

Tidal exchange of total mercury and methylmercury between a salt marsh and a Chesapeake Bay sub-estuary

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Abstract We examined the net exchange of total mercury (THg) and methylmercury (MeHg) between a tidal marsh and its adjacent estuary over a 1-year period from August 2007 to July 2008. Our objectives were to estimate the importance of tidal salt marshes as sources and sinks of mercury within the Chesapeake Bay system, and to examine the hydrologic and biogeochemical controls on mercury fate and transport in tidal marshes. Tidal flows and water chemistry were measured at an established tidal flume at the mouth of the principal tidal creek of a 3-ha marsh section at the Smithsonian Environmental Research Center. Fluxes were estimated by combining continuous tidal flow measurement for the entire study year, with discrete, hourly, flow-weighted measurements of filterable and particulate THg and MeHg, dissolved organic carbon (DOC), and suspended particulate matter (SPM) made

over 20 tidal cycles during the year. We found that the marsh was a relatively small net tidal source of MeHg, mainly during the warmer growing season. We also confirmed that the marsh was a substantial source of DOC to the adjacent estuary. DOC was a significant predictor of both filterable THg and MeHg fluxes. However, although the marsh was a source of filterable THg, it was overall a net sink for THg because of particulate trapping. The net per-area annual flux of MeHg from tidal marshes is greater than other MeHg pathways within Chesapeake Bay. The annual load of MeHg from tidal marshes into Chesapeake Bay, however, is likely small relative to fluvial fluxes and efflux from bottom sediment. This study suggests that MeHg production within the tidal marsh has greater consequences for biota inhabiting the marsh than for the efflux of MeHg from the marsh.

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Introduction

Tidal salt marshes are important zones of net methylmercury (MeHg) production and accumulation within coastal ecosystems (Marvin-Dipasquale et al. 2003; Canario et al. 2007; Heim et al. 2007; Hall et al. 2008; Mitchell and Gilmour 2008). In situ production and accumulation of MeHg in tidal marshes place biota that utilize tidal marshes at risk to MeHg

exposure (Eagles-Smith et al. 2009; Greenfield and Jahn 2010). However, there is little quantitative information on the magnitude of inorganic Hg and MeHg fluxes from tidal marshes, or even whether they serve as sources or sinks of inorganic Hg and MeHg to coastal waters. The amount of MeHg that tidal marshes may contribute to estuaries is currently unknown. Carrington et al. (2004) and Sunderland (2007) have estimated that more than 90% of commercially available seafood is of estuarine and marine origin. Knowing the predominant sources of MeHg to coastal ecosystems is thus critical to understanding risk to aquatic food webs (Munthe et al. 2007; Scheuhammer et al. 2007) and human consumers.

Within estuarine and coastal ecosystems, sources of MeHg may include fluxes from sub-tidal sediment (Hammerschmidt et al. 2004; Hollweg et al. 2009, 2010), water column methylation (Monperrus et al. 2007), riverine inputs (Mason et al. 1999; Riedel et al. 2000), groundwater (Black et al. 2009), and coastal wetlands (Langer et al. 2001; Hall et al. 2008; Bergamaschi et al. 2011). MeHg flux from sub-tidal sediment is the most studied pathway and possibly the dominant source of MeHg to estuarine and coastal waters (Hammerschmidt et al. 2004; Hollweg et al. 2010). However, in Chesapeake Bay, pore water MeHg concentrations are much higher in tidal marshes than in sub-tidal sediment (Heyes et al. 2006; Mitchell and Gilmour 2008; Hollweg et al. 2009), suggesting an important role for marsh-derived MeHg in the bay. Tidal marshes are a dominant feature of many estuarine coastlines and serve as important habitat to diverse biota, many of which are consumed by humans (Kneib and Wagner 1994). Tidal wetlands account for large areal fractions of coastal watersheds in many systems, like the US Gulf and southeastern coasts (Field et al. 1991). This, combined with their propensity to produce MeHg, suggests that tidal marshes could be important sources of MeHg to coastal waters. Nevertheless, while MeHg production rates in tidal marshes have been examined (Mitchell and Gilmour 2008), no comprehensive investigations of net MeHg flux have been undertaken. We do so here, using a well-studied salt marsh in mid-Chesapeake Bay.

Nutrient and particle fluxes in tidal marshes have been extensively studied and this work serves as a template for studying inorganic Hg and MeHg fluxes in tidal marshes. Tidal marshes, including the marsh studied here, are generally sinks for particulate matter

and sources of dissolved organic nutrients and carbon (Jordan et al. 1983; Correll et al. 1992; Childers et al. 2000; Tzortziou et al. 2008). In a South Carolinian marsh-estuarine system, the marsh acted as a net sink for most material, especially suspended sediment, and a source only of dissolved organic nitrogen (Dame et al. 1991). In studying more northerly marsh-estuarine systems of the St. Lawrence River, Poulin et al. (2009) found marshes to be consistent sinks of nitrate + nitrite and consistent sources of ammonium, but to vary between sink and source for phosphate and silicate, depending on season. Jordan et al. (1983) found that salt marshes of the Rhode River, including the marsh in this study, did not retain significant amounts of phosphorus or nitrogen, but rather were key transformers of particulate forms into dissolved forms. These studies highlight the important roles of seasonality, redox potential, and particle entrapment on material exchange, which are likely very important for Hg cycling in tidal marshes as well. Although attempts have been made to bracket the role of tidal marshes in net MeHg fluxes to the estuarine system (Langer et al. 2001; Hall et al. 2008), previous work has either been conducted over short time frames or has not included the direct hydrological measurements needed for net flux calculations.

In this paper, we report on the net exchange of both particulate and filterable total Hg (THg) and MeHg between a tidal marsh and its adjacent estuary over a 1-year period from August 2007 to July 2008. Fluxes were measured directly by combining continuous measurement of diurnal tidal flows with flow-weighted water sampling of a tidal creek that drains a 3-ha portion of a tidal marsh. On several occasions during the study, THg and MeHg fluxes were also examined at hourly intervals in order to assess hydrologic and biogeochemical details of flux within the tidal cycle. A detailed water budget for the marsh was constructed to help constrain the THg and MeHg budgets. Tidal exchange of THg and MeHg was monitored more frequently and over a much longer period than has previously been reported in the literature, leading to better-refined calculations of influx and efflux on semi-diurnal, monthly and annual time scales. The exchange of THg and MeHg was also contrasted to the net flux of other constituents, which may control the mobility of THg and MeHg from tidal marshes. Comparisons were then made between marsh derived MeHg loads and MeHg loads from other

sources within the Chesapeake Bay in an attempt to broadly bracket the potential role of tidal marshes in contributing MeHg to the estuarine system.

Experimental section

Study site

The study took place within a 3-ha drainage area of Kirkpatrick Marsh (38°52′26″N, 76°32′53″W), a 19-ha brackish marsh located near Edgewater, Maryland, at the head of the Rhode River, which is a sub-estuary of mid-Chesapeake Bay (Fig. 1). *Spartina patens*, *Distichlis spicata*, *Scirpus olneyi* and *Typha augustifolia* are the dominant vegetation types, although *Phragmites australis* is rapidly invading. In the 1980s, a flume and monitoring station were installed at the mouth of a creek draining the 3-ha section of the marsh (Jordan and Correll 1991), which we resurrected for this study. The mean tidal range in the Rhode River is 30 cm, but weather systems often cause much larger changes in water level. Salinity varies seasonally from 0 ppt in spring to 18 ppt in fall during years with low runoff.

