connecticut (Avery Point). Analytical methods have been outlined in detail in previous investigations (APHA 1995; Sharp et al. 1995; Bloom and Fitzgerald 1988, Hammerschmidt and Fitzgerald 2001; Tseng et al. 2004; Hollweg et al. 2009; Kim et al. 2006), thus will not be discussed further here. Analytical accuracy and precision for both sediment and water column measurements can be found in supporting information (SI; Tables S1 and S2). Sample results were corrected for field and preparation blanks as appropriate.

3 Results

3.1 Bulk Sediment

Sediment HgT concentrations ranged from $\sim$0.5 to 4.3 nmol g^{-1}, among all three sites and sampling events, with a peak observed at LM in November 2011 (Fig. 2a). Error bars reflect the differences in concentration between two sediment cores and two depths (0–2, 2–4 cm; vertical profiles presented in SI: Figure S1) at each site. Overall, mean HgT concentrations were not statistically different among either sites or seasons ($p > 0.05$, ANOVA). Additionally, paired t test comparisons of the average surface (0–2 cm) sediment HgT for each site demonstrate that the sites were not statistically different ($p > 0.1$, $n = 6$).

Average values for the surface sections (0–4 cm) and seasons were 1.80 $\pm$ 0.45 nmol g^{-1} for HC (RSD 25 %), 1.96 $\pm$ 0.86 nmol g^{-1} at LM (RSD 44 %), and 1.34 $\pm$ 0.16 nmol g^{-1} for site EGC (RSD 25 %). The higher variability at LM could potentially reflect local river inputs into this region, although that site also had the highest %LOI variability (6.1 $\pm$ 2.2 %; RSD 36 %). The %LOI exhibited considerable variation seasonally and among sites (SI: Tables S4, S5 and S6), which could also be a reflection of fluvial inputs to the DRE .

In contrast, sediment MeHg concentrations were more variable than HgT and displayed seasonal differences. Concentrations ranged from 0.3 to 5.3 pmol g^{-1} for November 2011 and 0.1 to 7.2 pmol g^{-1} for April 2012 (Fig. 2b). Sediment MeHg values were clearly elevated in July 2012 (4.7–6.0 pmol g^{-1}) compared to April and November (SI: Tables S4, S5 and S6). July surface MeHg concentrations (for 0–2 cm) were significantly different from April (t test, $p = 0.007$, $n = 6$) and November (t test, $p = 0.04$, $n = 6$); however, concentrations in April and November were not significantly different (t test, $p = 0.42$, $n = 6$). Similarly, concentrations at depth (8–10 cm) were also statistically different in July compared to April (t test, $p = 0.038$, $n = 6$). Methylmercury increased $\sim$200 % at sites HC and LM, and $\sim$40 % for site EGC, suggesting substantial production of MeHg in the sediment during the late spring/early summer. Accordingly, average sediment %MeHg (MeHg/HgT) was increased for each site in July (Fig. 2c). Notably, however, the average %MeHg was below 0.5 % overall for the ETM of the Delaware River.

3.2 Sediment Pore Water

Pore water HgT was elevated in April, with a peak observed at EGC (Fig. 3a). Pore water HgT was uniformly low at each site in July. Average pore water distribution coefficients (log K_d; K_d [l/kg] = [solid]/[pore water]) for HgT were reduced at site LM in November,

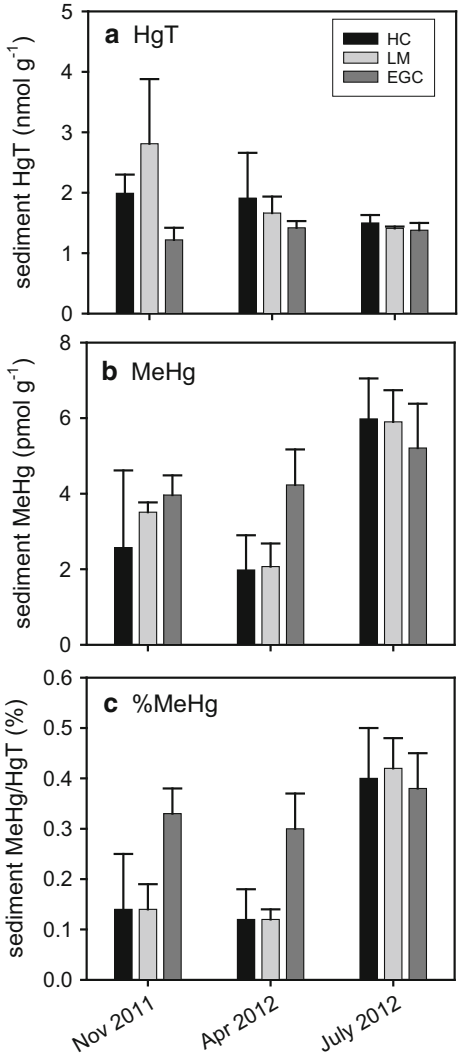

Fig. 2 Mean (SD) sediment (0–4 cm) **a** total mercury (HgT), **b** methylmercury (MeHg) and **c** %MeHg (MeHg/HgT) in November 2011, April 2012, and July 2012 at Hamburg Cove (HC), Lukens Marsh (LM), and Evraz-Gen Chem (EGC)

decreased at all sites in April, and were elevated at all sites in July (Table 1). Given the similarity in total sediment HgT between sites and season, these differences are driven primarily by differences in pore water concentrations. The average sediment pore water sulfide was highest in November at HC and EGC, and was lower and relatively uniform with depth at the other sites and seasons (0.1–1.1 μM; SI: Figure S2, Tables S4, S5 and S6).

Methylmercury pore water concentrations ranged from <0.1 to 2.3 pM among all three sites and sampling events (SI: Tables S4, S5 and S6), with a maximum concentration observed at EGC during July. Complementing sediment MeHg values, pore water MeHg concentrations were elevated in July at each site (Fig. 3b); however, the differences for the surface sediment (0–2 cm) were not significant given that only one core per site was used for pore water analysis. Additionally, average pore water %MeHg was higher at each site (26.8–62.7 % for 0–6 cm) in July (Fig. 3c), and %MeHg was greater in the pore water compared with sediment.

