

PENOBSCOT RIVER MERCURY STUDY

Chapter 18

Simulations of the rate of decline of mercury concentrations in the Penobscot estuary

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1 SUMMARY

Simulation modeling was carried out for the upper Penobscot estuary to examine whether field data are consistent with the hypothesis that a large pool of mobile solids governs the rate of recovery of mercury (Hg) concentrations in the system. The modeled area extended from Veazie Dam downstream to the end of Verona Island, and included Mendall Marsh and a portion of the Orland River. Hg concentrations in surface sediments have declined from peaks that averaged $6,700 \text{ ng g}^{-1}$ circa 1967-1970. Present-day concentrations (730 ng g^{-1} for all solids, 890 ng g^{-1} for fine material in depositional zones) remain elevated above background concentrations estimated in the range of 100 ng g^{-1} . Hg concentrations in sediments are estimated to be declining at a rate of 32 years to achieve 50% of the ultimate response. Although Hg concentrations are very low in the dissolved phase in the water column, although suspended solids are clearly contaminated. Field studies by Geyer and Ralston (Chapter 7) indicated however that the estuary is an effective particle trap, with only a small fraction of the mobile solids pool exported downstream each year. It is hypothesized that the rate of recovery of Hg concentrations in the system is governed by particle turnover in a large mass of sediment solids (318,000 tonnes) that is effectively mixed and laterally mobile in the upper estuary. Hg-contaminated particles are gradually being replaced by particles with lower Hg concentrations, reducing concentrations in mobile solids over time.

A mechanistic mass balance model of Hg cycling, the Dynamic Mercury Cycling Model (D-MCM Version 3.0) was used to simulate the upper estuary as a single cell with a well-mixed water column and well-mixed sediments that represented the mobile solids pool. While this was a coarse analysis, it indicated that field estimates of the mobile solids mass and turnover rate are not consistent with the hypothesis that the mobile solids pool controls the field-estimated rate of decline of Hg concentrations in sediments (mobile and depositional) in the upper estuary. If the best estimates of particle masses and fluxes are combined, the mobile solids would turn over particles with a half time of roughly 5 years, much faster than the 32 year half time estimated for Hg the upper estuary using sediment cores in depositional zones. This implies that the mass of solids involved in recovery is bigger than estimated, the particle loss rates are smaller, and/or the upper estuary is actually recovering faster than the current estimate of a 32 year half time. Alternatively, there could be an ongoing source of Hg contamination to the mobile bed that is slowing declining with time, governing the rate of recovery of the system. Based on the modeling, ongoing residual releases of Hg from the HoltraChem site, on the order of 2.2 kg yr^{-1} , are too small to meaningfully delay the rate of recovery of Hg levels in sediments.

Additional field studies are recommended to better constrain particle pool sizes and fluxes in the upper estuary with the objective of reconciling the rate of particle turnover with the observed rate of decline of Hg concentrations in sediments. Consideration should also be given to the potential for different sediment zones in the upper estuary to interact in a manner that affects the overall rate of recovery. If further field studies are carried out, additional modeling would be useful to help reconcile field data with the conceptual model, to simulate other contaminated zones of the Penobscot Estuary as

distinct areas (upper estuary, Mendall Marsh, Orland River, Fort Point Cove, Penobscot Bay), and to evaluate potential remediation actions.

2 INTRODUCTION

The HoltraChem Manufacturing Company, located in Orrington, Maine, operated on the banks of the Penobscot River from 1967 until September, 2000 (Maine DEP 2005) (Figure 18-1). The facility manufactured chlorine, caustic soda (sodium hydroxide), chlorine bleach (sodium hypochlorite), hydrochloric acid and the pesticide chloropicrin. Elemental mercury (Hg) was used as a cathode to collect sodium from water. Mercuric chloride and mercuric sulfide were present in the spent brine (EPA 2001). Large quantities of Hg, on the order of tonnes, were not accounted for in inventories. The fraction of missing inventories released to the Penobscot River and Bay is unknown, but Hg concentrations in sediments can be more than 10 times above background levels in some locations (Bodaly et al., 2008 – Appendix 1-2 Chapter 1). Hg contamination extends from the upstream limit of estuarine flow at Veazie Dam downstream to Fort Point Cove and into a portion of Penobscot Bay, with concentrations farther downstream declining to background concentrations. Contamination also exists in Mendall Marsh, a wetland area connected to the River, and a portion of the Orland River.

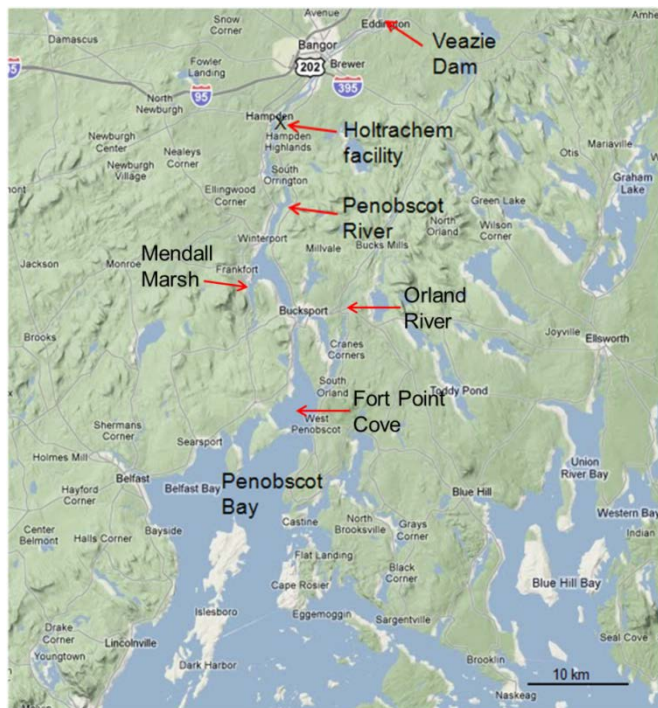


Figure 18-1. Penobscot River and Bay, Maine

Sediment cores collected in the estuary showed that Hg concentrations in contaminated sediments generally peaked in the late 1960s, and have declined since that time and are still recovering. This report describes mass balance Hg modeling carried out to help assess whether field estimates of particle masses and fluxes in mobile solids pool were consistent with the hypothesis that these particles govern the observed natural recovery of total Hg concentrations in the estuary. The Dynamic Mercury Cycling model (D-MCM Version 3.0, EPRI 2009), described further in later sections, was used to simulate total

Hg in the water column and sediments in the upper estuary. In this Chapter, the upper estuary is defined as including the main stem of the Penobscot River from Veazie Dam to the southern end of Verona Island, as well as Mendall Marsh and a portion of the lower Orland River (to a dam approximately 200 m downstream of the Castine Road Bridge).

3 OBJECTIVES

The primary objectives of the Hg modeling were to test the following hypotheses:

- Hypothesis 1: The rate of turnover of solids in the mobile pool controls the observed rate of decline of Hg concentrations in the mobile pool and depositional zones in the upper estuary.
- Hypothesis 2: Ongoing Hg releases from HoltraChem do not contribute significantly to current Hg concentrations in surface sediments or the rate of decline of Hg concentrations in surface sediments.

The modeling was not intended to predict the rate of recovery of sediment Hg concentrations in the estuary. The record of Hg contamination from intact sediment cores was considered to be the best evidence of the actual history of contamination and the ongoing rate of decline of Hg concentrations in sediments.

4 SITE DESCRIPTION – UPPER ESTUARY

General characteristics of the upper estuary are given in Table 18-1. The length of the upper estuary is ~46 km and the area is ~35 km². The mean hydraulic residence time based only on advective river flow is approximately 5 days. The entire reach of the river downstream of Veazie Dam is influenced by tides. The difference between mean high and mean low tide elevations is 3.3 m at Bucksport and 4.1 m at Bangor (NOAA 2010). Although information was not obtained regarding tidal flows past Verona Island, a rough estimate was developed using mean daily tidal amplitudes and the area of upper estuary. The resulting flow, equivalent to ~2800 m³ s⁻¹ on average, indicates that tidal flows are much greater than river flow on a daily basis.

The river reach from Veazie Dam to the end of Fort Point Cove exhibits vertical and horizontal salinity gradients (Chapter 7) indicating that the estuary water column is not uniformly mixed. Nevertheless, strong tidal flows, moving salinity fronts, and mixing do occur in the estuary. Salinity ranges from <1 to >30 PSU (Practical Salinity Units) (Chapter 7), depending on time and location, indicating varying degrees of mixing of fresh and seawater. Dissolved organic carbon (DOC) concentrations in freshwater inputs were in the range of 6-7 mg L⁻¹ (Kelly 2010), and tended to dilute conservatively in the downstream direction at salinity levels below ~12-14 PSU during sampling in July 2010 (Figure 18-2). At salinity levels above 15 PSU, DOC declined faster than would be expected due to dilution, indicating active removal. Dissolved Hg concentrations similarly showed an increased rate of decline where DOC concentrations declined faster than dilution would predict (data not shown).

The long term (1902-2011) average supply of solids over Veazie Dam is estimated to be approximately 43,000 tonnes year⁻¹ (Chapter 7). *In-situ* particle formation and degradation also occur. DOC coagulation is estimated to contribute approximately 25,000 tonnes of solids supply per year in the estuary, although a significant portion (e.g. 50%) decomposes rather than sedimenting permanently (Chapter 4). Additional solids are supplied by primary production, which is at least partially offset by decomposition. Approximately 18% of the upper estuary sediment area is classified as depositional (Chapter 1). The remaining 82% is characterized by cohesive sediments that are overlain by a pool of mobile sediment solids that can be 10 cm or greater in thickness (Chapter 7) in some locations. Geyer and Ralston (Chapter 7) concluded that solids in the mobile sediment pool are very effectively trapped in the estuary, with only a small fraction exported past Verona Island downstream (up to 7%, Chapter 1). Because of these features and the highly energetic state of the river, mobile solids are mixed effectively in the upper estuary and redistributed spatially during the year by changes in hydrodynamic conditions (Chapters 7 and 8). These solids are ultimately delivered to zones of long term sedimentation and buried, or exit to the lower estuary.

Parameter	Observed condition	Model input	Reference
Mean river flow	406 m ³ s ⁻¹ at Eddington for 1979-1996	406 m ³ s ⁻¹	Chapter 3
Mean tributary flow	75 m ³ s ⁻¹	75 m ³ s ⁻¹	Chapter 3, Appendix 3-8
Volume	~2.1x10 ⁸ m ³	~2.1x10 ⁸ m ³	Extracted from WASP simulation using aggregated grid from EFDC model
Area	~35 km ²	~35 km ²	Sum of segment areas from Chapter 7, Table 7-6
Mean depth	~6.1 m	~6.1 m	Estimated here
Hydraulic retention time	~5 days	n/a	Estimated here
pH	6.3 - 8.3	7.6	Kelly (2010)
DOC	Water: 1.1 - 7.4 mg L ⁻¹ Sediments: ~15 mg L ⁻¹	Water: 4.5 mg L ⁻¹ Sediments: 15 mg L ⁻¹	Water: Kelly (2010) Sediments: Chapter 11
Salinity/chloride	< 1 to >30 PSU salinity	~7 mg L ⁻¹ chloride	Intermediate value assumed between seawater and freshwater

