PENOBSCOT RIVER MERCURY STUDY

Chapter 1

A Synthesis of Mercury Studies on the Penobscot River Estuary

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1 INTRODUCTION

The Penobscot River in northern Maine (ME) is the second largest river in New England, draining an area of 22,300 km^2. Its estuary extends 35 km southward from Bangor, ME to about Searsport, with Penobscot Bay extending further southward. It is the largest estuary in New England with a surface area of about 90 km^2 (Figure 1-1).

Beginning in 1967, a chlor-alkali plant located in Orrington, ME ("HoltraChem") released large amounts of mercury (Hg) (about 6-12 tonnes, Chapter 3) into the Penobscot River. The amount of Hg released annually has greatly decreased since the early years, due to regulation, and it decreased further when the plant was closed in 2000 (Chapter 3).

Elevated levels of methyl Hg in sediments and biota led to legal action by the Maine People's Alliance in the 1990's. This group joined with the Natural Resources Defense Council (NRDC) to bring a suit against HoltraChem, which came to trial in 2002.

As a result of this trial in November of 2003, the U.S. District Court (District of Maine) ordered that there be an independent scientific study, and implemented the Penobscot River Mercury Study (PRMS) with the following three general objectives.

"The purpose of the Study Plan shall be to provide appropriate procedures and mechanisms to determine:

1. The extent of existing harm resulting from Hg from contamination to the Penobscot River/Bay system south of the HoltraChem plant site at Orrington, ME ("the site");

2. the need for, and feasibility of a remediation plan to effectively address the present effect of such existing harm, if any;

3. the elements and timetable for the execution of the appropriate remediation plan to address the harm existing as a result of Hg contamination "

The court order also listed the following specific questions:

a. "What physical, chemical and biological processes are presently at work that affect or govern the distribution and fate of mercury and methyl mercury in the sediments and biota of the Penobscot River/Bay system south of the immediate area of the site?

b. What is the extent to which any mercury in the Penobscot River/Bay system is being methylated and biomagnified in aquatic organisms and food webs of the Penobscot River/Bay system?

c. Is any mercury in the Penobscot River/Bay having significantly adverse effects on populations of organisms and food webs of the Penobscot River/Estuary system?

d. Is any mercury in the Penobscot River/Bay system posing an unacceptable risk to human health?

e. Do the scientific data lead to the conclusion that a mercury remediation program is necessary and feasible to effectively remediate the effects of any such harm by mercury contamination of the Penobscot River/Bay system?

f. If remediation is deemed necessary and feasible, what are the elements and schedule required for the execution and completion of such a remediation program, addressing the effects of mercury contamination in the Penobscot River/Bay system and what additional information is needed in order to design the remediation program?"

Two phases of the Study have now been completed. Phase I addressed Objective 1 of the Court order, concluding that there is extensive contamination of the estuary due to Hg released from HoltraChem site, which is sufficient to threaten the health of biota (Appendices 1-2 and 1-3). This warranted the initiation of Phase II of the study. Phase II of the study has addressed Objective 2, concluding that there is a need for a Remediation Program and that the remediation approaches, which are now recommended, are scientifically feasible. Data collected during Phase II have provided a scientific basis for our recommendation to the Court (Chapters 21 & 23) to proceed on to the 3rd objective of the implementing order, which is to order a Remediation Program to speed the recovery of the Penobscot from its present state of Hg contamination. The elements and schedule for a possible Remediation Program are given in Chapter 21.

This chapter is a synthesis of Phases I and II of PRMS. It is a big picture view of the transport, deposition, methylation and bioaccumulation of Hg in the Penobscot Estuary. This chapter primarily concentrates on the scientific interpretations of the data covering the past and present day characteristics of Hg in the system. Chapters 21 and 23 use these interpretations to predict the probable pace of recovery in the future if no active remediation occurs, and to make recommendations to the court about possible active remediation of the most contaminated reach of the Penobscot Estuary. This reach stretches from below the Veazie Dam to the southern tip of Verona Island and including Mendall Marsh and the Orland River. For the purposes of this report we refer to this most contaminated reach as the "upper estuary" (Figure 1-1).

This chapter presents evidence which shows that current elevated Hg concentrations in Penobscot sediments and biota are due primarily to legacy Hg released to the Penobscot River before 2000, and not to the present day discharges from the plant site or from Hg presently entering the upper estuary from the upstream watershed. We will also present evidence showing that the slow rate of recovery from the legacy Hg contamination from HoltraChem is caused by the efficient retention of Hg contaminated particles in the upper estuary in a large mobile pool of sediments, which slows the movement of particulate Hg seaward towards Penobscot Bay and to deep burial.

This chapter also presents what the Study Panel considers to be our best estimates of mass fluxes, inventories, and recovery times of Hg in the Penobscot estuary. Some of these are estimates provided by experts who prepared several of the following chapters. Others are estimates produced by the study group (Bodaly, Fisher, Kelly, Kopec, Rudd and Whipple). Together all of these estimates are used to produce the holistic view of Hg cycling in the Penobscot estuary described below. When some of these estimates

do not agree, they demonstrate the remaining uncertainty of our knowledge of Hg in the Penobscot estuary. In the last chapters of this report (Chapters 21 & 23) we recommend how these uncertainties could be further reduced by a few targeted data collections in the early stages of a recommended Remediation Program.

2 HIGH PRESENT-DAY <u>TOTAL HG</u> CONCENTRATIONS IN SEDIMENTS AND WETLAND SOILS ARE RESPONSIBLE FOR ONGOING TOXIC CONCENTRATIONS OF METHYL HG IN THE PENOBSCOT ESTUARY

The real concern in systems that become contaminated with Hg is not so much the inorganic Hg itself, which is the chemical form of Hg that was lost from the HoltraChem site, but the methyl Hg that is formed from it. Methyl Hg is an organic form of Hg that is efficiently bioaccumulated and biomagnified through food webs and that is most toxic. Methyl Hg concentrations are particularly high in the Penobscot system compared to concentrations in most other systems (Figure 1-2)[1].

Methyl Hg is produced from inorganic Hg by certain species of bacteria that live in sediments and wetland soils[2]. The amount of methyl Hg that the bacteria produce is affected by many environmental factors (Winfrey and Rudd 1990). The factor that appears to be most important in the Penobscot estuary is the concentration of inorganic Hg in surface sediments and wetland soils that is available for uptake and methylation (Figures 1-3a & b; Chapters 11 & 12). This means that at sites with higher amounts of inorganic Hg, more methyl Hg is produced. The Penobscot follows the general trend of many systems sampled throughout North America as illustrated by Figure 1-2, which shows that the concentration of methyl Hg is positively related to total Hg[3] at all of these locations. It is clearly evident that for a given total Hg concentration the Penobscot is notably higher in methyl Hg concentration than most of the other systems shown in Figure 1-2. This means that the methyl Hg production and accumulation in the Penobscot is particularly efficient[4].

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[1] Appendix 1-1 contains reports written during the study on the Quality Assurance/Quality Control program for the analyses of total Hg and methyl Hg in various media and for the radiochemical analyses done by Battelle Marine Sciences Laboratory, Texas A&M University - Galveston, Flett Research Ltd. and U. Kentucky.

[2] There are two groups of bacterial species in sediments and wetland soils that transform Hg to different chemical forms. One group, the methylators, produces methyl Hg from inorganic Hg. The other group, the demethylators, degrades methyl Hg back to inorganic Hg. Thus the methyl Hg present in sediments is the net result of these two opposing activities.

[3] In this chapter the term total Hg is used as a surrogate for inorganic Hg – the chemical substrate for methyl Hg production. The total Hg analysis includes about 3% methyl Hg. The remainder is inorganic Hg.

[4] The types and activity of bacteria that produce and degrade methyl Hg may contribute to high efficiency of net methyl Hg production in the Penobscot. Additionally, the chemistry of sediments and wetland soils impacts the activity of Hg methylating and methyl Hg degrading organisms, and importantly, also the bioavailability of the inorganic Hg for methylating bacteria. Inorganic Hg in Penobscot marshes appears to be highly bioavailable for methylation (Chapter 11). The biogeochemical factors that control net methyl Hg production, including (pH, dissolved organic carbon, and redox; Winfrey and Rudd 1990), must be optimal in the Penobscot system.