Experimental design

Using an approach similar to the tidal marsh nutrient cycling study of Jordan and Correll (1991), marsh

hydrology was measured continuously for a full year and tidal exchange of several chemical variables was measured on 20 different tidal cycles (generally 1–3 cycles per month) throughout the year to arrive at net fluxes. The tidal exchanges of THg, MeHg, dissolved organic carbon (DOC), suspended particulate matter (SPM), salinity, and sulfate between Kirkpatrick Marsh and the adjacent Rhode River estuary were computed monthly. Using our continuously collected hydrology data, a detailed water budget, including tidal creek fluxes, evapotranspiration, precipitation, and groundwater flow, was also constructed on a monthly basis. To measure tidal chemical fluxes, we combined the continuous bi-directional flow measurements in a small creek that floods and drains a 3-ha section of the marsh with time-series sampling of water within the creek. Flow across a tidal flume was monitored continuously at 5-min intervals throughout the 12-month study, using a combination of tidal height and velocity. On 12 occasions during the year, water was sampled hourly over a 24-h period (two tidal cycles). Sampling was not exactly monthly as we collected samples in winter only every other month. During Sep and Oct 2007, we collected samples twice monthly because of exceptionally high or low weather-driven tides during the first sampling period each month.

For most months, hourly water samples were composited into separate “ebb” or “flood” samples

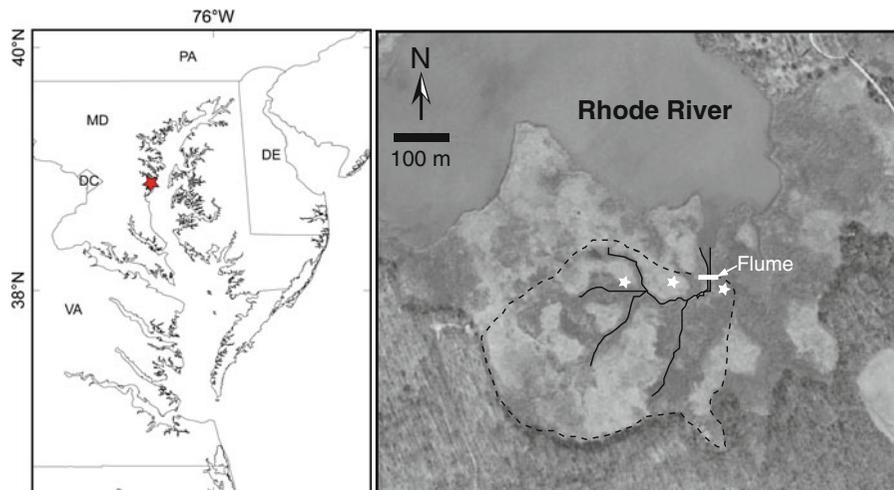


Fig. 1 The study site, Kirkpatrick Marsh, is located in the upper reaches of the Rhode River, a sub-estuary of Chesapeake Bay, near the cities of Washington, D.C. and Annapolis, MD (left). At right, the tidal flux measurement flume at the sampling platform

is labeled, as are precipitation and evapotranspiration measurement stations (stars). The dotted line delineates the maximum marsh drainage area for the flume measurement point

(two each) by flow-weighting. Tidal fluxes of the measured chemical variables were calculated monthly by: (1) separating tidal flow data into ebbing or flooding periods, (2) summing the ebbing and flooding hydrological fluxes separately for each month, and (3) multiplying monthly hydrological fluxes by mean “ebb” or “flood” chemical concentration from the flow-weighted samples for each month. Since we replicated concentration data for 2–3 tidal cycles in most months, we are able to bracket the variability in our monthly flux calculations. Chemical concentrations for Jan and March were estimated by linear interpolation of concentrations measured in Dec, Feb, and April. Net fluxes were then calculated by subtracting ebbing fluxes from flooding fluxes. Negative net fluxes denote a net source function for the tidal marsh whereas positive net fluxes denote a sink function.

For four of the sampled time periods (12–24-h periods in August and Oct 2007, Feb and July 2008), hourly samples were analyzed individually to assess temporal variability at a shorter time scale. Later, we also used these samples to arrive at flow-weighted composite concentration values, as explained above.

Hydrological measurements

Components of the water balance were measured directly and continuously and then compiled on a monthly basis, with the exception of upland freshwater inputs (upland groundwater plus upland surface water), which were modeled. Precipitation (P) was measured with triplicate bulk rain gauges. Evapotranspiration (ET) was measured using triplicate Mariotte systems attached to open-water lysimeters, which included marsh vegetation (Hussey and Odum 1992). On large tides, lysimeters were flooded and could not be used. Missing precipitation or ET data were estimated using linear relationships between rain gauges ($r^2 = 0.98$) or between the lysimeters and a nearby evaporation pan ($r^2 = 0.85$), respectively, at the Smithsonian Environmental Research Center, approximately 1 km away. Upland freshwater input to the marsh, which denotes a combination of upland surface runoff and groundwater fluxes, was estimated using a relationship between the estimated marsh contribution area and watershed runoff in the immediate area, previously established by Jordan and Correll (1991).

Tidal exchange between the marsh and the adjacent Rhode River (T_{in} and T_{out}) was measured directly using a site and methodology modified from Jordan and Correll (1991). A rectangular flume (2.4 m wide; 1.2 m high; 1.2 m long) was installed at the deepest cross-sectional point of the marsh’s principal tidal creek and flows were channeled into the flume by walls that extended from the flume to approximately 15 m into each creek-bank levee. Bi-directional current velocities were measured in the flume using an acoustic doppler velocimeter. The velocimeter was suspended in the flume and mounted to scan sideways, measuring the average velocity in the middle of the water column across a 0.6 m horizontal central section of the flume. The velocimeter was automatically and dynamically suspended in the middle of the flume water column at all stages of the tide by a system of pulleys, floats, and counterweights. Velocity measurements were digitally stored at 5-min intervals as the average of measurements taken every minute. The flume stage was monitored at 5-min intervals using a capacitance-based water level recorder in a stilling well attached to the flume. For each 5-min interval, discharge was calculated by using stage to determine the cross-sectional area of the flume and then multiplying by velocity.

The monthly water balance for the marsh was constructed based on an assumption of equal overall inputs and outputs and a zero monthly net change in storage, expressed as:

$$Tide_{out} + ET = Tide_{in} + P + UF \quad (1)$$

where $Tide_{out}$ and $Tide_{in}$ are the outgoing and incoming tidal fluxes, respectively, ET is evapotranspiration, P is precipitation, and UF is the estimated combined upland groundwater/surface water (upland freshwater) influx to the marsh. On an areal basis, fluxes were constrained to an estimated tidal flood area for the tidal creek of 3 ha, based on previous work by Jordan and Correll (1991). We re-confirmed the analysis of Jordan and Correll (1991) by plotting curves of water depth above mean low water versus flow per change in depth at 15-min intervals, which again led to an estimated 3 ha drainage area for the tidal creek (data not shown).

Similarly to Jordan and Correll (1991), we found that a slightly greater proportion (0–20%) of flood than ebb flow escaped measurement by bypassing the flume when the marsh was submerged. Because of this,

measured ebb flows often exceeded measured flood flows on a monthly basis, in excess of the balance between the other hydrological inputs and outputs. To account for this flow measurement bias we assumed that outgoing fluxes (ebb flow and ET) were equal to incoming fluxes (flood flow, precipitation, and groundwater/surface water inputs), as indicated in Eq. 1. We feel our balanced water budget is reasonable because of very weak differences in salinity between flooding and ebbing water. If freshwater inputs accounted for a large hydrological input, we would expect to observe considerably less saline water leaving the marsh. In fact, throughout the year we observed that the salinity of ebbing tidal water was slightly elevated (mean of 0.03 ppt) over the salinity of tidal water flooding into the marsh, which most likely represents the effect of evaporation of water resident within the marsh. Further, monthly differences in ebb versus flood salinity did not show any trend with precipitation inputs ($P = 0.9894$), leading us to believe that freshwater inputs were too small to cause measurable changes in salinity.

