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Tidal fluxes of mercury and methylmercury for Mendall Marsh, Penobscot River estuary, Maine

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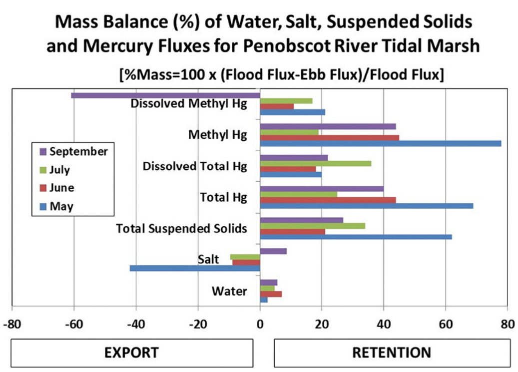
HIGHLIGHTS

- Studied fluxes of total and methyl Hg on a Hg-contaminated tidal marsh system at two spatial scales.
- Suspended matter and particulate total and methyl Hg fluxes were larger on flood than on ebb tides indicating retention.
- Larger system was less efficient as a sink of filter-passing Hg and spring tides made this system a net source of methyl Hg.
- Inorganic and methyl Hg content of exported particles was not significantly different from inflowing particles.
- The larger system was not a significant source (<3% of Penobscot River loading) of inorganic or methyl Hg fluxes to the Penobscot River estuary

GRAPHICAL ABSTRACT



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ABSTRACT

Tidal marshes are both important sites of in situ methylmercury production and can be landscape sources of methylmercury to adjacent estuarine systems. As part of a regional investigation of the Hg-contaminated Penobscot River and Bay system, the tidal fluxes of total suspended solids, total mercury and methylmercury into and out of a regionally important mesohaline fluvial marsh complex, Mendall Marsh, were intensively measured over several tidal cycles and at two spatial scales to assess the source-sink function of the marsh with respect to the Penobscot River. Over four tidal cycles on the South Marsh River, the main channel through which water enters and exits Mendall Marsh, the marsh was a consistent sink over typical 12-h tidal cycles for total suspended solids (8.2 to 41 g m^{-2}), total Hg (9.2 to 47 μg m^{-2}), total filter-passing Hg (0.4 to 1.1 μg m^{-2}), and total methylmercury (0.2 to 1.4 μg m^{-2}). The marsh's source-sink function was variable for filter-passing methylmercury, acting as a net source during a large spring tide that inundated much of the marsh area and that is likely to occur during approximately 17% of tidal cycles. Additional measurements on a small tidal channel draining approximately 1% of the larger marsh area supported findings at the larger scale, but differences in the flux magnitude of filter-passing fractions suggest a highly non-conservative transport of these fractions through the tidal channels. Overall the results of this investigation demonstrate that Mendall Marsh is not a significant source of mercury or

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methylmercury to the receiving aquatic systems (Penobscot River and Bay). While there is evidence of a small net export of filter-passing (<0.4 μm pore size) methylmercury under some tidal conditions, the mass involved represents <3% of the mass of filter-passing methylmercury carried by the Penobscot River.

1. Introduction

Mercury (Hg) is a potent neurotoxic and teratogenic contaminant, which has been used for centuries in numerous industrial applications, including the production of chlorine and caustic soda in chlor-alkali facilities (Nriagu, 1979). Historical discharges from such a facility on the Penobscot River, Maine, USA, have led to elevated Hg levels in sediment, water, and biota in this tidal river and bay system that continue to be well above background levels (Merritt and Amirbahman, 2007, 2008; Bodaly et al., this issue). One of the possible mechanisms linking this historical inorganic Hg contamination with high levels of Hg bioaccumulation in biota (e.g., Kopec et al., 2018) is the production of methylmercury (MeHg) in, and its release from, estuarine marshes within the river's watershed (Balcom et al., 2015).

Hydrologic transport and geochemical cycling of nutrient solutes and particulate matter in estuarine marshes have been studied throughout the world (e.g., Jordan et al., 1983) with the result that an extensive published literature exists, including many studies related to mercury cycling (e.g., Hall et al., 2008; Henry and Bigham, 2007; Bergamaschi et al., 2011; Mitchell et al., 2012; Balcom et al., 2015; Valega et al., 2008; Canario and Vale, 2004; Turner et al., 2001). Wetlands, particularly estuarine marshes, are habitats with biogeochemical conditions that lead to elevated activity of the anaerobic bacteria responsible for the conversion of inorganic Hg into MeHg, a highly bioavailable and toxic form of Hg (Mitchell and Gilmour, 2008). Biogeochemical conditions that favor MeHg production in wetlands and other aquatic ecosystems include anoxic sediments, abundant sources of labile carbon, and concentrations of sulfate that are neither too low to inhibit the activity of sulfate reducing bacteria or too high, wherein significant sulfide is produced and Hg bioavailability for methylation is reduced (Gilmour et al., 1992; Hsu-Kim et al., 2013). As discussed in Gilmour et al. (2018), the latter paradigm is being revised somewhat by results from the Penobscot marshes which indicate stronger role of dissolved organic matter in controlling complexation and bioavailability. Estuarine marshes with strong freshwater inputs and significant tidal exchange have this optimal biogeochemical milieu and can act as significant sources of MeHg to downstream receiving water bodies with net export rates ranging from approximately 0.7 ng m^{-2} day^{-1} (Mitchell et al., 2012) to 6.8 ng m^{-2} day^{-1} (Bergamaschi et al., 2011) for marshes without high levels of anthropogenic mercury contamination. Conversely, estuarine marshes are generally strong sinks of total Hg, particularly in particle-bound forms, on the order of 160 ng m^{-2} day^{-1} (Mitchell et al., 2012). Lastly, some marsh plant species have been implicated in mercury cycling in marine marshes (Windham et al., 2001; Valega et al., 2008).