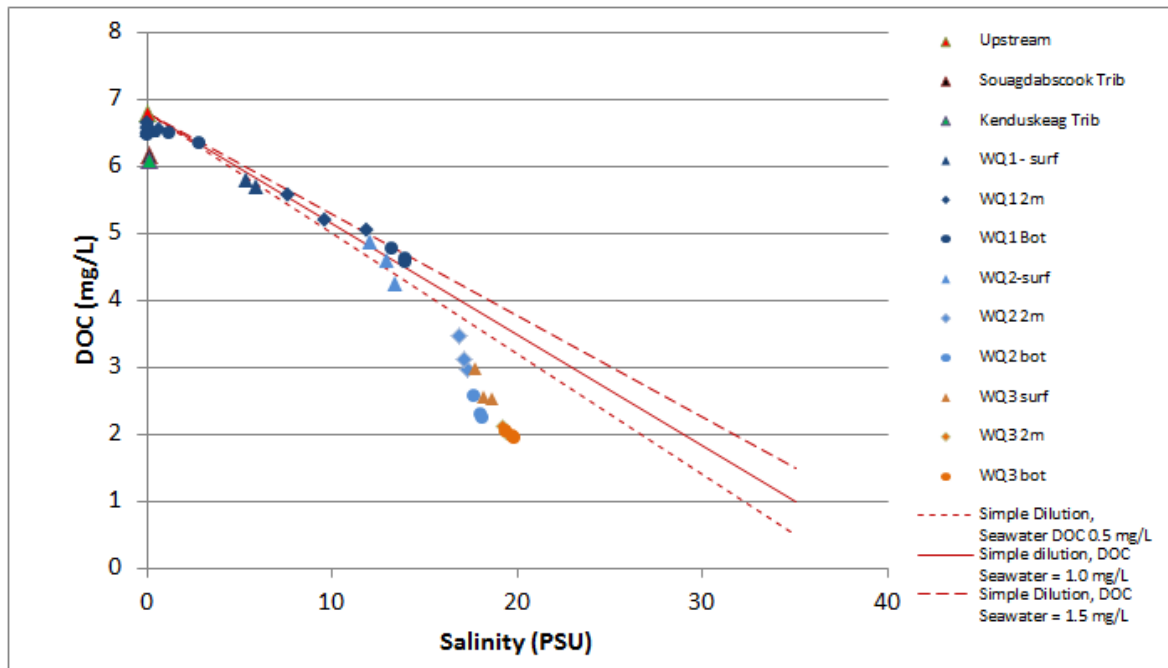


Figure 18-2. Dissolved organic carbon (DOC) concentrations in the water column of the Penobscot River, July 2010. WQ1, WQ2, and WQ3 are sampling locations near the HoltraChem facility, Winterport, and Bucksport respectively. Trib = tributary. Bot = bottom. Surf = surface, 2m = 2 m depth. Data from Kelly (2010).

4.1 Spatial trends for Hg contamination

Hg contamination is clearly evident in surface sediments downstream of Veazie Dam (Figure 18-3), where Hg concentrations rise sharply in the river above concentrations both upstream of Veazie Dam and downstream in Penobscot Bay. Hg contamination is also evident in water column particulates (Figure 18-4), with concentrations on suspended solids (TSS) that are intermediate between values upstream and in sediments. This suggests the contaminated sediments are resuspended into the water column and either mix with other solids in the water column to arrive at the observed concentrations, or Hg desorbs from resuspended solids, or both. Given the levels of TSS in the water column ($\sim 5\text{-}10 \text{ mg L}^{-1}$ average for 2006-2007 in surface waters, greater values in bottom waters; Bodaly et al. 2008), significant desorption of Hg from resuspended sediments would be expected to produce measurable increases in dissolved Hg concentrations in the water column. There is no apparent increase however in dissolved Hg concentrations in the water column along the contaminated reach of the river (Figure 318-5). As a result, the apparent partitioning (K_d) of Hg in the water column between solids and the filtered phase changes along the river, being higher in the contaminated reach than upstream or downstream (Figure 18-6).

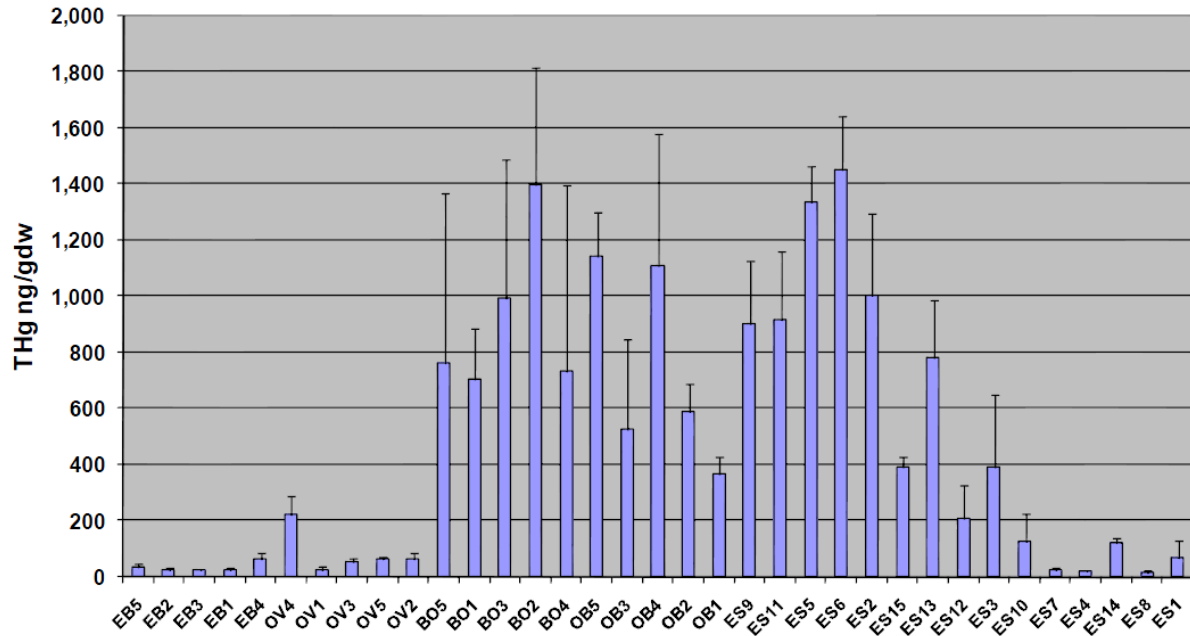


Figure 18-3. Mean concentrations of total Hg in near shore surficial sediments (0-3cm) between 2006-2007. EB=East Branch, OV=Old Town-Veazie, BO=Brewer-Orrington, OB=Orrington-Bucksport, ES=Estuary. Stations are ordered from upstream on the left to downstream (north to south) on the right. From Bodaly et al. 2008.

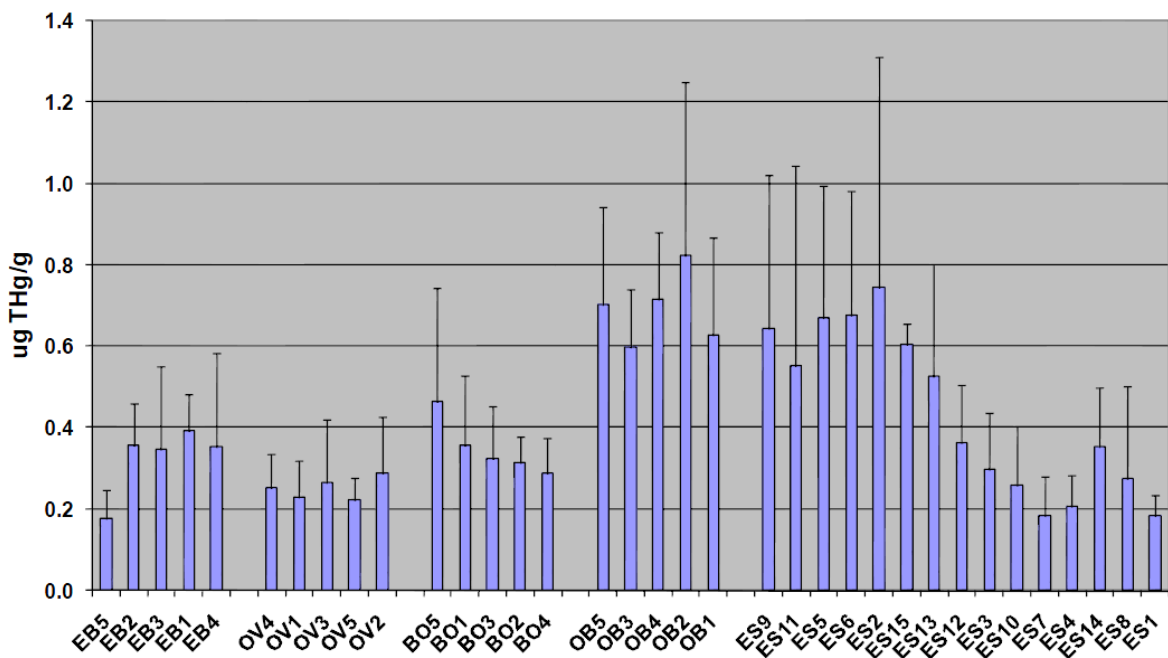


Figure 18-4. Mean concentrations of total Hg on particulates in surface water between 2006-2007. EB=East Branch, OV=Old Town-Veazie, BO=Brewer-Orrington, OB=Orrington-Bucksport, ES=Estuary. Stations are ordered from upstream to downstream (north to south). From Bodaly et al. 2008.

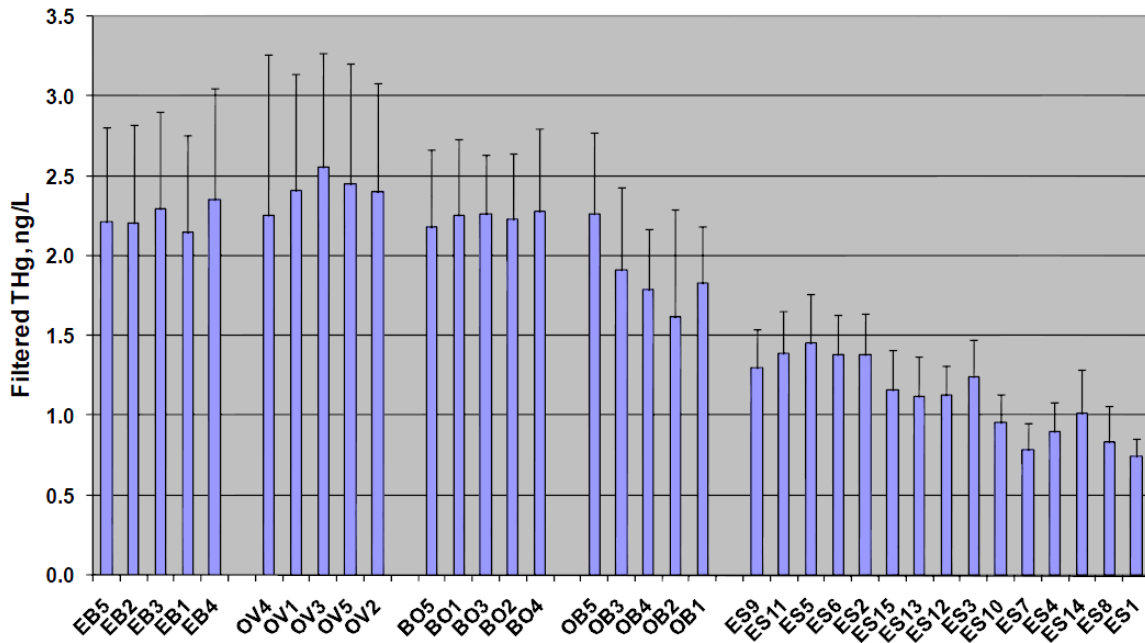


Figure 18-5. Mean concentrations of total Hg in filtered surface water between 2006-2007. EB=East Branch, OV=Old Town-Veazie, BO=Brewer-Orrington, OB=Orrington-Bucksport, ES=Estuary. Stations are ordered from upstream to downstream (north to south). From Bodaly et al. 2008.

