Science of the Total Environment 642 (2018) 1340–1352

Contents lists available at ScienceDirect

Science of the Total Environment

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

Fifty years after its discharge, methylation of legacy mercury trapped in the Penobscot Estuary sustains high mercury in biota

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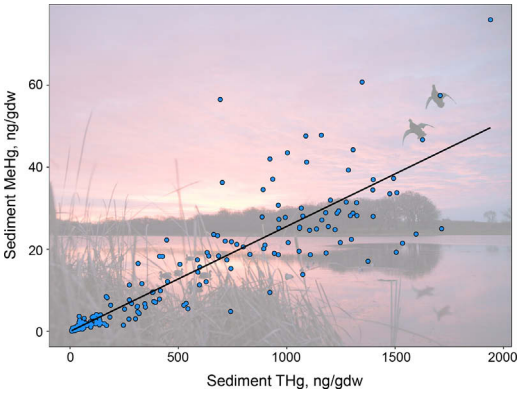
HIGHLIGHTS

- Legacy Hg discharged to Penobscot Estuary 50 years ago continues to be methylated.
- MeHg production in surface sediment is directly related to total Hg concentrations.
- Trapping of this legacy mercury above a salinity front slows the rate of recovery.
- Since the food web is sediment based, remediation needs to reduce sediment Hg.
- A novel remediation approach is discussed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 March 2018
Received in revised form 2 June 2018
Accepted 6 June 2018
Available online 21 June 2018

Keywords:
Mercury
Remediation
Estuary
Penobscot
Toxicity
Recovery
Methylation

ABSTRACT

Fifty years ago, the Penobscot Estuary was contaminated by mercury discharged from the chlor-alkali plant located in Orrington, Maine, USA. Almost all of the mercury was discharged from the plant during the late 1960s and early 1970s. Despite the much lower mercury discharges in recent decades, present-day concentrations in surface sediment remain high (averaging 350–1100 ng/g dw) and are still high in blood of marsh birds (up to 10.5 μg/g), black duck muscle (0.8 μg/g), and lobster muscle (0.4 μg/g). Methyl mercury (MeHg) concentrations in marsh birds exceed levels that impair reproduction. There are health advisories for duck hunters and closures of shellfish fisheries. These continuing high mercury concentrations are caused by the trapping of legacy mercury in a mobile pool of sediment that is retained in the upper estuary above a tidally forced salinity front, which travels up and down the estuary each tidal cycle - slowing the transport of particulate mercury to Penobscot Bay. The trapped legacy mercury continues to be available for methylation 50 years after it first entered the estuary. This is demonstrated by the fact that rates of MeHg production are positively related to the inorganic mercury concentration in parts of the estuary with elevated concentrations of legacy mercury. Thus, remediation measures that would lower the THg concentration in surface sediment would lower the MeHg in birds, fish and shellfish. All of this new information leads us to recommend two remediation options. Addition of mercury binding agents may lower mercury concentrations in birds in some wetland areas. System-wide, we also recommend Enhanced Natural Recovery (ENR), a novel approach that involves the partial removal of the contaminated

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https://doi.org/10.1016/j.scitotenv.2018.06.060

mobile sediment pool followed by replacement with clean-clay particulates to dilute inorganic mercury concentrations, which would lower methylation rates and mercury concentrations in biota.

1. Introduction

Between 1967 and 2012 about 9 metric tons of mercury were discharged into the Penobscot Estuary from the operation of the HoltraChem chemical plant in Orrington ME (Fig. 1, Turner et al., 2018a; Yeager et al., 2018a). Most of this mercury was discharged between 1967 and the early 1970s when chlor-alkali mercury cells were operational. After 1972, several efforts were made to further reduce mercury discharges to the river. The last of these efforts was the installation of a pump-and-treat plant in 2000 that treated both captured groundwater and sewer water draining from the plant. This treatment system was highly efficient resulting in greater than 90% removal of the mercury from the combined plant outfall. Present loss of mercury from the plant site (groundwater, surface water, and plant outfall) is estimated to be about 6 g/d which is much smaller than the estimated present-day downstream transport of mercury into the estuary by the Penobscot River (160 g/d; Turner et al., 2018a).

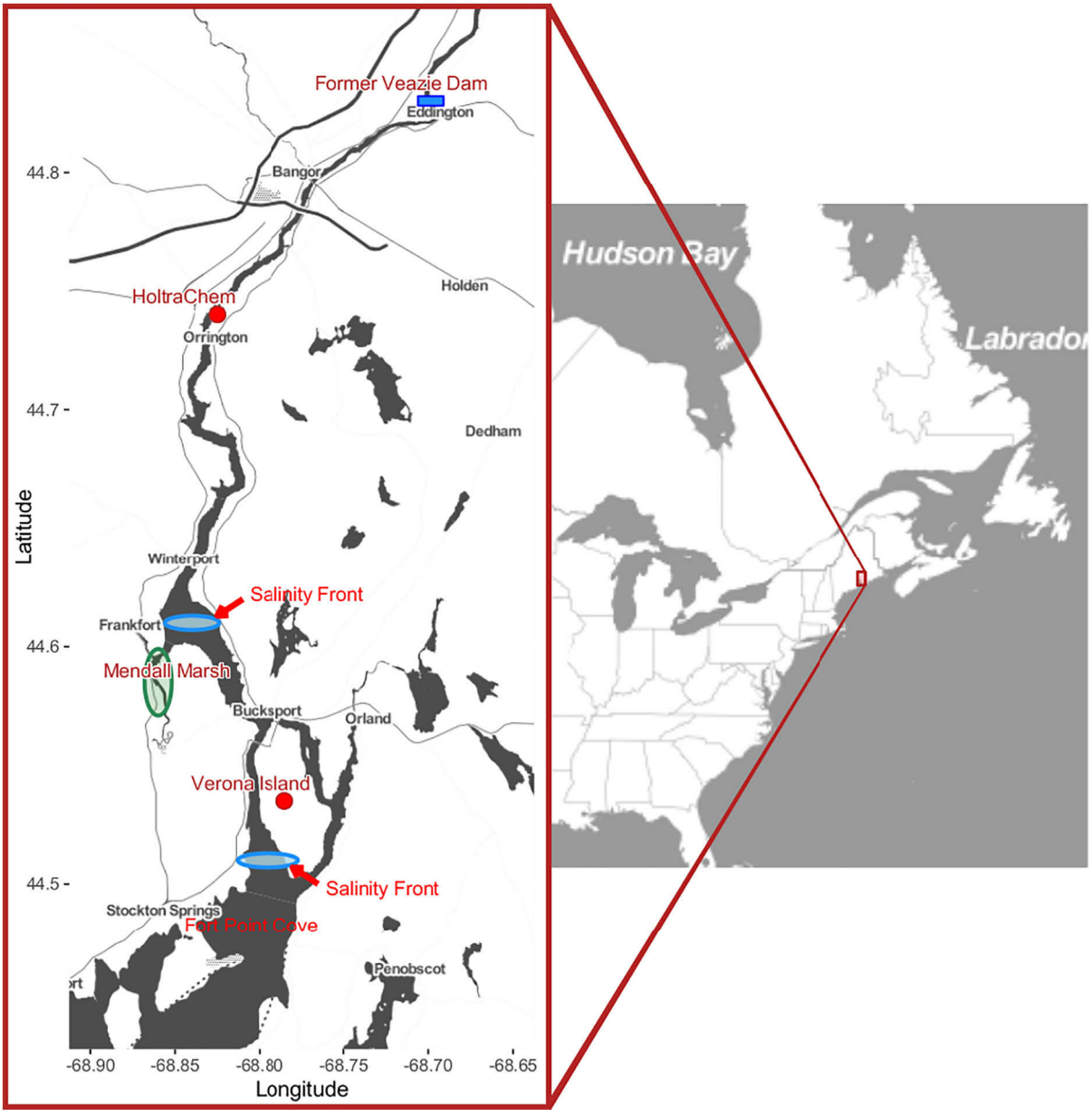

Fig. 1. The mercury contaminated *upper Penobscot Estuary* extends 46 river km from the former Veazie Dam (The Veazie Dam was in place at time of this study, but has since been removed.) to the southern tip of Verona Island. The salinity front (blue ellipses), which traps contaminated particles, moves upstream at flood tide and downstream at ebb tide. Mercury concentrations are highest in the Orland River, Mendall Marsh (green ellipse) and on the east site of Verona Island. Concentrations decrease progressively in a southerly direction from Fort Point Cove (Figs. S1, S3, S4).

Despite these site remediation efforts, MeHg concentrations in biota have remained high in the upper estuary, defined as the reach between Veazie Dam and the southern end of Verona Island (Fig. 1). Mercury concentrations are highest in marsh birds, especially Red-winged Blackbirds (mean total mercury (THg) 10.5 μg/g ww in blood) and Nelson's Sparrows (mean THg 7.2 μg/g ww), as well as other marsh bird species. These concentrations exceed levels reported to reduce reproduction (Kopec et al., 2018b). While not high enough to impair reproduction, concetrations were also high in bald eagles compared to reference areas (DeSorbo et al., 2018).