Table 1 Sampling information and mean sediment HgT and MeHg log K_d values (range) at each sampling site during each season

Survey/site	Time/date	Latitude (°W)	Longitude (°S)	log K_d HgT (l/kg)	log K_d MeHg (l/kg)
November 2011					
HC	0923/11-3-11	39.6031	−75.6121	5.49 (5.29–5.79)	3.69 (3.39–4.07)
LM	0900/11-2-11	39.6850	−75.5364	4.92 (4.54–5.17)	3.85 (3.68–4.07)
EGC	1130/11-2-11	39.8006	−75.4387	5.28 (5.17–5.44)	3.59 (3.36–3.86)
April 2012					
HC	0730/4-16-12	36.6038	−75.6101	5.29 (4.7–5.85)	3.49 (3.1–4.11)
LM	1045/4-16-12	39.6848	−75.5372	4.60 (3.59–6.07)	3.97 (3.69–4.25)
EGC	0940/4-16-12	39.8011	−75.4385	5.01 (4.37–5.53)	4.28 (3.58–6.06)
July 2012					
HC	0650/7-31-12	39.6038	−75.6101	5.55 (5.41–5.63)	3.65 (3.45–3.94)
LM	0930/7-31-12	39.6856	−75.5372	5.64 (5.38–6.25)	3.57 (3.15–3.89)
EGC	0830/7-31-12	39.8011	−75.4385	5.77 (5.42–6.22)	3.39 (3.13–3.67)

This is likely due to the comparatively stronger binding of inorganic Hg to solids than MeHg, as reflected in the log K_d values in Table 1. Seasonal average pore water MeHg log K_d values were uniform, though site averages were slightly lower in July (Table 1).

Methylation rates (k_{meth}) varied among sites and season with values of k_{meth} ranging from 1.3 to 5.1 % day^{-1} for November, 2.5–5.3 % day^{-1} in April, and 2.9–5.0 % day^{-1} during July (SI: Table S13). Rates were relatively uniform down core at each site. At HC, k_{meth} increased from an average of 1.4 ± 0.2 % day^{-1} (average of all depths, 2 cores) in November to 4.0 ± 2.4 % day^{-1} in April to 11.3 ± 9.3 % day^{-1} in July. However, in July the two HC cores yielded very different k_{meth} values (4.1 ± 0.5 % day^{-1} and 18.6 ± 7.9 % day^{-1}). While k_{meth} increases over the season concurrent with warming temperatures and associated higher microbial activity, it is evident from site HC that there is the capacity for high spatial variability within a site, especially during the summer. There was no increase in methylation rate with season at LM, and only a slight increase at EGC.

3.3 Water Column

Filtered HgT concentrations in surface and bottom water samples were consistent among surveys, ranging from 2.1 to 3.8 pM for November, 1.2–3.5 pM for April, and 1.7–4.0 pM in July (<20 % differences; Fig. 4a). Surface and bottom water concentrations for MeHg, on the other hand, varied among both surveys and seasons. Values were lowest in November, increased in April, and reached their highest concentrations in July (Fig. 4b). Methylmercury concentrations in November were all <0.07 pM (%MeHg < 2 %; SI: Tables S7, S8 and S9),

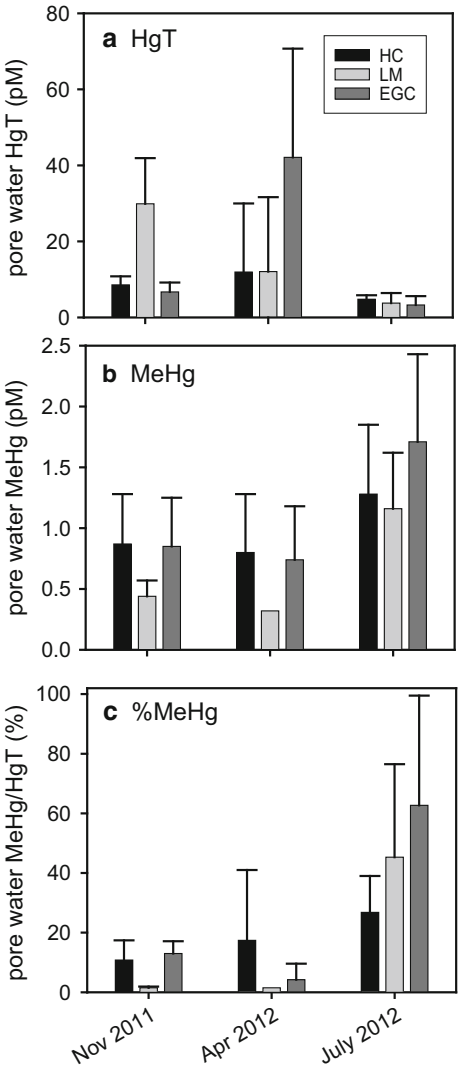

Fig. 3 Mean (SD) sediment pore water (0–6 cm) **a** total mercury (HgT), **b** methylmercury (MeHg) and **c** %MeHg (MeHg/HgT) in November 2011, April 2012, and July 2012 at Hamburg Cove (HC), Lukens Marsh (LM), and Evraz-Gen Chem (EGC)

and overall average filtered MeHg for April was 0.25 ± 0.10 pM. In July 2012 there was also a modest increase in surface concentrations over bottom water for several sites, as well as elevated concentrations for middle locations of the ETM compared to outer sites of the study. Average concentrations for bottom waters at these middle sites (0.73 ± 0.33 pM) were higher than the outer site concentrations (0.33 pM at MH and 0.45 pM at RI). Filtered %MeHg increased seasonally concurrently with increasing filtered MeHg (Fig. 4c). Average %MeHg increased from ~1.2 % in November, to 16 % for April, and up to 29 % in July.

Suspended particle HgT concentrations (surface and bottom) were generally in the range of 0.5–1.0 nmol g^{-1} during each survey (Fig. 5a). As indicated by the relatively uniform filtered and suspended particle HgT concentrations among seasons, log K_d values for water column HgT (K_d [l/kg] = [solid]/[dissolved]) in each season overlapped (Table 3). Suspended particle MeHg concentrations (surface and bottom) generally

