

PENOBSCOT RIVER MERCURY STUDY

Chapter 23

The Scientific Basis for Active Remediation of the Upper Penobscot Estuary

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1 PREAMBLE

This chapter steps through the scientific bases for our recommendation to pursue active remediation of the upper estuary of the Penobscot River¹. First, we will discuss the evidence demonstrating that the sediments need to be the focus of remediation, second, we will present the basis for concluding that the present rate of recovery of mercury (Hg) in the surface sediments is too slow, and third, we will provide the scientific bases for the remediation approaches recommended in Chapter 21, and for choosing to recommend that certain remediation procedures be further investigated to establish their feasibility.

2 THE FOCUS OF REMEDIATION SHOULD BE ON THE LEGACY HOLTRACHEM MERCURY STILL IN THE SURFACE SEDIMENTS, AND NOT ON ONGOING SOURCES OF MERCURY TO THE UPPER ESTUARY.

Before recommending active remediation of any kind, it is critical to firmly establish whether the high mercury (Hg) concentrations presently accumulating as methyl Hg in biota are caused mostly by legacy Hg that was released by HoltraChem mainly during the late 1960's and early 1970's, and not primarily from ongoing sources of Hg to the upper estuary (either from upstream Hg flowing into the upper estuary over Veazie Dam or from local tributaries or from local point sources located in the upper estuary; e.g. the HoltraChem site). This is a necessary distinction because if there are important ongoing sources, active remediation that focuses on the legacy Hg in the surface sediments would not help, and would be ill advised. The following discussion addresses this point.

We know that Hg concentrations in surface sediments are 10 – 20 fold higher in the upper estuary than in sediments either upstream of Veazie Dam or south of Fort Point (Figures 23-1 & 23-2), and we know that these high concentrations are caused by legacy Hg released from the HoltraChem site mostly during the late 1960's and early 1970's (Chapter 1). We also know that lowering total Hg concentrations in the upper estuary would lower methyl Hg concentrations in sediments (Chapter 1 and later discussion) because methyl Hg concentrations are positively related to total Hg concentrations. However, this does not necessarily mean that the high present-day methyl Hg concentrations in the biota in the upper estuary are caused by the legacy HoltraChem Hg stored in the upper estuary sediments. It is also possible that comparatively small ongoing sources of Hg to the upper estuary (the same zone of the estuary where the Hg was initially released from HoltraChem and where sediment concentrations are still high) are feeding the present-day production of methyl Hg and maintaining the methyl Hg at high levels in biota. This would be possible if the ongoing sources, which are small compared to the masses of legacy Hg still in the sediment,

¹ The upper estuary of the Penobscot includes the main stem of the river from the Veazie Dam to the southern tip of Verona Island including the Mendall Marsh and the tidal portion of the Orland River. This is the zone where mercury concentrations in surface sediments are highest (Figures 23-1 & 23-2) and where Hg concentrations in biota are highest (Chapter 14, Appendix 16-2, Chapter 16).

were much more bioavailable to the Hg methylators for methyl Hg production than the legacy HoltraChem Hg, which has been buried in sediments for decades.

Our mass budget estimates (Figure 23-3, Chapter 1) show a large inventory of Hg in the deeper sediments, which is presently buried deep enough to be unavailable for active biogeochemical cycling and methylation (Chapter 1), and a smaller but still large quantity of mostly HoltraChem Hg stored in shallower active sediments to a depth of 3 cm, and in the mobile sediment pool. Figure 23-3 also shows annual ongoing sources and outputs of Hg from the upper estuary. The sources are from upstream of Veazie Dam, from local tributaries below Veazie Dam, from present-day estimated inputs from the HoltraChem site and from municipal sources in the upper estuary, and from direct atmospheric deposition. Together, these ongoing inputs amount to about 57 kg/ yr. Hg flowing into the upper estuary over Veazie Dam, primarily in a dissolved form,² was estimated to be the largest ongoing source to the upper estuary (Chapters 1 & 4).

These ongoing inputs enter the water column, and could theoretically be important in providing inorganic Hg for methylation. However, there are four lines of evidence that lead us to conclude that it is the legacy HoltraChem Hg in surface sediments that is mostly responsible for the high present-day Hg concentrations in the food web, and not ongoing inputs to the water column of the upper estuary. The four lines of evidence are as follows:

First, in our data set we have one example of a species, the American eel, which inhabits both the most contaminated upper estuary as well as the much cleaner zone of the river upstream of the Veazie Dam. In these two zones the methyl Hg concentrations in water and sediment followed different patterns. Methyl Hg in water decreased, going from the cleaner zone to the more contaminated zone. In contrast, methyl Hg in sediments increased (Figure 23-5). The Hg concentrations in American eels closely mirrored the methyl Hg concentration in surficial sediments, not the concentrations in water. This demonstrated that the methyl Hg in the food web was sediment based, and that the legacy HoltraChem Hg below the Veazie Dam is responsible for the present-day high Hg concentrations found in eels below the Veazie Dam.

Second, the spatial patterns of methyl Hg in the eel data are supported by the stable isotope data for nitrogen and carbon, which show that the base of the eel's food web is sediment-dwelling organisms (Chapter 16). Similarly, the stomach-content data show a largely sediment based food web for most fish at most locations (Table 23-1).

Third, Hg concentrations in biota of the upper estuary are higher than in other unimpacted estuaries (Chapters 14 & 16; Appendix 1-2 and 1-3 of Chapter 1) even though the Hg concentrations in inflowing river water are not higher than other impacted rivers in North America. Concentrations of total Hg and methyl Hg in the water flowing over Veazie Dam (3.8 ng total Hg/L and 0.15 ng methyl Hg/L) are not elevated - they

² It is possible that some of the inflowing mercury over Veazie Dam is HoltraChem Hg, which originated as fugitive elemental Hg that was lost to the atmosphere from the HoltraChem Hg cells and then deposited in the Penobscot drainage basin upstream of Veazie Dam.

are very similar to concentrations in other rivers and streams of the northeastern, USA (Shanley et al. 2005). Nor are the biota above Veazie Dam elevated in Hg concentration (Appendix 1-2 and 1-3 of Chapter 1). In contrast, the sediments of the upper estuary are many times higher in Hg than the sediments of unimpacted estuaries in the region (Chapter 17), and biota are also higher in Hg concentration (Chapter 14).

Fourth, a recent whole-lake Hg addition experiment, where isotopically labeled Hg was added, demonstrated that newly added Hg is not preferentially methylated as compared to legacy Hg, which had been in the sediments for many decades (Rudd et al. in prep.). Instead, newly added isotopic inorganic Hg quickly becomes indistinguishable from legacy Hg to the Hg methylators. This experiment supports our Penobscot data, which say that it is very unlikely that the very small amount of Hg being added to the upper estuary from the HoltraChem site (compared to much larger amount in the mobile pool and surface sediments where methylation occurs, Figure 23-3) would be preferentially methylated. Instead this whole-lake experiment supports the view that the Hg supporting methylation is the legacy Hg, which is most abundant in the upper estuary and Fort Point Cove, and that it is causing the present-day high methyl Hg concentrations in biota.

We conclude that the Hg released by HoltraChem in the late 1960's and early 1970's is primarily responsible for present-day high Hg concentrations of the biota downstream of Veazie Dam in the upper estuary of the Penobscot River.

This does not imply that Hg from upstream sources does not enter the food web downstream of the Veazie Dam, just that its contribution to the methyl Hg accumulated in biota is minor. Thus we conclude that the active remediation procedures discussed below, which focus on the sediments in the contaminated areas, would be beneficial in decreasing the Hg concentrations in biota in the upper Penobscot estuary.

3 THE NEED FOR ACTIVE REMEDIATION IN THE UPPER ESTUARY OF THE PENOBSCOT RIVER

Chapter 1 concludes that average total Hg concentrations in the surface sediments of the upper estuary are today about 885 ng/g dry wt., and should be reduced to 450 ng/g dry wt. to have acceptable (target) Hg concentrations in biota (Chapter 2). Natural attenuation will decrease these Hg concentrations over time to the target concentration (about 33 years from 2013, Chapter 21). However, we have concluded that the rate of natural attenuation of the upper estuary is too slow³, and that active remediation should take place, if feasible.

The main scientific basis for this conclusion are the radiochemical and Hg profiles in sediment cores analyzed by Drs. Santschi and Yeager (Chapters 5 and 6). A synopsis of their key data and findings follows:

³ The primary scientific basis for the conclusion by the Study Panel that the natural attenuation rate of the upper estuary of the Penobscot is too slow, and that remediation is needed, are the high concentrations of methyl Hg in birds and fish in the upper estuary, which based on toxicological studies are above toxic levels, and that it is now 46 years after the major input of mercury to the Penobscot and concentrations in biota are still at toxic levels.

The current average rate of attenuation, or recovery, of Hg concentrations in the upper estuary of the Penobscot is much slower than it was initially, after the peak contamination occurred. Radiochemical dating and total Hg depth profiles from long sediment cores taken from the river, Penobscot Bay and Mendall Marsh have shown that Hg concentrations in sediments were highest during the period of high Hg releases from the HoltraChem site, which peaked the late 1960's to early 1970's. The Hg concentrations were initially highest in the main stem of the river in the upper estuary (Figure 23-4). This initial dispersal was then followed by a slower, wider ranging lateral dispersal of the Hg throughout the upper estuary, and into Fort Point Cove (Chapter 6). There was also dispersal below Fort Point (Chapter 5). Some areas of Fort Point Cove, the Orland River and Penobscot Bay, still have their highest Hg concentrations in sediments at the sediment/water interface. This indicates that the lateral dispersal of the HoltraChem Hg is still continuing – four decades after the peak Hg discharges from the HoltraChem site (Chapter 6). This very wide dispersal of the Hg in the upper estuary makes the remediation of the problem daunting, because the high Hg concentrations in the surface sediments (compared to present-day regional background concentrations) are now spread over such a wide area (Figure 23-1).

The two phase dispersal of the Hg from the HoltraChem site is illustrated by the shape of total Hg concentration depth profiles in most of the sediment cores. These profiles show an initial rapid decrease in Hg concentration from a late 1960's to early 1970's peak concentration, followed by a slower rate of decrease in Hg concentration in the last 21 years, as the lateral dispersal became almost complete (Chapter 6). It is this slower rate of recovery that is occurring now.