We also conducted an evaluation of the water budget error on a monthly basis using the equation:

$$\text{Error} = \sqrt{(E_P \cdot P)^2 + (E_{T_{in}} \cdot T_{in})^2 + (E_{T_{out}} \cdot T_{out})^2 + (E_{ET} \cdot ET)^2 + (E_{UF} \cdot UF)^2} \quad (2)$$

where E_x is the measurement error associated with each hydrological flux, and P , T_{in} , T_{out} , ET , and UF are the monthly hydrological measurements as outlined in Eq. 1. Precipitation measurement error was approximately 5% as per the manufacturer of the gauges. The error in our evapotranspiration measurements was 21%, based on our relationship between the SERC evaporation pan and our lysimeter measurements. The error in our estimation of upland freshwater input to the marsh was large, approximately 105%, but in absolute terms this error, as well as the errors in precipitation and evapotranspiration measurements, were minor because of the dominance of tidal fluxes in the water budget. On a depth basis, precipitation error accounts for 3 mm month⁻¹, evapotranspiration error accounts for 1.8 cm month⁻¹, and upland freshwater input error accounts for <1 mm month⁻¹. Tidal flux measurement error, a combination of error in velocity measurement and stage measurement, was 6%, which

accounts for ± 30 cm month⁻¹. The overall average monthly error was 6%.

Water sampling

Water entering and leaving the marsh through the flume was sampled using an automated discrete water sampler, outfitted with acid-washed Teflon components and acid-washed glass bottles. All handling of water samples was by strict ultra-clean methods. The inlet of the sampler was constantly suspended in the middle of the water column using the same system described above for the velocimeter. Water samples were retrieved at 12-h intervals and processed immediately. Ebb and flood samples were separated using discharge data from the flume. Composite, flow-weighted samples were mixed in acid-washed glass bottles by weight according to the proportional discharge at time of sampling. A known volume of the water sample was filtered through a Teflon filtration tower and directly into PETG bottles using ashed 0.7 μm glass fiber filters. For later THg and MeHg analysis, the filtrate (referred to as the filterable fraction) was preserved by addition of trace metal

grade, concentrated HCl, to 0.5% volume and then refrigerated in the dark until analysis. Prior to acid preservation, aliquots of the filtrate were separately bottled for analysis of ancillary chemical variables. Filters were frozen until analyzed for particulate THg and MeHg.

Analytical methods

All samples were analyzed for both filterable and particulate total mercury (THg) and MeHg, as well as for suspended particulate matter (SPM), dissolved organic carbon (DOC), sulfate, salinity, pH, and UV absorbance-based measurements of DOC character. THg and MeHg samples were analyzed by cold vapor atomic fluorescence spectroscopy (CVAFS) and isotope dilution gas chromatography inductively coupled plasma mass spectrometry (ID-GC-ICPMS), respectively, following procedures outlined in Mitchell and

Gilmour (2008). Detection limits for THg and MeHg concentrations were 0.22 and 0.02 ng l⁻¹, respectively.

Samples for DOC (Shimadzu TOC analyzer), sulfate (ion chromatography), and salinity (as chlorinity via ion chromatography) determination were stored at 4°C in polyethylene bottles and analyzed within 4 weeks. pH and UV absorbance measurements were conducted the same day as sample retrieval, usually within 4 h. UV absorbance-based measurements of DOC character included specific UV absorbance at 280 nm (SUVA; Chin et al. 1994; Weishaar et al. 2003) and the spectral slope ratio, S_R , defined as the ratio between absorbance slopes measured between 275–295 and 350–400 nm (Helms et al. 2008).

Results

Tidal marsh hydrology

To provide an accurate account of the net export or import of MeHg from tidal marshes, the water balance of the system must be well constrained. Bi-directional tidal fluxes into and out of the marsh dominated the water budget, while precipitation, evapotranspiration,

and groundwater flows were small components (Fig. 2). In this low-gradient mid-Atlantic marsh, tidal fluxes are complex. Forces related to local weather conditions can be as important as lunar forcing (Jordan and Correll 1991). For example, strong northwesterly wind conditions can push water out of Chesapeake Bay coastal areas for extended periods of time. Additionally, the magnitude of tidal fluxes has strong seasonal variation (Fig. 2), with tidal fluxes greatest during early fall and mid-spring and least during winter. Due to the complexity of these tidal fluxes, continuous hydrological records were critical to monitoring flow and to interpreting fluxes over a range of conditions.

Precipitation and evapotranspiration were minor components of the marsh's water balance, being less than 3 and 4%, respectively of the ebbing tidal volume (Fig. 2). Estimated upland freshwater inputs to the marsh ranged from 0% to possibly 9% of the ebbing tidal volume. Upland freshwater inputs were near nil from the start of the study until January 2008, with inputs peaking during May 2008. The seasonal variability in marsh water salinity supports this finding wherein salinity was elevated from August through January. The 2007–2008 study year was dry (total precipitation = 610 mm) compared to historic

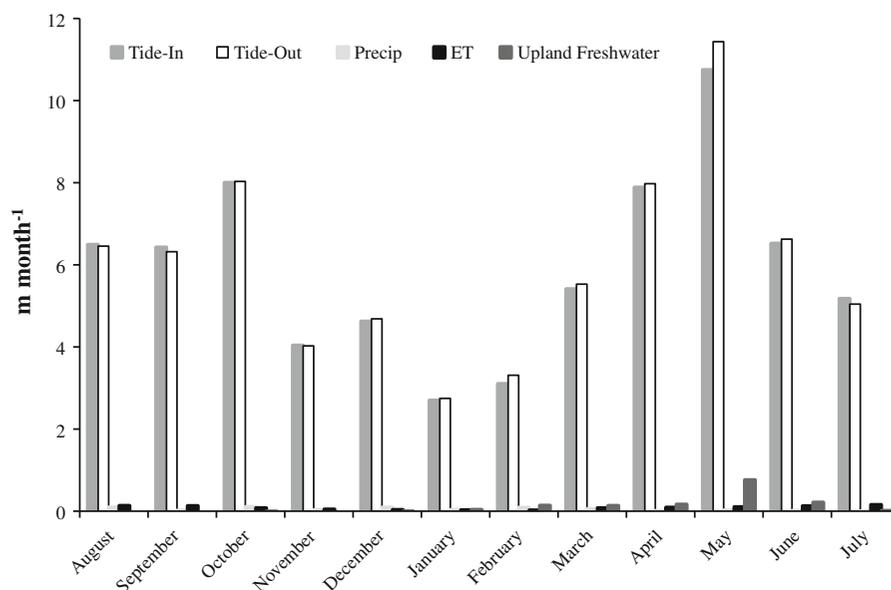


Fig. 2 Components of the monthly water balance for Kirkpatrick Marsh. Values are given as depths in meters. Tidal volumes and modeled freshwater input volumes were converted to depths by dividing through the marsh contributing area. Average

measurement error was ± 30 cm for tidal flows, ± 0.3 cm for precipitation, ± 1.8 cm for evapotranspiration (ET), and $\pm <0.1$ mm for upland freshwater input