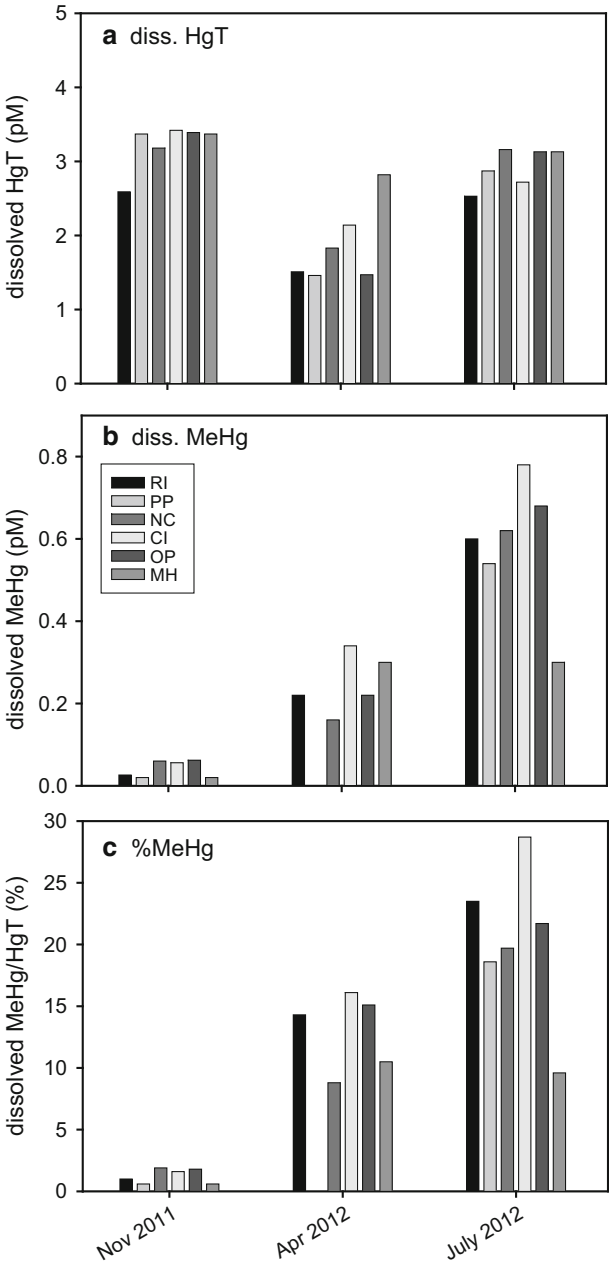

Fig. 4 Average water column (surface and bottom water) **a** dissolved total mercury (HgT), **b** dissolved methylmercury (MeHg) and **c** %MeHg (MeHg/HgT) at Reedy Island (RI), Pea Patch (PP), New Castle (NC), Cherry Island (CI), Oldmans Point (OP) and Marcus Hook (MH) in November 2011, April 2012, and July 2012

Table 2 Sampling information and mean water column HgT and MeHg log K_d values (range) at each sampling site during each season

Survey/site	Time/date	Latitude (°W)	Longitude (°S)	log K_d HgT (l/kg)	log K_d MeHg (l/kg)
November 2011					
Reedy Island	0759/11-2-11	39.5096	−75.5550	5.46 (5.33–5.59)	5.29 (5.11–5.47)
Pea Patch Island	1147/11-2-11	39.5916	−75.5626	5.57 (5.4–5.73)	5.29 (5.19–5.38)
New Castle	1320/11-3-11	39.6738	−75.5263	5.37	–
Cherry Island	1140/11-3-11	39.7289	−75.5033	5.09 (5.02–5.16)	4.88 (4.86–4.89)
Oldmans Point	0932/11-3-11	39.7790	−75.4650	5.58 (5.42–5.76)	5.07 (4.89–5.24)
Marcus Hook	0755/11-3-11	39.8108	−75.4047	5.32 (5.24–5.4)	5.11 (4.93–5.28)
April 2012					
Reedy Island	0745/4-16-12	39.5096	−75.5550	5.61 (5.58–5.65)	3.82 (3.44–4.19)
Pea Patch Island	1020/4-16-12	39.5916	−75.5626	5.66	–
New Castle	1250/4-16-12	39.6738	−75.5263	5.39 (5.3–5.48)	3.74 (3.6–3.87)
Cherry Island	1631/4-16-12	39.7290	−75.5033	5.54 (5.53–5.56)	4.05 (3.89–4.21)
Oldmans Point	1000/4-17-12	39.7790	−75.4650	5.79 (5.7–5.87)	4.43 (4.19–4.66)
Marcus Hook	1300/4-17-12	39.8108	−75.4047	5.80 (5.6–6.01)	4.56 (4.06–5.07)
July/August 2012					
Reedy Island	0655/8-2-12	39.5096	−75.5550	5.36 (5.33–5.4)	3.88 (3.70–4.06)
Pea Patch Island	0850/8-2-12	39.5916	−75.5626	5.48 (5.29–5.67)	3.96 (3.41–4.52)
New Castle	1055/8-2-12	39.6738	−75.5263	5.36 (5.2–5.53)	3.94 (3.88–4.01)
Cherry Island	0820/7-31-12	39.7290	−75.5033	5.57 (5.42–7.72)	3.54 (3.22–3.87)
Oldmans Point	1015/7-31-12	39.7790	−75.4650	5.60 (5.45–5.75)	4.20 (3.99–4.06)
Marcus Hook	1335/7-31-12	39.8108	−75.4047	5.61 (5.5–5.72)	4.34 (4.27–4.41)

ranged from 3 to 6 pmol g^{-1} in November and April, and 4 to 7 pmol g^{-1} in July (Fig. 5b). Unlike filtered MeHg levels, there was little evidence of a seasonal increase in suspended particle concentrations of MeHg or %MeHg (Fig. 5c). Due to seasonal changes in water-column-filtered MeHg, the average log K_d for MeHg was lower in April and July, and higher for the low water-column-filtered MeHg concentrations in November (Table 2).

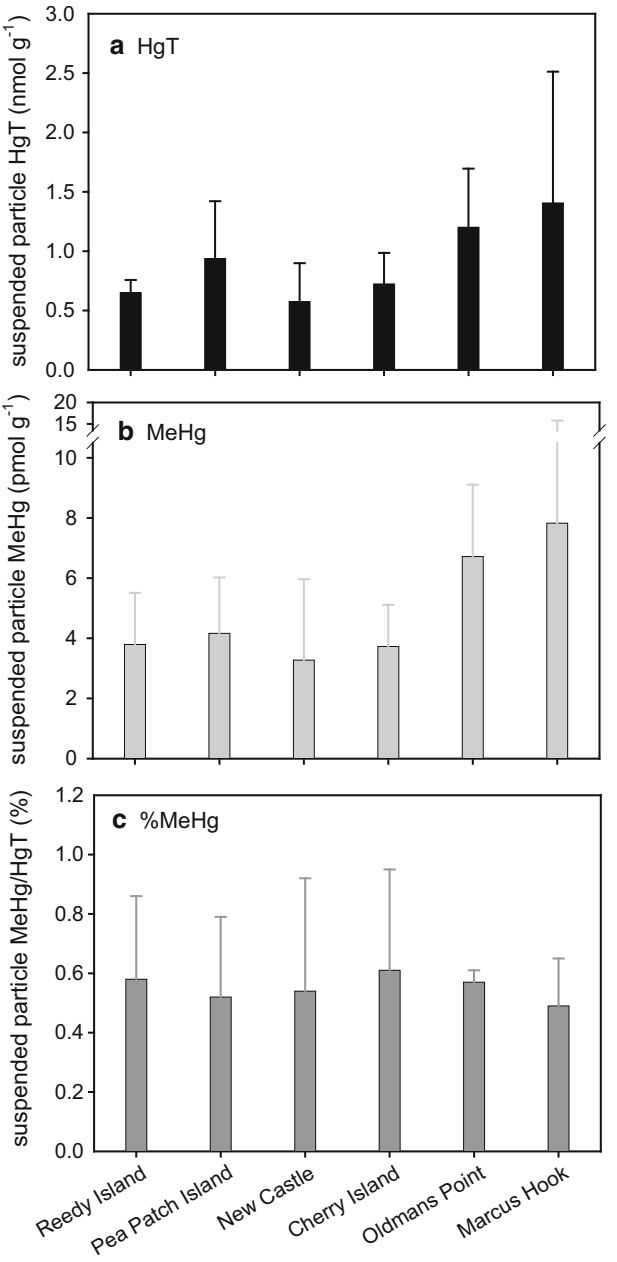

Fig. 5 Mean water column concentrations for: **a** suspended particle total mercury (HgT), **b** suspended particle methylmercury (MeHg) and **c** %MeHg (MeHg/HgT) for November 2011, April 2012, and July 2012 at each water sampling site

As expected, total suspended solids (TSS) were lower in surface waters (12–58 mg/L) than bottom waters (16–221 mg/L) during each survey (SI; Tables S7, S8 and S9). Bottom water TSS concentrations indicated no clear trends and remained relatively uniform. Salinity varied slightly depending on site and season within the sampling region (SI; Tables S10, S11 and S12). November salinities consistently ranged 'fresher,' from 4 to 6 ppt for all sites. In April the RI and PP sites (downstream) experienced an increase in salinity to 11–14 ppt, while in July the salinity averaged around 10 ppt for the sites from RI to NC. The upstream sites remained relatively consistent during the seasons.