Assuming that the rate of decrease of total Hg concentration in surface sediments during the past 21 years will continue into the future, we predict that it will be at least another 33 years from 2013 (i.e. about 2046) before Hg concentrations in the upper estuary reach the target concentration of Hg in surface sediments of 450 ng/g dry wt. (Figure 23-6), which we would expect to be protective of organisms and human consumers in the upper estuary (Chapter 2). We further predict that Hg concentrations in surface sediments will not decrease to within 20% of regional background levels of 100 ng/g dry wt. (Chapter 1) until about 2176, if natural attenuation is allowed to proceed without any active remediation and if there is no change in the attenuation rate in the coming decades (Figure 23-6).

4 ACTIVE REMEDIATION OPTIONS

The Study Panel first considered the possibility of conventional dredging of the soft depositional sediments in the upper estuary. However, based on the extensive dispersal of the Hg (Hg) in the soft sediments of the upper estuary, the Study Panel concluded that the very high estimated cost of dredging the upper estuary in a traditional manner is not warranted (Chapter 21). Extensive dredging also runs the risk of exposing previously buried high-Hg sediments, which could aggravate present situation.

Instead of conventional dredging, our recommendations to the Court are based on findings of the Phase II study, which point to remediation options that are much less expensive and much less disruptive of the natural ecosystem. The scientific bases for these options are as follows:

- Enhanced Natural Attenuation (ENA) in the upper estuary of the Penobscot River by removal of Hg contaminated mobile sediments and dispersal of clean mobile sediments.

In a previous section, we gave evidence that it is the legacy HoltraChem Hg in the sediments, not the ongoing inputs, that is responsible for the current unacceptable levels of methyl Hg in biota. Thus we are focusing our attention on the total Hg concentrations in surface sediments. Two lines of evidence lead us to conclude that removal of contaminated mobile sediments followed by dispersal of clean sediments in the upper estuary would reduce the Hg concentration in target organisms to acceptable levels, by reducing the Hg concentrations in the sediments. These are: 1) the positive relationship between methyl Hg production and inorganic Hg concentration in surface sediments, which means that lowering the inorganic Hg concentrations will reduce the methyl Hg concentrations; and 2) the presence of a Hg contaminated pool of mobile sediments in the upper estuary, which controls the rate of recovery of Hg concentrations in the surface sediments because this pool is so efficiently trapped in the upper estuary.

Evidence for the positive relationship between concentrations of methyl Hg and total Hg. We carried out extensive surveys of total Hg and methyl Hg concentrations in surface sediments of the river and bay (Figure 23-7, Appendix 1-2 and 1-3 of Chapter 1) and surface wetland soils in the estuary Penobscot system (Figure 23-8, Appendix 1-2 and 1-3 of Chapter 1). There was a positive linear relationship between the total Hg concentration in the surface sediments and soils and their methyl Hg concentrations. While the slope of the relationship is different in different habitats, it was clear that if total Hg concentrations could be reduced across all habitats, methyl Hg concentrations would also decrease. This relationship was found throughout the Penobscot system in river and bay sediments and in wetlands. It was also found in the mobile pool of sediments (Chapter 8). We have concluded that total Hg⁴ concentration is the primary driver of methyl Hg production in the Penobscot (Chapter 11,12). Thus a remediation

⁴ Total Hg concentration is used as a surrogate for Hg(II) (ionic mercury), which is the substrate for bacterial methyl Hg production. Measured total Hg concentrations in sediments and wetland soils include about 3% methyl Hg and about 97% inorganic Hg (Hg(II)).

procedure reducing total Hg concentration in the surface sediments and mobile sediments, where methyl Hg production occurs, would reduce methyl Hg concentrations in general in the upper estuary – including the food web fish and birds.

Importance of the Hg-contaminated mobile sediment pool. The primary explanation for the continuing high total Hg concentrations of the surface sediments in the upper estuary is the highly efficient retention of a large pool of Hg-contaminated *mobile sediments* in the upper estuary and in Fort Point Cove. Particles in the mobile pool feed sediment accumulation in the surface sediments of the long-term depositional areas of the upper estuary where methyl Hg production occurs. If the Hg concentration of the mobile pool were reduced by removal of contaminated sediments and replacement with clean sediments, this would reduce Hg concentrations in the surface sediments and mobile pool, where methyl Hg production occurs in the upper estuary.

The mobile sediments in the upper estuary consist of a variety of materials (sands, muds, and wood chips) of various sizes and Hg concentrations (Chapter 8), with an estimated total mass of 320,000 tons (Chapter 7). These contaminated mobile sediments are seasonally transported up and down the upper estuary by tidal and riverine currents, respectively, but they are mostly prevented from escaping downstream of the southern tip of Verona Island by trapping at tidal saline fronts in the vicinity of Verona Island (Chapter 7). The main trapping zones during high flow periods are shown in Figure 23-9. When river flows are low, the salt front moves upstream, and the mobile pool also migrates upstream to about as far as HoltraChem.

Most of the Hg in the mobile sediment pool is found in the smallest particle size fractions (i.e. the muds, Chapter 8). The muds in the mobile pool are referred to as “new muds”. The total Hg concentration of the new muds in the mobile pool are very similar to the “old muds” in the surface sediments (Figure 23-10). The old muds were deposited at sites of long term sediment accumulation, which are located in quiescent areas (Figure 23-11) where the muds are not readily resuspended.

Thus we conclude that the new muds in the mobile pool are controlling the total Hg concentration in the surface sediments at sites of long term deposition (i.e. in the coves and marshes) where methyl Hg production occurs. Because methyl Hg production (and concentration) are controlled by the total Hg concentrations in surface sediments (Figure 23-7 & 23-8) lowering the Hg concentration of the new muds in the mobile sediment pool would speed the recovery of total Hg concentrations in the surface sediments and thus lower methyl Hg concentrations in the sediments and biota. Our data lead us to conclude that replacing about half of the contaminated mobile sediments with clean muds obtained from within the system as described in Chapter 21 is a scientifically feasible remediation approach for the upper estuary of the Penobscot.

A clear understanding of the mobile sediment pool, its size, movements, and Hg concentrations in the upper estuary is a key to successful remediation of the Penobscot estuary (Chapters 1, 7, 18). Before the Phase II study, the importance of the mobile pool to recovery of estuaries from various types of contaminants, or specifically to the Penobscot, had not been recognized nor could it have been anticipated. This study has gone a long way towards understanding the important role of mobile sediments in

estuaries. However there was insufficient time for field sampling to quantify the size and turnover time of this pool to the extent needed to predict recovery of the upper estuary (Chapter 18). The reasons that we think our data on the mobile pool are insufficient are discussed in the next paragraph.

Our current data on the size of the mobile pool, and on exit rates of particles from the upper estuary, suggest that the **residence time** of particles in this pool is on the order of 6 years (Figure 1-14 in Chapter 1)⁵. If the residence time is correct, we would expect that after 6 years all of the particles in the mobile pool should have been replaced by new particles from upstream. The fine particles in the mobile pool are the particles that sediment at long term depositional site in the upper estuary - determining the total Hg concentrations in these surface sediments (Chapter 8). However, the natural attenuation data (i.e. core data Chapter 6) give average **recovery half-times** for total Hg in surface sediments of 32 years in the upper estuary. Also, the mass of total Hg below the southern tip of Verona Island (Chapter 1, 5) suggests that 77% of the Hg has left the upper estuary since 1967. This can be explained if only 3% of the pool exits each year, and this low rate of exit would be equivalent to a **recovery half-time** of 23 years. A recovery half-time is not the same as a residence time, as it is the rate of decline of Hg concentration in the mobile pool. Nevertheless, the two should not differ greatly. It is the opinion of the study team that the short residence time of the mobile pool and the much longer recovery time of the surface sediments are incompatible (Chapters 1, 5, 6, 18). While this incompatibility does not refute the scientific basis for our remediation recommendations, this does need to be resolved before the procedures should be implemented. Otherwise there could be an underestimation of costs or efficacy. There are possible explanations to address this incompatibility, which could be addressed with more field sampling. These include:

- The size of the mobile pool, which needs to be better quantified (Chapter 7). If the pool is bigger than is now estimated, this would mean a longer recovery time for the mobile pool.
- The amount of ongoing erosion of high Hg muds from riparian mudflats and wetlands (Chapter 18). This would constitute an ongoing internal source of legacy Hg to the mobile pool, which would lengthen the recovery half-time of Hg in the mobile pool (Chapter 18). Our data on this topic are limited, and this should be studied further before proceeding with this remediation option.

It is useful to consider the ramifications for remediation about differences in either the size of the mobile pool, or the amount of ongoing internal Hg contributions to this pool. If the pool is larger than now estimated, it would require a larger amount of sediment to be trapped, and a larger amount of clean material to be dispersed back into the surface waters of the upper estuary, which would increase the cost, but the overall concept would still apply. A bigger problem would be if there is an ongoing source from redistribution of Hg rich sediments to the mobile pool. If this source was large enough it

⁵ Other estimates made using different approaches as part of this study are 5-20 years (Chapter 7) and 6 years (Chapter 18).

would mean that the clean sediments added would be sufficient to lower the Hg concentrations to the intended target level but that concentrations might rebound in time rather than continue to decline, which is what would otherwise occur.

Once the size of the mobile pool is better known, and if ongoing erosion is deemed to be not a large contribution of Hg to this pool, this would be sufficient certainty to proceed with removing half of the contaminated mobile pool and replacing it by dispersal of clean muds into the upper estuary. This would lower Hg concentrations in the mobile pool by about a factor of two, achieving the target of 450 ng/g dry wt. These clean muds could be obtained from sediments located between Fort Point and the northern tip of Islesboro Island (Figure 23-13; Chapter 5). Muds in the deeper layers of these sediments were deposited decades ago, before Hg pollution of the Penobscot. The Hg concentration of this material is about 20 - 50 ng/g dry wt. (Figure 23-13, Chapter 5). The replacement of one-half of the mobile pool with clean muds would be sufficient to dilute the total Hg concentrations in the mobile pool to 450 ng/g dry wt. This would lower total Hg to target levels in surface sediments (Chapter 2). Total Hg concentrations would continue to decline thereafter because of the constant input of cleaner particles from upstream sources, which would further dilute the Hg concentrations in the mobile pool (Chapter 1). (As discussed in detail in Chapter 1, the Hg concentration of surface sediments in the upper estuary would be about 100 ng/g after they have recovered to regional background concentrations (Chapter 1).

Treatment of the entire upper estuary by mobile sediment removal and dispersal of clean sediments, as described above and in Chapter 21, would also reduce the concentration of Hg on particulates entering Mendall Marsh and the Orland River. However, because of the very long recovery half-time of the Orland River (Chapter 6) its recovery to target concentrations would be delayed. The proposed treatment of the upper estuary would also improve the situation more quickly in Fort Point Cove because it is downstream of the upper estuary.