In Mendall Marsh (Fig. 1), mercury concentrations in Black Ducks were 2 to 4 times above the Maine action level for mercury (0.2 μg/g ww), causing postings and health advisories for hunters (Figs. 1, 2; Sullivan and Kopec, 2018). Similarly, in Fort Point Cove and in upper Penobscot Bay, mercury concentrations in lobster and rock crab exceeded the Maine action level for mercury resulting in regional closures of the lobster and rock crab fisheries (Kopec et al., 2018a).

At the outset of this 7-year study, we hypothesized that present-day elevated concentrations of mercury in biota were most likely caused by continued, but small, discharges of mercury to the upper estuary, which has also occurred at other sites following closure of chlor-alkali plants (Gill et al., 1999; BCMOE, 2009). We further hypothesized that these smaller present-day discharges were more bioavailable to MeHg producers than older mercury in the system (Harris et al., 2007), and that this MeHg production was sustaining the mercury concentrations in biota. Instead, we found that recovery was being inhibited by the trapping of legacy mercury above salt fronts located in the upper estuary, and that this trapping continuously remobilized the legacy mercury making it bioavailable to mercury methylators in surface sediment. This new understanding was used to devise a novel remediation approach which would lower mercury concentrations in surface sediment and biota of the upper estuary.

2. Methods

Methods of sample collection and analyses for the data presented in this paper are described in detail in Appendix 1-1 Rudd et al. (2013a), and in papers included in this issue (Santschi et al., 2017; Yeager et al., 2018a, 2018b; Geyer and Ralston, 2018). Briefly, sediment was frozen and then dried and weighed prior to analyses. THg concentrations in sediment was determined using EPA Method 1631e, using acid digestion, BrCl oxidation, $SnCl_2$ reduction, purge and trap, followed by Cold Vapor Atomic Fluorescence Spectroscopy (CVAFS). MeHg was measured by distillation and ethylation, purge and trap, and CVAFS using EPA method 1630. Reference materials used were MESS-2 (Marine sediment, Beaufort Sea, National Research Council, Canada) for THg and International Atomic Energy Agency reference IAEA-405 for MeHg. Quality control/quality assurance included inter-lab comparisons with 4 mercury analytical laboratories (Appendix 1-1 of Rudd et al., 2013a).

Water samples were collected using ultra clean sample collection methods, EPA method 1669 and SG-004 EPA, and a peristaltic pump, with an in-line 0.45 μ filter, for filtered samples. THg concentrations in water samples were analyzed at Flett Research Ltd. by EPA Method EPA 1631e after oxidation followed by reduction, purge and trap, and CVAFS. MeHg concentrations in water were determined by EPA Method 1630, which involves distillation, ethylation, followed by purge and trap from water samples and quantification by CVAFS.

3. Production of MeHg in the Penobscot River and Estuary

Most of the mercury in fish and bird muscle is MeHg (Bloom, 1992; Sullivan and Kopec, 2018), which is produced from inorganic mercury (HgII) by bacteria active in sediment (Jensen and Jernolov, 1969), and then biomagnified up the food web. Most of this MeHg is produced in the top 3–5 cm of aquatic sediment and marsh soils (Rudd et al., 2013a; Gilmour et al., 2018a). Methylation is highest in sediment and marsh soils close to the sediment surface because fresh labile organic matter is continuously being deposited from the water above and consumed in the active surface layer of sediment where bacterial methylating activity is highest. In general, the rate of MeHg production in sediment is affected by several environmental factors including HgII concentration (which is the substrate for the methylation reaction), microbial activity, and the bioavailability of HgII to the methylating bacteria. The latter two factors can be combined into the term “efficiency of

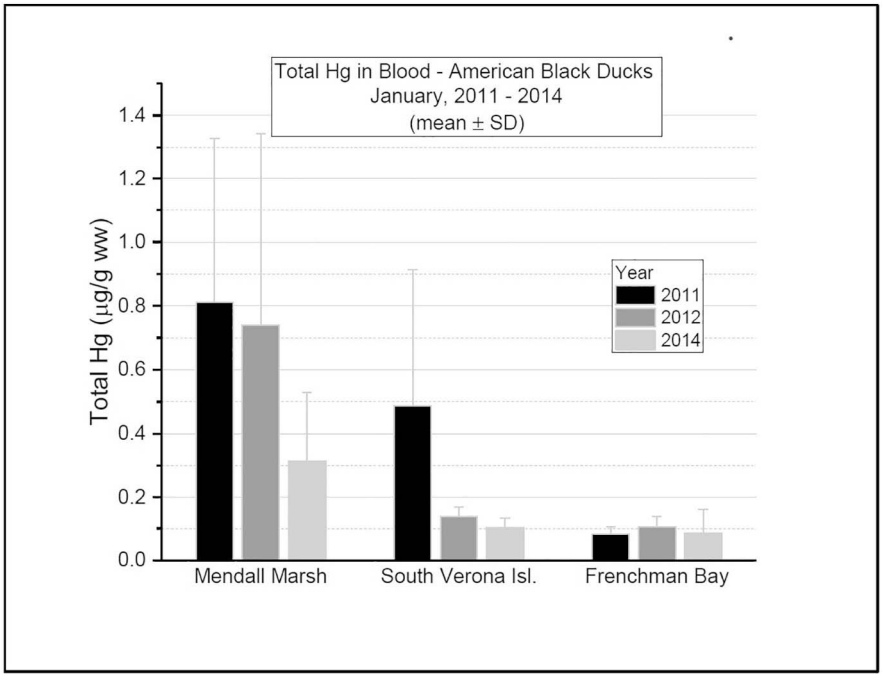

Fig. 2. In Mendall Marsh, mercury concentrations in black duck breast muscle averaged two to four times greater than Maine's action level for mercury in muscle, and about 8 times higher than at a nearby reference location, Frenchman Bay, by the end of the fall hunting season.
(Reprinted from Sullivan and Kopec, 2018, with copyright permission from Elsevier)

methylation". This efficiency of MeHg production per unit of THg can vary from one type of habitat to another (Winfrey and Rudd, 1990). In spite of the number of factors known to affect MeHg production, when we sampled surface sediment at 35 mudflat sites along the Penobscot River and estuary on 6 occasions in 2006–2007, a strong correlation was found between MeHg and THg, over a wide range of THg concentrations at an efficiency of about 3% (Fig. 3a). This robust relationship occurred over a distance of 160 km spanning freshwater Penobscot River sites to saline sites in Penobscot Bay (sampling sites shown in Fig. S3). Because of this strong relationship we concluded that these habitats for methylation must be fairly similar throughout, and that the primary controlling factor of MeHg production is the THg concentration.

This relationship is not always linear. Sediment was sampled in depositional locations in 28 coves in the upper and lower estuary (below Verona Island), a linear relationship was observed for intertidal mudflat sediment in front of wetlands (as in Fig. 3a), but in the wetland habitats at slightly higher elevations at the same locations the relationship with THg was hyperbolic (Fig. 3b). However, in all cases, MeHg concentration increased with increasing THg concentration at statistically significant levels.

Another example of a wetland habitat was the platform of Mendall Marsh, where methylation efficiencies (MeHg/THg) were found to be especially high compared to other habitats where efficiencies have also been measured (up to 10% at some sites, Gilmour et al., 2018a). In this case a combination of high THg concentration and high methylation efficiency resulted in very high MeHg concentrations in Mendall Marsh compared to five other sites in North America (Fig. S5). The high methylation efficiencies were the result of elevated concentrations of aromatic dissolved organic carbon in porewaters that increased partitioning of mercury to the liquid phase, as well as lower pH at some sites in Mendall Marsh (Gilmour et al., 2018a).

Even though MeHg production was very high in Mendall Marsh and MeHg concentrations in marsh birds were high enough to impact reproduction (Kopec et al., 2018b) the marsh was only a very small source (about 3%) of the MeHg flowing down the main stem of the Penobscot River (Turner et al., 2018b). This was because the MeHg was produced in the surface soils of the marsh platform that was only flooded briefly and intermittently during spring tides, which limited opportunity of transport from the marsh to the rest of the ecosystem.

Our finding that the MeHg concentrations in surface sediment respond strongly to higher concentrations of legacy mercury is important because the food webs in the upper estuary are sediment based. Highly contaminated marsh birds and ducks in the estuary that consume insects and benthic organisms have sediment-based food webs (Sullivan and Kopec, 2018). Similarly, using stable carbon isotopes and by analyses of stomach contents Kopec et al. (2018a) concluded that the fish species in the upper estuary (tomcod, American eels, mummichog, and rainbow smelt) have sediment-based food sources.

