Science of the Total Environment 640–641 (2018) 555–569

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Distribution and biogeochemical controls on net methylmercury production in Penobscot River marshes and sediment

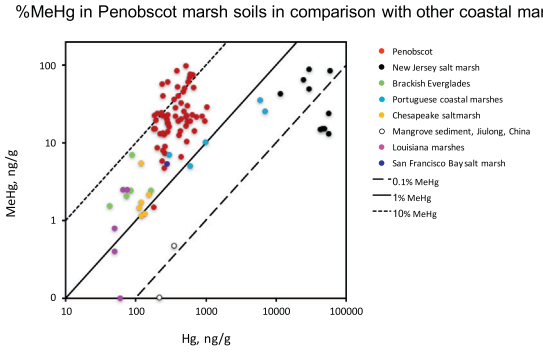
Cynthia Gilmour [a,*], James Tyler Bell [a], Ally Bullock Soren [a], Georgia Riedel [a], Gerhardt Riedel [a], A. Dianne Kopec [b,1], R.A. Bodaly [b,2]

[a] Smithsonian Environmental Research Center, 647 Contees Wharf Rd., Edgewater, MD 20657, United States
[b] Penobscot River Mercury Study, Bangor, ME, US

HIGHLIGHTS

- Penobscot methylmercury (MeHg) > other Hg-contaminated ecosystems
- Salt marshes are areas of particular concern for MeHg risk in the Penobscot.
- Penobscot salt marsh soil chemistry is particularly favorable for MeHg accumulation.
- HgS colloids in marsh porewaters enhance Hg availability for methylation.
- Low partitioning of MeHg to marsh soils suggests high bioavailability to animals.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 September 2017
Received in revised form 18 May 2018
Accepted 22 May 2018
Available online xxxx

Keywords:
Methylation
Bioavailability
Metal sulfides
Nanoparticulate
Saltmarsh
Estuary

ABSTRACT

The distribution of mercury and methylmercury (MeHg) in sediment, mudflats, and marsh soils of the Hg-contaminated tidal Penobscot River was investigated, along with biogeochemical controls on production. Average total Hg in surface samples (0–3 cm) ranged from 100 to 1200 ng/g; average MeHg ranged from 5 to 50 ng/g. MeHg was usually highest at or near the surface except in highly mobile mudflats. Although total Hg concentrations in the Penobscot are elevated, it is the accumulation of MeHg that stands out in comparison to other ecosystems. Surface soils in the large Mendall Marsh, about 17 km downstream from the contamination source, contained particularly high %MeHg (averaging 8%). In Mendall marsh soil porewaters, MeHg often accounted for more than half of total Hg.

Salt marshes are areas of particular concern in the Penobscot River, for they are depositional environments for a Hg-contaminated mobile pool of river sediment, hot spots for net MeHg production, and sources of risk to marsh animals. We hypothesized that exceptionally low mercury partitioning between the solid and aqueous phases (with log K_d averaging ~4.5) drives high MeHg in Penobscot marshes. The co-occurrence of iron and sulfide in filtered soil porewaters, sometimes both above 100 μM, suggests the presence of nanoparticulate and/or colloidal metal sulfides. These colloids may be stabilized by high concentrations of aromatic and potentially sulfurized dissolved organic matter (DOM) in marsh soils. Thus, Hg in Penobscot marsh soils appears to be in a highly available

* Corresponding author.
E-mail addresses: gilmourc@si.edu, (C. Gilmour), drewbodaly@gmail.com (R.A. Bodaly).
[1] Current address: University of Maine, Orono, ME, US.
[2] Current address: 115 Oystercatcher Place, Salt Spring Island, BC Canada V8K 2W5.

https://doi.org/10.1016/j.scitotenv.2018.05.276

for microbial methylation through the formation of DOM-associated HgS complexes. Additionally, low partitioning of MeHg to marsh soils suggests high MeHg bioavailability to animals. Overall, drivers of high MeHg in Penobscot marshes include elevated Hg in soils, low partitioning of Hg to solids, high Hg bioavailability for methylation, rapidly shifting redox conditions in surface marsh soils, and high rates of microbial activity.

1. Introduction

The tidal Penobscot River and estuary were contaminated with mercury releases from a mercury-cell chlor-alkali plant at Orrington, a few km downstream from Bangor, Maine, USA (Merritt and Amirbahman, 2007; Merritt and Amirbahman, 2008; Turner, 2018). Bottom sediment, mudflats and marsh soils have accumulated excess Hg from a chlor-alkali plant (HoltraChem) that operated on the banks of the river from 1967 to 2000 (Bodaly et al., 2008; Geyer and Ralston, 2018; Santschi et al., 2017; Yeager et al., 2018). Production of methylmercury (MeHg) from this contamination has resulted in risk to bird populations and human consumption advisories for fish, shellfish, and birds (Bodaly et al., this volume; Kopec et al., 2018; Sullivan and Kopec, 2017). In this study, the distribution of methylmercury (MeHg) in sediment and marsh soils of the ecosystem were evaluated along with, the biogeochemical controls on production and accumulation. This study was part of the larger Penobscot River Mercury Study (PRMS) (Bodaly et al., this volume; Rudd et al., 2018).