Within the Penobscot itself, concentrations of methyl Hg have a robust positive relationship with total Hg - in each type of habitat (Figure 1-3a,b, Chapter 12). However, the proportion of inorganic Hg that is transformed into methyl Hg is not the same across all habitats because of the other factors that also affect methyl Hg production[3]. For example, in Penobscot River and Bay sediments, about 2% to 3% (on average) of inorganic Hg is methyl Hg (Figure 1-3a), whereas in wetlands the average is 2% to 4% (Figure 1-3b). In some sites in Mendall Marsh, the proportion that is transformed is extremely high (averaging 8% but up to 22% (Chapter 11)). Within each type of habitat, however, methyl Hg concentrations are higher in sediments where inorganic Hg concentrations are higher (Chapter 12).

The top 3-5 cm of sediments and wetland soils are the most important for methyl Hg production and bioaccumulation by benthic organisms. In general, the bacterial activity (sulfur and iron reducing bacteria) that leads to production of methyl Hg is highest in sediments and wetland soils that are close to the surface. This is because these sediments receive fresh "food" for the bacteria, in the form of labile organic matter deposited from the water above. As sediments accumulate and are buried, the food becomes more degraded and the bacterial activity decreases. Thus, it is not surprising that in the Penobscot system, including in Mendall Marsh, the proportion of inorganic Hg that is methyl Hg is usually highest in the top 3-5 cm of river and bay sediments (Chapter 11, Appendix 11-2) and that methylation appears to be greatest in surficial marsh soils where there is an abundance of decaying vegetation (Figure 1-4). These observations have consequences for bioaccumulation of methyl Hg into the food web, because the upper few centimeters of sediment and marsh soils are also the place where the populations of benthic organisms most commonly feed. These organisms are an important part of the food web, and their methyl Hg is then bioaccumulated by other organisms higher in the food web.

Thus, we have concluded that the key to understanding methyl Hg production and natural attenuation of methyl Hg in the Penobscot is to clearly understand what controls **total Hg** concentrations in the upper few centimeters of aquatic sediments and wetland soils, because the rate at which these concentrations decline will determine the rate of recovery from Hg contamination in the Penobscot estuary. With this in mind the following biogeochemical discussions will focus primarily on total Hg, keeping in mind that processes that affect total Hg concentrations will also proportionately affect methyl Hg concentrations.

3   HISTORICAL AND PRESENT-DAY SOURCES AND CONCENTRATIONS OF TOTAL HG IN THE PENOBSCOT ESTUARY

3.1   Historical Hg sources and concentrations

Prior to 1850, when there was little industry in the watershed of the Penobscot River, background Hg concentrations in the sediments of the Penobscot estuary were very low- about 20-50 ng/g dry wt. (Figure 1-5). After industrialization of the Penobscot watershed (beginning in about 1850 to early 1940's), Hg concentrations in Fort Point Cove sediments increased slightly (to 50-100 ng/g dry wt., Figure 1-5). (Hg concentrations are expected to increase 2-3 times over preindustrial concentrations

because of anthropogenic increases in atmospheric deposition, as well as local industrial Hg sources.) The 1850-1950 concentrations in cores are similar to present-day surface sediments upstream of Veazie Dam, and in nearby reference estuaries, where there is no apparent point source of Hg contamination (Chapter 17, Appendix 17-2). We consider a total Hg concentration of about 55 ng/g dry wt. (with a range of 30-150 ng/g dry wt.) to be equivalent to present-day regional (New England) background concentrations of total Hg in surface sediments, as defined in Chapter 17.

Historical information on the amounts of Hg released into the Penobscot estuary since 1967 is incomplete. The only publicly available record of Hg discharges from the HoltraChem site begins in 1987. It includes only end-pipe discharges - not discharges to the river from the site in ground water or stream flow. Prior to 1987, we roughly estimated total losses of Hg to the river based on measurements made at other chlor-alkali plants (Chapter 3). This estimate suggests that releases in the early years of the plant's operation were likely 2 to 4 metric tonnes of Hg/year, between 1967 and 1970, when HoltraChem was first regulated in 1970 (Chapter 3). By 1987, when EPA records became available, reported discharges (from end-pipe discharges only) were 2-4 kg per year until plant closure in 2000, when they decreased to less than 0.1 kg/yr (Chapter 3). Presently we estimate that ongoing discharges from all sources at the HoltraChem site (end-pipe + stream flow + groundwater) are about 2.1 kg/yr (Chapter 3). The difference between this estimate and the reported end-pipe discharges, and the lack of data prior to 1987, make it difficult to go back in time to estimate total discharges of Hg to the river from the HoltraChem site. At a minimum, we estimate that the total amount of Hg released from the HoltraChem site into the Penobscot River prior to its closure in 2000 is about 6-12 tonnes, with most of that being released in the early years of operation (1967-1970's). Most of this Hg (9.3 tonnes) is estimated to still located in the sediments of the estuary (Chapter 5)

Hg released from chlor alkali plants to surface waters is usually in the ionic form (Hg^{2+}). This chemical form binds quickly and strongly to sediment particulates and to dissolved organic carbon (DOC) in the water column. Much of the Hg discharged by HoltraChem during the early years was deposited near or downstream of the plant site or was transported tidally upstream, above the HoltraChem site, as far upstream as Veazie Dam (Chapter 6). This is demonstrated by the maxima seen in many depth profiles of Hg concentration in sediment dated as 1967[5], which also corresponds to the 1967-1970 time period of maximum Hg discharge from the HoltraChem site (e.g. Figure 1-5).

The concentrations of total Hg in sediment laid down from about 1967 to 1970 in the upper estuary averaged about 6700 ng/g dry wt. (the average deep peak maxima in Penobscot River (PBR), Mendall Marsh (MM), and Orland River (OR) cores, Figure 1-

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[5]   Total Hg concentrations in depth profiles of Hg concentrations in Penobscot sediments are often elevated for a few cm depth below the depth at which sediments were deposited in 1967 (e.g. Figure 1-5), despite HoltraChem not having discharged Hg until 1967. The broadening of the Hg peak to depths below 1967 occurs because of mixing of the surface sediments by benthic organisms as the sediments were being deposited at the sediment surface in 1967.

6^6; Chapter 6). The highest 1967 concentrations are near the HoltraChem site (Figure 1-6). Peak concentrations decrease with distance from the HoltraChem site, but are still evident even in the most southerly cores taken from Penobscot Bay near Islesboro Island (Figure 1-6). The mechanisms by which this Hg is transported past Fort Point and into Penobscot Bay are presently not well understood and should be a topic of further study in a possible future remediation program[7].

Of the roughly 6-12 tonnes of Hg estimated to have been released to the Penobscot River prior to 2000 it is estimated that about 9.3 tonnes of this Hg remains in the consolidated sediments and mobile sediments in the estuary – mostly in Fort Point Cove and in Penobscot Bay (Chapter 5). An additional amount, which is difficult to quantify, remains in the soils of the adjacent wetlands. Inventories of the mass total Hg stored in areas of long term deposition in the estuary are shown in Figure 1-7. Of the 9.3 tonnes of total Hg that are presently estimated to be in the estuary, 77% is below the upper estuary in Fort Point Cove and in Penobscot Bay (Chapter 5). However the areal mass (mass per unit area) of total Hg in Fort Point Cove and in Penobscot Bay is much lower (0.13 tonnes/km^2) than in the upper estuary (0.36, 0.41, and 0.37 tonnes/km^2 in the Orland River, Mendall Marsh and main stem respectively). The highest areal inventories are in Southerly Cove - 1.5 tonnes/km^2.

These mass inventories of Hg can also be used to examine the rate of long term movement (natural attenuation) of total Hg out of the upper estuary since 1967 (Figure 1-7). 77% of the Hg in the entire estuary is now estimated to be south of the southern tip of Verona Island (Chapter 5). This amount (7.2 tonnes) is equal to the transport of 3% per year of the estimated 9.3 tonnes of Hg that has been released since 1967. This 3% per year export rate from the upper estuary is similar to the estimated needed losses of Hg from the mobile pool discussed later in this chapter. The agreement between two independent estimates (i.e. core studies & studies of Hg transport) gives us some confidence that we have a reasonably good understanding of the natural attenuation of Hg in the upper estuary.