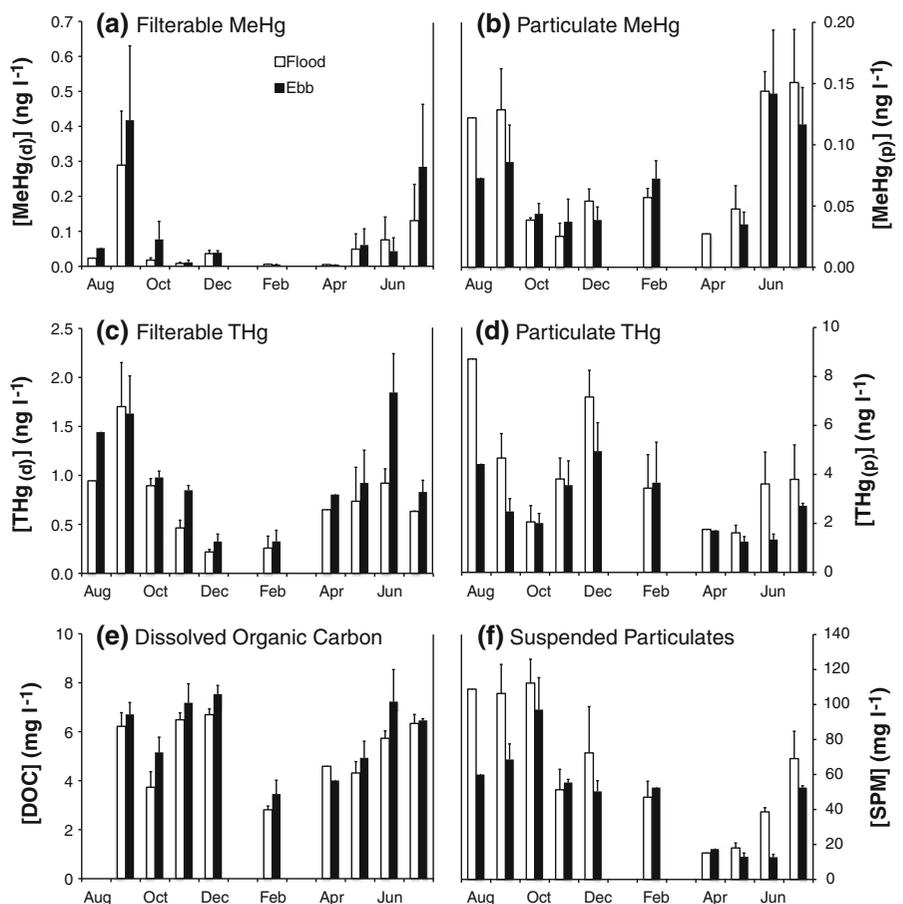
averages for the area ($\sim 1,100 \text{ mm year}^{-1}$; Maryland State Archives) and thus it is possible that in wetter years, upland freshwater inputs could play a more important role in both the water and Hg budgets of the marsh.

Tidal fluxes of Hg species, DOC, and suspended particulate matter

Given the dominant control of tidal forces on the marsh's water balance, we have focused on tidal fluxes for calculating the net THg and MeHg source/sink function of Kirkpatrick Marsh. Flow-weighted concentrations of THg and MeHg both entering (flood) and leaving (ebb) the marsh contrasted between particulate and filterable fractions (Fig. 3). For particulate species, flow-weighted THg and MeHg concentrations were generally higher in tidal waters entering the marsh than leaving it. On average, particulate THg concentrations were 1.15 ng l^{-1}

higher in flooding waters than in ebbing waters. For filterable species, concentrations were generally greater in tidal water leaving the marsh, but differences were not as large as those observed for particulate species. For example, the difference between flow-weighted filterable MeHg concentrations in ebbing and flooding waters varied considerably with season and we observed a much smaller mean difference (0.04 ng l^{-1}). Seasonally, both THg and MeHg (filterable and particulate) flow-weighted concentrations peaked in summer and early fall (Fig. 3). MeHg was seasonally more variable than THg, with differences between MeHg concentrations in incoming and outgoing tides most pronounced during the warmest seasons. Filterable THg showed similar seasonal variation, but particulate THg was less variable through seasons. During peak periods in the summer, flow-weighted filterable MeHg concentrations exceeded particulate MeHg concentrations by 2–4 times.

Fig. 3 Flow-weighted tidal concentrations of: **a** filterable MeHg, **b** particulate MeHg, **c** filterable total Hg, **d** particulate total Hg, **e** DOC and **f** suspended particulate matter in flooding and ebbing waters exiting/entering Kirkpatrick Marsh throughout 2007 and 2008. Error bars are standard error of the mean of multiple sampled cycles each month, where such replication exists



Using mean monthly tidal concentration values combined with our monthly water budget, Kirkpatrick Marsh was a net sink for particulate species (particulate THg, MeHg, and SPM) and net source of filterable species (filterable THg, MeHg, and DOC; Table 1). Overall, particulate THg net fluxes were, on average, 4.5–6.5 times larger than filterable THg net fluxes (Fig. 4; Table 1). Filterable MeHg net fluxes

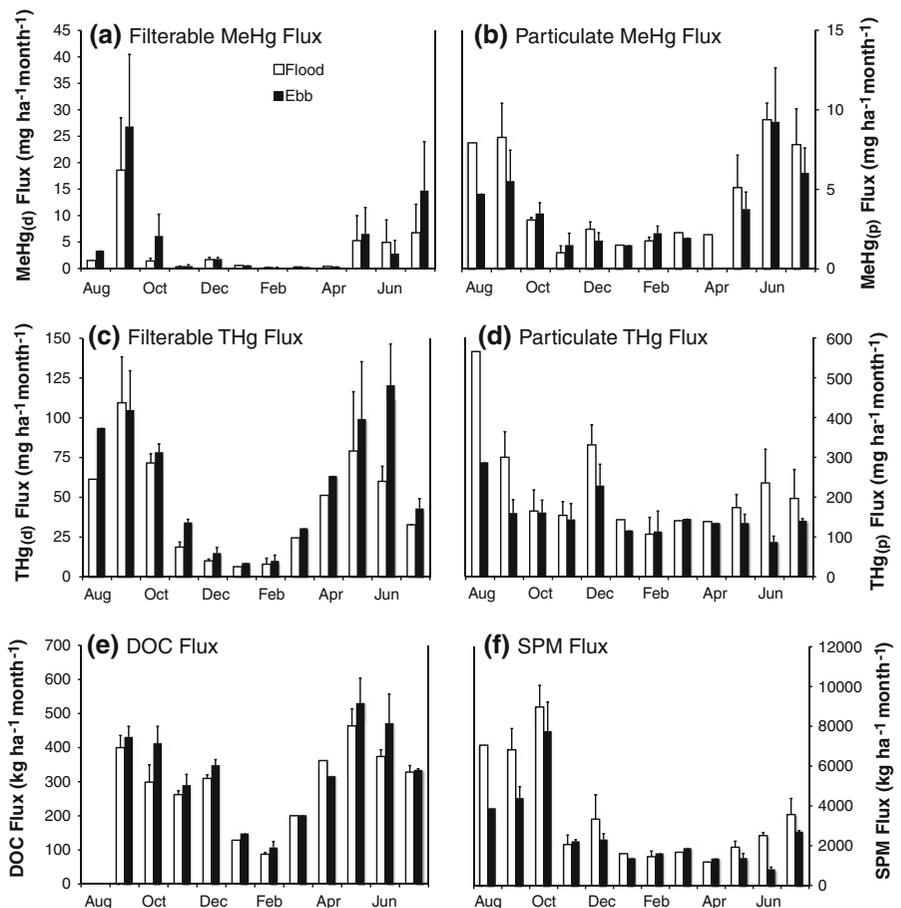
were, on average, 1.5–2 times larger than particulate MeHg net fluxes, but this difference was seasonally dependent. Filterable fluxes were more important in the warmer months of May through September. Outside of these warmer months, filterable and particulate MeHg fluxes were similar. We caution however that relatively large gross fluxes of both particulate and filterable Hg species are transported in

Table 1 Net annual fluxes of total mercury, methylmercury, dissolved organic carbon (DOC), and suspended particulate matter (SPM) between Kirkpatrick Marsh and the Rhode River estuary

	Total mercury		Methylmercury		DOC	SPM	
	Filterable	Particulate	Filterable	Particulate			
($\mu\text{g day}^{-1}$)	-1,300	6,200	-110	90	(g day^{-1})	-3100	8.1×10^4
($\text{ng m}^{-2} \text{day}^{-1}$)	-40	200	-3.6	2.9	($\text{mg m}^{-2} \text{day}^{-1}$)	-100	2,700
(mg year^{-1})	-500	2,400	-40	30	(tonne year^{-1})	-1.1	30

Negative fluxes signify a net loss by the marsh whereas positive fluxes signify a net gain by the marsh

Fig. 4 Monthly mean tidal fluxes of: **a** filterable MeHg, **b** particulate MeHg, **c** filterable total Hg, **d** particulate total Hg, **e** dissolved organic carbon, and **f** suspended particulate matter between Kirkpatrick Marsh and the adjacent Rhode River estuary throughout 2007 and 2008. Each monthly flux estimate is the average of up to three separate tidal cycle studies each month. Error bars are the standard deviation of that mean, and provide an estimate of the variability in Hg fluxes with the variability in tide



both directions, the result being a relatively small net flux for most species, with considerable variability around these numbers.