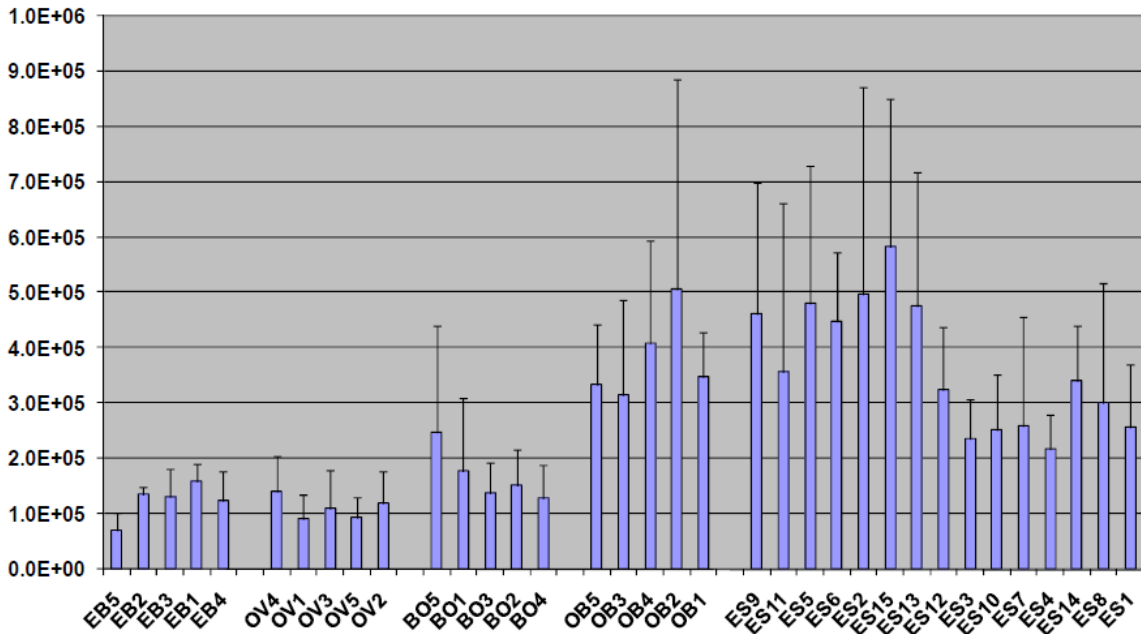


Figure 18-6. Mean apparent partitioning coefficients (K_d) of total Hg on suspended solids in surface waters in five reaches of the Penobscot system between 2006-2007. EB=East Branch, OV=Old Town-Veazie, BO=Brewer-Orrington, OB=Orrington-Bucksport, ES=Estuary. Stations are ordered from upstream (on the left) to downstream (on the right). Figure from Bodaly et al. 2008.

4.2 Temporal trends for Hg contamination

Peak Hg concentrations occurred circa 1967-1970, averaging $6,700 \text{ ng g}^{-1}$ and subsequently decreased in the majority of cores (Chapter 1). Surface sediment Hg concentrations in the Penobscot River remain contaminated, with variable concentrations depending on location, averaging $710 \pm 510 \text{ ng g}^{-1}$ in the upper estuary. Hg concentrations in surface sediments were lower on average in Fort Point Cove ($490 \pm 270 \text{ ng g}^{-1}$), and decline further traveling downstream. The average Hg concentration for fine grain material in long term depositional sites was 890 ng g^{-1} , and was used as the concentration that needed to be reduced to a target of 400 ng g^{-1} (Chapter 1). Mixing in surface sediments occurred to a depth of 3 cm or less. The decrease in Hg concentrations since 1967 has followed two phases, faster for the first 21 years up to 1988, followed by a slower decline since 1988 (Chapter 6). This shift in response rates is hypothesized to be related to the time required for Hg to be internally distributed within the estuary. Sediment cores sampled in areas with the highest initial contamination declined more quickly in the early years after 1967, as Hg was distributed to other locations. Conversely cores from some downstream estuarine areas displayed increasing concentrations towards the surface, consistent with the redistribution hypothesis.

Current rates of decline of Hg concentrations in sediments vary widely among locations. The main stem of the river between Veazie Dam and the end of Verona Island is currently estimated to be recovering at a rate that can be described as taking 32 years to achieve 50% of the ultimate response (Chapter 1) (referred to in the report as the “half time” or $t_{1/2}$). The estimated half time for the recovery of Hg in surface sediments in Fort Point Cove is 61 years (Chapter 1). Sedimentation rates also vary within each of these broader areas. Only about 18% of the upper estuary is depositional for solids in the long term (Chapter 1). The remaining 82% of the upper estuary area consists of areas with a large mass of mobile solids overlying more consolidated sediments. These solids are mobilized, transported and redeposited intermittently, at rates sufficient to cause extensive mixing and similar Hg concentrations for a given type of solids (e.g. mud). These mobile solids are estimated to play a large role in the rate of recovery of Hg concentrations in the system (Chapter 1).

5 MODELING APPROACH AND ASSUMPTIONS

Simulations were carried out to represent the upper estuary as shown in Figure 18-7. This reach of the estuary was selected for modeling because:

1. The rate of recovery of Hg concentrations is estimated to be relatively similar within this area, while areas farther downstream are estimated to be changing more slowly (although Hg concentrations are lower).
2. Field studies indicate that the mass of mobile solids mixes and moves extensively within this area (Chapter 7), resulting in similar Hg concentrations in different locations, for a given type of solids. An exception is Mendall Marsh, where about 40% of particles entering the Marsh are retained (Chapter 1). Given

that half or more of the solids are not trapped, it was therefore deemed more appropriate to include Mendall Marsh in the model domain rather than exclude it.

3. This is the portion of the estuary most contaminated with Hg (in terms of concentrations). Understanding the rate of recovery in this reach was considered important in order to understand the recovery of downstream areas.

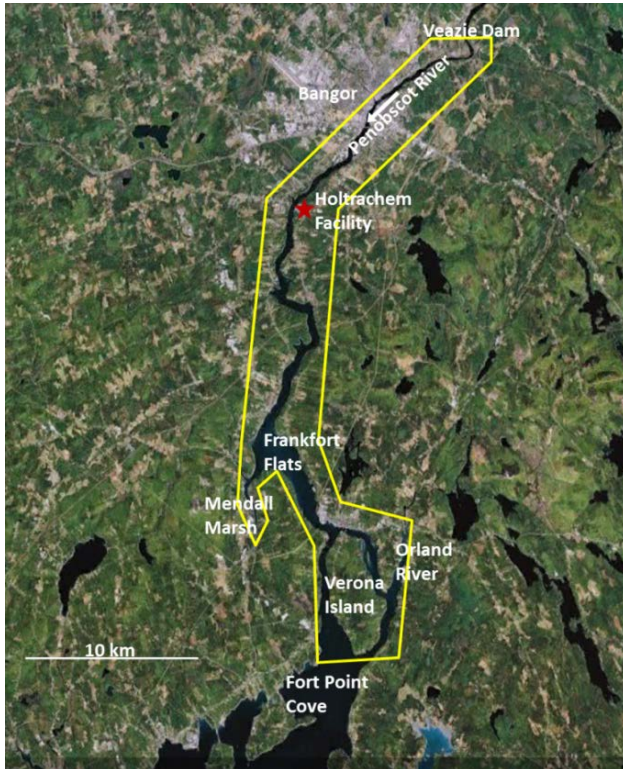


Figure 18-7. Simulated reach of Penobscot Estuary (outlined in yellow)

5.1 Modeling Assumptions

Key assumptions used for Hg modeling included the following:

1. There is complete mixing of mobile sediments in the main stem of the river in the upper estuary, Mendall Marsh, and the Orland River.
2. Mobile sediments supply solids to depositional areas, where burial occurs. There is no feedback of mobile solids from depositional zones to the mobile pool.
3. Sediment cores in depositional areas are good estimates of the rate of recovery of Hg in the mobile solids pool in the upper estuary.
4. Solids are also lost from the mobile pools via downstream export.
5. Hg contaminated solids lost from the mobile pool via burial and export are replaced by solids with background Hg concentrations. The mass of mobile solids is stable in the long term.

6. Hg on resuspended sediments is strongly bound and does not desorb appreciably into the dissolved phase.
7. None of the Hg entering the upper estuary via inflows was strongly bound on inflowing particles.
8. Atmospheric dry Hg deposition was assumed equal to wet Hg deposition.
9. Hg evasion from the water surface to the atmosphere was assumed to be comparable to literature estimates for natural aquatic systems.
10. The recovery of Hg in contaminated sediments in the upper estuary was not significantly affected by tidal flows.
11. Reduction of inorganic Hg(II) to elemental Hg in sediments was not important as a flux affecting the decline of Hg concentrations on solids.
12. The long term steady state concentration for total Hg in sediments in the upper estuary was 100 ng g^{-1} .
13. There is only one particle type for sediments in Version 3 of D-MCM. All sediment particles therefore have the same properties and concentrations. The same situation applies for suspended solids (although they may differ from sediment solids).

Additional discussion of these assumptions is given below.

5.1.1 Well mixed conditions for mobile solids in the upper estuary (Assumption 1)

Mixing is an important consideration when developing an approach for contaminant modeling. Model configurations can range from a single cell where conditions are assumed to be horizontally uniform throughout the modeled area, to many cells for sites where spatial gradients exist and the assumption of horizontally well mixed conditions is not valid. Ideally a model for the upper estuary would represent the spatial variability of conditions in the water column and include a range of sediment zones with mixing that occurs on different time scales, both laterally and horizontally. Contaminant models commonly have suspended solids that are transported and mixed horizontally in the same manner as bulk water (plus settling), and have sediment compartments with vertical particle fluxes including resuspension and burial. Mobile sediments in the Penobscot Estuary are not readily placed in either category, because lateral mixing occurs but in a different manner than occurs for truly suspended solids. No existing model was identified that could fully represent physical transport in the water column, sediments, and mobile solids. A single cell model approach would assume complete horizontal mixing in the water column and sediments. A multi-cell model approach would more realistically represent water column heterogeneity but would not realistically represent lateral transport of the mobile bed.

Because Hg contamination is primarily in sediments in the estuary, and the modeling was meant to represent processes governing the ongoing rate of recovery of Hg in mobile sediments, a well-mixed modeling approach was considered appropriate for this study. This was due to the extensive lateral mixing of mobile sediments described by Geyer and Ralston in Chapter 7. Spatial data for Hg concentrations in the upper estuary are also consistent with this approach. Although Hg contamination originated from a point source, surface sediment Hg concentrations in samples collected in 2011 were more strongly correlated with particle type than location (Chapter 8). Similarly, mobile solids in the Penobscot River and Mendall Marsh had relatively similar concentrations if adjusted for sediment type (e.g. mud, sand, silt) (Chapter 8).

5.1.2 Links between Hg in mobile solids and depositional zones (Assumptions 2 and 3)

Approximately 18% of the upper estuary area is depositional (Chapter 5). The conceptual model for Hg in the estuary includes transport of mobile solids around the estuary, eventually entering depositional areas and sedimenting (Chapter 1). There is little feedback of solids or Hg from depositional areas to the mobile bed (Chapter 6). Hg concentrations in mobile solids are similar to concentrations on non-mobile solids, for a given solids type (Chapter 8). While this could be a coincidence of different recovery rates that happen to currently have similar concentrations, it was assumed that the rate of recovery of Hg concentrations in mobile sediments is equal to the observed rate of recovery recorded in sediment cores in depositional areas.

5.1.3 Solids are also lost from the mobile pools via downstream export (Assumption 4)

This assumption is based on the observation that Hg contamination exists downstream of Verona Island. Water column transport must have occurred, at least in the particle phase, and possibly in the dissolved phase when the HoltraChem facility originally released Hg to the water column in the upper estuary. Geyer and Ralston (Chapter 7) also estimate that a small fraction of the mobile solids pool continues to be exported downstream.

5.1.4 Contaminated solids in the mobile pool are replaced by low-Hg solids (Assumption 5)

In the absence of information suggesting large changes in recent years regarding particle fluxes in the upper estuary, it is assumed that the mass of mobile solids is at steady state, *i.e.* solids are being replaced at the same rate as losses occur. The initial assumption that new solids loaded to the mobile pool have low Hg concentrations was considered a hypothesis to be evaluated with simulations. Implicit in this hypothesis is that cohesive sediments in non-depositional areas are not an ongoing source of Hg contamination for the mobile solids pool.