3.2   Present-day sources of Hg to the upper estuary

During Phases I and II of the PRMS we estimated annual loading of total Hg to the upper estuary of the Penobscot River (Figure 1-8). Annual loading was estimated to be about 57 kg/yr from all sources (Figure 1-8). Of this total, 86% was contributed by inflow

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[6] A number of maps plotted using data of various types, as well as maps showing all sampling locations for the PRMS study are located in Appendix 4 of this Chapter.

[7] There are several possible ways that Hg could have passed Fort Point and entered Penobscot Bay, but we are uncertain of their relative importance. During the peak years of mercury discharge form HoltraChem (1967-early 1970's), much of the Hg was apparently associated with lignosulfonates produced by the pulp and paper industry, which was active at that time (Chapter 6). During these years mercury was likely transported past Fort Point attached to either dissolved or particulate lignosulfonates. During more recent years, when lignosulfonates were not as abundant, Hg is likely being transported south of Fort Point in "wash load" attached to particulates or in a dissolved form attached to DOC. Some additional study using more intense instrumentation over a longer time period than was used in Phase II is necessary to understand the form and quantity of mercury being transported south of Fort Point, which will help to quantify the rate at which contaminated sediments in the mobile pool are naturally recovering, as recommended in Chapter 21.

over Veazie Dam and about 9% by tributary inflows below Veazie Dam. Ongoing loadings from HoltraChem, municipal sources, and by direct atmospheric deposition contributed 4%, 0.4% and 0.5% respectively.

While the mass of present day annual river inputs is large (Figure 1-8) compared to all other present-day sources, the concentration of unfiltered total Hg in the inflowing river water is very low (3.9 ng total Hg/l, Q weighted average, Chapter 3) and is very similar to concentrations in other unimpacted rivers and streams of the northeastern USA (Shanley et al. 2005) – so upstream inflow of cleaner water is a mechanism of clean-up for the estuary (not contamination). Furthermore, these annual inputs are very small compared to the large quantity of legacy total Hg still stored in the sediments and wetlands of the upper estuary and Fort Point Cove, which is perpetuating the problem (see later discussion).

For this reason, and for four other reasons discussed in detail in Chapter 23, we conclude that none of the ongoing external sources of Hg to the upper estuary contribute importantly to the present-day contamination of Hg in biota inhabiting the upper estuary. Instead, it is the legacy Hg discharged from HoltraChem in past years, some of which is still causing elevated total Hg in surface sediments, which is responsible for the present-day contamination.

3.3 Present-day concentrations of total Hg in the upper estuary of the Penobscot River

3.3.1 Mercury in water

Concentrations of total Hg on suspended particulates in the water column of the main stem of the river below the town of Brewer are similar to total Hg concentration in the surface sediments at these locations[8]. This similarity is probably because much of the suspended material in the water column is derived from mobile surface sediments, which are re-suspended by river currents during the twice daily tidal excursions. While Hg concentrations decrease with distance from the HoltraChem site (Figure 1-9), this tidal mixing has resulted in similar concentrations of Hg in surface sediments of the same sediment type throughout the reach of the river from south Brewer to the southern end of Verona Island (Chapter 8).

One would expect that dissolved total Hg concentrations in surface waters of the upper estuary would be high, because the sediments are high in total Hg concentration, but this is not the case. In fact, surface water concentrations in the upper estuary (about 2 ng/L, Appendix 1-2) are either similar to or lower than dissolved Hg concentrations above Veazie Dam. These low dissolved total Hg concentrations below the dam in the highly contaminated upper estuary are due to: 1) total Hg being tightly bound to

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[8] An exception to this is the Brewer to Orrington (BO) reach (Figure 1-1) of the river below Veazie Dam, where suspended particle concentrations were only slightly higher than those above the Veazie Dam, even though surface sediments in the south Brewer to Orrington (BO) reach were highly contaminated. We view this difference between suspended particles and surface sediments as being caused by the fact that we always sampled on the outgoing tide when cleaner upstream water was dominating this part of the river.

contaminated sediment particles and not dissolving when resuspended (Chapter 18). 2) Dissolved Hg being scavenged from the water by coagulation of DOC and the subsequent sedimentation of Hg-bearing particulate organic carbon (Chapter 4), and 3) dilution by incoming seawater.

3.3.2 Mercury concentrations in surface sediments

Presently, the highest total Hg concentrations in surface sediments (0-3 cm) in the Penobscot River and estuary are found between Brewer (about 4 miles below the Veazie Dam) and the southern end of Verona Island including the Orland River and Mendall Marsh (Figure 1-9). In this section of the river, total Hg concentrations in surface sediments are more than 10 times higher (averaging[9] about 710 ng/g dry wt., +/- 510, n=268) than concentrations in surface sediments upstream of Veazie Dam (Figure 1-9, Appendix 1-2), where there is no aquatic influence of contamination from HoltraChem[10]. We designate this zone of the estuary, where Hg concentrations are the highest (Table. 1-1), as the "upper estuary". Total Hg concentrations are also elevated in Fort Point Cove south of Verona Island, but to a lesser extent (490 +/- 270, n= 26, Table 1-1; Figure1- 9). Below Fort Point in Penobscot Bay surface sediment total Hg concentrations progressively decrease to background levels of about 50 ng/g dry wt. near Vinalhaven Island (Figure 1-9; Table 1-1; Appendix 1-2).

In addition to the upper estuary being the zone of highest contamination in surface sediments, it is the zone where Hg concentrations in biota are the highest (Chapter 14, Appendix 14-2, 14-3), it is the zone where mobile sediment trapping takes place (see later discussion), and it is the zone of the river that would be directly impacted by possible active remediation (Chapters 21 & 23). It should be noted that over time remediation activities in the upper estuary would also benefit Fort Point Cove and Penobscot Bay, which are downstream from the upper estuary.

Average concentrations of total Hg in sediments can be calculated for any reach of the river as was done for the upper estuary (e.g. 710 ng/g dry wt. for sediments between Brewer and southern Verona Island including Mendall Marsh and the Orland River, Figure 1-9). However, it should be understood that any average sediment concentration for an area depends on the types of samples included (Table 1-1). For example, in the main stem of the river, concentrations were higher in the samples from the low elevations of the wetlands, intertidal and depositional sites than in mid-river sites, where currents are greater and samples tended to be larger grain size. Larger grain size sediments have lower Hg concentrations (Chapter 8). In contrast, in the Orland River, which is more quiescent, average total Hg concentrations were higher because

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[9] This average concentration is for all types of surface sediments sampled (including fine grained, sands and other materials). The average of 710 ng/g dry wt. is somewhat lower than the average concentration of 890 ng/g dry wt., which is the average concentration for in fine grain sediments at long term depositional sites, and 890 is the number used for calculating sediments targets for remediation. Also see Table 1-1.

[10] There is a possibility that during the years of Hg cell operation that fugitive Hg from the HoltraChem site was transported atmospherically upstream of Veazie Dam and deposited in the watershed there. So it is possible that some portion of the Hg presently flowing over Veazie Dam has originated form the HoltraChem site.

sediments were finer grained, even in the middle of the river channel (Table 1-1; Chapters 7 and 8).

3.3.3 Monitoring of Hg concentrations in surface sediments

Because we have monitored total Hg and methyl Hg concentrations in surface sediments over the period of Phase I and Phase II of the Study (2006-2010), we have data that can serve as a test of natural attenuation of Hg in the Penobscot system over this relatively short period. That is, are concentrations declining fast enough that a difference can be observed in surface sediments over the period 2006 to 2010? In surface sediments of Fort Point Cove, where sedimentation is spatially more uniform than further up the river, and thus where time trends in Hg concentration should be most obvious, there was no detectable decrease in total Hg concentrations from 2007-2010 (1-10; Chapter 15). This confirms the relatively long recovery times predicted for Fort Point Cove (Chapter 6).There were also no significant changes over the period 2006 to 2010 at wetland high elevation, medium elevation or low elevation sites (Chapter 15). In fact, one out of seven intertidal sites showed a significant increase in total Hg whereas two out of six wetland – mudflat elevation sites showed significant decreases. Overall these results confirm that natural attenuation in other parts of the system is proceeding slowly (Chapters 5 & 6).