Despite intra-tidal variability and large seasonal variations, we found statistically significant sink/source functions in the marsh. Mean trends consistently demonstrated that the flux of particulate species flooding the marsh were nearly always greater than the fluxes of particulate species leaving the marsh (Fig. 4). The opposite was consistently observed for filterable species. Since the direction of differences in flux is consistent throughout the year, monthly fluxes can be treated as replicates and the flux measurements then statistically tested through a paired t-test for filterable THg, particulate MeHg, and DOC data, which were normally distributed, or a Wilcoxon ranked sign test for particulate THg, filterable MeHg, and SPM data, which were not normally distributed. These tests indicate that the tidal marsh acts as a statistically significant sink for particulate THg ($P = 0.0093$), particulate MeHg ($P = 0.033$), and SPM ($P = 0.021$) and a significant source of filterable THg ($P = 0.018$) and DOC ($P = 0.029$). Although mean fluxes of filterable MeHg were consistently higher with water leaving the marsh than entering it, the difference was marginally significant ($P = 0.054$). We note that the variance in our hydrological measurements is reflected within the variance of our flux measurements.

Diurnal variability in tidal exchange chemistry

On four occasions, individual hourly samples were obtained over 12–24-h periods (Fig. 5). The patterns of tidal stage and flow varied greatly among the four observed periods, as is typical in the upper Chesapeake Bay. Nevertheless, two consistent patterns were observed: (1) filterable MeHg and THg concentrations spiked during the end stages of marsh drainage, and (2) particulate THg concentrations closely followed the temporal variability in flow between the marsh and estuary. Peaks in filterable Hg species in the July sampling period, which was both warm and without significant weather-driven tidal anomalies, were especially elevated nearer the end stages of marsh drainage. There is a clockwise hysteresis in the concentration of particulate species in relation to tidal stage and a counter-clockwise hysteresis in the concentration of filterable species. An example of this hysteresis during the July 2008 sampling is shown in

Fig. 6. The hysteretic effect is especially large for both particulate THg and filterable MeHg, but there is variability between the two tidal cycles depicted, which are both from the same day.

DOC and SPM concentrations were strongly correlated with filterable and particulate THg concentrations, respectively, but were less correlated with filterable and particulate MeHg (Fig. 7), although all relationships were statistically significant ($P < 0.001$ in all cases). Significant relationships were also observed between both filterable THg and MeHg, and measures of DOM character, such as SUVA and S_R , but coefficients of determination were less than those observed using DOC concentrations. Both particulate THg and MeHg correlations with SPM were affected by low Hg concentrations during our October sampling, the effect of which has been removed from the linear regression analysis in Fig. 7. Upon further inspection, THg and MeHg concentration of the particles themselves during October (ng/g) were significantly lower than those found during the rest of the year, likely indicating a short-term change in the source of suspended particulate matter. This is potentially related to end-of-growing-season senescing vegetation and may be an important source of variability in the construction of annual Hg budgets.

Discussion

Hg source/sink function of tidal marsh

Similarly to the tidal dynamics of nutrients in tidal marshes (Teal 1962; Jordan et al. 1983; Jordan and Correll 1991), Kirkpatrick Marsh was a net sink for particulate species (particulate THg, MeHg, and SPM) and net source of filterable species (filterable THg, MeHg, and DOC; Table 1). We are most confident about the marsh being a sink for particulate total mercury because that showed the clearest differences between flooding and ebbing fluxes. In contrast, we are least certain that the marsh is a source for MeHg although there are consistent trends and marginal statistical significance in our measured net flux.

Our hypothetical conceptualization of THg and MeHg movement and transformations within the marsh is presented in Fig. 8. Generally, relatively small loads of filterable MeHg, filterable THg, and particulate MeHg are transported into the marsh with

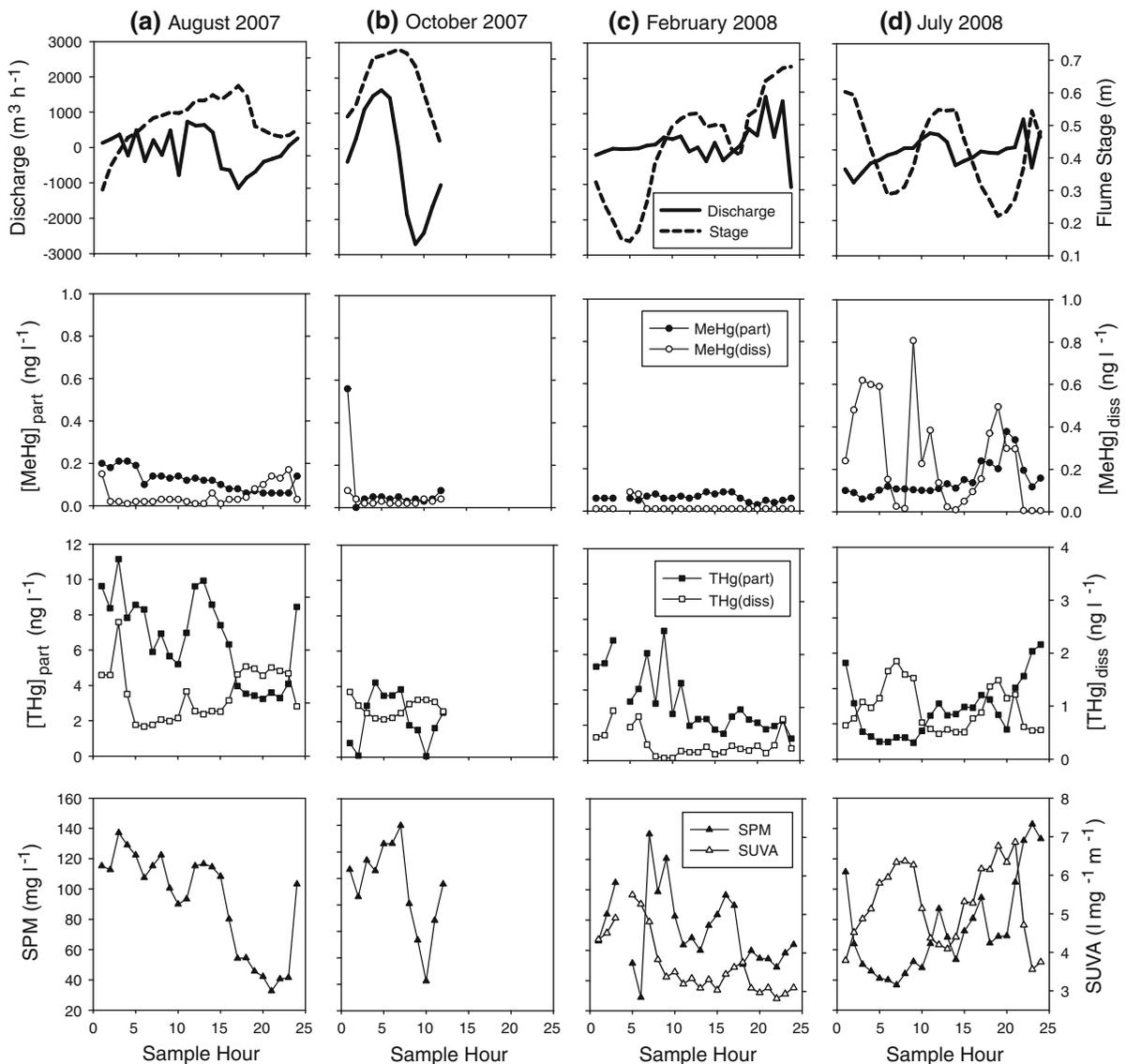


Fig. 5 Detailed time series of water chemistry at the marsh flume over four separate tidal cycles in different seasons, showing hourly measurements of particulate and filterable total Hg and MeHg concentrations, suspended particulate matter

(SPM), and specific UV absorbance (SUVA) in relation to tidal flux and stage (**a–d**). Negative discharge indicates water leaving the marsh whereas positive discharge indicates water entering the marsh

relatively large loads of particulate THg. Once flooded, particulate Hg and MeHg settle onto the marsh surface. It is probable that particle remineralization and redox-driven desorption release some of the particulate Hg delivered to the marsh, and we have previously observed that some of the Hg is methylated (Mitchell and Gilmour 2008). As the tide ebbs, particulate Hg still suspended in the water column is likely washed back into the estuary along with

aqueous Hg and MeHg that have accumulated in the water column during flooding. As the ebb proceeds, greater concentrations of filterable species are observed (Fig. 5), likely as a result of subsurface drainage through the banks of the tidal creek (Jordan and Correll 1985). The total load of filterable aqueous species exported during this time however is small because of the relatively small ebb tide water flow at the time.