5 ACTIVE REMEDIATION OF MENDALL MARSH

Concentrations of methyl Hg in Mendall Marsh soils and biota are extremely high (Table 23-2, Figure 23-14, Chapters 11, 14, 16; Appendix 1-2 and 1-3 of Chapter 1). This is because the mobile sediments entering the marsh from the river are just as contaminated as those in the river (Figure 23-15), and because Hg is methylated more efficiently in Mendall Marsh than in the river (Chapters 1, 11, 12). Additionally, bioaccumulation of the methyl Hg into the avian food chain is very efficient because methyl Hg is not as tightly bound to the marsh soils as it is in most other locations (Table 23-2, Chapter 11, 16).

The continuous input of contaminated particles to Mendall Marsh is facilitated by its location. There is a major trapping zone of mobile sediments in the main stem of the river near the mouth of the Marsh River (Figure 23-9). On each flood tide, some of the material trapped at this site moves up the Marsh River and into Mendall Marsh as depicted in Figure 23-16. We estimate that about 40% of this material is retained in the marsh channels on each tidal cycle (Chapter 10). During spring tides, when the entire marsh platform is flooded, this material is transported onto the Mendall Marsh platform.

Total Hg concentrations are lower by about one third on the marsh platform than in the marsh channels and on the levees at the edges of the marsh next to the channels. This is because of plant growth on the marsh platform, which dilutes the Hg in the surface soils with clean plant carbon (Chapter 1). If the methylation efficiency in the marsh were the same as that in the river, we would expect methyl Hg concentrations in the marsh to be lower than in the river. However, this is not the case. The high methyl Hg concentrations are because of the high methylation efficiency in the marsh (i.e. there is a higher percentage of methyl Hg per gram of total Hg in the marsh than elsewhere in the river; Figures 23-7, 23-8, 23-14, Chapter 12). This high methylation efficiency may be linked to high rates of microbial activity associated with decomposition of plant material in the marsh as has been seen in other situations (Bodaly et al. 2004; Rudd 1995), and also the low K_D 's for inorganic Hg in Mendall Marsh soils, which result in very high concentrations of methyl Hg in pore water (Figure 23-17; Chapter 11).

Within the marsh there is a positive linear relationship between methyl and total Hg (Figure 23-17). Therefore, if the total Hg concentrations in the marsh could be lowered, then methyl Hg concentrations should also be lowered.

Because of the high methylation efficiency in the marsh, we estimate that target concentrations of Hg for surface soils on the marsh platform should be about 100 ng/g Hg dry wt. (Chapters 2 & 21), which is somewhat above the estimated background concentration for the marsh (i.e. complete recovery, Chapter 1). Mendall Marsh is not estimated to reach target concentrations of 100 ng/g dry wt. until about 2073, if natural attenuation is allowed to proceed without any active remediation (Chapter 21), because the rate of recovery of Mendall Marsh is controlled by the rate of recovery of incoming Hg from the river (Figure 23-18).

We are recommending further design and testing of two types of active remediation options for Mendall Marsh (Chapter 21). These options could be applied separately or together to speed recovery.

5.1 Removal of contaminated mobile sediments entering Mendall Marsh and dispersal of clean sediments inside the marsh.

If it is decided by the Court to not remediate the entire upper estuary as discussed above, but to instead actively remediate only Mendall Marsh, one remedial option could be the trapping and removal of contaminated mobile sediment entering the marsh, followed by dispersal of low Hg sediments in the marsh. The clean sediments could be obtained from deeper layers of Penobscot Bay sediments (Figure 23-13). The trapping of incoming contaminated sediments could be accomplished at the mouth of the Marsh River, followed by its removal and dispersal of clean sediments as described in Chapter 21. We have concluded on a scientific basis that this option is feasible because the removal and replacement would lower Hg concentrations in the surface soils of the marsh platform, and decrease methyl Hg production proportionately (Figures 23-7, 23-8 and 23-14; Chapter 12).

If the main stem of the river was not remediated, sediment removal and replacement at the mouth of Mendall Marsh would need to be continued even after the 100 ng/g dry wt. target in surface soils in the marsh was achieved (Chapter 2 & 21). This is because recovery of the marsh is governed by the riverine Hg source, so it is estimated that recontamination of the marsh would continue until about 2176 (Figure 23-6), when Hg concentrations in the river will have recovered to background levels. However large improvements in the present serious situation could be achieved with periodic additions of clean sediments to maintain total Hg concentrations at about half of their present levels of 490 ng/g dry wt. (Chapter 1) on the marsh platform. If this approach of partial treatment was chosen, it could be ended in about 2046, at which time Hg concentrations in the river would be about half their present levels (Figure 23-6) and then would further decrease with time as natural attenuation in the river proceeded.

5.2 The Use Of Sedimite™ For Remediation Of Mendall Marsh

Several binding agents were added to Mendall Marsh soils in small-scale plots to determine if they reduced the concentrations of methyl Hg in porewaters of the marsh soils (Chapter 19), which would decrease movement of methyl Hg into the lower food web. This series of experiments (Chapter 19) was designed as initial screenings of possible binding agents, so that the most promising candidates could be further investigated and proven as part of a possible future Remediation Program. Two of the binding agents, biochar, and SediMite™ showed some promise.

Experiments were carried out at two sites on the Mendall Marsh platform (Figure 23-19; Chapter 19). From the perspective of methyl Hg bioaccumulation, the pore water data in Figure 23-19 c&d are most important because dissolved methyl Hg enters the base of the food web (Chapter 19).

For the biochar addition plots, concentrations of methyl Hg in pore waters were between about 20% and 60% of the controls over a 12 month period. SediMite™ additions were somewhat more effective (5-50% of controls), but the beneficial effect appeared to wane with time for the SediMite™ plots, but not for the biochar plots (Figure 23-19 c&d). Longer term results for methyl Hg concentrations in porewater will be available soon, when samples from the summer of 2012 have been analyzed.

The effects of biochar and SediMite™ on methyl Hg attached to soil particles (Figure 23-19 a & b) were opposite to the effects on porewater (Figure 23-19 c & d). In both cases methyl Hg in solids were greater, or similar to, concentrations on solids in the control plots, so methyl Hg production was not inhibited by either of the treatments. In the biochar plots, methyl Hg concentrations on the particles (Figure 23-19 a & b) increased with time (in one case up to 250% of control plot concentrations). In the SediMite plots, methyl Hg concentrations on soil particles changed only slightly. These results are consistent with other studies that have shown that binding agents do not necessarily inhibit methyl Hg production, but instead prevent the methyl Hg from moving into the porewater where it can be bioaccumulated (Chapter 19).

One negative effect of adding binding agents is that they could inhibit plant growth, and there was some evidence of this in our small-scale experimental plots (Chapter 19). In both the biochar and SediMite™ plots at the end of the experiment, there were plant species absent, compared to the control plots.

Overall, we recommend the continued exploration of SediMite™ mainly because of the apparent stimulation of methylation in the biochar plots (Figure 23-19 a & b), which could pose a risk at later dates if the methyl Hg stored on the soil particles was released into the soil pore water. The apparent decline of the SediMite™ effect with time on porewater methyl Hg concentrations should be investigated with longer term studies to determine how often SediMite™ would need to be added to the marsh. The minimum effective dosage required should also be investigated. Additionally, there should be more study of impacts on plant communities, for example through binding of essential trace metals like iron, and on methyl Hg concentrations in resident biota.

From a scientific perspective, the best possible treatment for Mendall Marsh would be a combination of either upper estuary mobile sediment removal and replacement (see 2 above), plus treatment with SediMite™, or mobile sediment removal and replacement (see 3 above) followed by treatment with SediMite™. This would quickly lower methyl Hg concentrations in the marsh. The high concentrations of methyl Hg in the porewater (Chapter 11) and biota on Mendall Marsh (Table 23-2, Figures 23-14 & 23-17, Chapter 14, Phase 1 report) require a target concentration of 100 ng/g dry wt., which would achieve a target concentration in bird blood (Chapters 2 & 21).

6 REFERENCES

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Table 23-1: Percent contribution of benthic-based food chain items to higher food chain organisms. Unless otherwise stated, the remainder of the 100% is from pelagic food sources. These results are obtained from stomach content analysis and/or stable isotope analyses, see Chapter 16 for detailed results.

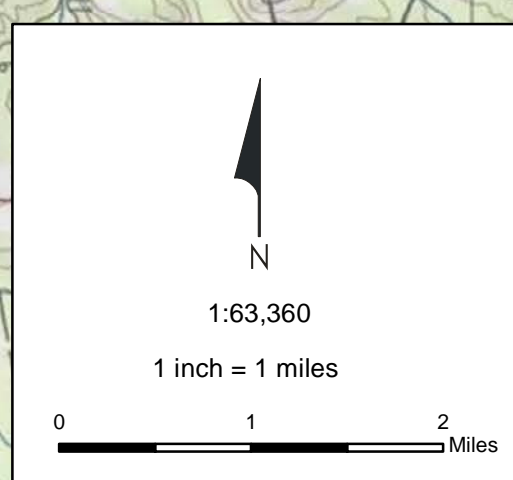
Species	OV %	BO %	OB %	ESTUARY %
Mussels				0
Lobster				55-671
Tomcod			742	442
Smelt			9	9
Mummichog			903	
Am. Eel	79	98	97	
Black duck ⁴			100	100
Winter flounder ⁴			100	100

1. estimates based on stable isotope analyses and reports in the literature; non-benthic prey consumed by lobster primarily trap bait (Atlantic herring)
2. Crangon shrimp and gammarids: epi-benthic invertebrates
3. 90 % of food was insects of terrestrial or benthic sources
4. benthic-based diet estimated from numerous reports in the literature (see Chapter 16)