5.1.5 Hg on resuspended sediments is strongly bound (Assumption 6)

Hg contamination was evident in water column particulates (Figure 18-4), while there was no apparent increase in dissolved Hg concentrations in the water column in the

upper estuary (Figure 18-5). Apparent partitioning (K_d) of Hg in the water column between solids and the filtered phase changed along the river (Figure 18-6). Two hypotheses were considered to explain these observations. The first hypothesis was that contaminated sediments were resuspended and mixed with the existing pool of suspended solids, but did not appreciably desorb Hg (*i.e.* Hg was strongly bound to particles). The second hypothesis also involved resuspension of contaminated sediments, but assumed instantaneous exchangeability of all Hg on solids. Given that dissolved Hg concentrations in surface waters were lower than in porewater (Bodaly et al. 2008 (Appendix 1-2 of Chapter 1); Chapter 11), the second hypothesis would require differences in the chemistry of surface waters and pore water such that there was little tendency for Hg to desorb when sediments were resuspended. For example, DOC competes with solids to bind Hg. If DOC concentrations were higher in pore water than the water column, and particles were resuspended, it is possible that the result would be little tendency for Hg to desorb in the water column. This hypothesis would also be consistent with increases in apparent Hg partitioning from river waters (with higher DOC) to estuarine waters (with lower DOC). Problems with this hypothesis arose in terms of explaining why the observed apparent partitioning (K_d) on TSS declined downstream of the contaminated zone, where DOC was low. While it is possible that Hg on solids is fully exchangeable and differences in water chemistry and/or the characteristics of particles along the estuary caused the observed increase in Hg partitioning in the contaminated zone, the simpler explanation was that Hg was strongly bound to solids, and did not desorb when resuspended.

5.1.6 None of the Hg entering the upper estuary via inflows was strongly bound on inflowing particles (Assumption 7)

This was a limitation of the model used for the analysis. Simulations were carried out to examine the implications of this feature of the model, in terms of the delivery of Hg in inflows to mobile sediments via settling.

5.1.7 Atmospheric dry Hg deposition was assumed equal to wet Hg deposition (Assumption 8)

No measurements were available of dry Hg deposition rates for the study area. In the absence of data, it was assumed that dry deposition was equal to wet deposition.

5.1.8 Hg evasion was assumed to be comparable to background rates (Assumption 9)

Given that (1) inorganic Hg(II) is the substrate for the photochemical production of DGM in surface waters, and (2) dissolved inorganic Hg(II) concentration in surface waters did not show evidence of significant contamination (Figure 18-5), it was assumed that dissolved concentrations of gaseous elemental Hg (DGM) and DGM evasion rates would not be elevated above background levels. In marine systems, Soerensen et al. (2010) estimated an evasion rate of $\sim 9 \mu\text{g m}^{-2} \text{yr}^{-1}$ for the oceans globally while Balcom et al. (2004) estimated a higher evasion rate for Long Island Sound ($24 \mu\text{g m}^{-2} \text{yr}^{-1}$). In freshwater systems, Southworth et al. (2007) estimated an evasion rate of approximately $7\text{-}8 \mu\text{g m}^{-2} \text{yr}^{-1}$ for ambient Hg over a 140 day period in the ice free

season for Lake 658, Ontario. For the Penobscot upper estuary, the model was calibrated to produce an evasion rate of $8 \mu\text{g m}^{-2} \text{yr}^{-1}$, within the range observed for other systems. A sensitivity analysis discussed later in this Chapter indicated that the rate of recovery of sediment Hg contamination was not sensitive to significant variations in this flux.

5.1.9 Tidal influences are not explicitly included in the modeling (Assumption 10)

Tides have the potential to accelerate the recovery of Hg concentrations in mobile sediments in the upper estuary by increasing advective losses during ebb tides or increasing the supply of low-Hg solids during flood tides, resulting in the faster replacement of contaminated solids with low-Hg solids. Conversely, flood tides could slow the recovery of Hg concentrations in mobile sediments in the upper estuary if Hg-contaminated solids from Fort Point Cove are transported back to the upper estuary. Current estimates of mobile solids fluxes from Fort Point Cove to the upper estuary are on the order of 10% gross transport past Verona Island, 3% returned during flood tides, up to 7% net export per year (J. Rudd, pers. comm.). Given the uncertainty in these numbers, there is currently insufficient information to accurately simulate tidal influences on the rate of recovery of Hg in mobile sediments in the upper estuary, above and beyond what can be inferred by including river transport and adjusting the net fraction of mobile solids exported downstream annually.

5.1.10 No reduction of inorganic Hg(II) to elemental Hg in sediments (Assumption 11)

As a result of this assumption, Hg reduction in sediments and subsequent loss from the upper estuary by evasion or DGM downstream transport was not a loss mechanism for Hg contamination in sediments. It is recognized that while it was not necessary to invoke Hg reduction in sediments to achieve the observed rate of decline of Hg concentrations in sediments, it is possible that this process occurs (e.g. microbially). If this assumption is in error, the system would recover faster than otherwise predicted, all else left unchanged. As discussed in the results section, the opposite inconsistency exists with simulations. The system should already recover faster than observed (without adding another removal mechanism) if the conceptual model and field estimates of particle masses and fluxes are correct.

5.1.11 Long term concentration for total Hg in sediments = 100 ng g^{-1} (Assumption 12)

This is discussed in Chapter 1.

5.2 Modeling Approach for Base Case Scenario

As a result of the assumptions used, simulations effectively modeled the mobile sediments but not sediments in depositional areas. Because mobile sediments were assumed not to receive any ongoing legacy Hg contamination mobilized from other sediments, the predicted rate of recovery was governed by the ability of mobile sediments to eliminate Hg, with the exception of small ongoing inputs of Hg from HoltraChem and municipal discharges.

The base case scenario for the upper estuary was developed using the following steps:

1. Assume that the mass of mobile pool solids is known (318,000 tonnes).
2. Use the observed Hg concentration in mobile sediments in 2010 and the field-estimated half time of 32 years for the rate of recovery to back-estimate Hg in 1988 (the starting year for simulations) for the initial concentration in sediments.
3. Adjust resuspension, settling and decomposition of solids to obtain the desired net burial and sufficient resuspension to produce elevated Hg concentrations observed on TSS.
4. Adjust the fraction of TSS exported in outflow to approach the target recovery rate for Hg in sediments ($t_{1/2} = 32$ years).
5. Adjust Hg partitioning in the water column and sediments to achieve the target long term background concentration of 100 ng g^{-1} on sediment solids and achieve minimal desorption of Hg when contaminated sediments are resuspended.
6. Iterate steps 3-5 to converge on a model calibration in which sediment Hg declines with a half time of 32 years, and model results are consistent with observed water column and sediment Hg concentrations on particles and in the dissolved phase.
7. Adjust the rate constant for photoreduction to produce the target rate of evasion ($8 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$).

The effects of storm events were not included in the scope of these simulations.

5.3 Model Description

The Dynamic Mercury Cycling Model (D-MCM) (EPRI 2009) is a process-based aquatic Hg cycling and bioaccumulation model, available in the public domain and currently being updated. D-MCM has been used on several large multidisciplinary Hg research studies, including the Gulf of Mexico (Harris et al. 2012), Florida Everglades (Harris et al. 2003a), METAALICUS (Harris et al. 2007), and Wisconsin Lakes (Hudson et al. 2004). It has also been used in TMDL-related studies in Florida (Atkeson et al. 2003), and Wisconsin (Harris et al. 2003b).

D-MCM simulates inorganic Hg(II), elemental Hg(0), and methyl Hg in water and sediments (solids and porewater) (Figure 18-8). A simplified food web is optionally available in Version 3.0, including phytoplankton, zooplankton, benthos and three fish species. Methyl Hg dynamics in individual fish cohorts are followed for each species using a bioenergetics approach (Harris and Bodaly 1998). Biota were not included in simulations for this study, which focused on total Hg in water and sediments.

D-MCM Version 3.0 assumes that aquatic systems are well mixed horizontally in the water column, but allows for an epilimnion and hypolimnion. In sediments, D-MCM can include up to three sediment zones laterally (e.g. littoral, profundal), each with one

active layer that is simulated and a boundary layer beneath. D-MCM maintains a constant sediment layer thickness and mass, solving for burial or erosion as the unknown.

D-MCM has the ability to include two types of Hg binding sites on solids. One component exchanges instantly with Hg in the dissolved phase. The other component uses adsorption and desorption kinetics to allow for slower exchange of Hg between solids and the dissolved phase. This feature made it possible for example to resuspend Hg on sediment solids into the water column without appreciably desorbing Hg into the dissolved phase.

D-MCM does not simulate full carbon and particle budgets in the water column. Particle fluxes relevant to total Hg are specified as inputs (settling, resuspension, TSS in outflows). Inflowing particle fluxes of Hg are implicitly included in model inputs which include suspended solids and unfiltered Hg concentrations in inflows. Additional information on D-MCM is available in Harris et al. (2012a) and EPRI (2009).

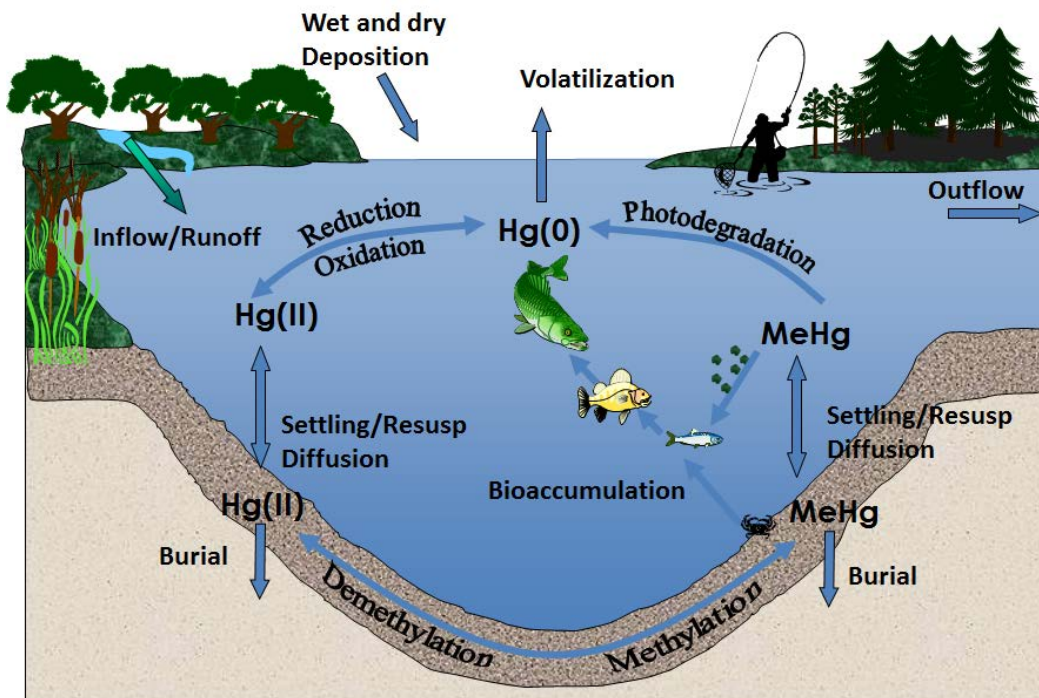


Figure 18-8. Conceptual diagram of Hg cycling and bioaccumulation in D-MCM Version 3.0

5.4 Defining the Rate of Recovery

In a model system where loss mechanisms are first-order expressions with respect to Hg concentrations, the recovery trajectory from one steady state to another tends to follow an exponential curve. Because background Hg loading remains after point source releases are eliminated, the long term concentrations that the river approaches in water and sediments are not zero. The idealized response then takes the general form shown in Equation 1:

$$C_t = (C_o * e^{-kt}) + C_\infty * (1 - e^{-kt}) \quad (1)$$

where:

C_t = Concentration at time t

C_o = Initial Hg concentration

C_∞ = Long term steady state concentration

k = Rate constant (units: time^{-1})

When the long term steady state concentration is not zero, the time required to achieve 50% of the ultimate response is not the same as the time to observe a 50% decline in concentration in absolute terms, which may not occur at all if the long term value is more than 50% of the initial value.

In this report, the term “half-time” is the time required to achieve 50% of the ultimate response, and is designated as $t_{1/2}$, where:

$$t_{1/2} = -\ln(0.5)/k = 0.693/k$$

The idealized exponential response and associated half time are valid only if Hg conditions and external loading do not change during a simulation. Because HoltraChem loading changed during the simulation, and because some aspects of the treatment of Hg cycling in D-MCM are not linear (thermodynamic complexation), model results may not strictly follow an exponential curve. This possibility was examined. Also examined was the time required for Hg concentrations in sediments to decline to 400 ng g^{-1} . (Note: this concentration is slightly lower than the target concentration to achieve acceptable concentrations in biota that is listed in Chapter 3 (450 ng g^{-1}), and came from an earlier exercise in setting targets).