There is one short (2 km, Figure 1-1) reach of the river below Veazie Dam (from Veazie Dam to Eaton Brook) where natural attenuation appears to be almost complete, at sites of long term deposition. Sediments at long term depositional sites in this reach of the river received high Hg concentrations in the early years of high discharge of Hg from HoltraChem (about 1967), as seen in the deep peaks in total Hg concentration (Figure 1-11), but surface concentrations are now almost at background levels (Chapters 6 & 9). Total Hg concentrations in surface sediments at these sites have recovered from peak concentrations of 1300-2700 ng/g dry wt. to near background concentrations – 100 ng/g dry wt. (Figure 1-11). This comparatively rapid 4 decadal recovery, compared to other locations in the Penobscot, has been facilitated by the high sedimentation rates at these sites (Figure 1-12) and by the continuous supply of cleaner (240 ng/g dry wt., Q-weighted average, Chapter 3) particulate material entering the upper estuary from above Veazie Dam.

This spatially limited example of recovery just below Veazie Dam together with much slower recovery further downstream is important as a demonstration of what surface sediment Hg concentrations could be when natural attenuation is finally complete in the main stem of the river.

4 NATURAL ATTENUATION OF MERCURY CONTAMINATION IN THE PENOBSCOT ESTUARY

Given the high present-day Hg concentrations in the upper estuary, it is important to estimate how long it will take for these concentrations to return to background levels. To do this one needs to know the rate at which Hg concentrations in surface sediments are decreasing over time, and also what final concentrations are expected to be after natural attenuation is complete, if no active remediation were to be undertaken. We

used a dated sediment core approach, which is our most trusted estimate of recovery rates in the Penobscot system.

4.1 Present-day background concentrations of Hg in the upper Penobscot estuary

Determining present–day background Hg concentration for the upper estuary is important because it is a lower bound below which surface sediment concentrations could not go if natural attenuation was allowed to proceed to completion, under present-day conditions. One approach to determine this concentration was to determine surface sediment total Hg concentrations at background sites in the region that had no known point source of Hg. Surface sediment concentrations found at such sites, in the East Branch of the upper Penobscot River, and in two reference coastal estuaries (the St. George and Narraguagus estuaries) averaged 55 ng/g dry wt. (30-150 ng/g dry wt., Chapter 17). These concentrations are somewhat higher than total Hg concentrations that were present in the Penobscot River in pre-industrial times (i.e. concentrations found at the bottom of long cores taken from Penobscot Bay (Figure 1-5). These somewhat higher Hg concentrations are very likely due to present-day elevated regional increases in atmospheric deposition of Hg caused by anthropogenic emissions of Hg to the atmosphere, which have generally raised Hg concentrations in the Penobscot watershed.

A second approach was the surface sediment concentrations at long term depositional sites in the short (2 km) reach of the river just below Veazie Dam (discussed above). At these sites, total Hg concentrations appear to have almost recovered and are now about 100 ng/g dry wt. (Figure 1-11), which is within the range of our low Hg reference sites (Chapter 17). These total Hg concentrations appear to be still declining (Figure 1-11), but have not changed much over the past 10 years. As a result, we have designated 100 ng/g dry wt. as a realistic expectation of surface sediment total Hg concentration when natural attenuation is complete. This is somewhat higher than the average regional background concentration presented in Chapter 17 of about 55 ng/g dry wt.).

It should be noted that the total Hg concentration on new particles entering the estuary from upstream of Veazie Dam is 240 ng/g dry wt., which is higher than our predicted background concentration after recovery of about 100 ng/g dry wt. The exact explanation for this observed difference has not been established, so we can only speculate, as follows, on the mechanisms responsible for our field observations. Diagenetic (microbial) processes in newly deposited sediments can release Hg from particles into pore waters during decomposition of newly sedimented particles. This diagenisis accounts for the higher Hg concentrations seen in sediment pore waters than in overlying surface water of the Penobscot (Chapter 11). These higher pore water total Hg concentrations could lead to loss of Hg from sediments in two ways: 1) by reduction of inorganic Hg to gaseous elemental Hg (Hg^0), which can volatilize to the atmosphere, or 2) by the binding of Hg(II) to DOC in pore water followed by its loss to the overlying surface water by diffusion. Whichever of these processes is responsible, our empirical field data (Figure 1-11) suggest that if natural attenuation is allowed to go to completion

surface sediment concentrations in the main stem of the river and in Penobscot Bay would be lowered to about 100 ng/g dry wt. total Hg.

4.2   Theory of natural attenuation

The rate of natural attenuation of Hg contamination in the upper Penobscot estuary is ultimately controlled by the rate at which the concentrations of particle-bound inorganic Hg are decreasing with time in the top few centimeters in wetland soils and river sediments (at long term depositional sites). The depth of this active mixing zone (which in long term depositional sites of the entire Penobscot is about 1-3 cm, Chapters 5 & 6) is determined by the physical mixing by the benthic organisms living in this zone. This is also the zone where much of the microbial methyl Hg production occurs, and where methyl Hg is bioaccumulated into the base of the benthic food web.

The average concentration of Hg in the particles in the surface sediment mixing zone will decrease with time if new particles being deposited on the surface sediments are lower in Hg concentration. Once particles enter the active mixing zone, they have a predictable residence time before they are buried into the deeper sediments by newly deposited particles. When a particle containing Hg is buried below the bottom of the active mixing zone, it leaves the zone of fastest methyl Hg production and accumulates permanently in the deeper sediments. As long as these deeper sediments below the mixing zone are not remobilized, the Hg in these sediments no longer contributes to the present Hg problem in the Penobscot. This burial process has already resulted in the burial of the sediments with the highest Hg concentrations to depths below the zone of methylation (Figures 1-4, 1-5, 1-6, 1-11), which means that methyl Hg concentrations in biota must have been much higher previously than they are now.

Three important factors that determine the rate of decrease of total Hg concentrations in the surface mixing zone in future years are: **1) the depth of the mixing zone and IHg concentration of these particles**, **2) the mass accumulation rate** (mg/cm^2/yr) of new particles being deposited to the sites of long term sediment accumulation in the river, bay and wetlands, and the **3) the Hg concentration of the new sedimenting particles.** These are discussed in some detail below.

The **depth of the mixing zone (1)** is determined by the physical mixing of the surface sediments by benthic organisms. We have estimated this depth for the Penobscot using concentrations of the short lived isotope ^{7}Be and the variability of porosity[11] with depth in sediment cores. Present estimates of the mixing zone depth are 1-3 cm (Chapters 5 & 6).

Determination of the ongoing **mass accumulation rate of new particles (2)** is done by radioisotope dating of the sediment layers. For example, if the sediment layer at 20 cm depth below the sediment surface is dated to be 40 years old, then the sediments at that sampling location are accumulating at an average rate of 0.5 cm/yr. Using this

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[11]   Aquatic sediments are composed of varying ratios of solid particulate material and water. Higher porosity sediments have a greater proportion of water compared to solid material.

approach at many locations in the estuary and in the wetlands the current rough estimate of the overall sedimentation is about 0.6 cm/yr of newly deposited sediment materials in the depositional areas of the estuary (Chapter 6). This average accumulation rate is dependent on:

a. the rate of supply of new particles to the estuary, including the inflow of new particles from upstream of Veazie Dam, from tributaries below the dam, and from the formation of new particles in situ by DOC coagulation and;

b. the efficiency with which these particles are being retained in the upper estuary - rather than being washed out to sea. As discussed below, the upper estuary is an efficient particle trap.

The **Hg concentration of the particles being deposited to the sediment surface (3)** is determined by the mixing of less contaminated particles entering the upper estuary from upstream (at about 240 ng /g dry wt.) with the more contaminated mobile sediments already in the upper estuary (730 ng/d dry wt., Chapter 8).

4.3   Studies of natural attenuation in the Penobscot

To make an accurate estimate of the natural attenuation rate of the Penobscot, an understanding of the system as described in the above paragraphs is required. To accomplish this, 58 sites at various locations in the river and wetlands were sampled (Chapter 6). We needed to evaluate this number of sites because of the high inherent variability[12] of sediments at different sampling locations, and because some sites are likely to have been disturbed in the past and so cores from these sites would be uninterpretable.