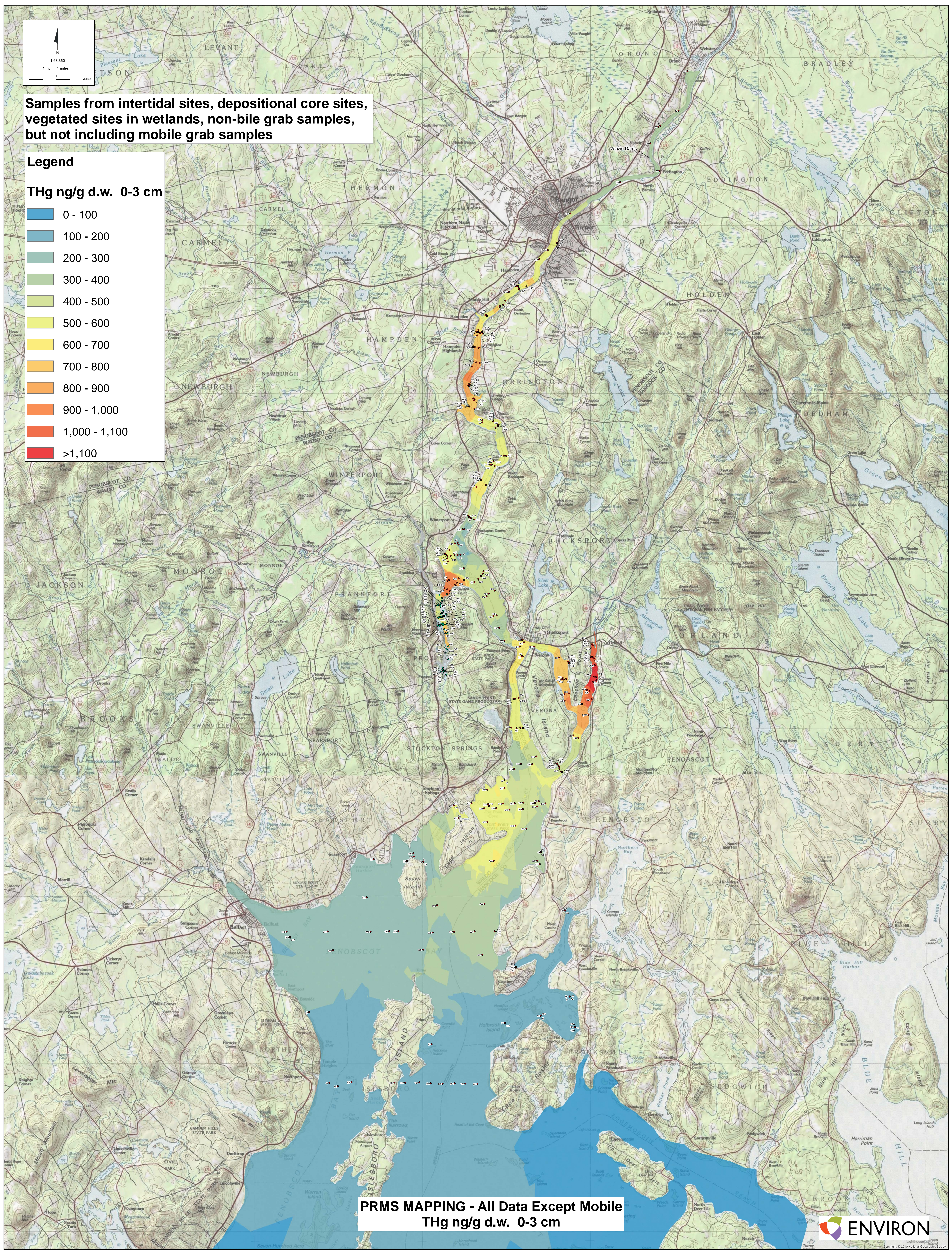
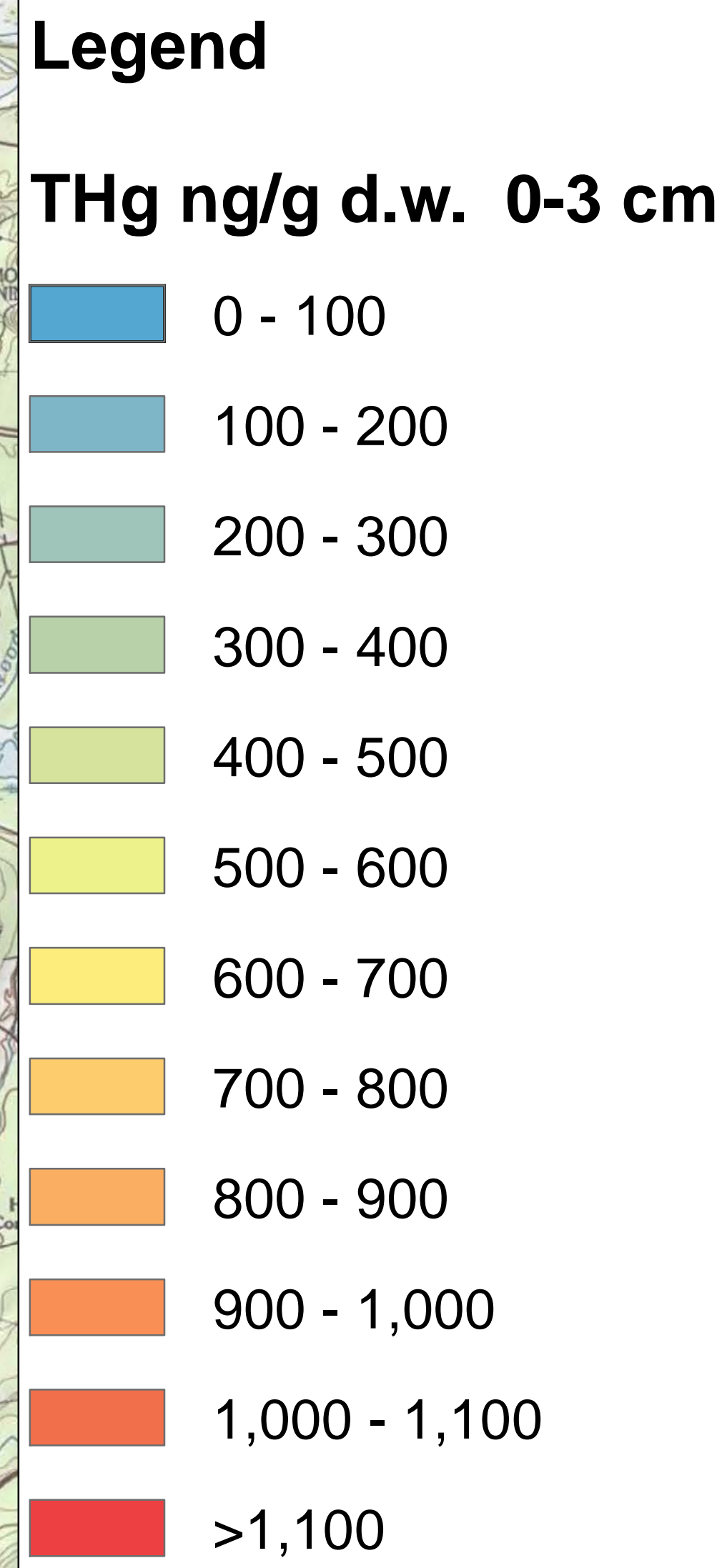
Table 23-2: Mean concentrations of Hg in birds and bivalves from the upper estuary of the Penobscot compared to reference sites in non-contaminated areas upstream or along the outer coast. See Chapters 2, 17, Appendix 1-2 & 1-3 of Chapter 1.

Biota group		Upper estuary Penobscot µg/g total Hg wet wt.	Non Hg contaminated estuaries. µg/g total Hg wet wt.	Remarks
Nelson's sparrows	blood	3-8	0.4-0.8	coastal reference sites
Song Sparrows	blood	0.5-3.5	0.01-0.5	upstream of Veazie Dam and coastal reference sites
Swamp sparrow	blood	1.5-3.5	0.06-0.7	upstream of Veazie Dam and coastal reference sites
Redwing blackbird	blood	2-8	0.2	coastal reference site
Black Duck	blood	0.8	0.1	coastal reference site
Virginia Rail	blood	1.5-3.5	0.2-0.4	Coastal and inland reference sites
Mussels	whole body	0.4-1.2 µg/g dry wt.	0.1-0.2 µg/g dry wt.	upper Estuary vs Penobscot Bay

Figure 23-1. Concentrations of total Hg in the top 3 cm of sediments in Penobscot Bay and in the Penobscot River downstream of Veazie Dam. These are kriged (smoothed) plots of Hg concentrations in surface sediments, which are intended to give a general understanding of the distribution of Hg concentrations in surface sediments over a wide area.



Samples from intertidal sites, depositional core sites, vegetated sites in wetlands, non-bile grab samples, but not including mobile grab samples



PRMS MAPPING - All Data Except Mobile
THg ng/g d.w. 0-3 cm

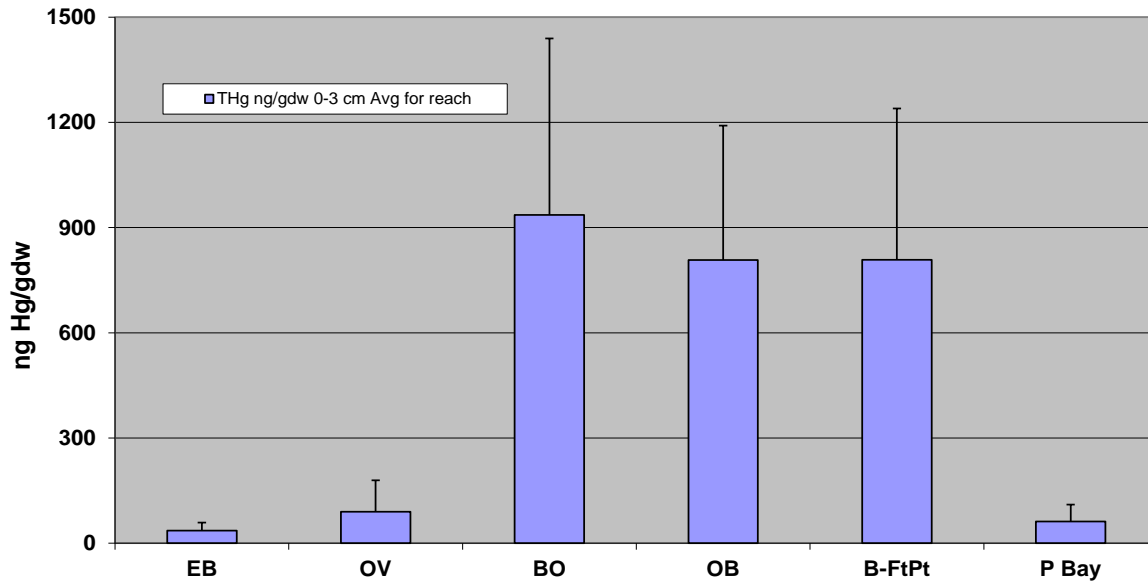


Figure 23-2. Total Hg concentrations in intertidal sediments (0-3 cm) in the Penobscot River and Estuary (average of 6 sampling periods in 2006 and 2007). EB = east branch of the river above all industries, OV = the reach of the river between old town and Veazie Dam, BO = the reach of the river from Brewer to Orrington, OB = the reach of the river from Orrington to Bucksport, B-FtPt = the river from Bucksport to Fort Point including the Orland River, and P. Bay = Penobscot Bay.