4 Discussion

4.1 Sediment and Pore Water

There were no significant seasonal changes in sediment HgT (Fig. 2a). These values are consistent with previous measurements in the DRE ETM (Hall and Burton 2005). This trend is also consistent with regional measurements from LIS and NY/NJ Harbor, where sediment HgT values overlapped among seasons (Hammerschmidt et al. 2008; Balcom et al. 2008). The lack of a sharp HgT concentration peak with depth could be an indication of enhanced particle mixing within the highly turbulent ETM region of the DRE. Pore water trends essentially paralleled with sediment HgT. Heyes et al. (2004) reported increased sediment mobilization during the arrival of the spring freshet and fresh particulate material showed advanced desorption of Hg from sediment particles to interstitial waters in the Hudson ETM. However, we did not find evidence for this process in the Delaware ETM. Seasonally consistent HgT is expected over the short term in this DRE study, as typical sedimentation rates are less than measured sampling intervals (i.e., 2-cm sections). Given the sources and sinks of Hg to this region of the estuary, and overall physical dynamics, the statistical tests confirm that differences in concentration likely reflect spatial heterogeneity. The vertical distributions of HgT in the top 10 cm indicate low variability with depth, suggesting no recent change in inputs of Hg to the sediment over the recent past (SI: Figure S1).

Average sediment MeHg concentrations were comparable for each site in November 2011 and April 2012 (Fig. 2b), though site EGC generally had elevated MeHg below 4 cm. Sampling in July 2012 revealed a different picture, as MeHg concentrations at each sediment station were clearly elevated relative to the other sampling times (Fig. 2b). Accordingly, there was suggestive evidence for a significant summertime increase in sediment MeHg content in the DRE. Pore water MeHg concentrations also subsequently increased during July for all sites. Similar amplifications in concentrations during summer have been observed for other regional estuaries (Table 3). Hammerschmidt et al. (2004) noted higher pore water MeHg in the upper 4 cm of sediment, coinciding with a peak in solid-phase MeHg in LIS. We, however, found no MeHg peak in surface sediment for the DRE. Hollweg et al. (2009) reported that seasonal variability in sediment MeHg was greater than for HgT in the Chesapeake Bay, moreover attributing the variance to seasonality driven changes in net MeHg production.

Seasonal variation in MeHg is indicative of in situ production of MeHg at warmer temperatures, with enhanced MeHg:Hg(II) concentration ratios. Temperature affects both sulfate-reducing bacteria (SRB) activity (King et al. 1999) and Hg methylation (Merritt and

Table 3 Range of sediment and pore water HgT and MeHg concentrations for estuaries adjacent to the Delaware River Estuary

Estuary	Sediment HgT (nmol g^{-1})	Sediment MeHg (pmol g^{-1})	Pore water HgT (pM)	Pore water MeHg (pM)	References
Chesapeake Bay					
Mid-estuary	0.3–0.9 0.3–1.0	1.0–5.0 0.5–3.5	4.0–23	0.05–1.0	Hollweg et al. (2009)[a] Mason et al. (1999)[b]
Near mouth	0.1	0.9–1.0	13–16	1.0–2.0	Hollweg et al. (2009)[a]
NY/NJ Harbor					
Mid-estuary	1.4–2.6	3.0–13	16–36	10–12	Hammerschmidt et al. 2008[c]
Near mouth	4.9–5.4	29–36	21–23	16–17	
Hudson River-ETM	2.5–10	3.0–15	5.0–75	n.d.–2.0	Heyes et al. (2004)[d]
Long Island Sound					
Western region	0.9–1.7	6.2–16	51–140	14–27	Hammerschmidt et al. (2004)[e]
Eastern region	0.2–0.3	1.0–2.0	90–190	10–30	
Delaware Estuary ETM	1.0–3.8	0.9–6.4	2.7–49	0.5–1.7	Current study[f]
	0.5–3.8				Hall and Burton (2005)[g]

[a] Mean mainstem concentrations for May, July, September 2005, April 2006; one high pore water MeHg mean of 13 pM in July 2005, 0–12 cm sed. HgT, sed. MeHg, and pore water HgT; 0–4 cm pore water MeHg

[b] Measured at Chesapeake Biological Laboratory in 1996/1997

[c] Mean mainstem concentrations for August. 2002 and May 2003, 0–6 cm for all parameters

[d] Mean concentrations for October 2000, February, March, June 2001; 0–20 cm for sediments and 0–12 cm for pore water

[e] Mean mainstem values for August 2001, March, June 2002; 0–4 m for all parameters

[f] Mean values for November 2011, April, July 2012; 0–10 cm for sediment and pore water

[g] Mean values for spring and summer 2001/2002

Amirbahman 2009), resulting in relatively more solid-phase MeHg during warmer intervals for a given Hg(II) concentration (Ullrich et al. 2001). Decreased pore water HgT and increased water-column-dissolved MeHg concentrations during July could further reflect this seasonal methylation trend, as HgT within the pore water could have been methylated and released into the overlying water column, leaving a smaller pool of HgT remaining in the pore water.

Overall, the LOI for these sites show similar variability to total Hg, suggesting that variability in sediment HgT may be associated with sediment organic content, as shown elsewhere (Lambertsson and Nilsson 2006; Hollweg et al. 2009; Hammerschmidt et al. 2008; Schäfer et al. 2010). But while the average sediment organic matter (%LOI) varied among sampling sites and seasons, neither HgT nor MeHg concentrations were correlated with LOI within sites or seasons. Ranges in %LOI for this study are equivalent to neighboring regions of the Chesapeake Bay, LIS and Hudson River estuary. The relatively low fraction of methylated average MeHg (0.5 %) in the DRE did not appear to be related to organic content of the sediment, which was suggested as a major controlling factor over methylation rates in LIS (Hammerschmidt et al. 2004).