4. Methylation of legacy mercury is the problem

Before recommending active remediation, it is critical to establish whether the high present-day mercury concentrations in biota result

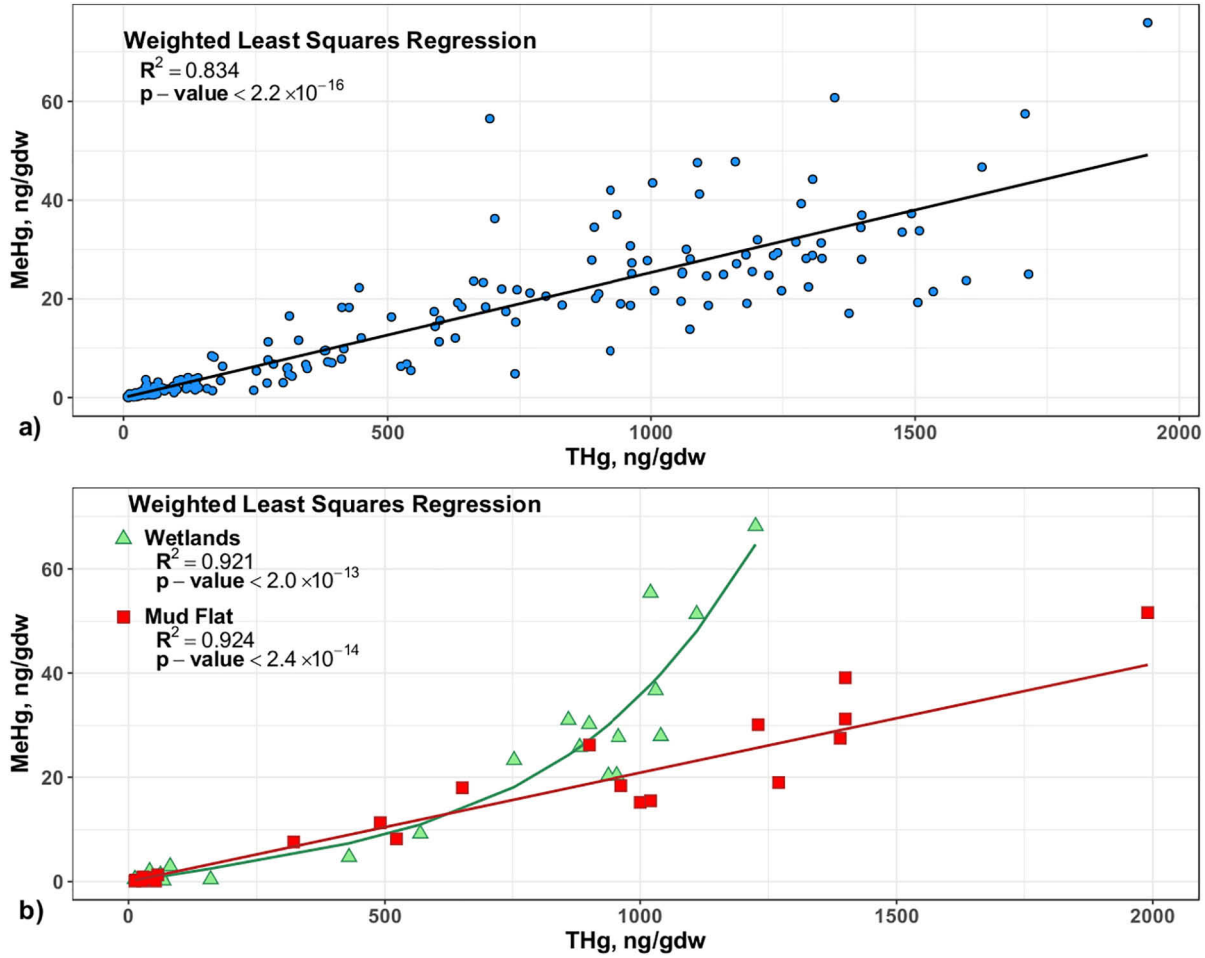

Fig. 3. MeHg concentrations are positively related to THg concentrations in mudflat sediment at 35 sampling sites between the east Branch of the Penobscot River and upper Penobscot Bay (panel a). Each site was sampled 6 times. In panel b at 28 sites, methylation was more efficient at higher elevation wetland sites (triangles) than in the mudflats in front of the wetlands (squares). Each site was sampled once.

mostly from methylation of legacy mercury released by the HoltraChem site mainly during the late 1960s and early 1970s, or from present-day sources of mercury (from upstream inflows over Veazie Dam, or from the HoltraChem site). This is a necessary distinction because if there are important ongoing sources or if new inputs are much more bioavailable to the methylators for methylation than is the legacy mercury, then active remediation that focuses on the legacy mercury would be ill advised. However, for several reasons listed below, we concluded that methylation of the legacy mercury is the primary reason for the continuing high MeHg in biota.

First, present-day inputs of mercury to the estuary from the Penobscot River above Veazie Dam and from the HoltraChem Site are not responsible for the elevated concentrations in the surface sediment of the upper estuary below Veazie Dam. Concentrations of mercury in the upstream river water are very low (3.8 ng THg/l and 0.15 ng MeHg/l, Rudd et al., 2013a). They are very similar to concentrations in other unimpacted rivers and streams of the northeastern USA (Shanley et al., 2005). The mass of mercury from the HoltraChem site today is a small fraction of the mercury delivered to the estuary by the Penobscot River (Turner et al., 2018a) and therefore does not have much effect. In the absence of the legacy mercury in the upper estuary, the sediment of the upper estuary should be like other unimpacted estuaries, such as the St. George (about 100 ng/g THg dw) that are background mercury concentration (Bodaly, 2013).

Second, this legacy THg is still being methylated even though it has been in the system for five decades. The statistically significant relationship of MeHg to THg in the sediment (Fig. 3a, b; Bodaly et al., 2013) showed that mercury at high concentrations, many times above background, are being methylated to the same or greater degree as THg at low concentrations. Since these high THg concentrations are due to legacy mercury, if the legacy mercury could not be methylated, as shown in Fig. 3a & b, we would not expect these relationships. Another example of old mercury being methylated is an experiment where a peatland was experimentally flooded to mimic reservoir construction (Kelly et al., 1997; St. Louis et al., 2003). In this case “old” mercury, which had been buried for centuries in the peatland was readily methylated when the peat column was disrupted by the flooding. Both the Penobscot data and the flooded peat experiment demonstrate the age of mercury in a system is not as important as if it is present in a location which is favorable for methylation. In both cases, it appears that when “old” mercury is moved into sites of active methylation, this inorganic mercury becomes available for methylation despite its age.

Third, the geographic distribution of MeHg concentrations in biota corresponded to mercury concentrations in sediment. The highest biota concentrations occurring in the upper estuary (Kopec et al., 2018a) where sediment mercury concentrations were highest, with lower concentrations being found in the lower mercury environments above the Veazie Dam and in Penobscot Bay (below Verona Island).

Because food webs in the upper estuary are primarily sediment based and because MeHg production in the sediment is directly proportional to THg concentration in the sediment (Fig. 3), we concluded that the key to remediating mercury concentrations in biota is to lower THg concentrations in the upper few centimeters of sediment and marsh soils.

5. What are the concentrations of mercury in the upper estuary?

5.1. THg concentrations in surface sediment

Presently, THg concentrations in surface sediment (0–3 cm), where methylation occurs, are more than 10 times higher in the upper estuary than in surface sediment upstream of the former Veazie Dam (Figs. S1, S3, S4). THg concentrations in the mainstem of the upper estuary, about 600 ng/g dw, were lower than in the side embayments of the Orland River (1000 ng/g dw) and Mendall Marsh (660 ng/g dw; Table 1). This is because the surface sediment in the lower-velocity side embayments receives more fine particulates, which have much higher mercury concentrations than the larger particulates (Kelly and Rudd, 2018). Concentrations were not as high in Mendall Marsh as in the Orland River, even though both side embayments were receiving the same high concentrations of mercury on the fine particles. This is because in Mendall Marsh the fine particles were diluted by organic material produced in the marsh by primary production (Gilmour et al., 2018a).

In support of the conclusion that fine particles with high mercury concentrations are deposited in side embayments (Kelly and Rudd, 2018), Turner et al. (2018b) found that Mendall Marsh was an overall net sink for THg with less mercury leaving the marsh at ebb tide than entering during flood tide.

5.2. THg concentrations in surface water

Concentrations of dissolved THg in surface waters were very low - about 2 ng/l in the upper part of the upper estuary (Fig. 4). These low concentrations are similar to dissolved mercury concentrations above Veazie Dam and in other unpolluted rivers (Shanley et al., 2005). Dissolved THg concentrations decreased further in the lower reaches of the upper estuary because dissolved THg was scavenged from the water by coagulation of dissolved organic carbon (DOC) in the estuary with subsequent sedimentation of mercury-bearing particulate organic carbon (Fig. 4; Turner et al., 2013).