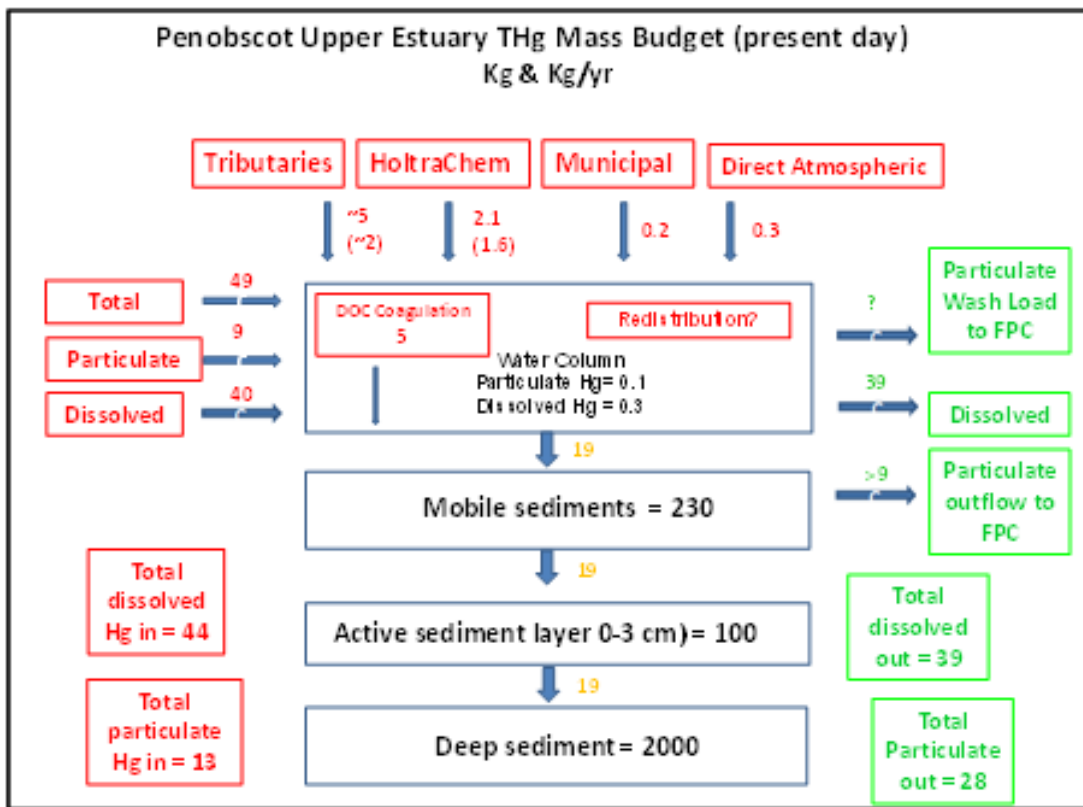


Figure 23-3. Estimated annual inputs (red), outflows (green) and burial (yellow) of total Hg in the Penobscot upper estuary. Masses of total Hg in the water column and sediments or wetland soils are in black lettering. Units of fluxes are Kg Hg/yr. Units of mass are Kg.

Total in = (49+5+2.1+0.2+0.3) = 57 Kg Hg/yr, total out = (39+19+9) = 67 Kg Hg/yr

Total out is greater because contaminated particles are settling and being replaced by cleaner particles, system not at steady state. Note that the Particulate outflow to FPC is a minimum estimate, based on sedimentation within FPC. Additional particulate Hg might sediment further south of Fort Point.

Dissolved and particulate total Hg over Veazie from Chapter 3.

Tributary inputs see Chapter 3.

Atmospheric input is direct input onto water surface, calculated from 10 $\mu\text{g}/\text{m}^2/\text{yr}$ and area of 31.6 km^2 from Veazie Dam to Fort Point

HoltraChem site and Municipal inputs from Chapter 3, R Turner

Water column masses from average Hg concentration and water column volume

Mobile sediment masses from Geyer et al., Chapter 7 and average total Hg concentration from Chapter 8.

Active sediment layer mass from average 0-3 cm THg concentration in surface sediments (885 g ng/g dry wt., Table 1, Chapter 1 in low elevation, intertidal, and depositional samples), average bulk density (0.67 g/cm^3) and depositional area = 5.6 km^2 (Chapter 5)

Deep sediment mass from Yeager-Santschi core inventories and depositional areas for each subarea, Chapter 5

Sediment Accumulation rates from Yeager-Santschi core data and depositional areas (Chapter 5), calculated individually for main stem of river, Mendall Marsh, and Orland River sub-areas, and summed.

Particulate outflow to Fort Point Cove (FPC) estimated as mass of Hg sedimenting onto depositional area, using sediment accumulation rates from Yeager-Santschi core data and depositional area from Chapter 5. This is a minimum estimate, because additional particles likely sediment south of Fort Point.

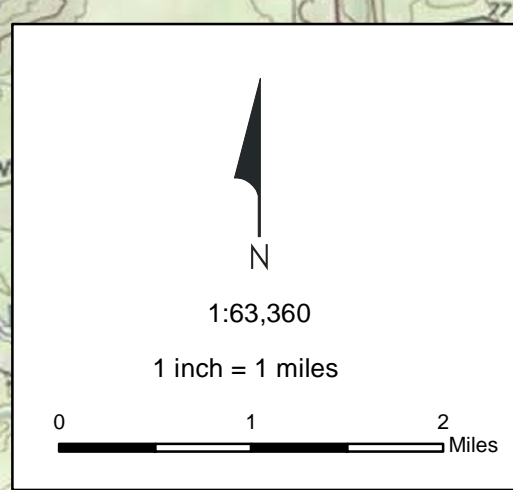
For calculations, all of the above, see "Upper Estuary Mass Balance September 23 CK Mar 27 2013.xlsx"

DOC coagulation from ratio of Hg to DOC = 0.36 in "WQ data lat long 2008_2009_2010 October 16_2011 CK Feb 13a.xlsx", and coagulation in "Upper Estuary Mass Balance September 23 CK Mar 27_2013.xlsx". Gross coagulation of Hg was used, because Hg not expected to return to water, even though we estimate that 50% of the OC will be decomposed.

Particles out = (19+9=28) Kg/yr. There could be some escape by "wash load", which is flow through of particles that enter over Veazie Dam and never mix with the mobile pool, and additional particles that don't sediment in FPC, but exit further to the south.

Dissolved Hg out = Dissolved in minus coagulation. This could be an overestimate, if some dissolved Hg adsorbs to particles as it passes through the system, or is converted to DGM and fluxes to the atmosphere.

Figure 23-4. Maximum total Hg concentrations in buried sediments estimated to have been deposited in 1967 -1970 during peak years of release of Hg from the HoltraChem plant (original data in Chapter 6).



Legend

Deep Peak (Hg maximum), ng THg/gdw

- 0 - 800
- 800 - 1,000
- 1,000 - 1,500
- 1,500 - 2,000
- 2,000 - 3,000
- 3,000 - 4,000
- 4,000 - 10,000
- 10,000 - 15,000
- 15,000 - 20,000
- >20,000

Note: Some higher deep peaks in MM than elsewhere, but not really high enough to predict the really high inventories at the distal end of the marsh.

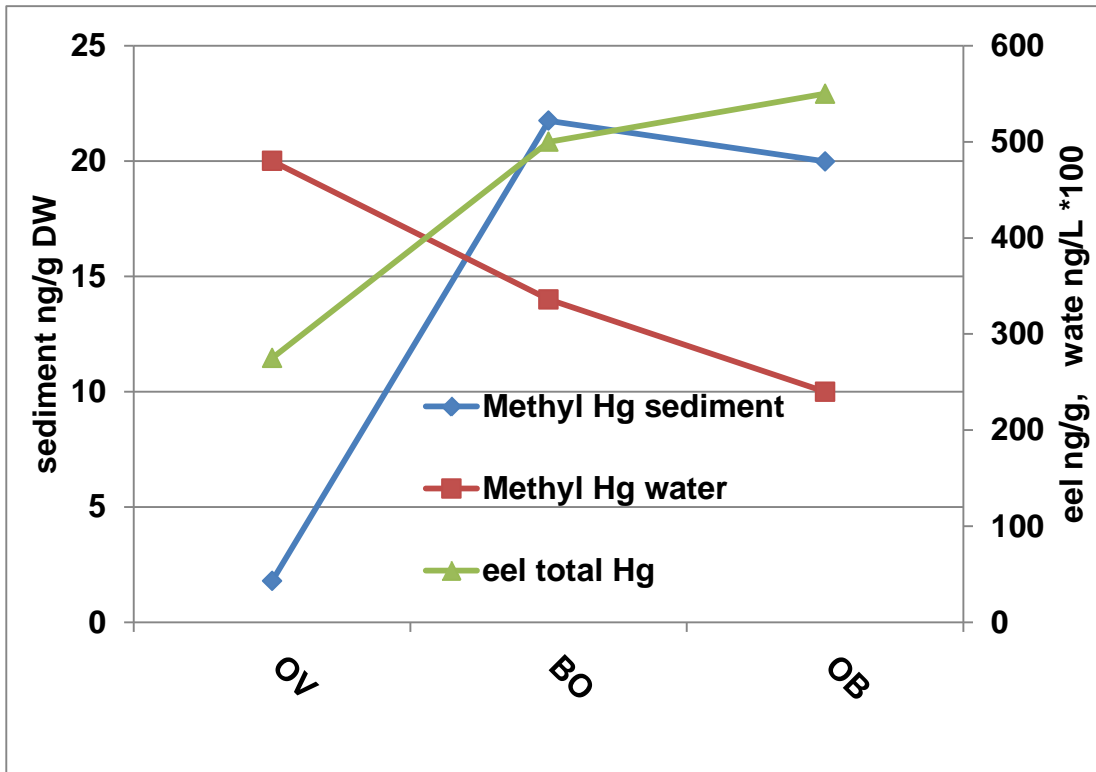


Figure 23-5. Concentrations of methyl Hg in surface sediments water and total Hg in American eels taken from the Old Town to Veazie (OV) reach, above Veazie Dam, and from the Brewer to Orrington (BO) and Orrington to Bucksport (BO) reaches below the Veazie Dam.