It is notable that we measured a significant increase in the range of sulfide concentrations during April (from <DL to 59 pM), but this did not appear to significantly impact

seasonal Hg concentrations in the DRE. Furthermore, sulfide concentrations were usually below 1 μM, and differences in sulfide levels are low compared with other estuarine locations. For example, Lambertsson and Nielsson (2006) measured pore water sulfide averages of ~2–100 μM in the Öre River estuary (Sweden), while Hollweg et al. (2009) found sulfide concentrations above 500 μM in mid Chesapeake Bay surface sediments, under the hypoxic summer water column. Schartup et al. (2013) suggested that the observed trend in LIS reflected a strong correlation between LOI and total sulfur (S), further suggesting that total S was a better predictor of net methylation across ecosystems than organic content. Additionally, sediment biogeochemical models (Skyllberg 2008; Drott et al. 2007; Driscoll et al. 2013) suggest that binding to sulfide is an important control over Hg distributions in estuarine environments. The relatively high Hg/C ratio for the Delaware River (~$10^{-6.5}$ mol/mol) compared to other locations (range $10^{-7.5}$ to 10^{-5}) examined by Schartup et al. (2013) further suggests that binding to reduced sulfur sites in sediments is important in this estuary. The Delaware River has relatively low %MeHg and a high Hg/C ratio, in comparison with areas, such as the Chesapeake Bay, which have a lower Hg/C ratio (<$10^{-6.8}$ mol/mol; Hollweg et al. 2009) and usually have higher methylation rates.

4.2 Sediment Methylation Rates

Methylmercury production is affected by the bioavailability of Hg(II) and the activity of Hg-methylating microbes, such as SRB. Both of these considerations are further influenced by biogeochemical changes across estuaries, with SRB typically becoming more active at higher temperatures (King et al. 1999). Methylmercury production is usually highest within the sediment just below the oxic/anoxic transition layer, where inhibiting sulfides are relatively low, but sulfate reduction is present (Bouchet et al. 2011; Lambertsson and Nilsson 2006). Furthermore, porosity of freshly deposited summer sediment can feasibly be greater than in spring, potentially increasing the flux of carbon and sulfate to SRB, the primary methylating bacteria (Merritt and Amirbahman 2009; Heyes et al. 2004). Our measurements among sites yielded results of k_{meth} ranging from 1.3 to 5.1 % day^{-1} for November, 2.5–5.3 % day^{-1} in April, and 2.9–5.0 % day^{-1} during July. Pore water sulfide levels were relatively low and steady through the sediment cores during the seasons (<0.5 to <5 μM); thus its inhabitation of methylation is unlikely (Merritt and Amirbahman 2009; Hollweg et al. 2009). Overall, values for k_{meth} were within the range of those measured in other east coast estuaries (Liu et al. 2015), but lower than measured in Gulf of Mexico sediments, and higher than rates in the Gironde Estuary (France) measured by Schäfer et al. (2010).

In the current study, k_{meth} was mostly independent of pore water Hg(II), as expected for a rate constant, and there was a positive relationship between k_{meth} and the %MeHg in the sediments. This suggests that differences in methylation rather than demethylation are driving sediment bulk concentrations. Enhancement in sediment methylation through the spring and summer resulted in an increase in sediment MeHg concentration and %MeHg in July. Sediment %MeHg was elevated at both sites EGC and HC in July, as well as at the EGC site in November and April, corresponding with elevated k_{meth}. These results indicate that MeHg was being produced in sediments at site EGC throughout all seasons. Pore water MeHg was also elevated at sites HC and LM in July (Fig. 3b); however, no increase in %MeHg was seen at these sites during November or April.

Methylation in sediment must produce an increase in pore water MeHg relative to overlying water in order to support a diffusive flux into the water column. As was the case

for sediment %MeHg, pore water MeHg was amplified at both sites EGC and HC in July (27.7 °C average temperature). However, unlike the trend for %MeHg, pore water MeHg was not enhanced in either November or April at EGC. This is likely due to a change in partitioning with season. These findings imply that sediment methylation and subsequent diffusion may not be the only factor supporting increases in July water column MeHg concentrations in the ETM. However, while diffusive exchange requires a difference in concentration to drive the flux, advective transport due to physical disturbance or from groundwater transport across the sediment–water interface could result in a substantial flux to the water column. Sommerfield and Wong (2011) measured a variable sediment advective movement of ~ 5 g m^{-2} s^{-1} throughout daily tidal cycles, though gravitational circulation in the DRE tends to primarily entrap sediment within the ETM region. We will discuss this further in Sect. 4.4.

4.3 Water Column

Average water column values for filtered HgT concentrations were relatively low in the DRE and fell within the range of values for mid-estuary east coast US sites (Table 4). Filtered HgT in the DRE was also equivalent to average surface values found in the San Francisco Bay estuary during April ($\sim$1–4.6 pM; Conaway et al. 2003), though lower then values measured during February, when precipitation and fluvial discharge is increased to that region along the western US coast. There was no apparent seasonal component for filtered HgT in the DRE. Conversely, filtered MeHg concentrations did increase with rising water temperatures. July concentrations were elevated for both surface and bottom water measurements in the DRE, indicating a relatively well mixed water column. November MeHg water concentrations were low compared with those found at the other sampling periods, and compared to other regional US east coast estuaries (Hollweg et al. 2009; Balcom et al. 2008). Furthermore, maxima for both %MeHg and the range of MeHg values occurred in July compared to the cooler months. Conaway et al. (2003) measured no seasonal differences in MeHg water concentrations during their investigation. To our knowledge, this is the first documented seasonal increase in water column filtered MeHg and %MeHg among estuaries along the eastern coast of North America.

There were elevated surface-filtered MeHg and %MeHg values in the ETM region compared to upstream and downstream locations (Fig. 6). In contrast to the filtered MeHg measurements, there was no consistent seasonal trend for suspended particle MeHg for any location within the ETM region. The relatively consistent particulate MeHg over time and the greater variability in filtered MeHg suggest that their concentrations are reflective of different sources and processes seasonally. Water sampling sites were located mid-channel in the Delaware River, while sediment sampling sites were near shore. Nonetheless, we propose that average sediment and suspended particle MeHg values show a relationship at each site in each season (Fig. 7b). This is a strong indication that sediment resuspension supplies particulate MeHg to the water column, and fluvial sources of suspended particulate MeHg to the ETM region of the DRE are of lesser significance.