The sediment coring work concentrated on sites in the river, bay and wetlands where there appeared to be long term accumulation of consolidated sediments. These sites were chosen because they are the locations where Hg is being removed (buried) from the upper estuary on the long term. Deeper in these sediments (often 20 - 40 cm below the sediment-water interface) there is usually a maximum in total Hg concentration that is on average 6 times higher (about 6700 ng/g dry wt.) than total Hg concentrations in present surface sediments (e.g. Figure 1-6). The deep peaks in total Hg concentrations coincide with the dated section of cores that were deposited in about 1967 (Chapter 6). This also coincides with early large releases of Hg from the HoltraChem site beginning in 1967 and until 1970 (Chapter 3).

The fact that these deep sediments and their high Hg concentrations have remained undisturbed for four decades at sites of long-term deposition indicates that eventually the system can recover if point sources of Hg to the estuary remain low and the highly contaminated sedimentary strata which are now buried, remain undisturbed. So long as these deep sediments containing high Hg concentrations remain buried they will not

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[12] This variability is caused by the turbulence of the river water which sorts the sediments into various particle sizes and deposits sediments of different particle sizes at different locations based on their size and the velocity of currents at that location.

contribute to the present-day Hg contamination of the food web. Assessing the risk of deep sediment disturbance by storm events was one of the goals of the natural attenuation study. This risk seems low because of the fact that most of the cores have discrete maximum peaks in Hg concentration suggests that little of the Hg been remobilized from these sediments by disturbances during the past 40 to 50 years, even though hurricanes have occurred in the Penobscot over this time span. However, it is possible that that some of these deeper highly- contaminated sediments could be being redistributed on an ongoing basis by erosion caused by tidal streams that meander across mudflats and marsh platforms, and this should be further investigated.

The natural attenuation study using dated sediment core profiles (Chapter 6), produced estimates of the rate of recovery in three zones of the upper estuary - Mendall Marsh, the Orland River, and the main stem of the river - and for Fort Point Cove, which is immediately downstream of the upper estuary (Table 1-2). Estimates of recovery half-times[13] varied from 22 years in Mendall Marsh to 77 years in the Orland River (Table 1-2). These recovery half-times were used in combination with current total Hg concentrations to estimate how long it would take these sediments to decline to within 20% of the estimated recovery concentrations. These estimates varied from 106 years in Mendall Marsh to 390 years in the Orland River (Table 1-2). This variation occurred because of differences in sedimentation rates in the different zones, and because of the different types of sediments, which had differing total Hg concentrations, that were deposited in the different zones (Figures 1-9 and 1-12; Table 1-1).

For the purposes of predicting recovery in the entire upper estuary and for formulating our recommendations to the Court we have used the average recovery half-time for all of the cores collected in the upper estuary, which is 32 years. (A special case is Mendall Marsh where we used its 22 recovery half-time to make predictions for the marsh itself).

We consider the core data and the recovery times calculated from these data (Chapter 6) to be the definitive data produced by the study on rates of recovery of the upper Penobscot estuary from Hg contamination. Other methods for estimating particle and Hg turnover times of the mobile pool and input-output fluxes, which are also discussed in this chapter, are less certain because of the large size and heterogeneity of the area in which these measurements were made. These measurements could be improved with some additional sampling, as outlined in Chapter 23.

The slow rates of recovery of the upper estuary during past decades could be caused by ongoing point source discharges of Hg to the upper estuary either from the HoltraChem site or from other municipal and industrial sources located in the upper estuary. However, we were unable to locate any large ongoing external sources to the upper estuary (Figure 1-8; Chapter 3), which suggests an alternative reason for the slow

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[13] The recovery half-time is the time required to reach 50% of the ultimate response. The time required to achieve 50% of the ultimate response is not the same as the time to observe a 50% decline in absolute terms because the ultimate response is not zero (Chapter 18). In the case the Penobscot upper estuary, our best estimate is that the ultimate response is 100 ng/g dry wt. total Hg.

recovery[14]. As discussed below, the more likely reason for the slow recovery of the upper estuary is the existence of a large pool of Hg-contaminated mobile pool of sediments, which is efficiently retained in the upper estuary.

4.4   Importance of mobile sediment trapping in determining rates of sediment deposition in the upper Penobscot estuary

During this study it was discovered (Chapter 7) that trapping of suspended particulate material in the upper estuary was a very important factor, which determines the rate of loss of particle bound Hg to Penobscot Bay, and the concentration of Hg on particles that accumulate at long-term particle depositional sites in the upper estuary[15]. The upper estuary, above the southern tip of Verona Island, is a zone of high turbulence and intense mixing due to the strong daily tidal excursions. It is also an efficient trap for suspended particles, which are largely retained at several trapping sites in the upper estuary, because of a saline front that acts as a barrier to movement of particles further out into Penobscot Bay (Figure 1-13; Chapter 7). Mobile sediments are frequently re-suspended and transported within the upper estuary, but do not readily escape to Fort Point Cove. These sediments are referred to as "mobile sediments" to distinguish them from "consolidated sediments" that stay intact on the bottom at sites of long-term sediment deposition, such as coves, mudflats in the river and the offshore bottom sediments of Fort Point Cove and Penobscot Bay. The trapping of mobile sediments has resulted in a pool of mobile sediments in the upper estuary estimated to be about 320,000 tonnes in size. Deposition of sediment particles from this mobile pool feeds sites of long-term sediment deposition and Hg burial in the upper estuary and in Fort Point Cove.

The contents of this large pool of mobile sediments are diluted with lower Hg particles entering in the inflows resulting in a gradual natural attenuation of the mobile pool. The turnover time of the mobile pool is estimated to be 6-20 years (Figure 1-14; Chapter 7). This slow turnover rate determines the rate of recovery of Hg concentrations in the mobile pool, which in turn determines the slow rate of recovery of the concentrations in the surface sediments of the long-term depositional sites. This in turn determines the methyl Hg concentration in surface sediments and the slow rate of recovery of the biota.

The fine sediment particles of the mobile sediment pool are the source of particles for the long-term depositional areas of the upper estuary, and so Hg concentrations of the

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[14] Another type of ongoing source to the upper estuary could be the erosion of mudflats by meandering streams that cross the mudflats. We know this erosion is occurring on mudflats and on marsh platforms, but we do not yet know if it results in significant inputs of Hg to the upper estuary. We do however have some circumstantial evidence that this may be the case because the turnover time of Hg in the mobile pool of sediments appears to be much faster than in the surface layer of sediments in depositional areas (Chapter 18). An explanation for this difference could be an unquantified total Hg input to the mobile pool from erosion of Hg in mudflats and wetlands. This should be a topic of study in a possible future Remediation Program.

[15] All presently available hydrodynamic contaminant models, which predict rates of recovery, do not have the capability of including mobile sediments in their modeling procedures. The discovery, by this study (Chapter 7), of a large pool of mobile sediments in the upper estuary, which determines the rate of recovery of the upper estuary of the Penobscot from Hg contamination, prevented the use of multi-cell hydrodynamic modeling to predict recovery of the Penobscot estuary.

fine mobile sediments determine concentrations in surface sediments in the long term depositional areas (Chapter 8). Surface sediment samples were collected at 267 sites in the upper estuary to determine types of bottom material, their distribution and Hg concentrations (Chapters 7 & 8). The mobile sediments spend most of their time on the bottom, but are periodically (days to months) picked up by currents and moved to other locations[16]. These mobile sediments are sorted by the currents into the lighter sawdust fraction, which can accumulate (but not always) separately from the more fine grained mobile sediments (brown muds), which are composed of both inorganic and organic materials. Hg concentrations of the fine mobile sediment particles are uniform throughout the upper estuary because of this mixing process (Chapter 8). Evidence for this was the similarity of total Hg concentrations in the mobile muds (high % fine particles) and the surface sediments at long-term depositional sites, which also contain mostly fine particles (Chapter 8).

In the mobile pool, the percentage of total Hg that was methyl Hg (1% to 3%) and concentrations of methyl Hg were similar to those found in surface sediments (Chapter 8). An exception was the wood chip fraction of the mobile pool which had high total Hg concentrations (1380 ng/g dry wt.) and therefore high methyl Hg concentrations (43 ng/g dry wt.). These data suggest that there is methyl Hg production in the mobile pool as well as in the surface sediments and wetland soils, so removal of the Hg contaminated mobile pool would result in an immediate improvement in the situation in the upper estuary.