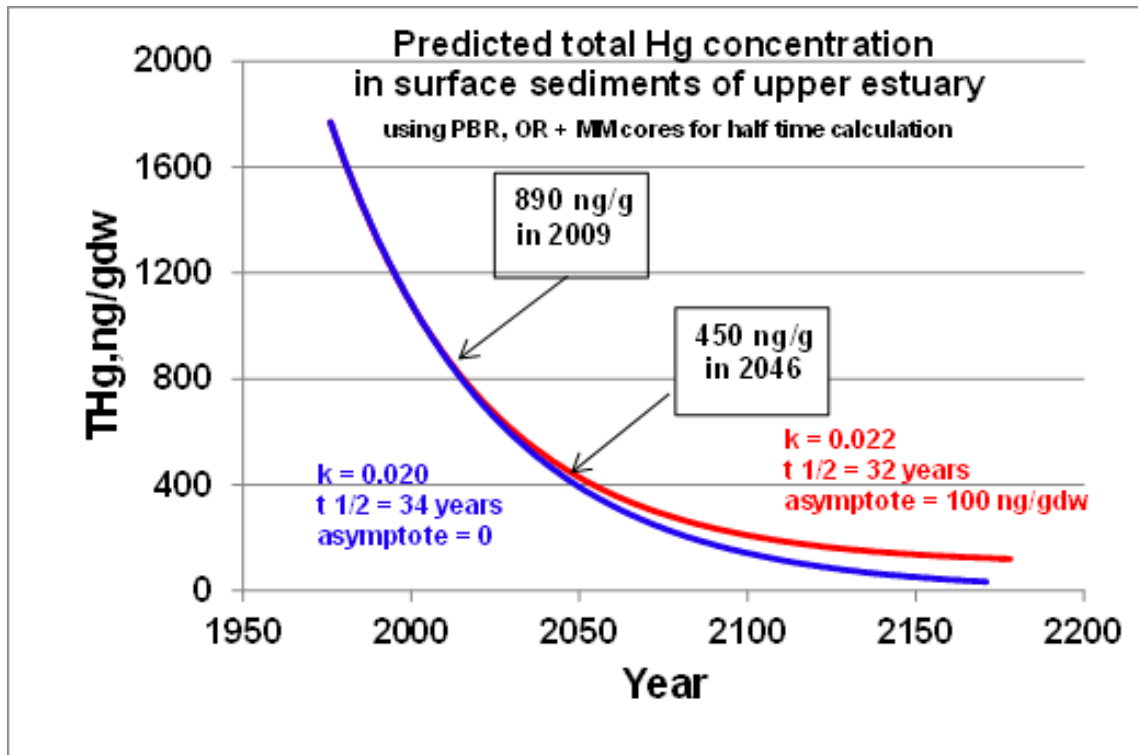


Figure 23-6. Predicted natural attenuation of total Hg concentrations in sediments of the main stem of the Penobscot River. The blue line is from the core data, using an expected asymptote of zero; the red line is adjusted to fit the past time period of 21 years of data, and also to fit an eventual background concentration of 100 ng/g dry wt.

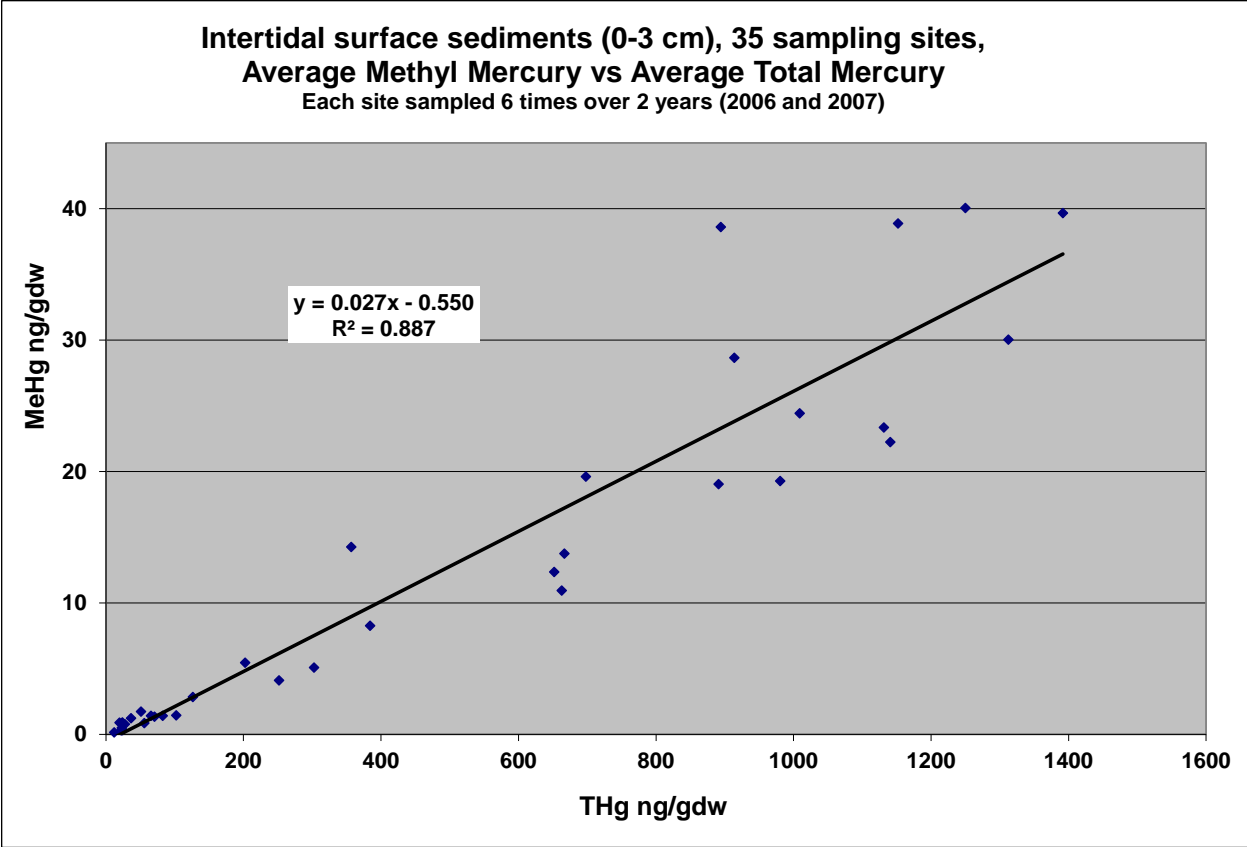


Figure 23-7. Concentrations of total Hg vs. methyl Hg in surface intertidal sediments of the Penobscot River and Estuary, demonstrating that concentrations of methyl Hg produced in the sediments are directly related to concentrations of total Hg.

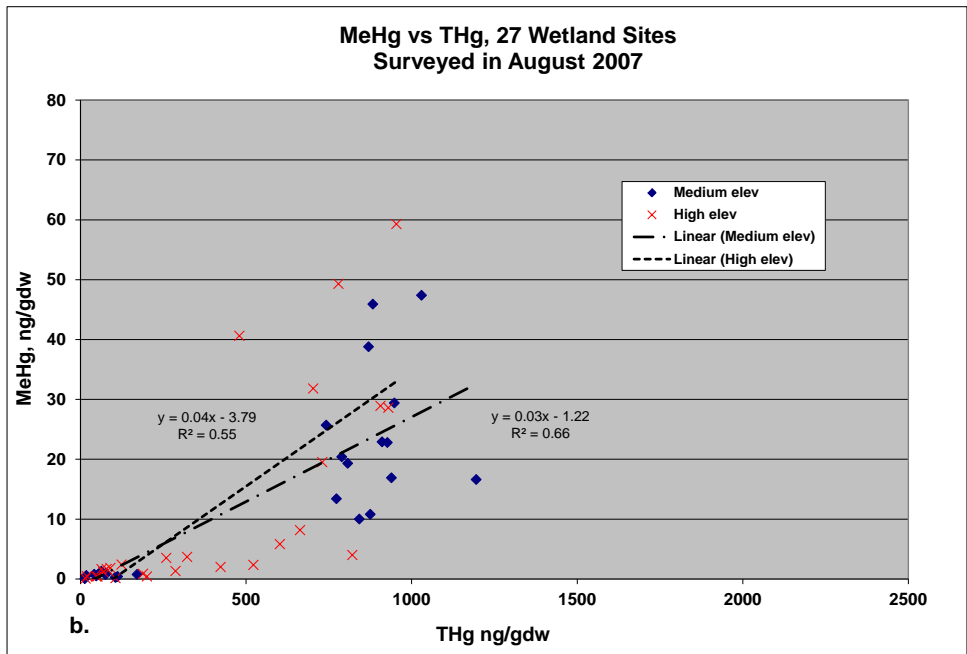
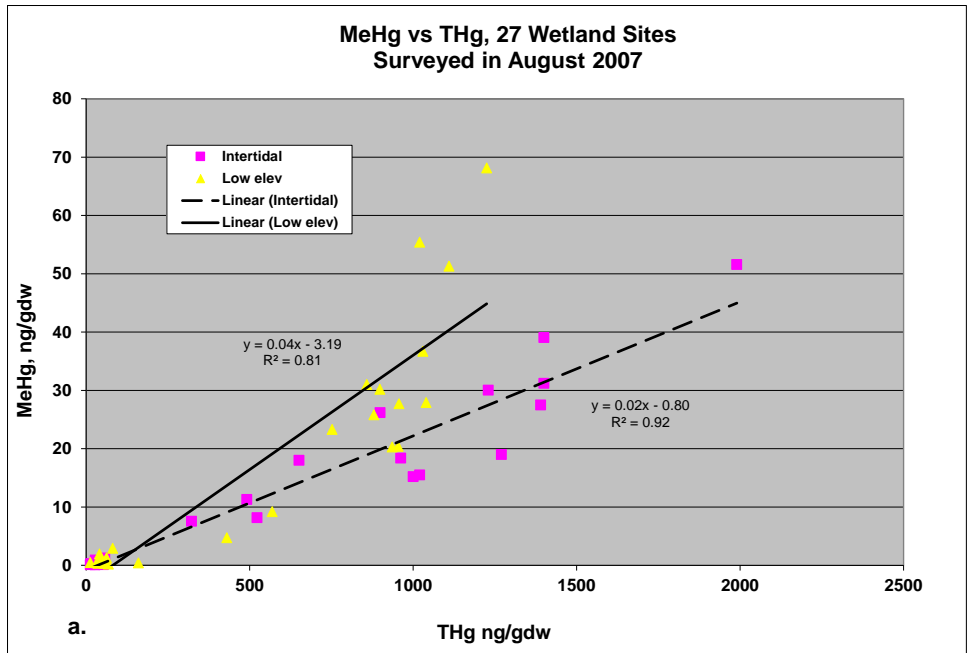


Figure 23-8. Concentrations of total Hg vs. methyl Hg in the surficial wetland soils, demonstrating that concentrations of methyl Hg, which is produced in the surface soils, are directly related to concentrations of total Hg in the surface soils.