Filtered MeHg and pore water MeHg were comparably elevated in July for all sites (Fig. 7a), further demonstrating the role of seasonally enhanced sediment microbial activity in estuarine MeHg production. Methylmercury concentrations for mean surface sediment (0–4 cm) and suspended particles also correlated with the ETM sites during each season (Fig. 7b). This further suggests that there was a potential connection between water column and sediment MeHg. The strong association strengthens the contention that sediment was supplying suspended solids, and therefore associated MeHg, to the water

Table 4 Range of water column HgT and MeHg concentrations for estuaries adjacent to the Delaware River Estuary

Estuary	Filtered HgT (pM)	Filtered MeHg (pM)	Part. HgT (nmol g^{-1})	Part. MeHg (pmol g^{-1})	Total HgT (pM)	Total MeHg (pM)	TSS (mg/l)	References
Chesapeake Bay								
Mid-estuary					2.5–15	0.05–0.45	12–16	Mason et al. (1999)[a]
NY/NJ Harbor								
Mid-estuary	1.2–3.8	0.05–0.15	1.9–6.9	5.4–27	42–82	0.23–0.4	7.1–57	Balcom et al. (2008)[b]
Near mouth	2.7–13	0.09–0.19	3.1–4.3	10–41	26–170	0.31–0.71	5.4–51	
Hudson River–ETM								
Surface water	1.1–58	0.05–0.8			87–580	0.3–0.65		Heyes et al. (2004)[c]
Bottom water	20–130	0.2–0.45	2.0–7.0	4.0–18			50–600	Heyes et al. (2004)[d]
Long Island Sound								
Western region	1.7–6.6				1.9–44			Rolfhus and Fitzgerald (2001)[e]
	3.6–10	0.24–0.64	0.1–0.3	0.8–3.9	6.6–23	0.34–0.81	40–43	Balcom et al. in prep.[f]
Eastern region	2.7–4.7				2.3–7.4			Rolfhus and Fitzgerald (2001)[e]
	5.1–6.8	0.42–0.61	0.1–0.3	1.1–2.3	9.2–16	0.44–0.61	27–39	Balcom et al. in prep.[f]
Delaware Estuary–ETM	1.5–3.4	0.02–1.0	0.4–2.2	1.1–14	17–260	0.06–2.8	14–250	Current study[g]
Delaware River Estuary	2.2–27	–	0.2–1.5	–	6.4–75	0.15–1.2	6.6–150	Reinfelder and Totten, (2006)[h]

[a] Mainstem surface water, February and July 1997

[b] Surface and bottom water, August 2002 and February, May 2003

[c] Surface water, October 2000 and February, June 2001(ETM 14 to 22 km north of Battery)

[d] Samples from 0.5 and 1.5 m off bottom, November 2001 tidal cycle study

[e] Mainstem mean HgT concentrations in surface and bottom water, August 1995, February and October 1996, May and October 1997

[f] Mainstem HgT and MeHg in surface and bottom water, one vertical profile in each region, August 2009

[g] Mean concentrations in surface and bottom water, November 2011, April, July/August 2012

[h] Mean concentrations in surface water, May, August, November 2002; one high filtered HgT value of 50 pM in November 2002

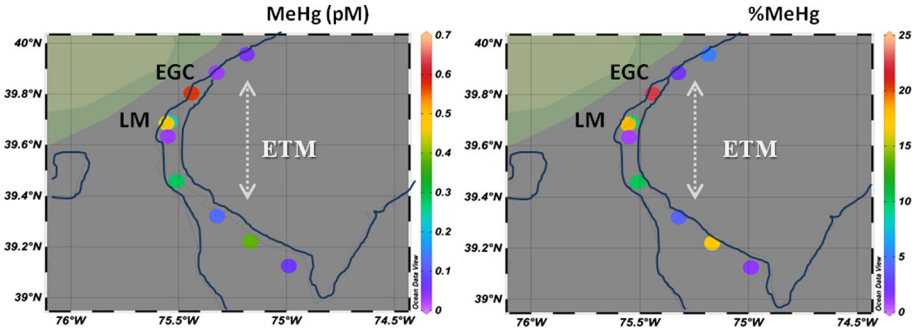

Fig. 6 Surface water dissolved methylmercury (MeHg) and %MeHg at intertidal sampling sites on the Delaware River and Estuary in July 2012 (data from Buckman et al. in prep.). Sites EGC and LM were the same location as in the current study, and were collected from the DE shoreline. All other sampling sites pictured were collected from the NJ shore. Position of the estuarine turbidity maximum (ETM) is indicated

column. This contrasts studies in other estuaries where particulate MeHg concentrations were substantially higher than the sediment (Balcom et al. in review), indicating that resuspension was not the major source of particulate MeHg to those ecosystems.

The concentrations of HgT on suspended particulate matter (Fig. 5a) were mostly similar to those of the surface sediment at the comparable sampling sites (Fig. 2a) (HC compared with PP and RI; LM compared to CI and NC; EGC compared to MH and OP), suggesting that the sediment is likely providing particulate matter through resuspension. Comparable water column particulate and sediment HgT has been found in other locations such as the NY/NJ Harbor (Balcom et al. 2008), and in sediment mesocosm resuspension experiments (Kim et al. 2004, 2006). We exhibit that average sediment (0–4 cm) and suspended particle MeHg values also appeared to imply a relationship at each site in each season (Fig. 7b). This is likewise a strong indication that sediment resuspension supplies particulate MeHg to the water column, and fluvial sources of suspended particulate MeHg to the ETM region of the DRE do not impart a different signal in the water column.

4.4 Sediment–Water Column Coupling and Mass Balance

Methylmercury in the DRE sediments is delivered into the water column via both particles (resuspension) and dissolved phase diffusive exchange. However, particle resuspension is not likely to increase the dissolved MeHg in the ETM (Kim et al. 2008). It is hypothesized that dissolved exchange between the sediment and water column is a more important factor for influencing filtered MeHg in the water column. The chemical gradient and pore water MeHg speciation are both factors that influence the diffusive flux of MeHg from the sediment into the water column. In pore water, depending on the sulfide and DOC levels, MeHg is either complexed as inorganic sulfide ligands or to DOC. he diffusion coefficient for MeHg bound to organic matter ($D = 2 \times 10^{-6}$ cm^2 s^{-1}) is smaller than that for the inorganic sulfide species ($D = 1.2 \times 10^{-5}$ cm^2 s^{-1} for CH_3HgSH and CH_3HgS^-; Hollweg et al. 2009). Due to differences in the molecular weight of the complexes, speciation has an important impact on flux (Hollweg et al. 2010; Schäfer et al. 2010; Mason et al. 2006). Diffusion, however, is not the only mechanism of transport as bioturbation and physical forces, such as tidal forcing, turbulence, and wave movement can also enhance exchange of dissolved chemical species by enhancing advection from the sediments to the