The mobile sediments are trapped in three locations, at Frankfort Flats, at the north end of the river channel on the west side of Verona Island, and on the east side of Verona Island (Figure 1-13). More work is needed to accurately determine the efficiency of particle trapping in the upper estuary. Our present best estimate is that the net export of sediment particles from the mobile sediment pool past the trapping zone is only about 3% to 7% per year of the total mass in the mobile pool (this chapter and Chapters 5 & 7). Improving the accuracy of estimated export rate, as well as the total tonnage of particulates in the mobile sediment pool should be an important task of the Remediation Program, if approved by the Court. Our current estimates of the size, and export rate of the mobile pool out of the upper estuary were used to develop the recommended Remediation Program. These estimates must be confirmed to determine the actual feasibility of our recommendations.

4.5   Sources of particles to the estuary

We attempted to do a mass budget of particle fluxes and burial in the upper estuary (Figure 1-14), as discussed below. The main objective of this exercise was to determine if our data on particle pools and fluxes were sufficiently robust, or if we needed some additional information before the remediation procedures that we recommend should be implemented.

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[16] The mobile sediment pool tends to accumulate at the trapping sites (Figure 1-13) during freshets and then is redistributed more broadly back up the river when river discharge is lower (Chapter 7).

There are two sources of new particles to the upper estuary. One source is the inflow of particles to the main stem of the Penobscot River over Veazie Dam and from tributaries that flow into the Penobscot below Veazie Dam. The average annual mass of suspended particles flowing over the Dam is estimated to be about 44,000 tonnes/yr and tributaries are estimated to contribute 9,700 tonnes/yr, for a total of 53,700 tonnes/yr of particulates in inflows (Figure 1-14). A second source of new particles is the *in-situ* formation of particles in the surface water of the upper estuary. These particles form in the surface water as a result of coagulation of inflowing DOC, which enters the estuary in a dissolved form either over Veazie Dam or from tributaries, and then coagulates to form particles (Figure 1-15; Chapter 4). The particle formation is likely promoted by the mixing of the fresh river water containing DOC with the saltier seawater. It is estimated that a 25,000 tons of particles are formed by this process (Chapter 4), but that about half of this mass is decomposed in the upper estuary (Bauer and Bianchi 2011). The remaining 12,500 tonnes is an internal source of particles, which enters the large pool of mobile sediments. This internal addition of particles also retards the overall recovery rate from Hg pollution. This is because the DOC contains Hg, and when it coagulates this particle formation adds Hg to the mobile pool slowing the recovery rate.

Together these two sources provide an estimated total of about 66,200 (net) tonnes of particles to the upper estuary annually (Figure 1-14).

4.6   Losses of particles

Particles are lost from the mobile pool through sedimentation within the upper estuary and by outflow (Figure 1-14). About 23,000 tonnes per year are estimated to be buried in the long term depositional sites of the upper estuary (Table 1-3; Figure 1-14 & Chapter 5). We don't have a direct measurement of loss of particles from the upper estuary past the southern tip of Verona Island and into Fort Point Cove. One estimate is that about 7% of the mobile pool exits via this route each year – based on particle inputs to the upper estuary and the estimated size of the mobile pool (R. Geyer pers. comm.), which would be about 22, 000 tonnes per year. Another independent estimate, based the depositional area of Fort Point Cove combined with mean sediment accumulation rates in cores taken from Fort Point Cove, indicates about 26,000 tonnes of deposition per year, assuming that none of the particles leave Fort Point Cove. Our present data (Chapter 7) are suggestive of efficient particle retention in Fort Point Cove, but additional more intensive measurements of particle fluxes at Fort Point are strongly recommended by Dr. Geyer.

Thus at least a total of 49,000 tonnes per year of particles leave the estuary, which leaves about 17,000 tonnes 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, Figure 1-14). The mass balance as presented in Figure 1-14 has an excess of 17,000 tonnes per year of particles entering the upper estuary. This suggests that some additional work is needed to account for this difference. 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 to Fort Point Cove by wash load[17], which could lead to an underestimate of total particle losses from the upper estuary. Because particle fluxes are such an important mechanism for Hg recovery, the Study Panel is of the opinion that these fluxes should be better understood before the remediation procedures we recommend are implemented. This additional work is recommended as part of a possible future remediation program (Chapter 21).

4.7   Mass fluxes and inventories of total Hg in the upper estuary

We also attempted to construct a mass budget for total Hg in the upper estuary – to investigate possible shortcomings of our understanding of mass fluxes of Hg. A schematic representation of total Hg inputs, outputs, and storage in the upper estuary is presented in Figure 1-17. A total of 57 kg of total Hg is estimated to enter the upper estuary annually (Figure 1-17). Of this total, 44 kg is in the dissolved form bound to DOC. It is estimated that about 12% of the dissolved total Hg is retained in the upper estuary when DOC flocculates, forming particulate Hg, which joins the mobile pool (Chapter 4). The remainder of the DOC-bound Hg is assumed to flow through the upper estuary to Penobscot Bay. In addition to inputs of Hg from flocculated DOC, the mobile pool of sediment also receives particulate Hg from Hg in particles that enter over Veazie Dam and from tributaries south of Veazie Dam, as well as from ongoing inputs from HoltraChem and municipal sources (Figure 1-17). However, much of the Hg in the mobile pool is still legacy Hg that originated from the HoltraChem plant. The present average concentration of Hg in the mobile sediments in the upper estuary is 730 ng/g dry wt. (Chapter 8). The newly arrived particulate Hg from upstream and from flocculation of DOC has lower Hg concentrations (240 and 30-240 ng/g dry wt., respectively, Chapter 4). These newly arrived and formed particles dilute the particulate Hg already in the mobile pool, enabling natural attenuation. Fine particulate Hg in the mobile pool feeds sedimentation at long-term burial sites at a rate of 19 kg/yr (Figure 1-17), so as Hg concentrations in the mobile pool decline with time surface sediment concentrations also decline. Once the particulates enter the surface active layer in zones with consolidated sediments they undergo diagenisis, which further reduces their total Hg concentration to about 100 ng/g dry wt. (as described above).

Approximately 18% of the surface area of the upper estuary above the southern tip of Verona Island is depositional on the long term (Table 1-3; Chapter 5). In the upper estuary, sites of long term Hg deposition are located in wetlands, in coves along the main stem of the river, in Mendall Marsh, and in the Orland River (Figure 1-16). A main route of exit of particulate total Hg from the upper estuary is the long-term burial (19 kg/yr, Figure 1-17) at these sites of long-term deposition. In addition to this burial, other total Hg outputs from the upper estuary are the outflows of particulate Hg and the dissolved Hg attached to DOC. Our present understanding is that at least 9 kg/yr of particulate Hg exits the upper estuary annually (Figure 1-17), and much of this

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[17] Wash load is sediment carried by river flow such that it always remains close the surface of a river. It is transported without deposition, essentially passing straight through the upper estuary to Penobscot Bay. It consists of the finest particles, which remain suspended because the turbulent mixing velocity of the river water is far greater than the settling velocity.

particulate Hg is deposited on the long term in Fort Point Cove[18]. Much (about 88%) of the dissolved (DOC-bound) Hg does not coagulate in the upper estuary, and it exits to Fort Point Cove and then further south to Penobscot Bay.

Our present estimates of total outputs of Hg from the upper estuary of 67 Kg/yr (19 kg burial + 39 Kg outflow +9 particulate outflow) are greater than the total inflows (57 kg/yr, Figure 1-17). This is consistent with the fact that the upper estuary is not in steady state -it is losing Hg because it is still undergoing natural attenuation.

Even though the above estimate of net loss of Hg from the upper estuary seems reasonable, the absolute quantity of Hg lost does not easily reconcile with expected turnover time of Hg in the mobile pool in the upper estuary. If the mass budget was functioning properly, the recovery half-time of Hg concentrations in the mobile pool should equal the recovery half-time of Hg concentration in the surface sediments of the upper estuary because the mobile pool feeds the surface sediments with the Hg-contaminated particles. The calculated half-time in the mobile pool is only 8 years (Figure 1-17) as compared to 32 years for the surface sediments (Chapter 23), which suggests that there is still some work to be done (in tandem with the particle work discussed above) before our remediation procedures should be implemented. The most likely explanations for the differences in the calculated mobile pool recovery half-time as compared to the observed surface sediment recovery half-time could be that the size of the mobile pool is presently underestimated, and/or that there is an ongoing internal source of legacy Hg to the upper estuary from the remobilization of highly Hg contaminated sediments from mudflats or wetlands, as discussed in Chapters 18 and 23.