6. Recovery from legacy mercury contamination is slow

The high surface sediment mercury concentrations in the estuary today (Table 1) in the absence of a significant point source (Turner et al., 2018a) means that the system is still recovering from the earlier

Table 1
Average THg concentrations in surface (0–3 cm) sediment in the upper Penobscot Estuary, including coves in the main stem of the upper estuary and its side embayments, the Orland River and Mendall Marsh. Also shown are THg concentrations in surface sediment of Fort Point Cove immediately downstream of Verona Island and in Penobscot Bay (Fig. 1, S1). The averages include sites sampled by the Penobscot River Mercury Study (PRMS) in surveys taken in 2006–2009 (Appendix 1-3 of Rudd et al., 2013a), sites in coves and protected areas sampled for natural recovery studies (Santschi et al., 2017; Yeager et al., 2018a, 2018b) and subtidal sites sampled by PRMS and by the Woods Hole Oceanographic Institution (WHOI) during their study of mobile sediment (Kelly and Rudd, 2018).

	Wetland intertidal & mudflat sites			Wetland soils			Subtidal sites			All samples		
THg, ng/g dw, 0–3 cm	Avg	Std dev	n	Avg	Std dev	n	Avg	Std dev	n	Avg	Std dev	n
Main river stem, from Brewer to southern tip of Verona Island, not including Mendall or the Orland River	890	370	57	700	300	20	360	490	79	600	500	156
Mendall Marsh	750	250	21	500	230	36	910	810	16	660	460	73
Orland River	1100	420	11	780	140	4	1000	420	7	1000	390	22
Ft Point Cove	350	360	14	110	110	7	470	230	12	350	300	33
Penobscot Bay, South of Fort Point to Islesboro Island	200	220	30	76	30	16	110	78	48	130	140	94

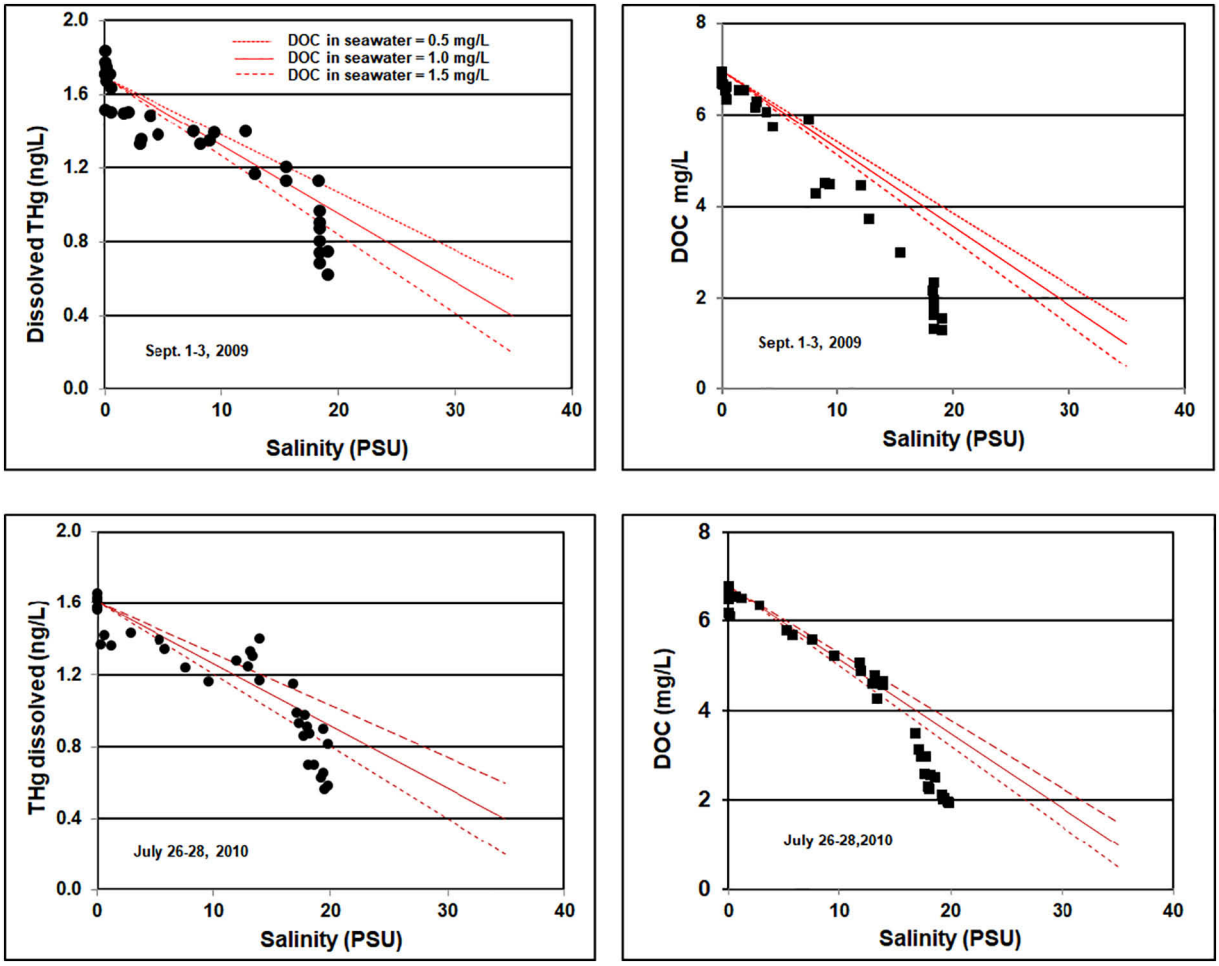

Fig. 4. Concentrations of dissolved THg and DOC in surface waters of the upper estuary of the Penobscot Estuary. The decrease in concentrations of THg and DOC at a salinity of 18 psu is indicative of DOC coagulation and removal of DOC and mercury from the dissolved phase. The three lines are simulations showing expected dilutions by seawater at assumed DOC concentrations of 0.5, 1.0 and 1.5 mg/l of Penobscot River freshwater with a DOC concentration of 35 mg/l.

legacy discharges. To determine the current rate of recovery, cores were taken from 56 stations in the estuary in 2009 (Santschi et al., 2017). Analyses of depth profiles of radionuclides (^{7}Be, ^{137}Cs, ^{239,240}Pu, ^{210}Pb) and THg concentrations were used to determine sedimentation rates and THg burial.

The geographic pattern of THg in the upper estuary has changed markedly since the time of maximum discharges (about 1967). At that time, the highest mercury concentrations (46,000–73,000 ng/g dw) were found near the HoltraChem site in Orrington, ME (Fig. S2). THg concentrations decreased precipitously with distance downstream from the HoltraChem site. Presently, surface THg concentrations are lower everywhere and more homogeneous throughout the estuary (Fig. S1), although there are still areas of higher concentration near the HoltraChem site. There are also areas of higher concentration in Mendall Marsh, and the Orland River because of sedimentation of fine particulates in these two areas (Kelly and Rudd, 2018).

There was a fast initial recovery during the first 21 years after closure of the mercury cells. During this first phase of recovery, sites nearest the HoltraChem plant recovered most quickly as the mercury was redistributed throughout the upper estuary and downstream past the trapping zone. Recovery in the upper estuary was much slower thereafter. In southern Penobscot Bay, surface concentrations of THg are continuing to rise as the plume of mercury slowly moves away from the HoltraChem plant site (Santschi et al., 2017; Yeager et al., 2018a).

Santschi et al., 2017 produced estimates of the current rate of recovery ($T_{1/2}$) in three zones of the upper estuary over a recent 21 year period: for the mainstem (31 y), Mendall Marsh (22 y), and the Orland River (77 y). But Santschi et al. (2017) emphasize that these estimated half-times are only indicators – particularly for the mainstem of the river and the Orland River where core variability was higher than in Mendall Marsh. The best indicator of whole-ecosystem recovery (22 y) is derived from the Mendall Marsh cores (Geyer and Ralston, 2018) because this quiescent side embayment receives mercury from the mainstem of the estuary and deposits it on the long-term, with least disturbance (Santschi et al., 2017).

7. Why is the ecosystem recovering so slowly?

The reason for the slow recovery discussed above is due to efficient trapping of mercury-contaminated particulates in the upper estuary above the southern tip of Verona Island (Geyer and Ralston, 2018). The upper estuary is the most contaminated zone of the Penobscot and it is also a zone of high turbulence and intense mixing due to daily tidal cycles. Mobile sediment is re-suspended and homogenized as it is moved up and down the mainstem of the upper estuary, but it does not readily escape to Fort Point Cove because of a tidally forced saline trapping front, which travels up and down the estuary restricting the movement of particles into Fort Point Cove (Fig. 5; Geyer and Ralston, 2018). This trapping of results in a pool of mobile sediment in the upper estuary estimated to be ~317,000 tonnes.