Fig. 6 Progression of Hg species concentration through two sequential full tidal cycles in July 2008, showing hysteresis between flooding and ebbing water. Panes are for particulate total Hg, particulate MeHg, filterable total Hg, and filterable MeHg (a–d). Numbers 1 and 2 indicate the two tidal cycles and arrows follow the sequence of each cycle

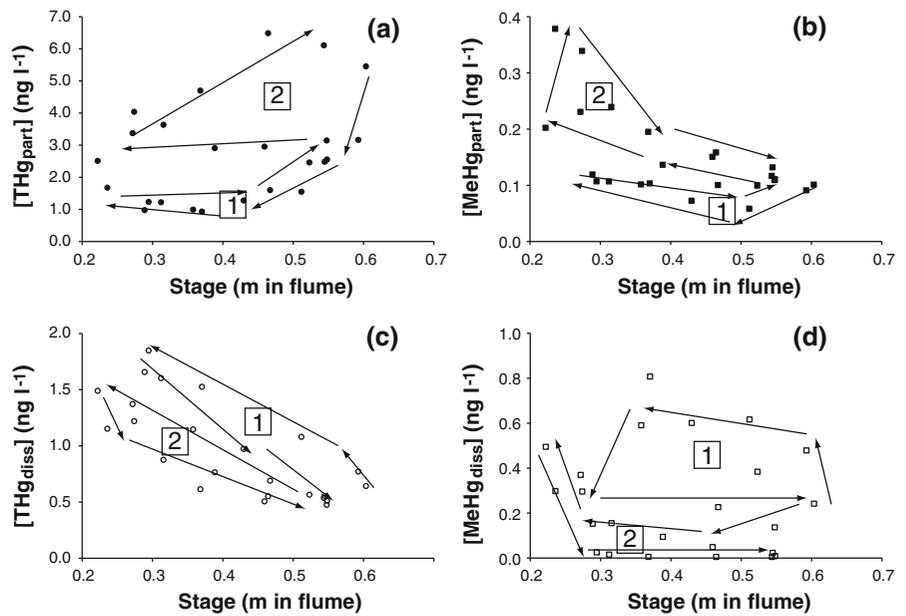
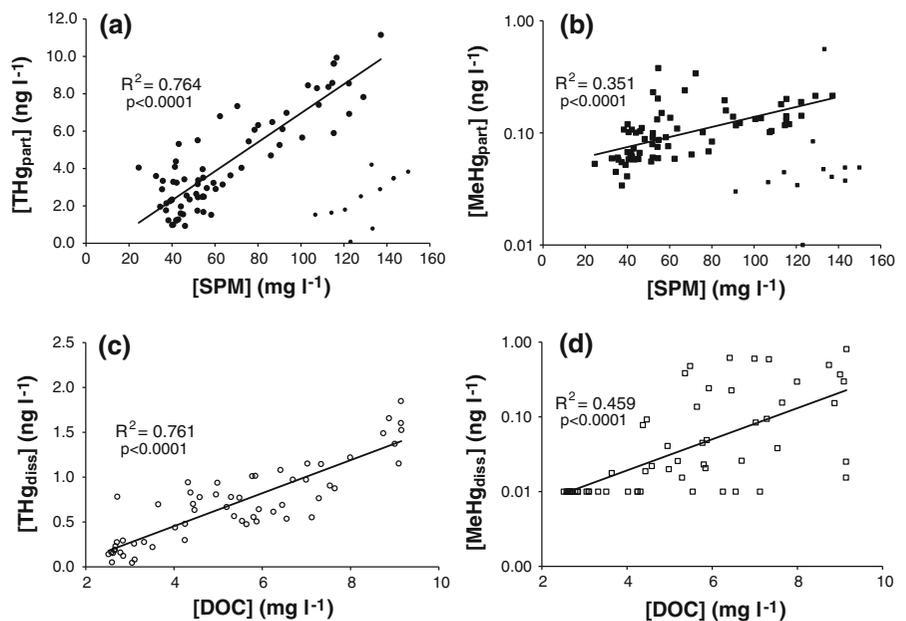


Fig. 7 Relationships between particulate total Hg and suspended particulate matter (SPM) (a), particulate MeHg and SPM (b), filterable total Hg and DOC (c), and filterable MeHg and DOC (d). Small data points in a, b are for the October sampling, when Hg concentrations were anomalously low compared to SPM concentrations



Combined with the tidal pattern of higher DOC in outflowing tide (Fig. 5), the strongly significant correlative relationships between both filterable THg and MeHg and DOC support the idea that Hg and MeHg are exported from the marsh primarily as DOC complexes (Fig. 7). This has previously been observed in a number of studies in a number of different wetland

ecosystems, both freshwater and saline (Driscoll et al. 1995; Galloway and Branfireun 2004; Hall et al. 2008; Selvendiran et al. 2008). The r^2 values between THg or MeHg and proxy measures of DOC aromaticity and molecular size (SUVA and S_R) were no better than those observed with DOC (data not shown). In this context, the large differences in DOC concentration on

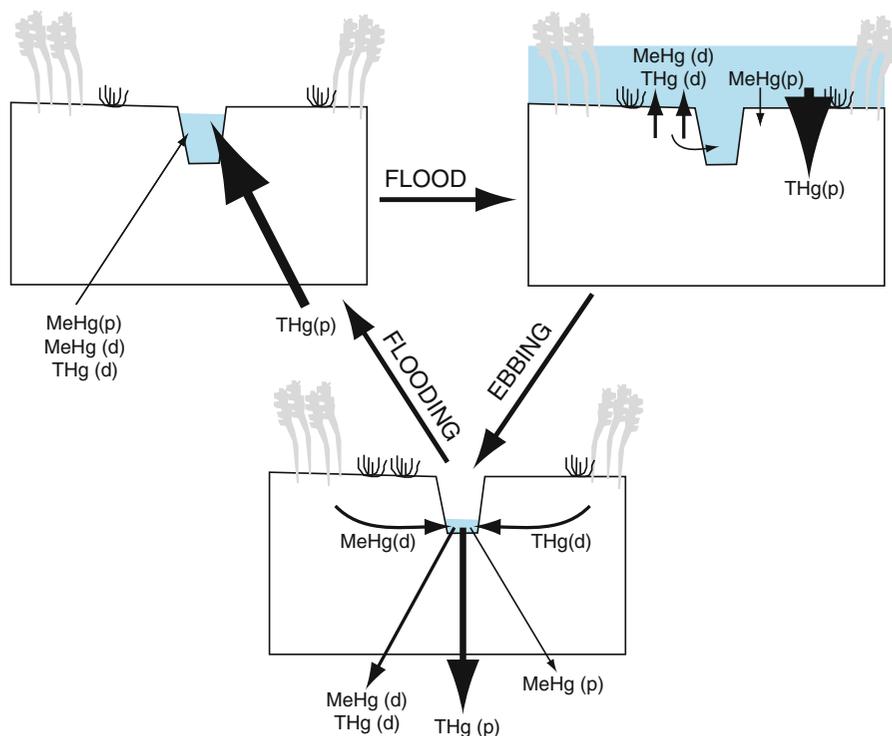


Fig. 8 Conceptual model of THg and MeHg entering and leaving Kirkpatrick Marsh during a typical tidal cycle. The weight of arrows is relatively proportional to flux magnitude

incoming and outflowing tides appear to be the primary driver of the Hg:DOC relationship, rather than differences in DOC character.