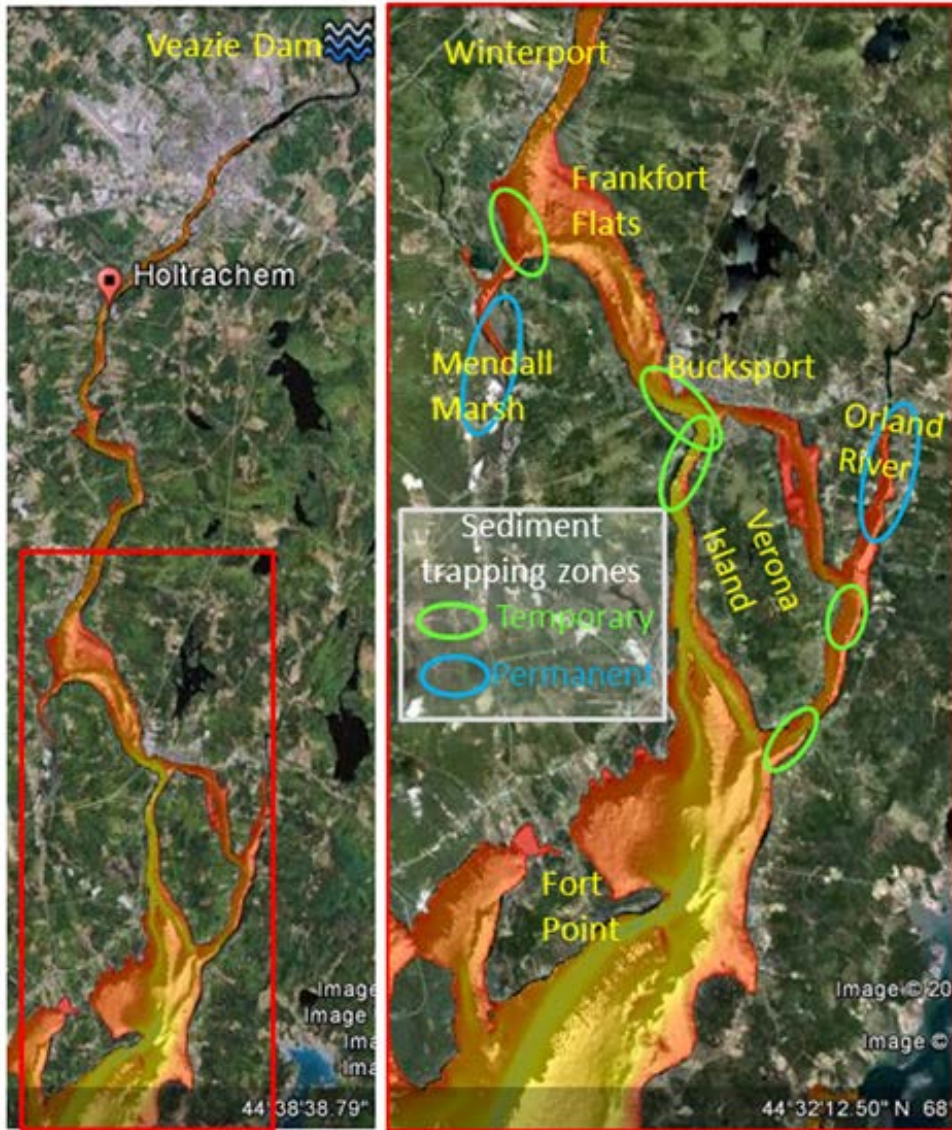


Figure 23-9. Aerial image of the Penobscot River study area. NOAA bathymetry is shown and the HoltraChem site, Veazie Dam, and other locations of interest are noted. On the right, regions of enhanced estuarine sediment trapping at temporary (seasonal) and longer time scales are indicated.