Most of the mercury in the mobile pool and in the surface sediment is bound to the finest particles in the muds (fine silts and clays, Kelly and Rudd, 2018) found in a class of sediment known as the “muds”. These fine particles are transported the furthest into low energy

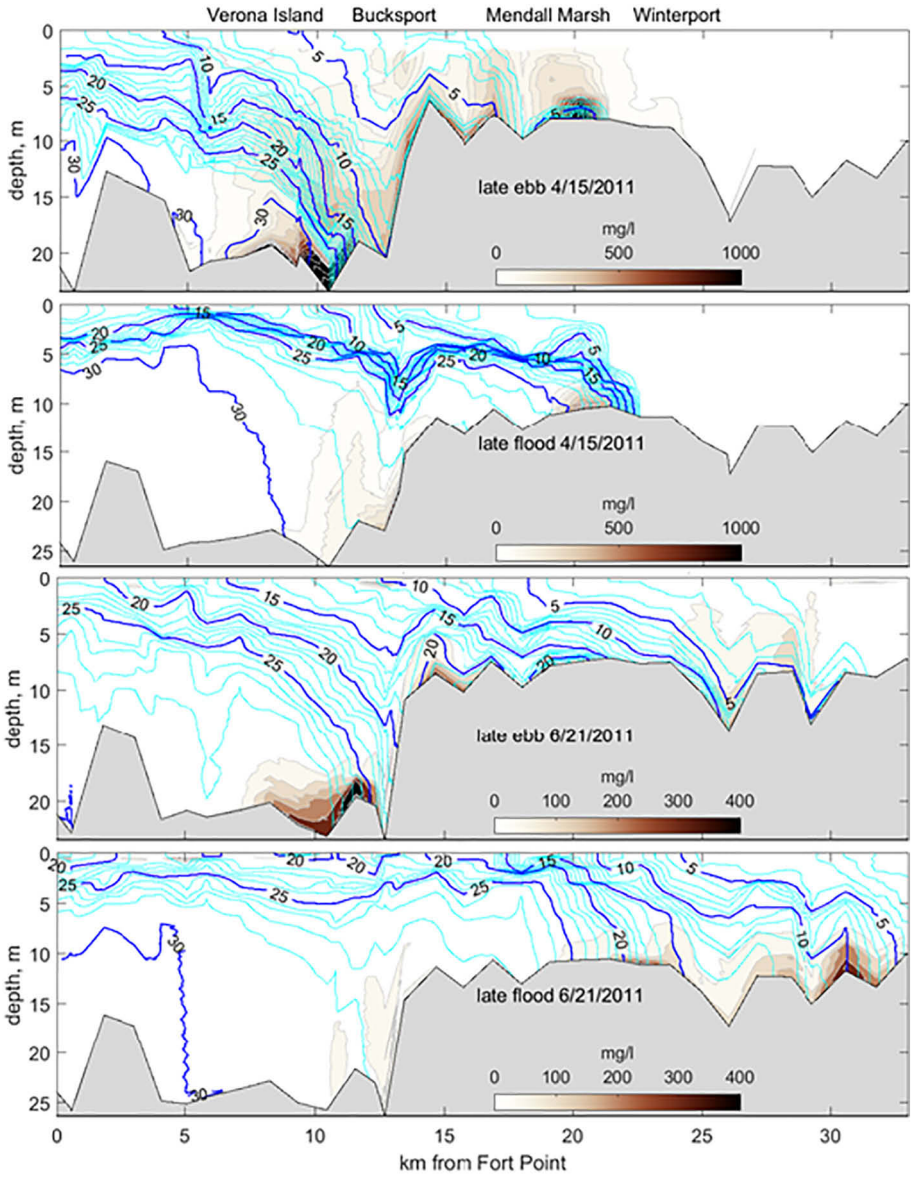

Fig. 5. Cross-sections on two sampling dates during high river discharge (upper panels) and low discharge (lower panels) along the axis of the Penobscot Estuary (the mouth to the left) near the end of late ebb and late flood tide, showing salinity (psu) in blue contours and suspended sediment (mg/l) with brown shading. The sediment concentration scale changes between the upper and lower panels, reflecting the marked decrease in suspended sediment concentrations during low river discharge. Note the change in position of the front (zone of closely spaced salinity contours intersecting the bottom) between ebb and flood and between high discharge and low discharge conditions.
(Reprinted from Geyer and Ralston, 2018, with copyright permission from Elsevier)

environments, such as coves and side embayments, and this accounts for the higher surface mercury concentrations in Mendall Marsh and the Orland River as compared to the mainstem of the estuary (Table 1; Kelly and Rudd, 2018; Yeager et al., 2018a).

The link between mercury concentrations in the mobile pool and in the surface sediment is demonstrated by comparing concentrations in the muds in the mobile pool with the muds in surface sediment (Fig. 6). Throughout the main stem of the upper estuary, because of tidal mixing, THg concentrations of the mobile muds were spatially very similar. Muds in the surface sediment had a similar spatial pattern to the mobile muds, and similar mercury concentrations (Fig. 6), and because there is little vertical mixing in surface sediments (Yeager et al., 2018b), these data together demonstrate that the particles in the mobile pool were the source of mercury to the surface sediment.

Particulate mercury in the mobile pool is constantly diluted by lower mercury containing particles entering in the inflows, resulting in a gradual natural recovery of the mobile pool. If this mobile pool was not there, the surface sediment of the estuary would receive the relatively clean incoming particles directly, and the legacy mercury would have been buried by now. It appears that this direct deposition of clean particles has occurred in the sediment closest to Veazie Dam (within 4 km) where surface concentrations have returned to background concentrations of 110 ng/g dw (Fig. 7). In contrast, surface concentrations are still elevated in Mendall Marsh (680 ng/g dw, Fig. 7), which is continuously receiving contaminated particulates from the large slowly recovering mobile pool.

8. Mass balance budgets in the upper Penobscot Estuary

There are several important reasons for constructing particle and mercury mass balances. First, it provides a conceptual model of the

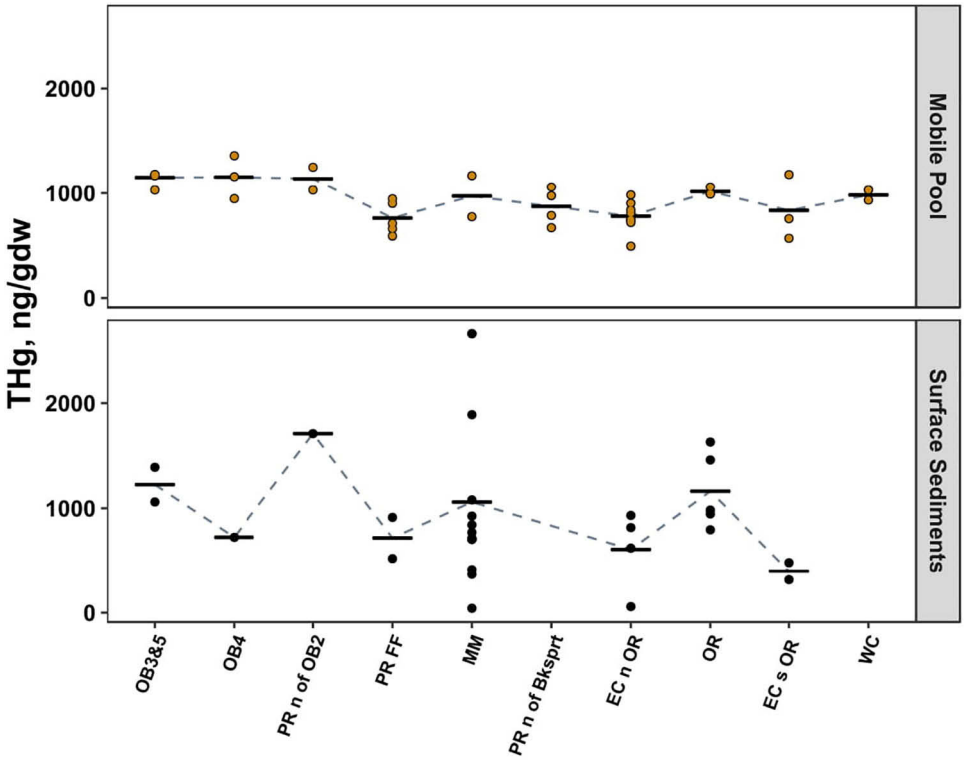

Fig. 6. Average THg concentrations in muds in mobile pool and muds in surface sediment, at geographic sub-areas, ordered north to south in the upper estuary of the Penobscot (OB = Orrington to Bucksport reach, PR = Penobscot River, FF = Frankfort Flats, MM = Mendall Marsh, Bksprt = Bucksport, EC = East Channel round Verona Island, OR = Orland River, WC = West Channel around Verona Island). The locations of the sampling sites are shown in Kelly and Rudd (2018).

transport, long-term storage, and loss of particles and mercury from the upper estuary. Second, if the mass balance that contains data produced by all of the Penobscot River studies has a reasonable degree of internal consistency, it gives confidence that mercury in the upper estuary is fairly well understood. Third, this understanding can then be used to design remediation measures.