As part of the Penobscot River Mercury Study, commissioned to investigate the severity of Hg contamination in the Penobscot River system (Rudd et al., this volume), the purpose of this study is to characterize the total Hg and MeHg loading and flux from a regionally-important mesohaline fluvial marsh (Mendall Marsh) that is hydrologically connected to the Penobscot River. As indicated in Gilmour et al. (this issue) Penobscot marsh soils, and especially to in Mendall Marsh, are unusual in their capacity to produce and retain MeHg. Several hypotheses, mostly suggested by results of other studies, were tested in this study: 1) Mendall Marsh is a net sink for particle-bound Hg; 2) inorganic Hg and MeHg are predominantly associated with particles, but filter-passing (<0.4 μm pore size) concentrations in exported water during ebb (outward flow) tide are greater than during flood (inward flow) tide; 3) this Hg-contaminated marsh, while still being a net sink for particle-bound Hg, exports particles with higher inorganic Hg and MeHg concentrations; and 4) ebb tide fluxes of filter passing inorganic Hg and MeHg are greater than flood tide fluxes of these forms, and especially so within smaller tidal channels. This study represents a means for contextualizing estuarine marsh MeHg production and transport to the Penobscot River in relation to other sources of MeHg within the Penobscot River ecosystem (Gilmour et al., 2018).

2. Materials and methods

2.1. Investigative approach and study sites

We measured net fluxes of mercury from the South Marsh River and its fringing marshes (collectively referred to as Mendall Marsh) over four full tidal cycles using a combination of moving boat discharge measurements and manual water sampling. Hydrologic measurements and sampling for mercury over full tidal cycles were focused mainly on the South Marsh River (SMR) at two locations (Fig. 1a), referred to hereafter as “boat launch” (BL) and “peninsula” (P). The BL site was immediately adjacent to the moored water quality and hydrologic monitoring station operated by Woods Hole Oceanographic Institute (WHOI) between April and June 2010 (see companion paper by Geyer et al., in this volume) and represented a convenient location for intensive water sampling. The P location was selected for installation of an upward facing Acoustic Doppler Current Profiler (ADCP) because of its proximity to an onshore location where battery and data logger could be securely installed and accessed without a boat. We also used a Doppler velocimeter (FloTracker®) to manually measure discharge over two tidal cycles on the small tidal channel within Mendall Marsh referred to here as Cindy's Slough (station CS in Fig. 1b). As discussed subsequently, the contributing area for this channel is uncertain but is estimated to range from 3 to 10 ha depending on how the area is calculated. We also investigated how the speciation of mercury (e.g., % filter-passing, % MeHg) varied along the length of this tidal channel.

From data (see Appendix B, Tables SM7-SM9) previously collected as part of the Penobscot River Mercury Study (PRMS), mainstem river concentrations of filter-passing MeHg nearest the marsh were quite low (~0.05 to 0.2 ng L^{-1}). Thus, detection of minor changes in concentration upstream and downstream of the marsh within the Penobscot River itself was expected to be unresolvable as a means of assessing contributions of MeHg from the marsh to the river. This difficulty would be compounded by the uncertainty involved in trying to quantify potentially very small differences in water discharge upstream and downstream of the marsh such that a net contribution by the marsh could be calculated (see Appendix B, Tables SM7-SM9 for upstream-downstream data and evaluation). There were also important possible interferences from the tributary (North Marsh River) that passes through Frankfort, Maine and empties at the northern end of Mendall Marsh (Fig. 1). Separating flows originating from this tributary from those from the marsh would have been impossible in an upstream-downstream sampling approach. To reduce these uncertainties, we quantified flood and ebb tidal concentrations and discharges within the South Marsh River that drains the Mendall Marsh (~200 ha) and a relatively small upland watershed (~6500 ha). At our sampling location (BL) on the lower South Marsh River the summer-time influence of the upland drainage was expected to be minor compared the tidal exchange volumes. For all four of our tidal cycle studies 2 to 3 million cubic meters