5.5 Model Scenarios

5.5.1 Base Case Scenario

Simulations began in 1988, the approximate year estimated by Santschi (Chapter 6) as the beginning of the current slower phase of recovery, and spanned 140 years to 2128, to ensure sufficient time for simulations to reach long term steady state conditions. Atmospheric Hg deposition, upstream Hg inputs, and Hg inputs from municipal waste treatment were assumed constant from year to year, as were annual solids fluxes. Site specific estimates for atmospheric deposition were not available. Wet deposition ($6.7 \mu\text{g m}^{-2} \text{ yr}^{-1}$ average) was calculated from Mercury Deposition Network data for Hg concentrations in precipitation (6.28 ng L^{-1} average from 1996-2012; NADP 2012) and mean monthly precipitation from 1980-2010 climate normal data for the region (NOAA 2012). Dry Hg deposition is not known but was assumed to be approximately equal to wet deposition. Freshwater Hg inputs from the upstream Penobscot River were estimated using a mean annual flow of $406 \text{ m}^3 \text{ s}^{-1}$ (Chapter 3) and an unfiltered total Hg concentration of 2.9 ng L^{-1} (average of 2008-2010 samples upstream of Veazie Dam;

Kelly 2010). Inflow from 18 tributaries totaled $75 \text{ m}^3 \text{ s}^{-1}$ (Chapter 3). Hg inputs from HoltraChem were assumed to decline with time as shown in Table 18-2.

Table 18-2: HoltraChem Hg loading rates to the Penobscot River used in simulations. Current estimate (post 2006) from Chapter 3. Earlier loads assumed.

Year	Hg Load to River (kg yr^{-1})
1988	15
2001	11
2006	2.2

5.5.2 Sensitivity Simulations

Additional simulations were performed to examine the sensitivity of model results to selected inputs and assumptions. The base case simulation was calibrated such that Hg concentrations in sediments would decline at a rate of 50% of the ultimate response within approximately 32 years. Other combinations of mobile solids pool sizes and particle fluxes (burial and downstream export) could achieve the same rate of recovery. An alternative scenario was tested that maintained a 32 year half-time but used a different combination of solids pool size and mass sedimentation rate:

- 23,000 tonnes yr^{-1} of mass sedimentation and 1.2 million tonnes of solids:** Kelly (2013b) estimated a mass sedimentation rate of 23,000 tonnes per year for the upper estuary (including Mendall Marsh and a portion of the Orland River). This would result in too fast a recovery in model simulations if the mobile solids pool was maintained at 318,000 tonnes. To maintain a recovery half time of 32 years for sediment solids, the mobile solids pool was iteratively adjusted in simulations to 1.2 million tonnes (other factors held constant).

Additional simulations were also carried out to examine the effects of (1) a different long term steady state Hg concentration in sediments, (2) less resuspension, and (3) greater export of particles in outflow:

- Higher long term steady state sediment Hg concentration:** For a given recovery half time (e.g. 32 years), the long term Hg concentration in sediments also affects the amount of time required to achieve an Hg concentration of 400 ng g^{-1} in sediments. For example, if the long term concentration was 500 ng g^{-1} , the sediments would never decline to 400 ng g^{-1} . A sensitivity test was carried out where the long term Hg concentration for sediments was raised to 200 ng g^{-1} . This was accomplished by increasing the partition coefficient in the water column by approximately 3 times.
- No resuspension:** Resuspension of contaminated solids from the sediments was an important factor determining Hg concentrations on suspended solids in

the water column. A sensitivity analysis was performed where resuspension of particles from the sediment layer was set to zero and settling was reduced to maintain the same solids burial rate as the base scenario (~3,500 tonnes yr⁻¹). It is recognized that zero resuspension is not realistic. The purpose of the simulation was primarily to examine the importance of resuspension regarding elevated Hg concentrations on suspended solids in the water column.

- **Greater export of particles in outflow:** A simulation was carried out to examine the sensitivity of the recovery rate of Hg concentrations in sediments to the assumed fraction of water column solids that are trapped in the estuary, unable to be exported in outflow. The based case simulation assumed that only 3% of water column solids were exported. A sensitivity test doubled the fraction of particles that were exported in outflow to 6%.

5.5.3 Conceptual River Simulation with Two Sediment Zones

Simulations were also performed using two hypothetical sediment zones, one depositional, the other non-depositional. The purpose of these simulations was to conceptually investigate interactions between the two zones that affected rates of recovery. Specifically, what if the mobile bed could respond faster than $t_{1/2} = 32$ years but interacts with another sediment zone that is non-depositional in terms of solids, but is contaminated? For these scenarios, 50% of the total area was assumed depositional, burying 23,000 tonnes year⁻¹, the field estimate of mass sedimentation in the upper estuary (Chapter 1). The remaining 50% of the modeled area was assumed to be non-depositional for solids (*i.e.* no net burial or erosion), but had significant settling and resuspension. Areas, sedimentation rates, resuspension rates, and solids pool sizes are given for the two hypothetical sediment zones in Table 18-3. The 50/50 allocation between mobile solids and non-depositional solids was used in the absence of quantitative estimates for the relative areas associated with these pools. Because of the structure of the D-MCM model, solids could not be exchanged directly from one sediment zone to the other. Instead, particles were resuspended from one zone, mixed into the water column, and some of this material settled back into both sediment zones. The supply of settling solids to both zones was the same on an areal basis (per m²). Particles were replaced with half times of 3.7 and 7.5 years respectively in the mobile and non-depositional sediments. Overall, the two sediment zones had significant indirect mixing of solids when considering time periods relevant to the long term recovery of the system (decades).

Three scenarios were tested, differing only in terms of the initial Hg concentrations in each zone. In one scenario, the initial concentrations were equal in each zone. In a second scenario, the initial Hg concentration was higher in the mobile sediments, while the opposite was the case for the third scenario.

These simulations were considered conceptual rather than quantitative, because the surface areas and conditions in each sediment zone were hypothetical and because D-MCM Version 3.0 does not have the ability to simulate a large mass of mobile sediments that moves laterally among sediment zones.

Sediment zone	Area (km²)	Solids pool size (tonnes)	Sedimentation rate (tonnes yr⁻¹)	Resuspension rate (tonnes yr⁻¹)
Mobile pool	13.3	318,000	23,000	37,500
Rate limiting pool	13.3	636,000	0	58,800
Total	26.6	954,000	23,000	96,300

6 SIMULATION RESULTS

6.1 Base Scenario for Natural Attenuation

Particle fluxes for the base case simulation are shown in Figure 18-4. Burial was the largest removal mechanism for sediment particles, 3,500 tonnes per year. To accommodate efficient particle trapping in the estuary, only 1,600 tonnes of solids were lost to downstream export from the sediment pool. These fluxes were adjusted to produce a recovery half time of 32 years for Hg in sediments, in combination diffusion from sediments (the three significant loss mechanisms in model scenarios). The upper limit for particle losses from the mobile bed is 6,900 tonnes per year, if the recovery half time is 32 years for Hg in the mobile bed and the mobile solids mass is 318,000 tonnes.

Large settling and resuspension fluxes were required to adequately calibrate the elevated Hg concentrations on water column solids, as discussed below. When water column particle fluxes in Figure 18-4 are summed, inputs exceeded outputs by 63,700 tonnes yr⁻¹. Possible explanations included decomposition of solids in the upper estuary, or a large flux of solids in outflow that enters the estuary from upstream and passes through, effectively bypassing interaction with the mobile bed.

Simulated inorganic Hg fluxes in the upper estuary for 2010 are shown in Figure 18-5. Simulations included two point sources of Hg to the river reach: a HoltraChem load that decreased over time and a constant load from municipal sources. In 2010, inflow represented 92% of Hg inputs in the simulation, while HoltraChem Hg inputs represented 6% to 7% of inputs. Atmospheric Hg deposition and municipal inputs were each 1% or less of 2010 Hg inputs. There was a net loss of Hg from sediments, as concentrations continued to decline. The largest Hg loss was from outflow (93%), nearly all of which was in the filtered phase, as only a small fraction of suspended solids were carried out of the system. Burial represented 6% of Hg losses from the system, but was an important loss pathway for Hg contaminated sediments (>50%). Given that the net flux of Hg from sediments to the water was 70 µg m⁻² yr⁻¹ (roughly half on particles and half dissolved) only a small component of the Hg exported downstream (1,220 µg m⁻² yr⁻¹) was associated with Hg losses from the sediment pool. Most of the Hg in outflow was supplied by river inputs that passed through the system.

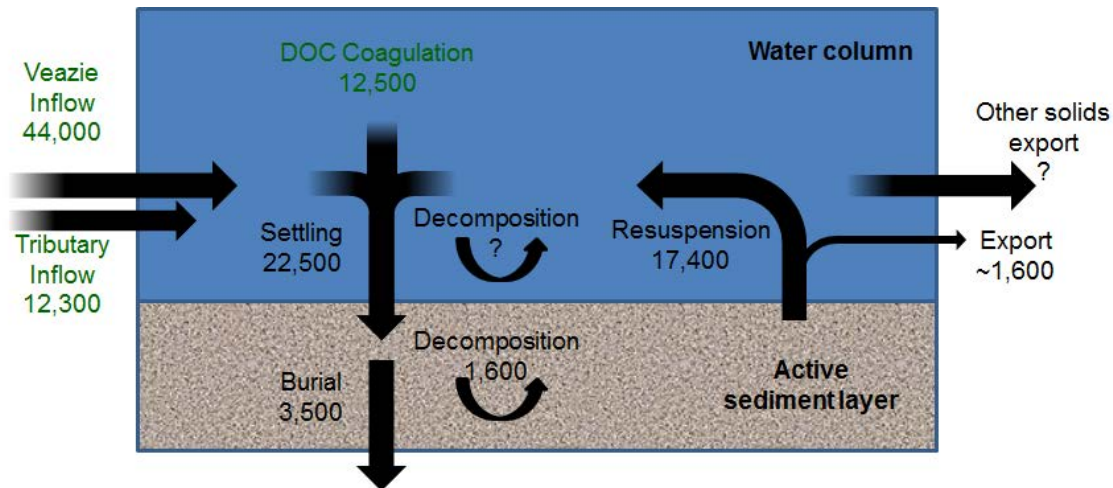


Figure 18-4. Estimated particle fluxes in model reach (tonnes per year) for base case scenario. Sediment fluxes balance (Burial = Settling – Resuspension – Decomposition). DOC coagulation is net production assuming 50% decomposition (Chapter 4). Fluxes shown in green are based on field data. Other fluxes are modeled.

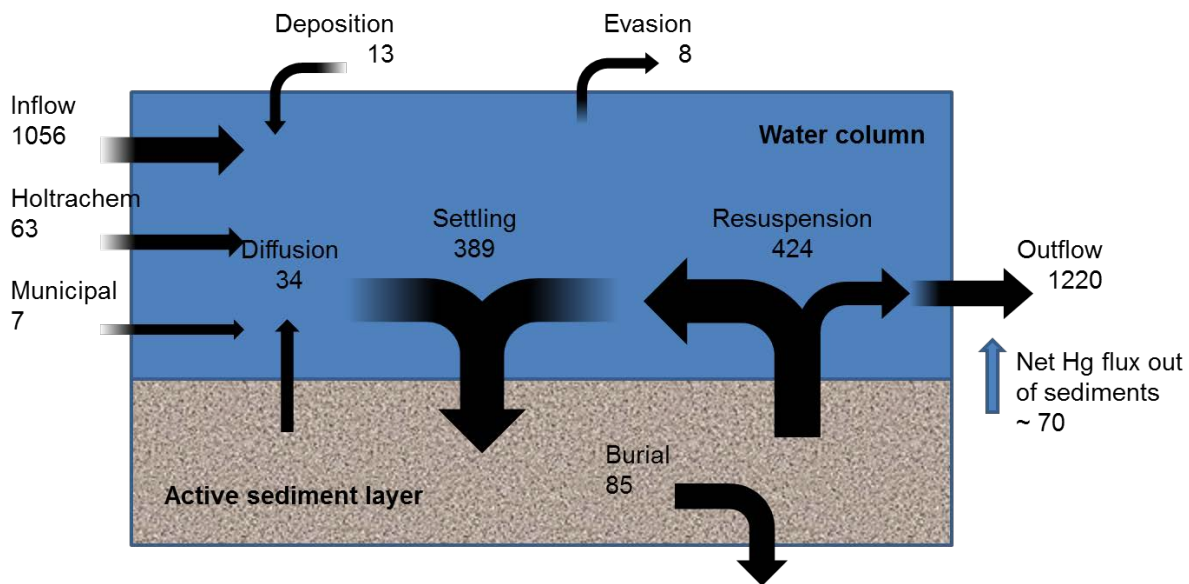


Figure 18-5. Simulated inorganic Hg fluxes in model reach in 2010 ($\mu\text{g m}^{-2} \text{yr}^{-1}$). Hg losses exceed inputs in sediments because system is still recovering.