Methylmercury is produced from inorganic mercury (Hg) in anaerobic estuarine sediment (Hammerschmidt et al., 2004; Hollweg et al., 2009; Marvin-DiPasquale and Agee, 2003; Sunderland et al., 2004) and salt marsh soils (Hall et al., 2008; Marvin-DiPasquale et al., 2003; Mitchell and Gilmour, 2008). The microorganisms that participate in MeHg production include sulfate and iron-reducing bacteria, methanogens, and a few fermentative organisms and syntrophs (Compeau and Bartha, 1985; Gilmour et al., 2013a; Gilmour et al., 2018b; Gilmour et al., 2011; Graham et al., 2012b; Kerin et al., 2006; King et al., 2000; Parks et al., 2013; Podar et al., 2015; Yu et al., 2013). The relative importance of each group is still being studied, and varies by setting (Acha et al., 2012; Christensen et al., 2016; Correia et al., 2012; Podar et al., 2015; St Pierre et al., 2014; Yu et al., 2012). However, sulfate-reducing bacteria play an important role in marine settings where sulfate is abundant, based on co-correlation with sulfate utilization (King et al., 1999; Mitchell and Gilmour, 2008), the effect of inhibitors (St Pierre et al., 2014), and early metagenomic evaluation of the distribution of a gene pair (*hgcAB*) responsible for Hg methylation (Podar et al., 2015).

The Penobscot River watershed is the second largest drainage basin in New England (~22,400 km^2). The river is recovering from decades of pollution, including pulp and paper mills and sewage that led to anoxic conditions and depletion of fisheries (Haefner Jr, 1967; Rabeni et al., 1985). The macro-tidal river flows for ~35 km below the head of tide (near Bangor) before emptying into Penobscot Bay. Along the river are two large marsh complexes, the Mendall Marsh complex on the Marsh River and the Orland River marsh complex (Fig. 1), in addition to several small fringe marshes on protected coves (Jacobson et al., 1987). These marsh systems are net depositional environments (Santschi et al., 2017; Turner et al., 2018) and traps for riverine particulate Hg.

The main goals of this component of the larger PRMS study were to evaluate the distribution of MeHg in Penobscot sediment and soils, define the habitats within the Penobscot River system where mercury contamination is most efficiently converted to MeHg, and to understand the biogeochemical drivers of net MeHg production in the Penobscot system, building on prior work in the ecosystem (Bodaly et al., 2008; Merritt and Amirbahman, 2007; Merritt and Amirbahman, 2008). We hypothesized that anaerobic bottom sediment and marsh soils, locations where Hg-methylating bacteria are known to be active (Hsu-Kim et al., 2018), would be the dominant sites of net MeHg accumulation in the river system. More specifically, prior work led us to hypothesize that the combination of high levels of microbial activity and highly bioavailable Hg in salt marsh soils (Canário et al., 2007b; Hall et al., 2008; Merritt and Amirbahman, 2008; Mitchell and Gilmour, 2008) would provide an environment where Hg contamination would be readily converted to MeHg. Our overarching goal was to define the biogeochemistry of Penobscot marsh soils and bottom sediment in a way that would allow us to define the factors that most impact net MeHg accumulation.

Our approach was to intensively examine the geochemical indicators of MeHg production, including Hg methylation rate constants, at a suite of study areas along the salinity and Hg contamination gradients of the Penobscot. Sampling was confined to the tidal river reach between Bangor and Fort Point (Fig. 1) The study focused on marsh soils mudflats, and to limited extent bottom sediment, as these have been repeatedly identified as the main zones of MeHg production and accumulation in estuarine systems.

2. Methods

2.1. Study sites and dates

Cross-ecosystem surveys of sediment and marsh soils in the tidal portion of the Penobscot estuary, from just below Bangor to Fort Point (Fig. 1), were conducted in August 2009 and May/June 2010. The sites examined spanned a salinity gradient from <5 ppt to >30 psu. Additional spatial detail on Mendall Marsh was collected from late 2010 though fall of 2012. This in-depth look provided information on the distribution of total Hg and MeHg across different habitat types, salinities, and with soil depth, along with associated biogeochemistry.

Marsh sampling focused on four marsh complexes, chosen based on prior surveys by Normandeau Associates and the Penobscot River Mercury Project (Bodaly et al., 2008). The marsh complexes were numbered based on distance in river miles from the Veazie Dam at Bangor. Marsh W10 (Bald Hill Cove) is a fringing marsh in the oligohaline reach of the Penobscot. Marsh W17 is a mesohaline fringing marsh along the main Penobscot River. The fringing marshes (W10, W17 and W26) are narrow marshes in which the distance from the river to the trees is generally <100 yards. They slope up from the water with a generally smooth elevation gradient from the mudflats to the trees; and sometimes have a small lip near the water edge of plant growth (Fig. S1). Mendall Marsh (W21) is a large marsh (>50 ha) complex on the Marsh River, a sub-estuary of the Penobscot. It comprises 3 main marsh platforms (east, west, south), plus additional marsh area. Each platform is at least 0.4 km wide (distance between the river and trees), and at least 10 ha in size. Marsh complex W26, also mesohaline is along the upper Orland River. The full set of sampling sites is listed in Table S1 with coordinates in Table S2.

2.1.1. Survey of marshes and bottom sediment

In August 2009 and again in May/June 2010, samples were collected in each marsh complex across a gradient from the tidal mudflat to the upper marsh. In each marsh complex, up to four habitats were sampled: mudflats, low marsh, mid-marsh and high marsh (Figs. S1–6). Mudflats (MF) were sampled within walking distance seaward from the edge of