8.1. Mass fluxes and inventories of particles in the upper estuary

There are two sources of new low-mercury particles to the upper estuary. One is the inflow of particles to the upper estuary over Veazie Dam and from tributaries that flow into the estuary below Veazie Dam. The average annual mass of suspended particles flowing over

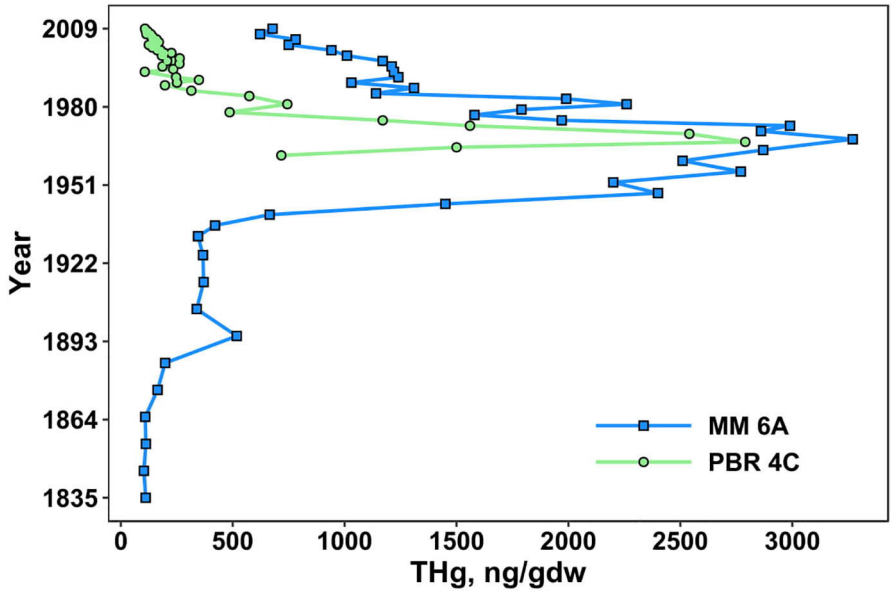

Fig. 7. Depth profiles of THg concentration 4 km downstream from Veazie Dam, where surface sediment mercury concentrations have recovered (Site PBR 4C), and at a site in Mendall Marsh (Mendall Marsh 6A) where surface sediment is still contaminated because of ongoing deposition of contaminated material from the mobile pool. Deposition dates for core sections were determined by pegging the maximum THg concentration for each core to 1967 and by using the sedimentation rate appropriate for each core (1.85 cm/y, core PBR 4C; 0.50 cm/y, core MM 6A, Santschi et al., 2017). The relative percent difference (RPD) for duplicate THg analyses in sediment for the method used was 5.7% (Appendix 1-1, Rudd et al., 2013a).

the Dam is estimated to be about 44,000 tonnes/y and tributaries are estimated to contribute 9700 tonnes/y, for a total of 53,700 tonnes/y of particulates in inflows (Fig. 8). A second source is the *in-situ* formation of particles in the surface water of the upper estuary. These particles form by coagulation of inflowing dissolved organic carbon (DOC), which enters the estuary in freshwater, either over Veazie Dam or from tributaries, and then coagulates to form particles (Fig. 4b). This particle formation is promoted by the mixing of the fresh river water containing DOC with the saltier seawater. It is estimated that 25,000 tonnes of particles are formed by this process, but that about half of this mass is likely decomposed in the upper estuary (Bauer and Bianchi, 2011). The remaining 12,500 tonnes is an internal source of particles that enters the large pool of mobile sediment. Together these sources provide an estimated total input of about 67,200 (net) tonnes of particles to the upper estuary annually (Fig. 8). This input becomes part of the mobile pool, which is estimated to be a size of 317,000 tonnes (Geyer and Ralston, 2018).

Particles are lost from the mobile pool through long-term sedimentation in the upper estuary and its embayments, and by outflow to Fort Point Cove. Approximately 18% of the surface area of the upper estuary above the southern tip of Verona Island is depositional on the long term (Yeager et al., 2018b). About 23,000 tonnes per year are estimated to be buried in these long-term depositional sites of the upper estuary (Fig. 8). A direct measurement of loss of particles past the salinity front and into Fort Point Cove is not available and based on the depositional area of Fort Point Cove combined with mean sediment accumulation rates in cores taken from Fort Point Coveit is estimated by deposition is ~26,000 tonnes/y (Table S1). This is a minimum estimate because loss below Fort Point Cove is not included.

In total about 49,000 tonnes per year of particles leave the upper estuary by transport (260,000 tonnes) or burial (23,000 tonnes), which leaves about 18,000 tonnes of output unaccounted for. If it is assumed that the particle fluxes in the upper estuary are in steady state, then the inputs of particles to the upper estuary (from upstream of Veazie Dam + the tributaries) should equal the losses from the upper estuary to Fort Point Cove (outflow + burial, Fig. 8). The difference could be accounted for by decomposition of particulate organic carbon entering the upper estuary, or additional losses of particles from the upper estuary and through to Fort Point Cove by wash load that occurs at high river flows, and would transport particles directly from upstream to the lower estuary without interacting with the mobile pool or sedimenting in Fort Point Cove.

8.2. Mass fluxes and inventories of THg in the upper estuary

A total of 59 kg of THg is estimated to enter the upper estuary over Veazie Dam annually (Fig. 9). A much smaller quantity of mercury (about 4% of the total input) enters from residual discharge from HoltraChem, municipal, and atmospheric sources (Fig. 9). Of the 59 kg entering over Veazie Dam, 48 kg is dissolved, and bound to DOC. It is estimated that about 4% of the dissolved THg is retained in the upper estuary when DOC flocculates (Table S1), forming particulate mercury, which joins the mobile pool. The remainder of the dissolved mercury is assumed to flow through the upper estuary to Penobscot Bay as wash flow.

In addition to inputs of mercury from flocculated DOC, the mobile pool of sediment also receives particulate mercury from particles that enter over Veazie Dam and from tributaries south of Veazie Dam (11 kg/y). The present average concentration of mercury in the mobile sediment in the upper estuary is 730 ng/g dw (Kelly and Rudd, 2018). The newly arrived particulate mercury from upstream and from flocculation of DOC has lower mercury concentrations (150–230 ng/g dw and 30–204 ng/g dw, respectively, Turner, 2013). These newly arrived and formed particles dilute the particulate mercury already in the mobile pool, enabling natural recovery. Particulate mercury in the mobile pool feeds long-term sedimentation at long-term burial sites (Fig. 9), and so as mercury concentrations in the mobile pool decline, surface sediment concentrations, where mercury methylation occurs, also decline.

The outputs of THg are long-term burial and flows of dissolved and particulate mercury out of the trapping zone. About 19 kg/y (Fig. 9) is deposited in coves along the main stem of the river, in Mendall Marsh,

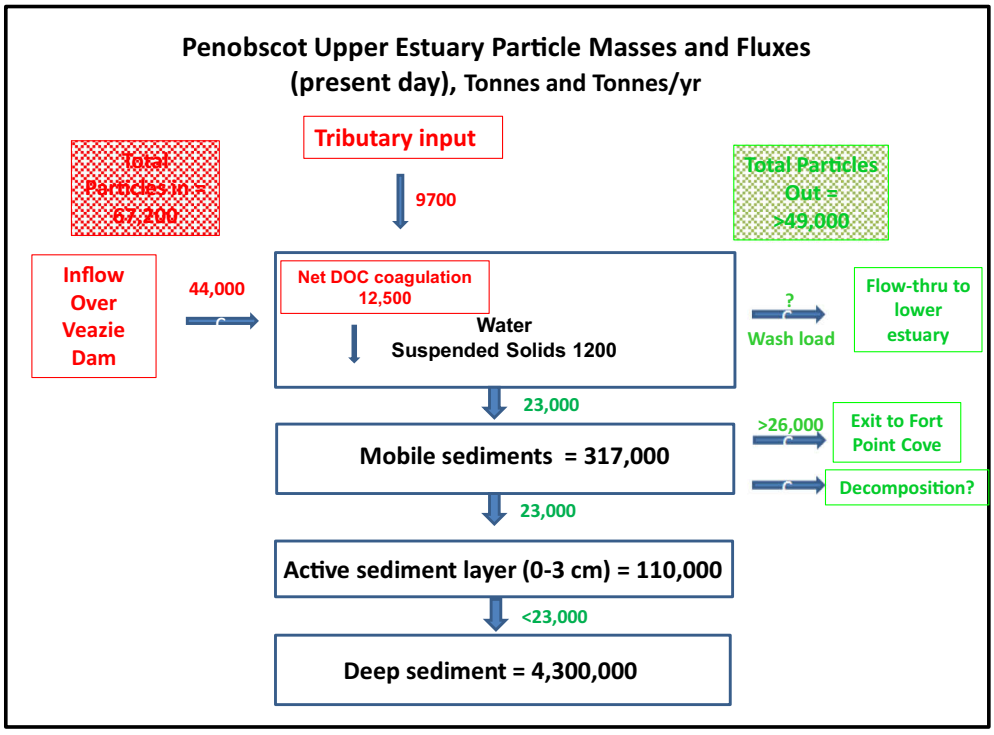

Fig. 8. Estimated annual fluxes of particles into and out of the Penobscot upper estuary and to the sediment, and masses of particles in the sediment of the upper estuary. Fluxes are in units of tonnes/y and masses in units of tonnes. Full referencing and calculations are in Table S1.