Calibrated Hg concentrations in the dissolved and particle phases in the water column and sediments reasonably reflected observations in 2006-2010 (Figures 18-6 and 18-7). The time required to achieve 50% of the full response was 32 years, consistent with the target. Total Hg concentrations on sediments declined to 400 ng g^{-1} by ~2052. This concentration was the threshold for the recovery of river biota to acceptable Hg levels (Chapter 2). The long term Hg concentration was 100 ng g^{-1} in sediments (based on a curve fit to the model results and long term extrapolation).

Rapid resuspension and settling particle fluxes were required to produce Hg concentrations on suspended solids in the water column in the range of 600 ng g^{-1} in

2010, the observed value (Figure 18-6a). The model was also calibrated such that very little desorption of Hg occurred from resuspended sediments. In this manner, increased Hg concentrations were observed in the particle phase in the water column, consistent with observations (compare Figures 18-4 18-6a), but there was little evidence of increased Hg concentrations in the dissolved phase in observations or the model calibration (compare Figures 18-5 and 18-6b).

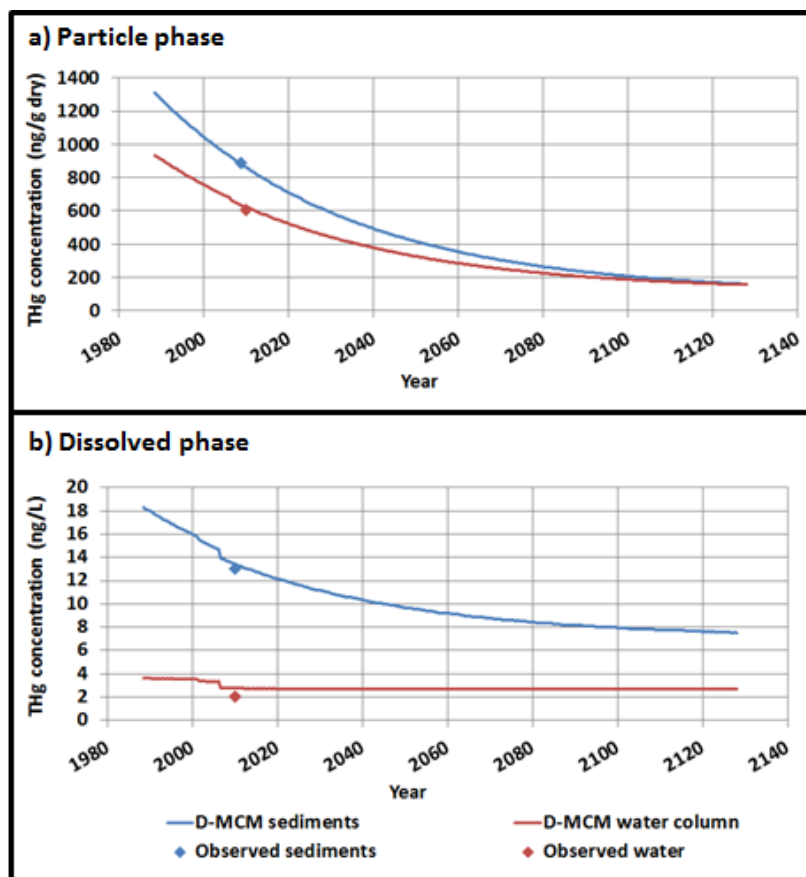


Figure 18-6. Simulated total Hg concentrations in particle and dissolved phases of sediments and water column from 1988-2128. Observations: Sediment particle phase: 885 ng g⁻¹, from Chapter 1). Sediment dissolved phase: 13 ng L⁻¹ (Chapter 11). Water particle and dissolved phases: Approximate averages of measurements in the Brewer-Orrington and Orrington-Bucksport reaches between 2006-2007 derived from Bodaly et al. (2008).

While dissolved Hg concentrations in the water column were relatively stable with time and showed little if any evidence of contamination, the unfiltered phase, which includes particulate and dissolved Hg, was predicted to decline with time (Figure 18-7). Sampling conducted between 2009-2010 showed highly variable unfiltered total Hg concentrations in the river reach (2-81 ng L⁻¹, mean 8.2 ng L⁻¹) (Kelly 2010). The predicted apparent partitioning (K_d) for total Hg in the water column and sediments also decreased over time in simulations, as contaminated particles were gradually replaced by cleaner solids (Figure 18-8).

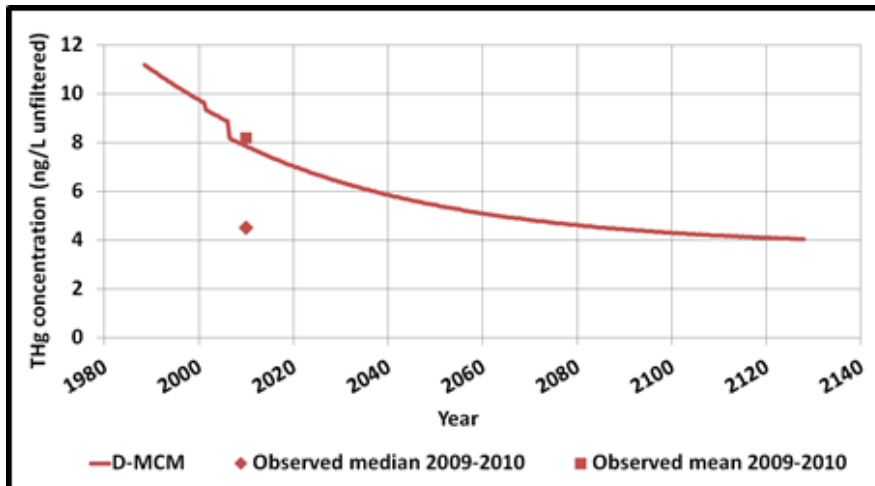


Figure 18-7. Simulated unfiltered total Hg concentrations in water column from 1988-2128. Observed median and mean are from samples collected at various depths throughout the modeled reach between April 2009 and July 2010 (Kelly 2010).

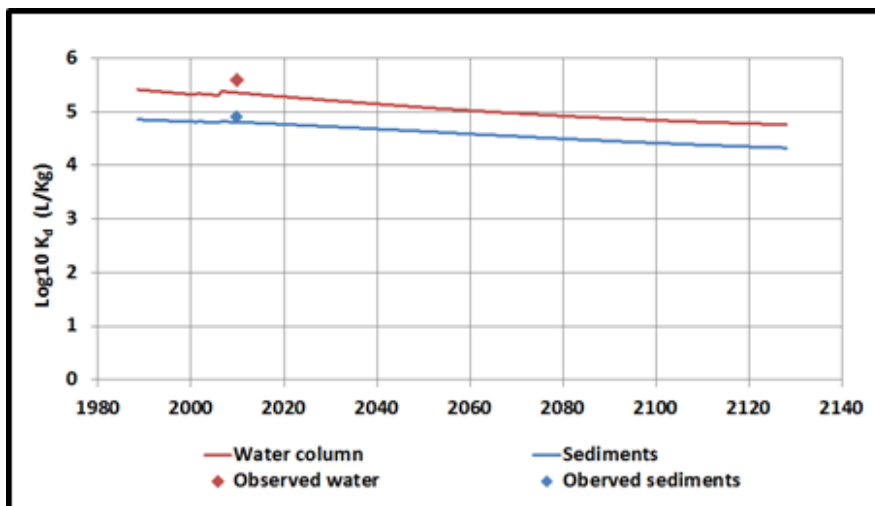


Figure 18-8. Simulated partition coefficient (K_d) in water column and sediments from 1988-2128. Observed water K_d is the approximate average of measurements in the Orrington-Bucksport reach between 2006-2007 (Bodaly et al. 2008). Observed sediment K_d of 4.9 (log10) from C. Kelly.

6.2 Sensitivity Analysis Results

Sensitivity test results are summarized in Table 18-4. The simulation with a greater mass of solids and increased mass sedimentation confirmed that it is possible to achieve the same rate of recovery in simulations with different combinations of solids pool size and mass sedimentation. A simple set of calculations was also done to approximate different combinations of solids masses and turnover rates that would produce a 32 year half time for recovery. It was assumed that the only process affecting the recovery of Hg in solids was the rate of replacement of contaminated solids with solids that have a lower Hg concentration that is constant with time. The rate of recovery was calculated by dividing the rate of solids turnover by the mass of the solids pool. For example if 100,000 tonnes of solids were replaced at a rate of 20,000 tonnes

per year, the rate constant for recovery would be $20,000/100,000 = 0.2$ per year. This number can be converted to a half time as follows: Half time = $\ln(2)/0.2 = 3.5$ years. This calculation was performed for different combinations of pool sizes and particle turnover rates as shown in Figure 18-9. Also shown in Figure 18-9 is a point based on field estimates of the mobile bed mass (318,000 tonnes) and field estimates of particle losses via sedimentation and downstream export of mobile solids ($23,000 + 22,000 = 45,000$ tonnes yr^{-1} ; Chapter 1). The resulting recovery half time would be ~ 5 years, much faster than observed. Even if no downstream export of solids occurred, burial alone would produce a recovery half time of 10 years, still much faster than observed for Hg. This indicates that field estimates of mobile solids mass and turnover rate are not consistent with the conceptual model where the mobile solids pools controls the rate of decline of Hg concentrations in sediments. Either the field estimates are inaccurate or the conceptual model needs adjustment to include additional processes affecting the rate of recovery.

The simulation with no resuspension predicted a suspended solids Hg concentration of ~ 60 ng g^{-1} in 2010, an order of magnitude below observed values, indicative of the importance of resuspension to explain observed Hg contamination in the water column.

Sensitivity simulations also demonstrated resuspension and downstream export played an important role in the rate of recovery in the base case simulation. When resuspension was eliminated, the time required to reach 400 ng g^{-1} lengthened from 2052 to 2080. Conversely when particle export was increased (6% of TSS exported with outflow compared to 3% in the base case), the target concentration of 400 ng g^{-1} was achieved by 2037 ($t_{1/2} = 25$ years). These results indicate that it is important to obtain realistic estimates of the rate of loss of sediment solids via downstream export in order to understand processes governing the recovery of the system.

While eliminating resuspension strongly affected predicted Hg concentrations on TSS, dissolved Hg in the water column was not appreciably different than the base case simulation (~ 2.7 ng L^{-1}). These results indicate that little of the Hg load entering the estuary over Veazie Dam adsorbed onto TSS and settled in the base case simulation. Most of the inflowing Hg was exported downstream. This was due to the slow kinetics of adsorption and desorption that governed Hg concentrations on solids in simulations. The version of D-MCM used for these simulations did not have the ability to designate a portion of inflowing Hg loads as strongly bound to particles.

The simulation with a higher long term concentration for sediments (200 ng g^{-1}) confirmed that it would take longer for sediment Hg concentrations to decline to 400 ng g^{-1} (year 2069) compared to simulations with lower long term concentrations (Table 18-4). These results point to the importance of establishing a realistic estimate of the long term Hg concentration that sediments are likely to reach.