5 MERCURY CONCENTRATIONS IN BIOTA OF THE PENOBSCOT RIVER/ESTUARY

Although about 87% of the Hg entering the upper estuary of the Penobscot comes from upstream inflows (Figure 1-8), concentrations in this inflowing water are low, about 3.9 ng/L (Chapter 3). We do not consider this Hg to presently be the major source of Hg to the food web. Instead there are four lines of evidence indicating that the surface sediments and mobile sediments, where legacy Hg is still found, are the main source of Hg for the food web in the upper estuary of the Penobscot (Chapter 23). With this in mind, concentrations of Hg in the food web of the Penobscot estuary are described below.

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[18] There are two independent estimates of particulate total Hg loss from the upper estuary. An estimate of 9 kg/yr (based data from Chapter 5) assumes that all of the Hg that enters Fort Point Cove from upstream is retained din Fort Point Cove. Available data supports this assumption (Chapter 7), but the data are not robust and should be improved because there is likely some transport of particulate Hg south of Fort Point. The second estimate of 16 kg/yr is a rough estimate from Dr. Geyer based on his understanding of the efficiency of trapping of particulates in the upper estuary and the size of the mobile pool. A robust estate of the loss rate of total Hg form the upper estuary is needed because modest changes in the mass budget of Hg inputs or outputs to/from the upper estuary have large implications with respect to the feasibility of option 1 for remediation of the upper estuary (see Chapter 21).

5.1 Geographic distribution of Hg in biota in the Penobscot River and Bay

As noted in the Phase I Update report (Appendix 3) and in Chapter 14 Hg concentrations in many species of biota showed geographic patterns that were consistent with the HoltraChem site being the major source of Hg to the lower river and bay. Because of downstream changes in environmental conditions in the upper estuary, especially salinity differences, there were no aquatic species that occurred throughout the whole contaminated zone. However, we were able to make observations of the relationships between Hg in biota in relation to the distance from HoltraChem or in different reaches of the river in relation to HoltraChem. The species that showed geographic patterns of Hg related to the location of HoltraChem included periwinkles, lobster, mussels, *Nereis* worms, soft-shelled clams, *Macoma* clams, green crabs, tomcod, eels, rainbow smelt, cormorants, and osprey (Table 1-4).

On the other hand, geographic patterns of Hg concentrations in six species of biota did not appear to be related to HoltraChem. The lack of relationships in these six species was due to limited occurrence of the species within the lower Penobscot watershed because of habitat restrictions (e.g. Nelson's sparrow), small sample sizes (e.g. otters, eagles), physiological differences among animals inhabiting different river reaches (e.g. freshwater snails), or highly mobile species that probably feed in tributaries rather than the river itself (e.g. kingfishers and otters).

We now have data for Hg concentrations in selected aquatic biota for the period 2007 – 2010, including mussels, lobsters, tomcod, rainbow smelt, winter flounder, American eels, song sparrows, swamp sparrow, cormorants, black ducks, and little brown bats. Similar geographic patterns of Hg concentrations consistent with a Hg source at the HoltraChem plant site have been observed in most years for all of these species in the Penobscot. For example, Figure 1-18 shows the concentrations of total Hg in mussels over the period 2006-2010, confirming the geographic trends presented in the Phase I Update report (appendix 3). All of these observations strengthen our previous conclusions that HoltraChem was the major source of Hg to the Penobscot estuary.

5.2 Year-to-year monitoring of Hg concentrations in aquatic biota of the Penobscot system

In some cases, Hg concentrations in biota at the base of the food chain have shown decreasing trends in concentration during the years that we monitored them (since 2006 or 2007 to 2010, Chapter 14). The most notable example is blue mussels, which showed statistically significant decreases in Hg at most sites monitored, but mussels do appear to naturally undergo very significant multi-year changes in Hg, as seen in the NOAA Mussel Watch data set (see Chapter 14). Hg concentrations in other lower food chain organisms such as rainbow, smelt, and mummichogs have shown decreasing concentrations at some sites, but not others. In lobster, there were no significant trends at most sites.

In prey fish, Hg declined significantly in tomcod at 1 site sampled in the OB reach (the most contaminated reach for this species), but remained unchanged at all sites in the estuarine (ES) reach. There were declines in Hg in rainbow smelt at 3 sites, all sampled

in 3 or more years. Smelt also had significant trends at an additional 6 sites, but those sites were monitored in only 2 years, and the trends, of both increasing and decreasing, may represent inter annual variation, and so should be interpreted with caution. There were declines at both sites with multiple year comparisons in the mummichog. However, there was no evidence of overall trends in the prey fish winter flounder. Animals low in the food chain are generally short-lived and small and would be expected to reflect changes in the supply of Hg to the food chain faster than larger, long-lived animals feeding higher in the food chain. And, indeed, in predatory fish and in birds, little trend was observed in Hg over the period 2006 or 2007 to 2010. In the American eel, there were no significant temporal trends seen at any of the 11 sites monitored over the period 2007 – 2010. In all bird species monitored, including songbirds, shorebirds, and the fish-eating cormorant, there were no consistent trends of declining Hg concentrations.

So, we have seen little evidence of decreases in the total Hg concentrations in surface sediments, but some evidence for decline in some animals at some locations, but not others. The short time frame of the current monitoring period limits our ability to document Hg trends in biota. Furthermore, known inter-annual changes in methyl Hg production rates and concentration in sediments (in the absence of changes in total Hg concentrations) could explain some of this variation over the short term. To clearly observe changes with time (i.e. on the expected time scale of total Hg concentration changes in the surface sediments,) longer term monitoring is required as recommended in Chapter 21.

5.3 Mercury concentrations in biota inhabiting wetlands in the Penobscot system

In the Phase I Update report (Appendix 3), we presented data for Hg concentrations in a number of bird species that were collected from wetlands in the system in 2006 and 2007, including Nelson's sparrows, song sparrows, swamp sparrows, red-winged blackbirds and Virginia rail. These species have been re-sampled over the period 2008 – 2010 and we now have data from these additional years for all these species. For example, Figure 1-19 shows total Hg concentrations in the blood of Nelson's sparrows over the period 2006 – 2010. These data confirm the high concentrations seen in this species in 2006 and 2007, especially as compared to the reference area. There are notable differences among years, but in general, no consistent temporal trends are evident. Swamp sparrows, song sparrows and red-winged blackbirds were also resampled at Mendall Marsh and levels in later years were similar to those found in 2007. There appeared to be no temporal trends in Hg in these species as well. In Virginia rails, Hg concentrations in blood and feathers were much higher than those at a reference area in 2007 (Phase I Update report), and levels were also high over the period 2008 – 2010. As noted in the Phase I Update report (Appendix 3), levels of Hg in species such as sparrows and rails are high enough to be of concern for toxic effects. Our more recent results (Chapter 14) confirm the high levels of Hg in songbirds and shorebirds in the area of Mendall Marsh and the special concern regarding Hg contamination and the bioaccumulation of methyl Hg in this area.

5.4 Concentrations of Hg in biota in relation to human health, wildlife health protection, and toxic effects to wildlife

In the Executive Summary of the Phase I Update report (Appendix 3), we presented a summary of conclusions regarding Hg concentrations in 24 species of biota in relation to reference areas, in relation to the geographic location of HoltraChem, in relation to levels of concern for human consumption, and in relation to levels of concern for toxic effects to the animals themselves. We have updated that summary by the addition of black ducks and by adding an additional criterion - aquatic animal health -for organisms eating species lower on the food chain and by applying the additional information from sampling various species of biota until 2010 (Table 1-4).

Black ducks inhabiting the Penobscot system, particularly in Mendall Marsh, have methyl Hg levels that are high relative to other non-Penobscot sites. They also show a geographic pattern consistent with HoltraChem being the major source of Hg. Our data show that black ducks from the lower Penobscot exceed levels of concern for human consumption (Figure 1-20; Chapter 14).