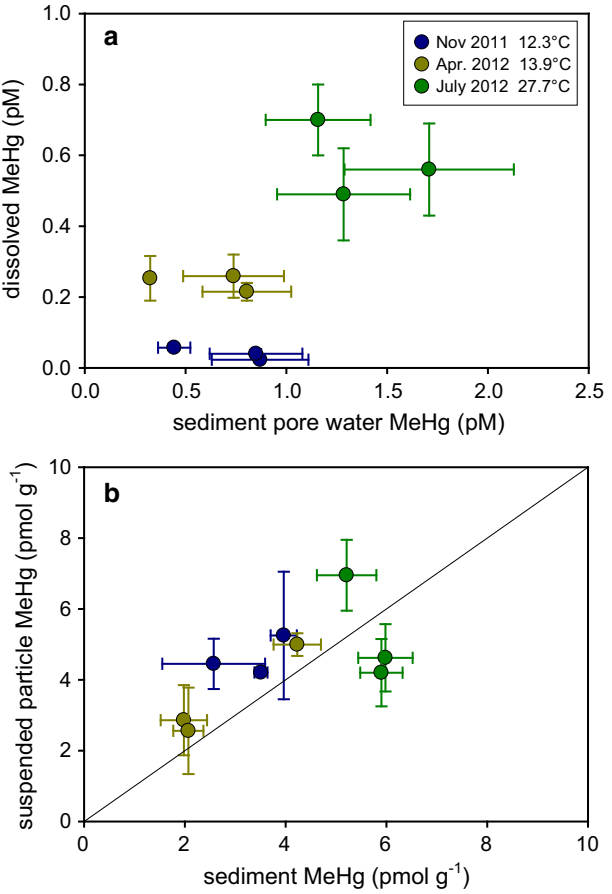

Fig. 7 **a** Average (SE) water column dissolved methylmercury (MeHg) plotted against sediment pore water MeHg (0–6 cm) and **b** average (SE) suspended particle MeHg plotted against sediment MeHg (0–4 cm; 1:1 line plotted for reference) for each sediment sampling site in November 2011, April 2012, and July 2012 (no error bars when $n = 1$ or 2). Average water column concentrations for sites PP/RI, CIF/NC, and MH/OP were used for comparison to sediment sites HC, LM, and EGC, respectively. Average water temperature (surface and bottom) shown for each survey

water (Lerman 1978; Gill et al. 1999; Benoit et al. 2009; Hollweg et al. 2010). Furthermore, groundwater flow may also be enhancing the flux. Such enhancement can lead to an increase that is more than 50 times the estimated passive diffusive flux, based on the studies summarized in Hollweg et al. (2010). Given the dynamic nature of the Delaware estuary (Cook et al. 2007; Sommerfield and Wong 2011), and comparing the Delaware to other systems, the flux could be 5–50 times greater than estimated by passive diffusion, due to additional advective mechanisms. In further support of such enhancement, a previous study of the impact of groundwater input into the region of the ETM used measurements of radon (Rn) and radium (Ra) to construct a Rn budget for the ETM, and estimated the groundwater flux to range from 14 to 29 $m^3\ s^{-1}$ (Schwartz 2003). The study concluded that the average estimated groundwater flux was equivalent to 40 times the estimated diffusive flux derived from Rn pore water measurements.

We calculated diffusive fluxes using Fick's law, considering the change in concentration between MeHg in filtered bottom water and the pore water of surficial sediments (upper 2 cm) (SI: Tables S4, S5 and S6). The overall flux was assessed by estimating the fraction of MeHg in pore water and the overlying water complexed to DOC and sulfide, using the binding constants and approach in Hollweg et al. (2010). As DOC was not measured in

pore water, it was estimated from %LOI, assuming 40 % carbon, and using the formulations in Hollweg et al. (2010) for estimating the reactive thiol concentration (RSH) from the particulate organic carbon (POC) content. Using this approach, for example, the pore water RSH concentration for 7 % LOI was estimated at 0.7 μM. Given the relatively low sulfide levels in the sediment, the fraction of the MeHg bound as inorganic sulfides ranges from 40 % (5 % LOI, 5 μM sulfide) to <1 % (7 % LOI, 0.1 μM sulfide). Due to the undetectable sulfide in the water column, organic complexation dominates MeHg speciation in the water (Hollweg et al. 2010). The flux for the organic complexes and inorganic complexes were estimated based on their relevant change in concentration across the interface as well as their respective diffusion coefficients.

At each sediment site, estimated diffusive fluxes varied by a factor of 3–5 for the various sampling periods. Since measured pore water sulfide was highest in November (>0.5 pM), estimated fluxes were higher for all sites in November compared with April, as pore water concentrations were relatively similar for these two sampling periods (Fig. 3). Fluxes were higher in July compared with that in April. The averages estimated diffusive flux for the three sites was 1.6 ± 0.21 pmol m^{-2} day^{-1} in November, 0.38 ± 0.16 pmol m^{-2} day^{-1} in April, and 1.2 ± 1.2 pmol m^{-2} day^{-1} in July. These flux values occur at the low end of numbers reported in the literature (<1–150 pmol m^{-2} day^{-1}, as summarized in Hollweg et al. 2010), though they are comparable to the range of diffusive fluxes estimated for the Chesapeake Bay and adjacent continental shelf (Hollweg et al. 2009, 2010).

The diffusive MeHg flux calculation is a minimum estimate for the overall MeHg exchange, as processes such as physical forcing and bioturbation could substantially increase fluxes, as discussed above (Gill et al. 1999; Benoit et al. 2009; Hammerschmidt et al. 2008). The low pore water concentrations found in this study compared to other regional estuaries (Table 3) is likely indicative of the strong advective transport occurring in this estuary (Sommerfield and Wong 2011), and is characteristic of the ETM region.

Using the range of values for the relative influence of advection (5–50 times enhancement, average 10 times), based on the literature and on the Rn study in the DRE ETM (Hollweg et al. 2009; Schwartz 2003), the overall fluxes for the different sampling periods are estimated to range from 1.9 to 60 pmol m^{-2} day^{-1} (Table 5). These estimates are well within the range of literature values reported for coastal MeHg sediment passive diffusion plus advective flux, which span a range up to 4000 pmol m^{-2} day^{-1} (Hollweg et al. 2010).

5 Regional Budget Balancing and Overview

The relative importance of dissolved MeHg flux from sediment input compared to estimated watershed and atmospheric inputs was evaluated to provide a broader scale perspective (Table 5). Gay and O'Donnell (2009) reported that the net water volume flux was seaward from the DRE to the continental shelf. However, the tidal volume is much larger than the net advective freshwater flow, as even during times of high flow, the freshwater flow is still <5 % of the tidal flow (Sommerfield and Wong 2011). Therefore there is likely no net input of MeHg from the ocean to the estuary, as total MeHg concentrations are lower on the continental shelf than in the DRE (Hammerschmidt and Fitzgerald 2006; Hollweg et al. 2010). In our calculations, it is assumed that there is no net contribution of MeHg from seawater flux to the ETM. Methylmercury flux from sediments in Table 5 is scaled, using the average estimated advective + diffusive flux based on the three sites,

Table 5 Seasonal comparison of sediment, river, and atmospheric MeHg fluxes to the Delaware River estuary ETM

Month	Sediment MeHg flux (pmol m^{-2} day^{-1})	ETM Sediment flux[a] (mmol day^{-1})	Average Streamflow[b] ($\times 10^7$ m^3 day^{-1})	Total MeHg (pM)[c]	River flux (mmol day^{-1})	Atm. flux (mmol day^{-1})
Nov	8.2–82	1.6–16 (29–80 %)	3.4	0.11	3.4 (17–62 %)	0.48 (2.4–8.8 %)
April	1.9–19	0.38–3.8 (1–12 %)	7.0	0.47	28.1 (87–97 %)	0.48 (1–2 %)
July	6–60	1.2–12 (14–62 %)	2.3	0.36	6.8 (35–80 %)	0.48 (2.5–6 %)
		mol $year^{-1}$		mol $year^{-1}$		mol $year^{-1}$
Annual		0.42–4.2 (10–53 %)		3.6 (45–86 %)		6 (2.3–4.3 %)