Table 18-4: Sensitivity test results for key indicators of system recovery

Scenario	Mass sedimentation rate (tonnes yr ⁻¹)	Long term sediment Hg concentration (ng g ⁻¹)	Time to achieve half of response, t _{1/2} (years)	Year to reach 400 ng g ⁻¹ sediment Hg
Base case (318,000 tonnes solids)	3,500	100	32	2052
More solids (1.2 million tonnes)	23,000	137	32	2057
Higher long term Hg concentration in sediments (200 ng g ⁻¹)	3,500	200	33	2069
No resuspension	3,500	75	48	2080
Greater particle export of resuspended sediments in outflow (~3,200 tonnes)	3,500	81	25	2037
Lower estimate of 2009 Hg concentration in mobile sediments (730 ng g ⁻¹)	3,500	100	32	2042

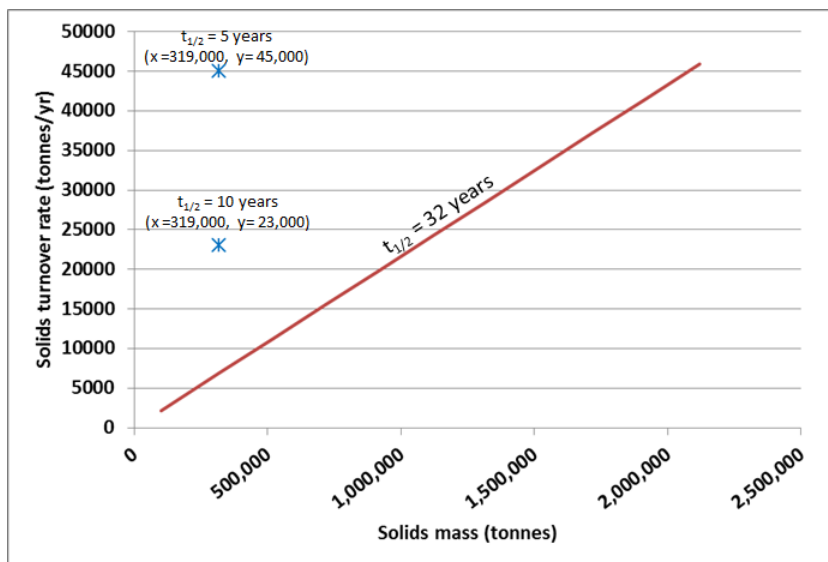


Figure 18-9. Combination of solids pool sizes and solids turnover fluxes associated with 32 year half time for recovery. The simple calculation assumes that Hg recovery is affected only by particle losses. The red line is based on the following calculation: Half time = 32 years; The rate constant associated with the 32 year half time is $\ln(2)/32 = 0.0217$. All points on the red line have this ratio. Also shown is a point based on field estimates of the mobile bed (318,000 tonnes) and combined particle losses via sedimentation (23,000 tonnes yr⁻¹) and downstream export of mobile solids (22,000 tonnes yr⁻¹) (Chapter 1). The resulting half time would be ~5 years.

6.3 Simulation Results with Two Sediment Zones

In all simulations with two sediment zones, the response of the mobile sediment pool was slowed by the presence of the non-depositional zone (Figure 18-18 a-c). The dashed lines in Figure 18-10 show theoretical recovery rates in mobile sediments, based on the internal ability to remove Hg via particle turnover. The slowed response of the mobile bed occurred because the two zones mixed particles fast enough that the simulation began to approach the behavior of one large well mixed mass of solids (both zones combined) that could still only eliminate Hg via burial losses from the mobile pool or downstream export. If resuspension of solids from the mobile zone had been minimal in these simulations, the results would have been more representative of two boxes in series. In such a case, the rate of decline of Hg concentrations in the mobile sediments would still be affected, and potentially slowed down, by the rate of recovery of the non-depositional sediments.

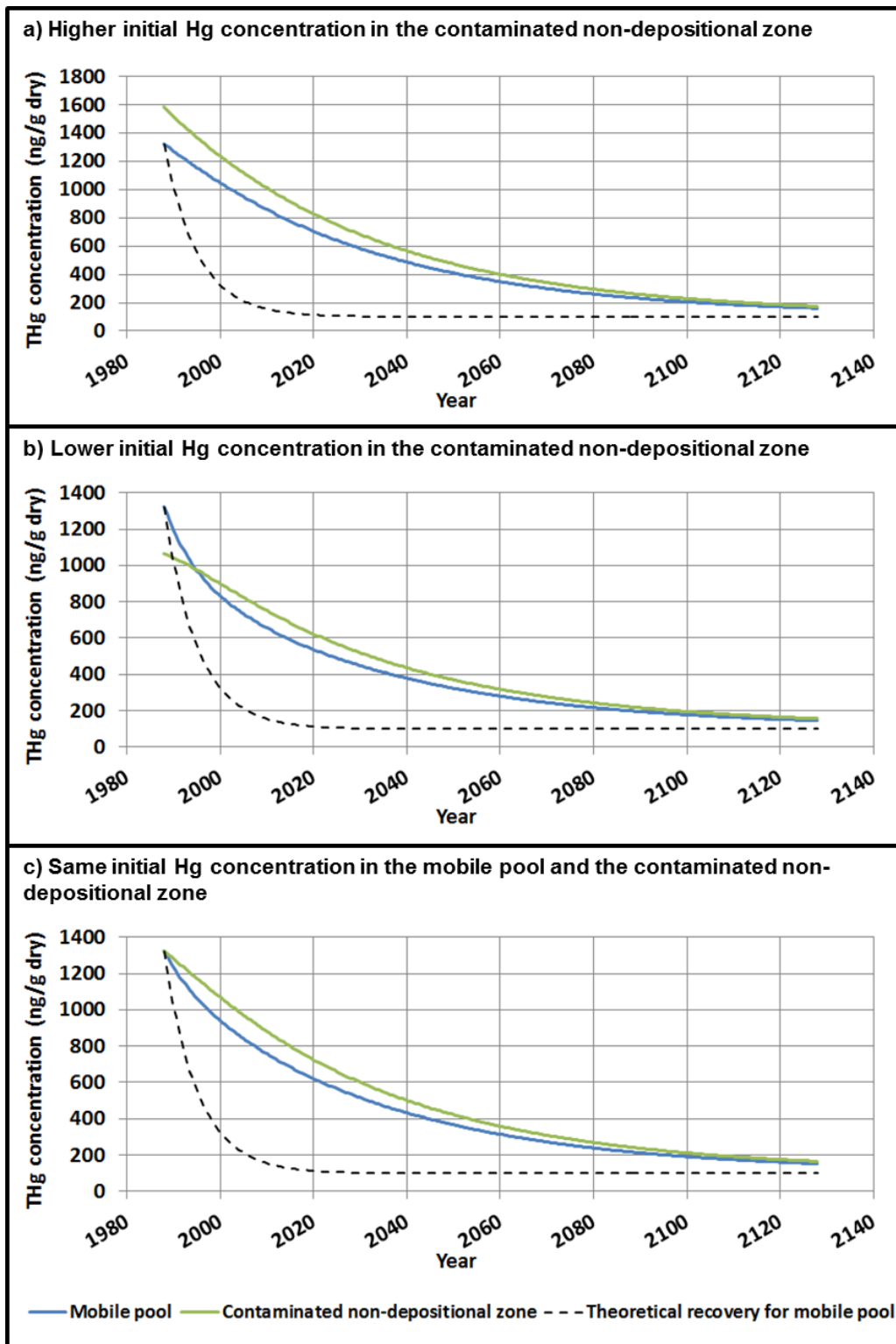


Figure 18-10. Predicted Hg concentrations in sediments for conceptual simulations with two sediment zones. The contaminated non-depositional zone has settling and resuspension, but no net burial.

7 DISCUSSION

The model analysis presented in this Chapter was a coarse-level examination of whether field data are consistent with some fundamental features of the conceptual model of Hg cycling in the upper estuary. It is recognized that the Penobscot estuary is a complex system with spatial heterogeneity and different scales of mixing that cannot be fully represented with this analysis.

7.1 Are field data and the conceptual model consistent?

The model analysis indicates that existing field estimates of mobile solids mass and turnover rate are not consistent with the hypothesis that the mobile solids pools controls the rate of decline of Hg concentrations in sediments (mobile and depositional) in the upper estuary. Either the field estimates are inaccurate or the conceptual model needs adjustment to include additional processes affecting the rate of recovery. Based on estimates of the mass of mobile solids in the estuary (318,000 tonnes) and estimates of solids burial ($\sim 23,000$ tonnes yr^{-1}) and downstream export of solids from the mobile pool in the upper estuary ($\sim 22,000$ tonnes yr^{-1}), Hg concentrations would decline faster than the observed 32 year half time if these pools and fluxes governed the recovery of the system. If burial and downstream export of solids are combined, Hg concentrations in the mobile bed would be expected to recover with a half time on the order of 5 years. Even if just one of these removal mechanisms applied, the half time for recovery would be on the order of 10 years.

Possibilities to explain the discrepancy between field estimates of the rate of recovery of Hg concentrations in sediments and rates that would apply solely due to particle turnover in the mobile bed include:

1. A larger pool of solids:
 - a. **The mobile pool could be larger than 318,000 tonnes.** If particle losses from mobile solids are $45,000$ tonnes yr^{-1} , mobile solids would have to be 2 million tonnes for this factor alone to explain the discrepancy between observed and expected recovery rates if the mobile pool is the governing factor.
 - b. **There is greater mixing between the mobile pool and depositional zone solids**, such that the mass of mixed solids relevant to recovery is bigger than just the mobile solids. Roughly $110,000$ tonnes of solids are estimated to reside in the upper 3 cm of the depositional zone in the upper estuary (Chapter 1). If this mass is added to the mobile pool, the total is $430,000$ tonnes, only about $1/3$ of the total solids pool needed to achieve the observed recovery with solids losses of $45,000$ tonnes yr^{-1} . Other mechanisms would also have to be invoked.
 - c. **There are additional sediment zones in non-depositional areas that are contaminated and interacting with the mobile bed.** This hypothesis was tested conceptually in simulations with two sediment zones, and found to be plausible.

2. **Mass sedimentation and particle export fluxes could be smaller.** If the mobile bed is 318,000 tonnes, burial + particle losses could not exceed 7,000 tonnes (with no ongoing source of Hg contamination)). This is one sixth of the current estimate for particle turnover.
3. **The recovery rate for the upper estuary could be faster than the 32 year half time currently estimated.** Given the magnitude of the discrepancy between the half times based on sediment cores (32 years) and a simple calculation based on existing estimates of the mobile solids mass and turnover rate (5 years), it is unlikely that the sediment core data are in error to this degree.
4. **There could be a lag between changes in Hg concentrations in the mobile bed and the response in depositional zones.** The depositional zone was assumed to respond instantly to changes in loading from the mobile bed in the analysis presented here. The time required for depositional zones to respond to changes in Hg concentrations supplied from the mobile bed is difficult to quantify given the high variability of Hg concentrations in both mobile and depositional area solids (standard deviations of 61% and 110% respectively; Chapter 8). It is unlikely however that the mobile pool would respond with a half life of 5-10 years and the depositional zone half life would be 32 years, without a quantifiably higher concentration in the depositional zone. Other mechanisms would also likely need to apply.

7.2 Effects of Hg partitioning and particle trapping on recovery

Geyer and Ralston (Chapter 7) concluded that only a small fraction of mobile sediments in the upper estuary are transported out to Penobscot Bay annually. Simulations predicted that the rate of recovery was sensitive to particle trapping, and further field quantification of this process would be beneficial. Simulations also predicted that resuspension of contaminated sediments solids is an essential mechanism to explain the elevated Hg concentrations observed on suspended solids (Figure 18-4). In order to also be consistent with observations that the dissolved phase showed little if any evidence of contamination as water flowed through the upper estuary (Figure 18-5), low desorption rates of Hg from suspended sediments into the dissolved phase were imposed in simulations. This also slowed the recovery of the system, as Hg on resuspended sediments settled back into sediments. While different mechanisms could explain the lack of desorption, the hypothesis considered most consistent with observations, including changes in apparent partitioning (K_d) along the estuary, was that Hg on resuspended sediments was strongly bound to solids, with slow rates of release.