The protection of wildlife health can now be added as a criterion to the table presented in the Phase I Update report (Appendix 3). There is now growing evidence of concern for toxic effects in predatory animals that eat other animals with elevated concentrations of methyl Hg (Depew et al. 2012; Burgess and Meyer 2007; Evers et al. 2007; Friedman et al. 1997). The effects level is now thought to be approximately 50 ng/g wet wt. (0.05 µg/g wet wt.) on a whole body basis for fish, or about 63 ng/g wet wt. (0.06 µg/g) in muscle, assuming a conversion factor of about 25% between whole body and muscle concentrations. Species that may be of concern for protection of wildlife health include tomcod, mummichog, rainbow smelt, winter flounder and golden shiner (Table 1-4). These species are in addition to the bird species discussed above.

6 MERCURY IN MENDALL MARSH

As discussed above, methyl Hg concentrations in songbirds and shorebirds are especially high in Mendall Marsh. This is a result of a combination of factors, most notably the location of Mendall Marsh in the Penobscot system, as well as the high efficiency of Hg methylation and bioaccumulation there.

The mouth of the Marsh River, which is the entrance to Mendall Marsh, is located adjacent to one of the major trapping zones for particles in the main stem of the Penobscot River (Figure 1-13; Chapter 7). Studies of particle movement into Mendall Marsh have shown that under particular hydrodynamic conditions, particles are efficiently transported laterally into the Marsh (Chapter 7). About 40% of the particles that enter Mendall Marsh are retained in the marsh (Chapter 10). The Hg-contaminated mobile sediment particles are initially deposited in the bed of the Marsh River, as transitional sediments but over time they are resuspended and moved onto the marsh levees and platform, where they are retained in the vegetation. This deposition of sediment particles, originating from the main stem of the river, onto the marsh platform is the major source of Hg to the marsh. This is why Mendall Marsh cannot recover from Hg contamination more quickly than the main stem of the river.

Total Hg concentrations (750 ng/g dry wt.) in sediments on the marsh levees, which run alongside the main channels of the Marsh River, are much higher than concentrations on the marsh platform (490 ng/g dry wt., Table 1-1). This is because plant growth on the platform continuously adds clean organic material to the marsh soils (Chapter 11), which dilutes the Hg that comes in with the river particles.

Even though Hg concentrations in the marsh soils are lower than in the river sediments, methyl Hg concentrations on the marsh platform are higher (Chapters 11 & 12). This is because of the high efficiency of methyl Hg production in the marsh soils. Methyl Hg as a fraction of total Hg in Mendall Marsh soils and soil interstitial waters, in fact, stand out as some of the highest reported in the literature (Chapter 11). Saltmarsh biogeochemistry appears to be highly favorable for efficient conversion of Hg to methyl Hg, including these factors:

- There is a greater tendency of inorganic Hg to be in porewater rather than attached to soil particles, as compared to other types of aquatic sediments and soils (Chapter 11). This makes the inorganic Hg more available to the methylating bacteria.

- It appears that methyl Hg production in Mendall Marsh is stimulated, as it is in reservoirs and freshwater marshes, by high rates of microbial decomposition of organic plant carbon, which results in lower pH (Kelly et al, 1997, 2003; Winfrey and Rudd 1990), both of which stimulate methyl Hg production. In Mendall Marsh, methylation is positively correlated with organic matter concentration and negatively correlated with pH (Chapter 11).

- Salt marshes also have additional unique characteristics that further enhance the efficiency of methyl Hg production. Shifting redox conditions associated with the daily tidal cycle promote high rates of Hg methylation (Chapter 11).

- Shifting redox favors the formation of iron-sulfide-DOC complexes that hold Hg in pore water and are highly available for methylation by bacteria (Chapter 11).

The concentrations of total Hg in Mendall Marsh are higher than in less contaminated ecosystems. Even on the marsh platform, where total Hg is diluted with new organic matter from vegetation, concentrations are 4-5 times background, and concentrations are 7-8 times background on the levees close to the river. As discussed in section 1, methyl Hg concentrations are highly correlated with total Hg concentrations, and so the combination of high efficiency of methylation with high concentrations of Hg leads to the very high concentrations of methyl Hg found in Mendall Marsh. In addition, in Mendall Marsh as compared to other locations, there is greater tendency for methyl Hg to be in porewater rather than on the solid particles, which makes it more available for bioaccumulation by lower food web organisms (Chapter 11).

The end result of all of the factors discussed above is that there are very high concentrations of methyl Hg in pore water in Mendall Marsh compared to other ecosystems (Figure 1-2), which elevates methyl Hg concentrations in the lower food chain (Chapter 16), and eventually in the resident birds (Chapters 14 &16).

Because of these particular conditions in Mendall Marsh, inorganic Hg concentrations need to be decreased to a greater degree in the marsh than in the main stem of the river to achieve reductions to target Hg concentrations in key biota. To lower methyl Hg concentrations in birds to target levels (Chapter 2), the concentrations need to decrease by about 80% (Chapter 2). This would be achievable if total Hg concentrations in the marsh soils also declined by 80%. However this is likely close to regional background for marsh habitats with high organic carbon concentrations. So unless some specific active remediation procedure is executed in Mendall Marsh, as described in Chapters 21 and 23, methyl Hg in the biota of Mendall Marsh will not achieve their targets until total Hg concentrations in the marsh have returned to background concentrations, about 106 years, or 2119 (Table 1-2).

7 CONCLUSIONS

Legacy Hg discharged from the HoltraChem facility mostly between 1967 - 1970's, and to a much lesser extent until 2000 contaminated the Penobscot Estuary. This legacy Hg is still largely responsible for present-day elevated Hg concentrations in sediments and biota.

Of the estimated 6-12 tonnes of Hg that were discharged from the HoltraChem facility prior to its closure in 2000, about 9.3 tonnes still remain in the estuary. Most of this Hg is now located in Fort Point Cove and further south in Penobscot Bay.

Present concentrations of total Hg in sediments and biota are highest in the upper estuary between Brewer and the southern tip of Verona Island.

Our Hg mass flux data and modeling results suggest that a small loss of Hg from either the HoltraChem site or from Southerly Cove during any future clean-up operations of Southerly Cove or at the HoltraChem site, would have a significant deleterious impact on the estuary.

Different zones of the estuary are recovering at different rates. In general the northern zones (the main stem and Mendall Marsh) are recovering more quickly than the more southerly zones (Orland River, Fort Point Cove and Penobscot Bay). Some sites, particularly in Penobscot Bay, still have increasing surface Hg concentrations as the Hg contamination continues to spread.

In the upper estuary, we estimate that without active remediation biota will reach target levels in about 2046 (Chapter 21), but in Mendall Marsh, without intervention, target concentrations in birds will not be reached until about 2073 (Chapter 21). This longer recovery time is related to the exceptionally efficient methyl Hg production in Mendall Marsh.

Present-day inputs of Hg to the upper estuary are about 86% from upstream sources, but they are very dilute and do not contribute importantly to the present-day concentrations of Hg in biota in the reaches contaminated by HoltraChem.

Within each habitat (river sediments, wetland soils), methyl Hg production is directly proportional to total Hg concentration, so remediation procedures that reduce total Hg concentrations will speed recovery.

Methyl Hg production is particularly efficient in marsh soils in the Penobscot, relative to mud flats and bottom sediments in the Penobscot, and also in comparison to many marshes in other ecosystems.

Mendall Marsh is a sink for total Hg and is not an important source of methyl Hg to the upper estuary.

Concentrations of methyl Hg are particularly high in birds inhabiting Mendall Marsh. These high concentrations are caused by the high efficiency of Hg methylation in Mendall Marsh, and high bioavailability of methyl Hg to the food web. The continued accretion of historically-contaminated mobile sediments into marsh soils is the main driver of methyl Hg in the marshes where wildlife is most at risk.

Remediation of Hg contamination in the upper Penobscot estuary will be challenging because of the wide dispersal of Hg in the estuary, and because of the complicated hydrodynamics of the estuary.

A crucial finding of the Phase II study was the importance of mobile sediments in slowing the rate of natural attenuation in the upper estuary. A few important aspects of the mobile sediment pool in are still not understood, and should be examined by some targeted future studies to ensure that proposed remediation procedures will be effective.

Our studies of methyl Hg production, abundance, and bioaccumulation in the Penobscot system reveal a substantial risk for harmful exposures to methyl Hg for fish and wildlife that are supported by food webs in reaches of the Penobscot system polluted by Hg from the HoltraChem facility - to a lesser extent human consumers of ducks, lobster, rock crabs and eels may also be at risk.

8   ACKNOWLEDGMENTS

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