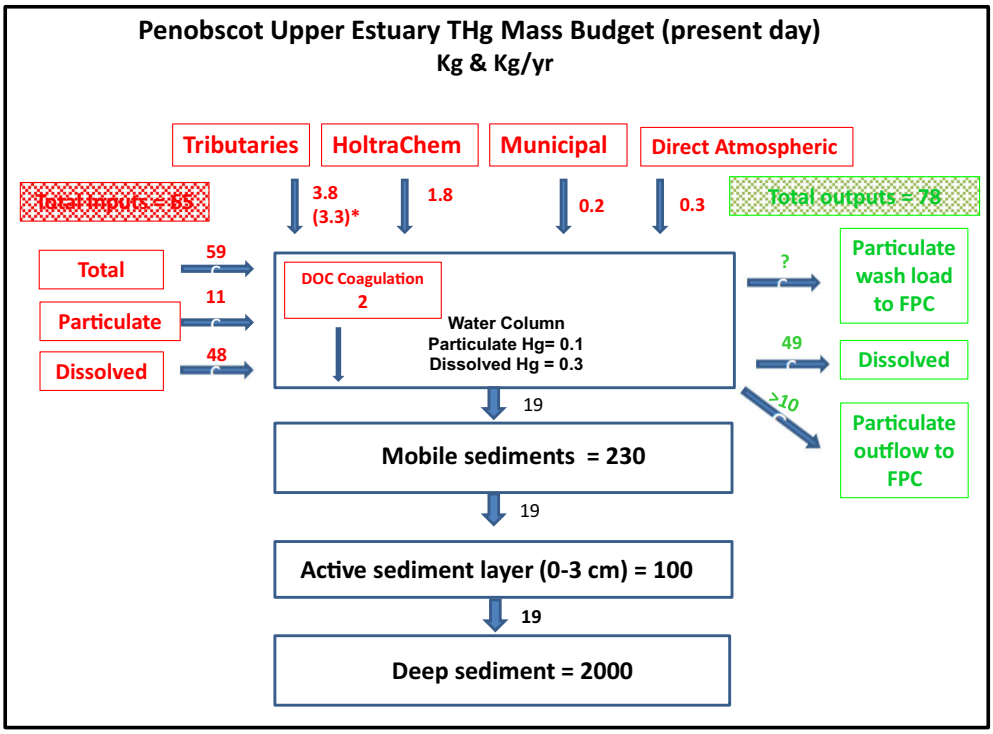

Fig. 9. Estimated annual inputs, outflows and burial of THg in the Penobscot upper estuary. FPC = Fort Point Cove, * = dissolved mercury. This does not include remobilization of mercury from sites of long-term burial. Full referencing and calculations are given in Table S2.

on the east side of Verona Island, and in the Orland River. In addition to this burial, other THg outputs are outflows of particulate mercury and the dissolved mercury attached to DOC. It is estimated that at least 9 kg/y of particulate mercury exits the upper estuary annually (Fig. 9), and much of this particulate mercury is deposited on the long term in Fort Point Cove.

Our present estimate of total outputs of mercury from the upper estuary of 78 kg/y (19 kg burial + 49 kg dissolved outflow + 10 kg particulate outflow) is greater than the total inflows (65 kg/y). This is consistent with the fact that the upper estuary is not in steady state – *i.e.* burial > inputs because the estuary is undergoing natural recovery (Fig. 9).

There is an internal inconsistency between the mass balance results and rates of recovery measured with core data (Harris et al., 2013; Santschi et al., 2017; Geyer and Ralston, 2018). The inconsistency is that the estimated residence times in the mobile pool for both particles and THg are too short to account for the slow rates of recovery ($T_{1/2}$ = 22 years, Santschi et al., 2017). For particles, the estimated residence time is about 6 years (317,000 tonnes/49,000 tonnes/y, Fig. 8), and for THg it is about 8 y (230 kg/29 kg/y, Fig. 9). It is possible that the size of the mobile pool may be underestimated. Also, Geyer and Ralston (2018) concluded that there must also be an ongoing remobilization of mercury contaminated particles to the mobile pool from previously deposited sediment, which could reconcile these different estimates. This is a challenge for remediation, because this constitutes an ongoing source of mercury to the mobile pool that may slow the recovery rate.

9. Remediation

9.1. Targets for biota

The main objective of the PRMS was to recommend mercury remediation goals and options to the U.S. Federal Court in Maine. The criteria for setting mercury reduction targets included toxicity of the mercury to the biota themselves, which were established by review of the peer reviewed literature on the toxicity of mercury to human and animal consumers of fish, shellfish, and ducks (Bodaly et al., 2013). It was concluded that reductions of mercury concentrations of 35–80% are needed for the aquatic biota in the mainstem of the upper estuary (Table 2). To reach targets for breeding marsh birds and wintering ducks that inhabit the marshes, reductions of about 80% from present concentrations are needed. For lobster, which are found in Fort Point Cove and the lower bay, reductions up to 50% are needed.

9.2. Targets for sediment

Based on the work described in the previous sections, a major conclusion for the PRMS was that remediation should focus on lowering the concentration of legacy THg in the surface sediment of the upper

Table 2
Summary of species considered to be in need of reductions in mercury concentrations, their primary habitat, and the amount of reduction from present concentrations that would be required to meet targets for animal toxicity and/or for human consumption, from Bodaly et al. (2013).

Species	Habitat	Reductions needed
Lobster	Fort Point Cove & Upper Penobscot Bay	Up to 50%
Rock crabs	Fort Point Cove & Upper Penobscot Bay	10 to 15%
Eels	Upper Estuary	50%
Rainbow smelt	Upper Estuary, Fort Point Cove & Upper Bay	Up to 60%
Fundulus	Upper Estuary, Fort Point Cove & Upper Bay	50% to 80%
Tomcod	Upper Estuary, Fort Point Cove & Upper Bay	35% to 80%
Cormorants	Fort Point Cove & Upper Penobscot Bay	None
Nelson's sparrows	Mendall Marsh & other Marshes in the Upper Estuary	Up to 75%
Other songbirds and shorebirds	Mendall Marsh and other Marshes in the Upper Estuary	Up to 80%
Black guillemots	Upper Penobscot Bay	35%
Black ducks	Marshes in the Upper Estuary	75%

Table 3
On average, concentrations of mercury in blood (MeHg) in bird species in Mendall Marsh are 10 times higher than in reference areas. Total mercury concentrations in marsh sediment soils are 7 times higher in Mendall Marsh than at uncontaminated reference sites.

Species	Mendall Marsh blood (μg/g ww)[a]	Reference Wetland blood (μg/g ww)[a]	Mendall Marsh soil (μg/g dw)[b]	Reference soil (μg/g dw)[c]
Black duck	0.8	0.1	0.5	0.07
Nelson's sparrow	5.1	0.5	0.5	0.07
Swamp sparrow	2.1	0.3	0.5	0.07
Song sparrow	1.4	0.2	0.5	0.07
Redwing blackbird	4.7	0.3	0.5	0.07
Virginia rail	2.3	0.2	0.5	0.07

[a] THg (MeHg) in blood of birds from Mendall Marsh (Kopec et al., 2018b).
[b] Average THg concentrations in Mendall Marsh wetland surface soils (0-3 cm), Table 1.
[c] PRMS wetland survey data most southerly sites in Penobscot Bay, Appendix 2 of Rudd et al. (2013a).

estuary and associated marshes, with the percent reduction for sediment coinciding with the percent reductions needed for biota (Table 2).

For the biota in the mainstem of the upper estuary, a lowering of THg concentrations in surface sediment by 50% to 450 ng/g dw, would be mostly protective (Table 2). A concentration of 450 ng/g dw would lower MeHg production rates by 50% (Figs. 3, S5), which would achieve the target for mercury in biota, because the food web of fish species in the upper estuary is sediment based (Kopec et al., 2018a). Concentrations of mercury in the marsh birds also reflect surface concentrations of THg in marshes (Table 3). For Mendall Marsh, a reduction in mercury concentrations of about 80% is required to protect the marsh bird species (Table 2). This would require a surface mercury concentration of about 100 ng/g dw (Table 4). The reason for the lower sediment target concentration in Mendall Marsh, in comparison to the mainstem, is that the marsh has much higher efficiencies of mercury methylation (Fig. S5, Gilmour et al., 2018a).