Percent contribution to total MeHg inputs is shown in parentheses

[a] Area of 2.0×10^8 m^2 (est. from Cook et al., 2007)

[b] Average of USGS daily means for 2-week period (2007–2011) at Trenton, NJ; corrected (30 % increase) for increased drainage area between Trenton and zone 5 (Schwartz, 2003; Sommerfield and Wong 2011)

[c] Surface water concentrations at Marcus Hook in current study

over the area of the ETM. This area is estimated at 200 km^2 from Cook et al. (2007), assuming the median cross-sectional distance of the river near New Castle is 2.5 km. Cook et al. (2007) established that suspended sediment concentrations are elevated between 50 and 130 km (80 km) upstream from the mouth of Delaware Bay, but concluded that there is little net transport of sediment out of the ETM to the lower estuary. Sommerfield and Wong (2011) concluded that this region of the estuary traps sediment and limits sediment export to Delaware Bay, thus sediment input of MeHg is not expected to be important due to these geological parameters constraints.

River inputs were estimated to be about 28 mmol MeHg day^{-1} in April, using the flow data measured at Tenton, NJ (www.waterdata.usgs.gov). The ETM sediment–water flux in April was estimated to range from 0.4 to 3.8 mmol MeHg day^{-1} (diffusive + advective) which is <1 % of the river inputs. This indicates that river inputs of MeHg are likely the dominant MeHg source to the ETM in the spring, or during any high river flow period (Table 5). In July, on the other hand, river inputs are smaller than in April due to reduced summer flow, and the upper range in sediment flux estimates (12 mmol MeHg day^{-1}) is twice the estimated river input of MeHg. Overall, the river flux of MeHg has decreased by about a factor of 3 between April and July, while the sediment flux has increased by a factor of 6. Thus, fluvial MeHg flux may not be the source of increased water column MeHg in the ETM during the summer, or at any period when flow rates are low. Based on the estimated fluxes in November, it is feasible that sediment inputs are important in winter as well, although pore water and water column filtered MeHg was low.

Examining the long-term flow record from USGS, the average monthly flow is highest in March/April, about a factor of 3 lower in summer (June–Sept), and about half the April flow in winter (Nov–Feb). Using the long-term flow estimates, and the measured water column concentrations and sediment flux estimates (Table 5), an overall yearly flux was estimated. The yearly river input at Marcus Hook is estimated at 3.6 mol MeHg $year^{-1}$ while the sediment flux estimate is 0.4–4 mol $year^{-1}$. For comparison, using the groundwater flux estimates of Schwartz (2003) and pore water MeHg concentrations, a yearly groundwater input flux of 0.2–1.5 mol $year^{-1}$ is estimated. Clearly, more measurements are needed, including in situ flux measurements, to confirm these estimations. Nonetheless, given the similar magnitude of sediment flux estimates over the seasons, and the comparatively similar concentrations of MeHg measured at the upstream site (MH), it is likely that the dissolved MeHg input from the sediment is an important source during low-flow seasons, but not during occasions of high river flow.

On an annual basis, we estimate that 10–50 % of the input of MeHg to the ETM is from the sediment. Sources of MeHg to the sediment are either in situ formation of MeHg from inorganic Hg in sediment, or from release due to diagenesis of MeHg deposited with the settling of particles. The river flux estimates in Table 5 were based on total MeHg, though a fraction of this total is particulate and would be deposited mostly within the ETM, based on the conclusions of Sommerfield and Wong (2011). Based on the MeHg in the particulate fraction at Marcus Hook (17–83 %), the estimated particulate flux is 1.5–3 mol $year^{-1}$. That value is somewhat lower, but comparable to the range in values for sediment input. An alternative estimate can be made based on the average amount of suspended sediment delivered to the estuary each year (1–2 $\times$ 10^9 kg/year; Sommerfield and Wong 2011) and the measured particulate MeHg concentrations. This estimate (3–10 mol/year) is somewhat higher than the estimate above, but within the same order of magnitude.

As an aside, and within the context of mass balance, it is notable that approximately 2.5 M cubic yards of sediment are removed annually via maintenance dredging from the main navigation channel, primarily in the ETM. Mercury is therefore removed with those

sediments, which are pumped into large confined disposal facilities. A combination of measurements and modeling indicate that approximately 181 kg (0.91 kmol) of HgT and potentially 2.7 mol of MeHg (assuming 0.3 % MeHg in sediments) could be extracted from the open waters and subtidal bottom of the DRE, and out of the estuarine habitat. This is equivalent to 7.4 mmol MeHg day^{-1}, on average, and comparable to 20–60 % of the total MeHg flux from external sources (river and atmospheric flux; Table 5). Dredging is therefore an important sink for Hg and MeHg from the Delaware ETM. Thus, future MeHg flux could be tapered due to lessening of the sediment Hg source material.

Generally, the sediment flux could be sustained by the external input of MeHg deposited with settling particles to the sediment. However, MeHg can be demethylated throughout the sediment column (Lambertsson and Nilsson 2006; Hollweg et al. 2009), and therefore, the formation of MeHg is required in the sediment to balance the demethylation. Unfortunately, we were unable to obtain reliable rate constants for demethylation during this study due to various factors, but given the relative rates of demethylation and methylation in estuarine sediments (Liu et al. 2015; Hollweg et al. 2009, 2010; Kim et al. 2006; Heyes et al. 2006; Hammerschmidt and Fitzgerald 2006), and the measured methylation rates during this study, we conclude that there is rapid cycling of MeHg within the sediments. Additionally, the rates of formation and destruction of MeHg in sediments are much higher than the net fluxes at the sediment surface. Using the methylation rate constants measured here, assuming 2 % bioavailable Hg (inorganic sulfide complexes) and taking pore water volume into account (integrating production over the top 10 cm of sediment), the methylation flux is up to 5 times the maximum estimated sediment flux to the water column. In this sense, the situation in the Delaware River is comparable to that of Passamaquoddy Bay, within the Bay of Fundy, modeled by Sunderland et al. (2010). In their study, MeHg production and destruction due to methylation and demethylation in sediments were very similar in magnitude, and about 6 times greater than the net MeHg input from particles at the sediment surface. It was also 10 times greater than the diffusive flux to the water column. Therefore, as found by others (Sunderland et al. 2010; Hollweg et al. 2010), we conclude that the flux at the sediment surface is a relatively small fraction of the methylation that is occurring within the sediment, with most of the MeHg produced likewise being degraded within the sediment. Overall, in situ MeHg production is more than sufficient to balance efflux. Any factors that enhance efflux will therefore greatly enhance MeHg transfer from sediments to the pelagic food chain, before it can become degraded and destroyed within the sediment.

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