Similarly, the strong correlations between both particulate THg and MeHg and SPM, combined with the pattern of high SPM on incoming tides, support the finding that Hg and MeHg influx to Kirkpatrick Marsh are dominantly in particulate form. Mean particle THg and MeHg concentrations of 74 and 1.1 ng g⁻¹ dw, respectively, settled on the marsh surface. These concentrations are less than we have previously observed in surface sediment (0–3 cm) of this same marsh for both THg (mean ± standard deviation: 125 ± 15 ng g⁻¹ dw) and MeHg (2.2 ± 1.6 ng g⁻¹ dw; Mitchell and Gilmour 2008). Part of this discrepancy is due to the coarser resolution of our previous profiling (3 cm increments) whereas the sediment accretion rate in Kirkpatrick Marsh is on the order of 2–4 mm year⁻¹ (Childers et al. 1993). Additionally for THg, these differences may derive from Hg concentration in soil matter during diagenesis (Heyes et al. 1998), or may represent decreasing contemporary Hg loads to the marsh. Indeed, THg

concentrations in Kirkpatrick Marsh tend to increase with depth (Mitchell and Gilmour 2008). Unlike inorganic Hg, we previously observed the highest MeHg concentrations in surface soils within Kirkpatrick Marsh and this pattern paralleled the pattern of MeHg production with depth in marsh soils (Mitchell and Gilmour 2008). This supports the idea that net MeHg formation within the marsh elevates soil concentrations relative to incoming particulate matter. MeHg production in the surface sediment, partitioning into the filterable phase, and diffusion and/or advection of filterable MeHg into overlying water or through creek banks are thus the most likely mechanisms of MeHg leaving the marsh.

It is well known that freshwater wetlands are large sinks for THg inputs (StLouis et al. 1996; Driscoll et al. 1998; Grigal 2003; Galloway and Branfireun 2004), but much less is known about the magnitude of THg sequestration in tidal marsh systems. In general, the net annual fluxes of THg into Kirkpatrick Marsh compare similarly to other studies. Conaway et al. (2004) used core analysis and radiocarbon dating to assess historic Hg deposition in a tidal marsh of San

Francisco Bay. Values for the period preceding historic Hg mining in the area ($495 \text{ ng m}^{-2} \text{ day}^{-1}$ during the period 1570–1870) are elevated compared to what we observed in Kirkpatrick Marsh, but this is a function of lesser overall sedimentation rates in our study marsh and not of large differences in THg concentration [82 ng g^{-1} in Conaway et al. (2000) during this period]. Our finding of a net accumulation of $160 \text{ ng m}^{-2} \text{ day}^{-1}$ THg in the marsh (Table 1) is also within the range of observations of Hung and Chmura (2006), but at the lower end of their net accumulation flux estimates. In a 5-year study of both low and high marshes in Canada's Bay of Fundy, Hung and Chmura (2006) found a wide range in both surface sediment concentrations ($7\text{--}79 \text{ ng g}^{-1}$) and Hg accumulation rates ($55\text{--}700 \text{ ng m}^{-2} \text{ day}^{-1}$).

In our study, the measurement of MeHg drainage from the marsh through the tidal creek provides indirect information about specific pathways of MeHg release from the marsh soils, but it is superior to measurements of sediment–water transfer for integrating the role of marsh physiology in controlling the retention and/or export of the MeHg produced within it. Overall, given the apparently negligible input of MeHg from upland freshwater sources through the marsh during the relatively dry study year, our method provides both a spatially and temporally integrated means of assessing both net Hg methylation within the marsh and sink/source function. A previous study found significant outwelling of MeHg and THg discharged into coastal waters in groundwater coming from upland sources (Black et al. 2009), but our hydrological measurements suggest that upland sources are not important in our marsh. Groundwater is likely very important to mercury cycling within the marsh, but specific to groundwater derived from infiltrating flood tide water.

The only other studies we are aware of to have made similar direct tidal mercury flux measurements are Langer et al. (2001) and Bergamaschi et al. (2011), but their measurements were extrapolated from single tidal cycle measurements. Langer et al. (2001) found a net retention of particulate MeHg and net export of filterable MeHg from a salt marsh in Connecticut, with an overall net export of approximately $9 \text{ ng MeHg m}^{-2} \text{ day}^{-1}$. Bergamaschi et al. (2011) used a proxy modeling approach to estimate an overall net export of approximately $7 \text{ ng MeHg m}^{-2} \text{ day}^{-1}$, which was dominated by a net efflux of particulate MeHg from

the wetland in the San Francisco estuary. We observed a smaller total MeHg net export of approximately $0.7 \text{ ng m}^{-2} \text{ day}^{-1}$. While the agreement in the direction of net fluxes between these studies further supports our hypothesis that most tidal marshes including Kirkpatrick Marsh are net exporters of MeHg, the difference in export fluxes between studies may be a combined function of the frequency and seasonal distribution of measurements as well as regional differences in mercury concentrations, methylation potential, and sediment fate.

Importance of intra-tidal and seasonal variability in constraining Hg budgets

Our observations through a 12-month period support the hypothesis that seasonal variation in temperature and productivity within the marsh-estuary system is a critical factor in determining both MeHg net production and net fluxes of filterable Hg species and particulate MeHg, but less important in controlling particulate THg fluxes (Figs. 3, 4). Moreover, the seasonal trends and predominance of filterable MeHg over particulate MeHg in the summer months suggests that most MeHg is released from tidal marsh soils and pore water and is not controlled by marsh erosion or biomass-derived particulates. Although the seasonal MeHg patterns are not surprising, given the microbial control of MeHg production in saline sediment (Berman and Bartha 1986; King et al. 2001), elucidating this pattern is critical for accurately determining an annual net flux.

Since these calculations involve relatively large gross fluxes of both particulate and filterable Hg species in opposite directions with a resulting small net flux for most species (Fig. 4), there is considerable variability in our estimates of net flux. However, we are confident in our conclusions because of the consistency in Hg flux differences observed entering and leaving the tidal marsh and the statistical significance of the consistency in this pattern (Fig. 3). It would be impossible to fully account for all sources of variability, however we feel that this study, with the application of continuous hydrological measurements, modern analytical techniques and multiple sampling periods, advances our understanding of Hg cycling in tidal marshes and provides a clearer picture of the rigor required in accurately assessing seasonal variability over the annual time scale.

Likely the greatest source of uncertainty/variability in our estimates of net flux is the uncaptured variability in flow-weighted Hg concentrations across tidal cycles. Although the average tidal range is only ~30 cm in this marsh, the absolute range, and the difference in the two daily tides, change across lunar cycles. Further, these lunar cycles are often overshadowed by tides driven by wind and atmospheric pressure. We generally captured only one 24 h period in each month. The stage data in Fig. 5 highlight the differences in tides across the four detailed sampling periods. The hysteretic patterns in Fig. 6 detail the differences in Hg flux patterns across tides. On some tides, particulate Hg input to the marsh largely stays in the marsh. Outflowing marsh runoff is often well mixed, and little export from the marsh is washed directly back into it. However, on other tides, material exported from the marsh is being washed back into it on subsequent tides, with little prior mixing in the estuary. Often, differences between ebbing and flooding concentrations were very distinct for one 12-h period and then less so for the next or previous 12-h period, especially during sampling periods when the two daily tides were very different in height. It is largely this diurnal difference in tidal cycles that leads to the variability observed at the daily time scale and subsequently our extrapolation to the monthly time scale. Overall, this intra-tidal variability is larger than our analytical or hydrological uncertainty and presumably both the analytical and hydrological

uncertainty are embedded within this variability. Still, these distinct tidal patterns and the direction of different hysteretic relationships between different Hg species and tidal stage support our integrated estimates of net fluxes based on flow-weighted sampling and our statistical analyses, specifically that the marsh is a source of filterable Hg and MeHg, and a sink for particulate Hg and MeHg.