7.3 Diffusion

The predicted diffusive flux of Hg in the base case simulation ($34 \mu\text{g m}^{-2} \text{yr}^{-1}$) was small compared to the predicted annual flux of dissolved Hg past Verona Island ($1200 \mu\text{g m}^{-2} \text{yr}^{-1}$). It would not be possible to detect such a flux in terms of increased dissolved Hg concentrations in the water column. There is considerable uncertainty in the actual dissolved flux of Hg from sediments, especially given that the mobile bed mixes with the

water column more than occurs in consolidated sediments. However, even if all the Hg losses associated with the observed rate of decline of Hg in the mobile bed (about $155 \mu\text{g m}^{-2} \text{yr}^{-1}$) occurred by diffusion and downstream export, the increase in Hg concentration in the dissolved phase would still be small compared to advective Hg inputs and outputs, and could be difficult to detect as an increase in concentration. Tidal flows are not considered in this analysis but could also reduce increases in dissolved Hg concentrations that might otherwise occur in the water column. This interpretation depends on the size of the mobile bed. If the mobile bed is significantly larger than 318,000 tonnes, the Hg fluxes needed to explain the observed rate of recovery would be larger, and possibly easier to detect in the dissolved phase if diffusion was an important loss mechanism for Hg from mobile sediments.

7.4 Importance of estimated existing and long term steady state Hg concentration in sediments.

In the base case simulation with a long term concentration of 100 ng g^{-1} in sediments, the target concentration of 400 ng g^{-1} was reached by the year 2052. If the long term concentration is actually higher, the time required to reach 400 ng g^{-1} , in the absence of remediation, would be longer than predicted for the base case. For example, the time to reach 400 ng g^{-1} in sediments lengthened by 17 years to 2069 when the long term concentration was 200 ng g^{-1} . Estimates of the existing concentration of Hg in mobile sediments also have uncertainty and affect the time required to recovery to 400 ng g^{-1} . A simulation with a lower current Hg concentration in mobile sediments (730 ng g^{-1} versus the base case of 885 ng g^{-1} in 2009) shortened the time required to reach 400 ng g^{-1} by a decade. These model results indicate that that projections of the time required to recover to 400 ng g^{-1} are sensitive to existing and final concentrations but the time scale is on the order of decades in all cases tested.

7.5 Role of ongoing HoltraChem Hg releases

Simulations indicate that ongoing residual releases of Hg from the HoltraChem site, estimated to be 2.2 kg yr^{-1} , are small (< 6%) compared to other ongoing Hg inputs to the upper estuary. To the extent that these releases occur in dissolved form, which could be more available for methylation than particulate Hg inputs, there is no obvious increase in dissolved Hg concentrations in the water column. To the extent that residual Hg releases from the HoltraChem site occur in particulate form, these inputs would be small compared to other sources. It is therefore not expected that this source significantly affects the rate of recovery of Hg concentrations in sediments.

7.6 Implications of model results for remediation

The model results indicate that it is not yet possible to determine the quantity of solids that would have to be removed or isolated to achieve the desired target concentration of 400 ng g^{-1} in sediments. This is because of the inconsistencies described above between field observations and the conceptual model that would guide remediation. This issue needs to be resolved before specific plans are made for remediation. Also, the modeling did not consider the potential for storm events to affect the rate of recovery of the system or interfere with the benefits of remediation. Storms could, for example,

remobilize previously deposited Hg into the solids pool ultimately relevant to methyl Hg accumulation by biota. Additional consideration should be given to the likelihood of such a scenario. Finally, the modeling suggests that further attention should be given to the possibility that sediments in non-depositional areas, other than the mobile bed, could influence and delay the overall recovery rate of the estuary. If true, targeted remediation of these specific areas could be considered.

8 Recommendations

The following recommendations emerged from the modeling analysis:

- Better constrain particle pool sizes and fluxes with the objective of reconciling the rate of particle turnover with the observed rate of decline of Hg concentrations in sediments. Carry out field studies as needed to meet this goal.
- Further evaluate the potential for different rates of recovery for Hg contamination in different sediment zones of the upper estuary, and interactions among these zones that could affect the overall rate of recovery.
- If additional field studies are carried out in connection with the above recommendations, consider additional simulation modeling with a limited number of connected cells to support field studies. Additional modeling would be useful to:
 - Expand the modeling analysis to include the broader area of contamination.
 - Help establish if the conceptual model and field data fit together in a consistent view of factors controlling the rate of recovery of Hg in different parts of the Penobscot Estuary, and
 - Improve the ability to test remediation scenarios.

The broader modeled area could include the Upper estuary, Mendall Marsh, Fort Point Cove, Orland River and Penobscot Bay. Mendall Marsh in particular is of interest due to concerns about methyl Hg exposure for biota in this area. Model simulations could include each of the above areas as distinct but linked cells, and could include a limited number of sediment zones with different recovery rates within each cell. Finally, a new version of D-MCM is being updated in 2013 to better simulate mobile sediments. The status of these updates should be evaluated if additional modeling is considered.

9 Conclusions

A simplified Hg modeling analysis has been carried out to help assess if field data are consistent with the conceptual model that a large pool of mobile solids governs the rate of recovery of Hg concentrations in the upper Penobscot Estuary. A mechanistic mass balance model of Hg cycling was used to simulate the upper estuary as a single cell with a well-mixed water column and well-mixed sediments representing the mobile solids pool. While this was a coarse analysis, it indicated that field estimates of the

mobile solids mass and turnover rate are not consistent with the hypothesis that the mobile solids pool controls the field-estimated rate of decline of Hg concentrations in sediments (mobile and depositional) in the upper estuary. If the best estimates of particle masses and fluxes are combined, the mobile solids would turn over particles with a half time of roughly 5 years, much faster than the 32 year half time estimated for Hg in the upper estuary using sediment cores in depositional zones. This implies that the mass of solids involved is bigger, the particle loss rates are smaller, and/or the upper estuary is actually recovering faster than the current estimate of a 32 year half time. Alternatively, there could be an ongoing source of Hg contamination to the mobile bed that has been declining with time, governing the rate of recovery of the system, rather than the mobile bed particle dynamics. Based on the modeling, ongoing residual releases of Hg from the HoltraChem site are too small to meaningfully delay the rate of recovery of Hg levels in sediments.

Additional field studies are recommended to better constrain particle pool sizes and fluxes in the upper estuary with the objective of reconciling the rate of particle turnover with the observed rate of decline of Hg concentrations in sediments. Consideration should also be given to the potential for different sediment zones in the upper estuary to interact in a manner that affects the overall rate of recovery. If further field studies are carried out, additional modeling would be useful to help reconcile field data with the conceptual model, to simulate other contaminated zones of the Penobscot Estuary as distinct areas (upper estuary, Mendall Marsh, Orland River, Fort Point Cove, Penobscot Bay), and to evaluate potential remediation actions.

10 References

- Atkeson, T.D., D.M. Axelrad, C.D. Pollman, G.J. Keeler. 2003. Integrating Atmospheric Mercury Deposition with Aquatic Cycling in the Florida Everglades: An Approach for Conducting a Total Maximum Daily Load Analysis for an Atmospherically Derived Pollutant. Integrated Summary, Final Report.
- Balcom, P.H., W.F. Fitzgerald, G.M. Vandal, C.H. Lamborg, K.R. Rolfhus, C.S. Langer, and C.R. Hammerschmidt (2004) Mercury sources and cycling in the Connecticut River and Long Island Sound. *Marine Chemistry*. 90:53–74.
- Bodaly, R.A., J.W.M. Rudd, N.S. Fisher, C.G. Whipple. 2008. Penobscot River Mercury Study Phase I of the Study: 2006-2007. Report to Judge Gene Carter, U.S. District Court (District of Maine), Portland, Maine. January 24, 2008.
- EPRI.2009. Dynamic Mercury Cycling Model for Windows XP and Vista - A Model for Mercury Cycling in Lakes. D-MCM Version 3.0. User's Guide and Technical Reference. December 2009.
- Hamrick, J. M. 1992. A three-dimensional environmental fluid dynamics computer code: Theoretical and computational aspects. The College of William and Mary, Virginia Institute of Marine Science, Special Report 317, 63 pp
- Harris, R.C., C. Pollman, D. Hutchinson, W. Landing, D. Axelrad, S.L. Morey, D. Dukhovskoy, K. Vijayaraghavan. 2012. A screening model analysis of mercury sources, fate and bioaccumulation in the Gulf of Mexico. *Environmental Research*. 119: 53–63.
- Harris R.C., J.W.M. Rudd, M. Amyot, C. Babiarz, K.G. Beaty, P.J. Blanchfield, R.A. Bodaly, B.A. Branfireun, C.C. Gilmour, J.A. Graydon, A. Heyes, H. Hintelmann, J.P. Hurley, C.A. Kelly, D.P. Krabbenhoft, S.E. Lindberg, R.P. Mason, M.J. Paterson, C.L. Podemski, A. Robinson, K.A. Sandilands, G.R. Southworth, V.L. St. Louis and M.T. Tate. 2007 Whole-ecosystem study shows rapid fish-mercury response to changes in mercury deposition. *Proceedings of the National Academy of Sciences of the United States of America*. 104(42):16586–16591.
- Harris, R., C. Pollman, D. Beals, D. Hutchinson. 2003a. Modeling Mercury Cycling and Bioaccumulation in Everglades Marshes with the Everglades Mercury Cycling Model (E-MCM). Final Report. Prepared for the Florida Department of Environmental Protection and South Florida Water Management District. June 2003
- Harris, R.C., C.D. Pollman, D. Hutchinson. 2003b. Wisconsin Pilot Mercury Total Maximum Daily Load (TMDL) Study: Application of the Dynamic Mercury Cycling Model (D-MCM) to Devil's Lake, Wisconsin. Submitted to the United States Environmental Protection Agency Office of Wetlands Oceans and Watersheds. December 2003.

- Harris, R.C. and R.A. Bodaly. 1998. Temperature, growth and dietary effects on fish mercury dynamics in two Ontario Lakes. *Biogeochemistry*. 40:175-187.
- Hudson, R.J.M., S.A. Gherini, C.J. Watras, D.B. Porcella. 1994. Modeling the Biogeochemical Cycle of Mercury in Lakes: The Mercury Cycling Model (MCM) and Its Application to the MTL Study Lakes. In *Mercury Pollution - Integration and Synthesis*. C.J. Watras and J.W. Huckabee (Eds.). CRC Press Inc. Lewis Publishers.
- Kelly, C. 2010. Spreadsheet titled "WQ data lat long 2008 2009 2010 edited CK December 16_2010.xlsx" sent to R. Harris by email on December 16, 2010.
- Maine Department of Environmental Protection (2005)
<http://www.maine.gov/dep/rwm/holtrachem/site.htm>
- NADP (National Atmospheric Deposition Program). 2012. Sample data for Acadia National Park-McFarland Hill (Station ME98), Maine. November 30, 2012.
<http://nadp.sws.uiuc.edu/sites/siteinfo.asp?net=MDN&id=ME98>
- NOAA (National Oceanic and Atmospheric Administration). 2012. Summary of Monthly Normal 1981-2010 (Station: Bangor International Airport, ME). National Oceanic & Atmospheric Administration: National Climatic Data Center, Asheville, NC.
- NOAA (National Oceanic and Atmospheric Administration). 2010. Chart 13309 Penobscot River; Belfast Harbor Edition 29. August 1, 2010.
<http://www.oceangrafix.com/chart/detail/13309-Penobscot-River-Belfast-Harbor>
- Soerensen, A.L., E.M. Sunderland, C.D. Holmes, D.J. Jacob, R.M. Yantosca, H. Skov, J.H. Christensen, S.A. Strode, R.P. Mason. 2010. An improved global model for air-sea exchange of mercury: high concentrations over the North Atlantic. *Environmental Science & Technology*. 44:8574-8580.
- Southworth G., S. Lindberg, H. Hintelmann, M. Amyot, A. Poulain, M. Bogle, M. Peterson, J. Rudd, R. Harris, K. Sandilands, et al. 2007, *Environmental Toxicology & Chemistry*. 26:53-60.
- Turner, R. and D. Kopec. 2012. Field Data and Experiments on in situ Particle Formation in Penobscot River – Summary.
- U.S. Environmental Protection Agency (EPA). 2001 Region 1 - No. 3 September - HoltraChem Manufacturing Site
- U.S. Environmental Protection Agency (EPA). 2009a.
<http://www.epa.gov/ceampubl/swater/efdc/index.html>
- U.S. Environmental Protection Agency (EPA). 2009b.
<http://www.epa.gov/athens/wwqtsc/html/wasp.html>