The natural recovery half-time of surface sediment established by dated cores (Santschi et al., 2017) for Mendall Marsh are considered to the best estimate of the recovery rate of the upper estuary as a whole[1] (Geyer and Ralston, 2018). This half-time was used in combination with present THg concentrations to estimate how long it would take sediment in the mainstem of the upper estuary and in Mendall Marsh to decline to estimated background concentrations (100 ng/g for the mainstem and 50 ng/g for Mendall Marsh, Bodaly et al., 2013). Without intervention, we estimated that it would take about 96 years for the sediment in the mainstem of the river to recover to within 20% of background concentrations, and about 100 years for Mendall Marsh (Table 4).

Since target sediment concentrations estimated to be protective of biota were 2–5 times higher than the background concentrations, less time should be required to reach target concentrations. To reach sediment concentrations of 450 ng/g dw for the mainstem and 100 ng/g dw for Mendall Marsh we estimated it would take 14 and 55 yrs. respectively (Table 4).

9.3. Remediation options

Since the mobile pool of sediment is the source of depositing material to the long-term sites of sedimentation in the coves of the mainstem of the river and in Mendall Marsh as well as the Orland River (Kelly and Rudd, 2018), it was concluded that a remediation option that lowered the THg concentrations in the mobile pool of the upper estuary would also lower surface sediment THg concentrations, and MeHg and the biota would follow (Table 4, Fig. 3; Kopec et al., 2018a; Kopec et al., 2018b).

Any remediation that lowered mobile pool concentrations in the upper estuary above the salinity front would also benefit biota in Fort Point Cove and Penobscot Bay, because of cleaner particulate outflows from the upper estuary. In Fort Point Cove and parts of the Penobscot Bay, lobster and rock crab fisheries are presently closed because of high mercury concentrations in these species. This is the case even though sediment concentrations in Fort Point Cove (345 ng/g dw, Table 1; Figs. S1, S4) are much lower than in the upper estuary (but still several times higher than background). Absent remediation of the mobile pool above the salinity front in the upper estuary mercury concentrations in Fort Point Cove and Penobscot Bay are likely to increase in the future (Santschi et al., 2017). Remediation of the mobile pool in the upper estuary would reverse this trend.

The PRMS examined several options to remediate the upper estuary (Rudd et al., 2013b, 2013c) where mercury concentrations are highest. Bank-to-bank dredging was not favored because of the very large area of contaminated sediment (Yeager et al., 2018a) and because of the possibility of aggravating the situation by exposing deeper mercury-rich sediment (Fig. S2; NRC, 2007). Capping the surface sediment was also not favored because of the large areas that would need to be treated, and because this remedy would not address mercury in the mobile pool of sediment, which would continue to contaminate a clean cap. Further, mercury methylation has been shown to be stimulated under sediment caps (Johnson et al., 2010).

Instead, the Study Panel recommended Enhanced Natural Recovery (ENR, Rudd et al., 1983; Rudd and Turner, 1983; Parks and Hamilton, 1987) in which high THg concentration in sediment is diluted by addition of clean clay particulates to lower inorganic mercury concentrations and methylation rates. In the case of the Penobscot, it was proposed that about 1/2 of the mobile pool of sediment be removed in the main stem of the upper estuary and that this material be replaced by clean clay rich sediment taken from Penobscot Bay (Rudd et al., 2013b, 2013c). The mobile pool contains a woodchip fraction that had both the highest THg concentrations (1380 ng/g dw) and highest MeHg concentrations (43 ng/g dw). Overall there is a linear relationship between MeHg and THg in the mobile sediment (Kelly and Rudd, 2018) similar to that seen in the surface sediment (Fig. 3), which suggests that there may also be MeHg production in the mobile pool, so removal of the mercury contaminated mobile pool including woodchips would result in an immediate improvement in the upper estuary.

An important uncertainty, mentioned above, is the extent of redistribution of previously deposited high-mercury sediment into the mobile pool (Geyer and Ralston, 2018). This would effectively increase the size of the mobile pool, and retard recovery. The extent of this redistribution needs to be better understood before proceeding with remediation.

The contaminated mobile sediment would be disposed of by confined aquatic disposal (CAD, Palermo et al., 1998). For example, diluting the mercury concentrations in the mobile pool over a five-year period by a factor of two would lower mercury concentration in the mobile pool by a factor of two and enhance the rate of recovery of THg and MeHg concentrations in the surface sediment and biota.

An important advantage of this ENR approach is that it is causes minimal disturbance of the ecosystem because the clean-clay material used for remediation is native to the ecosystem.

If half of the mobile pool of sediments was removed and replaced by clean clay-rich sediment from lower Penobscot Bay, estimated THg

[1] The turnover rate of the mobile pool was not used because of the uncertainty of the size of the mobile pool.

Table 4
Approximate years to reach target concentrations in sediment in the main stem of the upper estuary and on the platform of Mendall Marsh.

	2009 concentration, ng Hg/g dw	% reduction needed	Target concentration, ng/g dw	Approximate year reaching target	Approximate year reaching 20% of background
Mainstem	890	50%	450	2032[a] (14 yrs.)	2114[a] (96 yrs.)
Mendall Marsh platform	490	80%	100	2073[b] (55 yrs.)	2119[b] (101 yrs.)

[a] Using a half-time of 20 years, to an asymptote of 100 ng/g dw (expected background concentration in the mainstem after natural recovery is complete) (Santschi et al., 2017).
[b] Using a half-time of 20 years, to an asymptote of 50 ng/g dw (expected background concentration in the Mendall Marsh platform after natural recovery is complete).

concentrations in the surface sediment in the main stem of the upper estuary, the would approach target levels of about 450 ng/g dw THg within about 7 years. This estimate is based on a mixing depth in surface sediment of 3 cm and an average deposition rate of 0.6 cm/y (Santschi et al., 2017).

Mendall Marsh is a special case because of the high efficiency of mercury methylation in the marsh, which required a target sediment concentration of 100 ng/g dw. We estimated that lowering the mercury concentration in the mobile pool of the mainstem of the upper estuary by ENR as described above would reduce the recovery time by about a factor of two. Our recommendation was to further speed recovery in Mendall Marsh by doing additional treatments of ENR during spring tides when the marsh platform is flooded and/or to explore the possibility of adding activated carbon to the marsh platform, which was found to lower porewater concentrations of MeHg (but not production) in Mendall Marsh (Gilmour et al., 2018b).

10. Conclusions

The key findings in this paper are that inorganic mercury is efficiently retained in the Penobscot Estuary and this legacy mercury continues to be methylated 50 y after discharge. This explains why biota in the Penobscot Estuary are taking so long to recover from the large mercury discharges in the early 1970s, and also points the way towards remediation.

The PRMS demonstrated that there is not an ongoing source of mercury from the HoltraChem site that is sustaining the high mercury concentrations in the upper estuary today. Instead we found that loss of legacy mercury that originally entered the upper estuary in the early 1970s has been slowed by the existence of a large mobile pool of sediment above a salinity front that retards movement of contaminated particles downstream to Penobscot Bay. The contaminated particles in the mobile pool feed sedimentation of mercury to surface sediments. Because this legacy mercury was recently deposited it is still available for methylation 50 years after it was discharged from the HoltraChem site, as demonstrated by the finding that MeHg concentrations were proportional to THg. This is quite different from stratified lakes and deeper ocean environments, where mercury is permanently buried below the surface-active zone, becoming unavailable for methylation.

All of this understanding leads us to suggest a novel remediation strategy (ENR) whereby half of the contaminated mobile pool would be removed and replaced with clean native sediment. This would dilute THg concentrations in surface sediments, reducing the rate of MeHg production and speeding recovery.

Acknowledgments

The PMRS was a collaborative multidisciplinary effort funded by the U.S. Federal Court in Maine. The Court-appointed Study Panel (Rudd (Chair), Fisher, Whipple) was responsible for overall study design. They hired a number of experts, R.A. Bodaly, D. Kopec, C. DeSorbo, D. Evers, R. Geyer, C.A. Kelly, C. Gilmour, D. Ralston, P. Santschi, R. Turner, and K. Yeager, who capably undertook studies to understand mercury accumulation in biota, mercury inputs to the ecosystem, MeHg production, trapping and mercury transport out of the ecosystem as well as storage and recovery of surface mercury concentrations in the surface sediment. R. Harris collaborated on studies of DOC coagulation and particle mercury formation in surface waters of the Penobscot estuary, and in discussions about mass balance budgets of mercury in the estuary. Two highly proficient analytical laboratories, Flett Research Ltd. (mercury analyses in sediment and water, sediment radioisotopes) and the Battelle Marine Science Laboratory (mercury in biota), analyzed most of the samples taken for this study. Normandeau Associates expertly collected sediment, water and biota samples. We thank Mathew Parker and Rob James for their statistical advice. Fig. 1 map tiles by Stamen Design, under CC BY 3.0. Data by OpenStreetMap, under ODbL.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.06.060.

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