Relative importance of tidal marshes to Hg cycling

Compared to fluxes of MeHg from other known sources to Chesapeake Bay waters, net fluxes of MeHg from Chesapeake Bay tidal marshes are comparably large on a per-area basis (Table 2). However, since tidal marsh coverage around Chesapeake Bay is much smaller (1,150 km²; Chesapeake Bay Program 2011) than the area of Chesapeake Bay itself (11,600 km²), which is used to calculate bottom sediment and atmospheric loads, the overall annual load of MeHg to Chesapeake Bay from tidal marshes is probably relatively minor, <12% of potential inputs, assuming that all tidal wetlands in Chesapeake Bay, regardless of salinity and elevation, release MeHg at the same rate as Kirkpatrick Marsh. Furthermore, there are other poorly quantified sources of MeHg into this system, which would likely reduce the proportional role of tidal marsh efflux (see Table 2). Our assumption of the representativeness of this marsh is clearly tentative, and further study into annual net MeHg

Table 2 Major input fluxes of MeHg to Chesapeake Bay

MeHg source	Annual flux (ng m ⁻² year ⁻¹)	Annual load (g year ⁻¹)	References
Tidal marsh ^a	260	300	This study
Wet atmospheric deposition ^b	70	800	Mason et al. (2000)
Riverine flux ^c		3,600	Mason et al. (1999); Riedel et al. (2000)
Diffusive flux from bottom sediment ^d	95	1,600	Hollweg et al. (2009)

Input from the ocean and from small shoreline watersheds, de novo production in anoxic bottom waters, and net flux of particulates from bottom sediment are additional, possibly important sources that are poorly quantified. Estimates of diffusive MeHg efflux from bottom sediment are minimum fluxes that do not account for advective processes

^a Annual load is estimated based on a total Chesapeake Bay tidal marsh coverage of 1,150 km² (Chesapeake Bay Program 2011)

^b Estimate based on an assumption of 0.1 ng l⁻¹ MeHg in rain from the Chesapeake area (Mason et al. 2000); the assumption that MeHg in rain is 0.5% of THg in urban areas and 1% of THg in non-urban areas gives roughly the same value, using local Mercury Deposition Network data for the 2005–2009 period

^c Rough estimate based on a small number of observation of %MeHg in particulate and filterable fall line samples. No value is given for annual flux because an unknown area of the Chesapeake Bay watershed actually contributes to MeHg runoff

^d Based on reported diffusive fluxes in Hollweg et al. (2009) and applied to appropriate bottom areas of Chesapeake Bay

fluxes both across a salinity gradient and within marshes of differing elevation in the Chesapeake Bay would help in further refining this estimate, as these characteristics are likely to influence particle settling, the degree of tidal inundation, and MeHg production and/or accumulation. Moreover, further study and at least seasonal hydrographic measurements coupled to sampling in other coastal marsh systems is necessary to extend the findings from this study to other tidal marsh systems in the U.S. and elsewhere in the world. For example, given the much greater areal coverage of coastal marshes along the southeastern U.S. Atlantic coast and along the coast of the Gulf of Mexico (Field et al. 1991), tidal marsh contributions of MeHg to the coastal zone could be significantly more important to those ecosystems than we have observed in Chesapeake Bay. Other studies have indeed demonstrated a considerable ability for brackish marshes in the Gulf of Mexico region to produce MeHg, but have not yet linked production to net fluxes in the region (Hall et al. 2008).

Full consideration of seasonal variability, as has been undertaken in this study, and which explicitly considers the potential first order control of temperature on Hg cycling, is vital to interpreting the representativeness of scaling discrete tidal sampling to estimates of annual net flux. For example, if we had only collected samples during the major growing season of May through September, as is often the case in the literature, and then extrapolated these findings to produce a net annual flux, this value would have been more than eight times higher ($2,200 \text{ ng m}^{-2} \text{ year}^{-1}$) than our more rigorous estimate using data from all seasons ($260 \text{ ng m}^{-2} \text{ year}^{-1}$; Table 2). If calculated this way, our annual load estimates would also have been 1.5 times greater than estimates of load from Chesapeake Bay bottom sediment (Hollweg et al. 2009), rather than $<1/4$ as large. Whereas several research studies have clearly shown the potential for tidal marshes to produce and accumulate MeHg (Langer et al. 2001; Marvin-Dipasquale et al. 2003; Mitchell and Gilmour 2008), we know of no other studies that have directly measured fluxes throughout the seasons to estimate net annual flux of MeHg from tidal marshes. We therefore suggest that future research should focus on several seasonally spread measurements, such that limited measurement during periods of high net Hg flux do not bias annual estimates. Alternatively, continuous measurement of

proxy variables (Downing et al. 2009; Bergamaschi et al. 2011) could prove useful, but would require strong relationships between the proxy measure and the Hg species. According to our findings, DOC concentration and/or absorbance measurements may be useful for monitoring THg fluxes, but would certainly not be precise enough for continuous estimation of MeHg fluxes or concentrations.

Although tidal marshes are likely smaller sources of MeHg to Chesapeake Bay than is the flux from bottom sediment, the MeHg released from marshes is likely to have a different fate within the bay. MeHg released from marshes is predominantly in the filterable phase, which may increase surface water residence time (Hines and Brezonik 2007) and consequently uptake by biota. Conversely, this may also increase the potential for photo- and biological demethylation (Hintelmann et al. 2000; Li et al. 2010). Particulate MeHg entering from rivers can be another significant mass transfer to estuaries but as the particles rapidly settle the significance beyond the very near coastal zone is unclear (Sunderland et al. 2010). Thus, while the flux of MeHg from marshes is small relative to other loads, the significance of this flux to biota may be greater.

Finally, this study suggests that if other tidal marshes behave similarly to Kirkpatrick Marsh, then more focus should be placed on the study of biotic exposure within the marshes. Given that tidal marshes are potent transformers of inorganic Hg into MeHg (Mitchell and Gilmour 2008), and that tidal marshes are important habitat and breeding grounds for fishes, crustaceans, and other nekton (Kneib and Wagner 1994; King et al. 2005; Eagles-Smith et al. 2009), the exposure risk related to in situ MeHg production in tidal marshes is more important for organisms inhabiting marshes than for organisms inhabiting adjacent coastal waters. The net efflux of MeHg from Chesapeake Bay tidal marshes is not a negligible component of the overall bay MeHg balance, but accumulation of particulate THg in tidal marshes probably plays a more significant role in the Bay's overall Hg balance.

Conclusion

Over a year of continuous monitoring, Kirkpatrick Marsh, a brackish tidal marsh on upper Chesapeake Bay, was a net sink for inorganic Hg (mainly in particulate form) and a small net source of MeHg

(mainly filterable MeHg associated with DOC) to its adjacent estuary. By examining Hg and MeHg concentrations in tidal water flows at a tidal flume on the main drainage creek, along with measurements of ET, precipitation, and upland freshwater inputs, we were able to construct accurate water and Hg budgets for the marsh. This study represents the most rigorous and detailed budget for Hg cycling in a tidal marsh to date. A novel contribution of this work is its quantification of seasonal variability, which is especially important for MeHg fluxes. We have also shown that DOC and particulates are important transport vectors for THg and MeHg, but more so for THg. Although areal MeHg production in this tidal marsh is relatively high (Mitchell and Gilmour 2008), and MeHg is exported, a rough mass balance for the Chesapeake Bay suggests that tidal marshes are likely a minor source of MeHg to the Bay overall. Mercury contamination within the salt marsh food web likely has more serious consequences than does the net efflux of MeHg from marshes into the coastal zone.

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