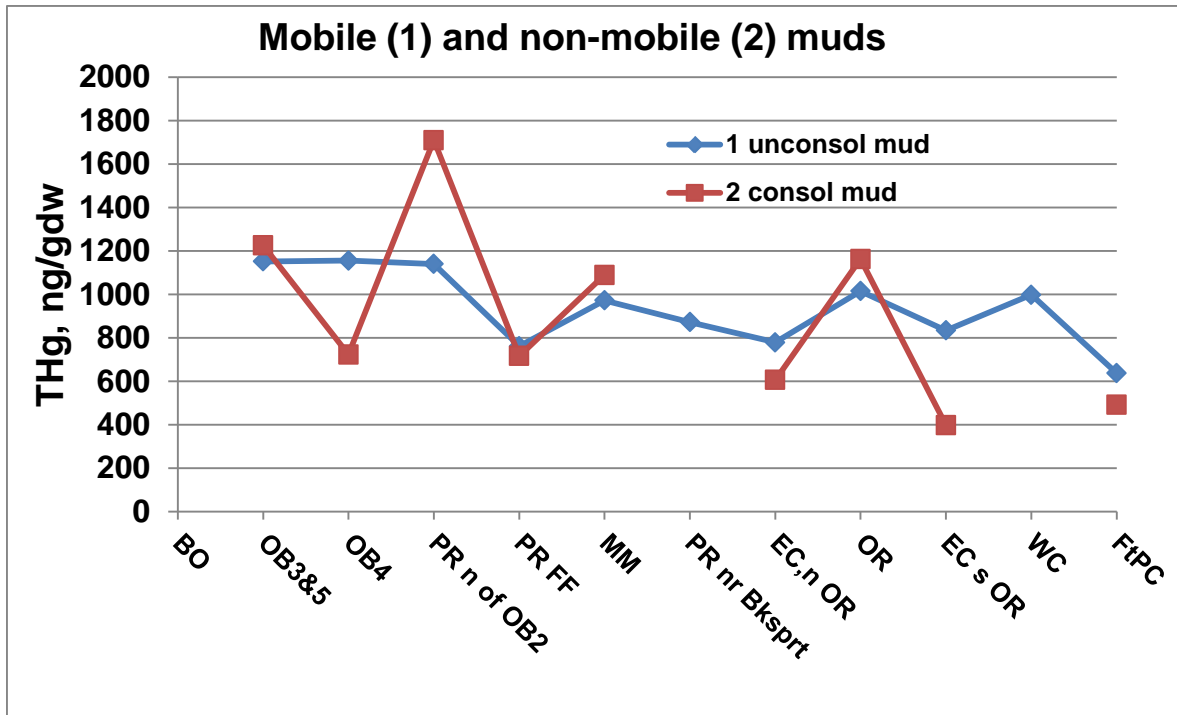
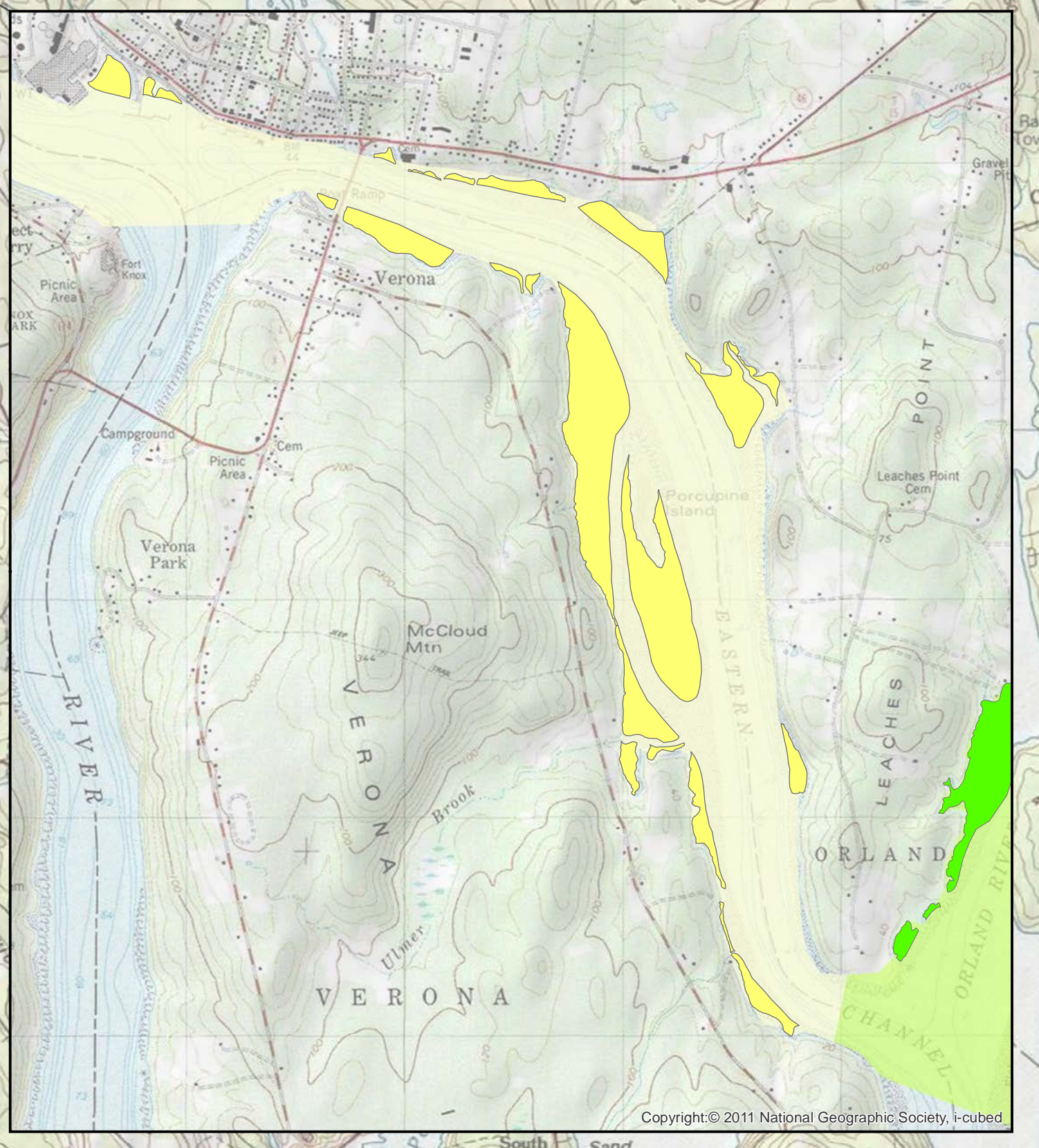
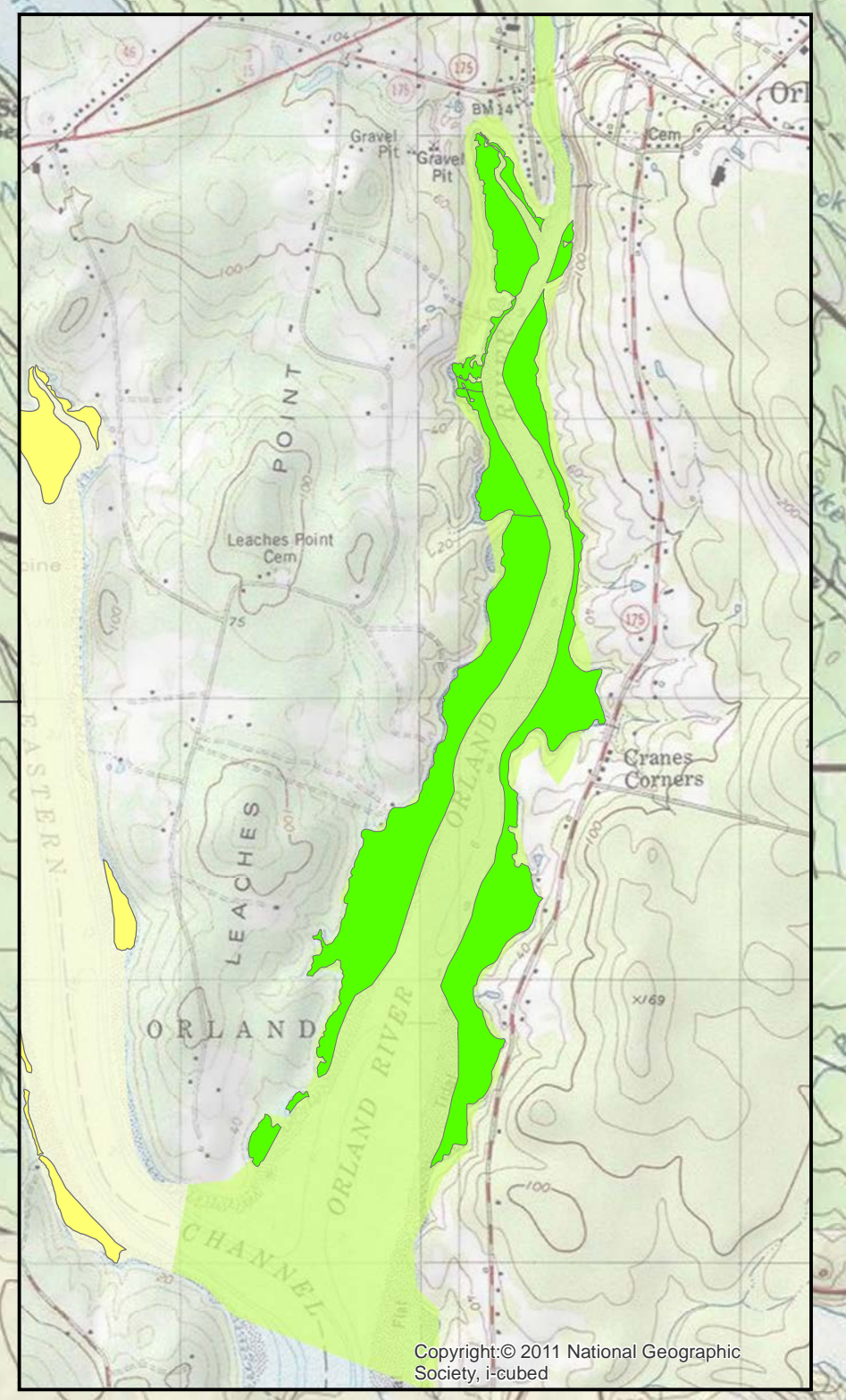
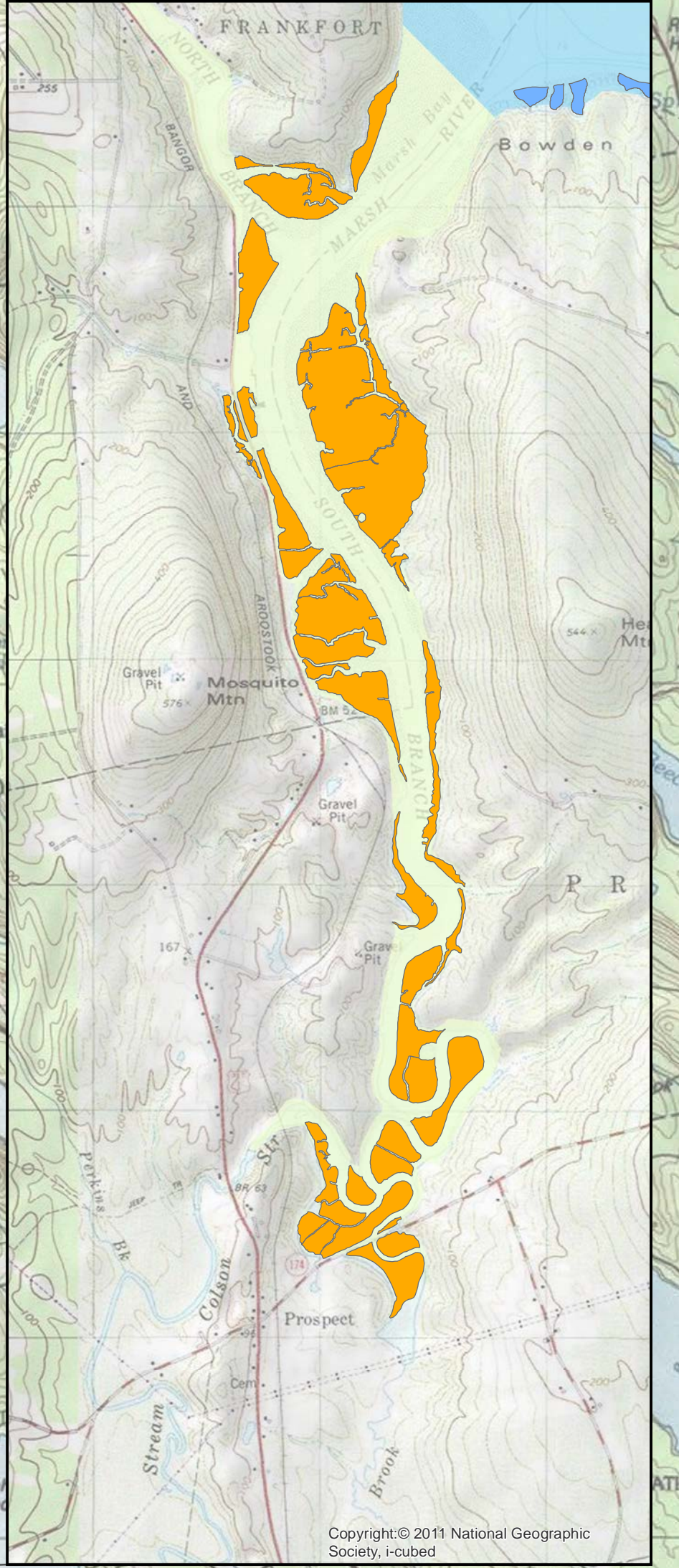
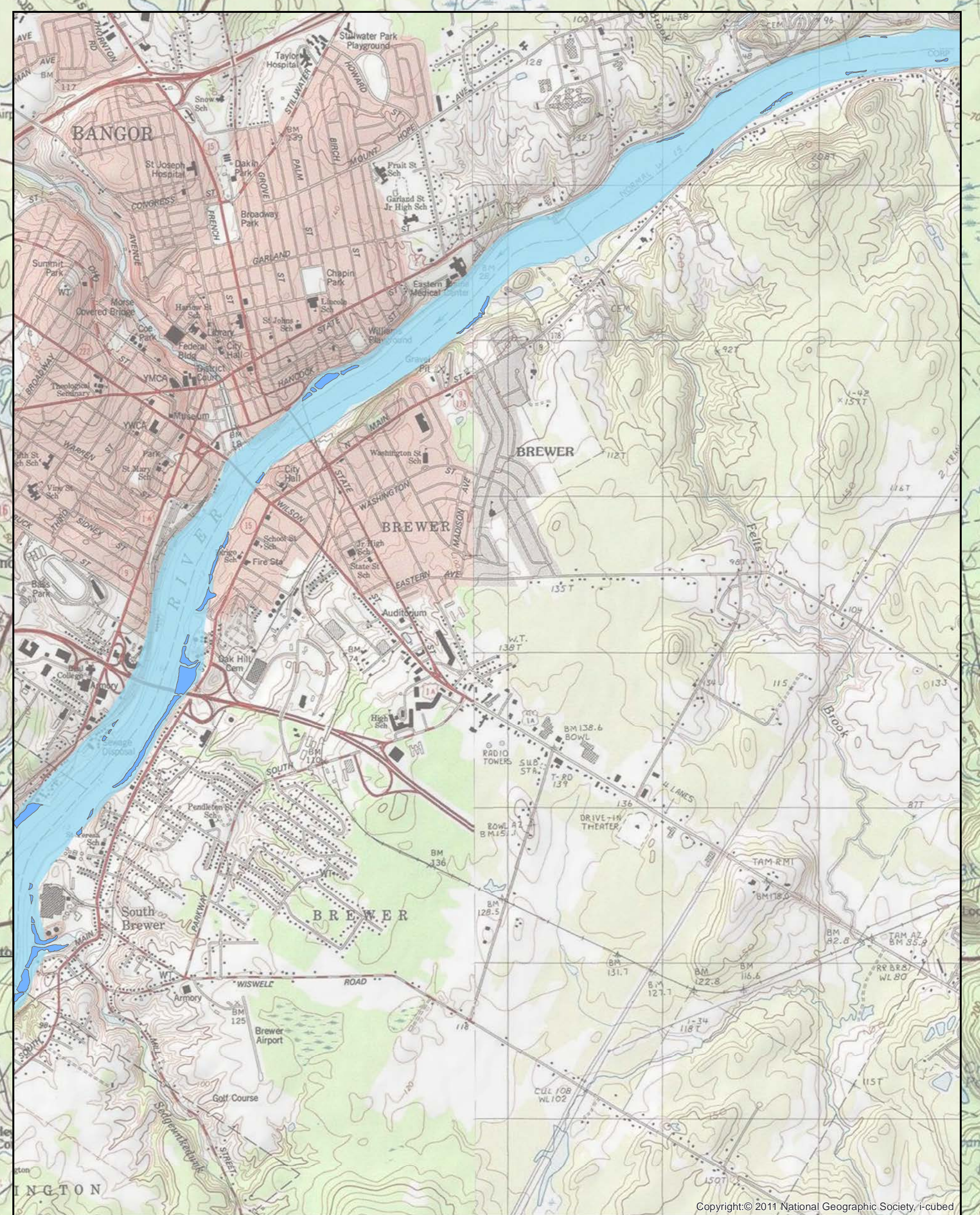
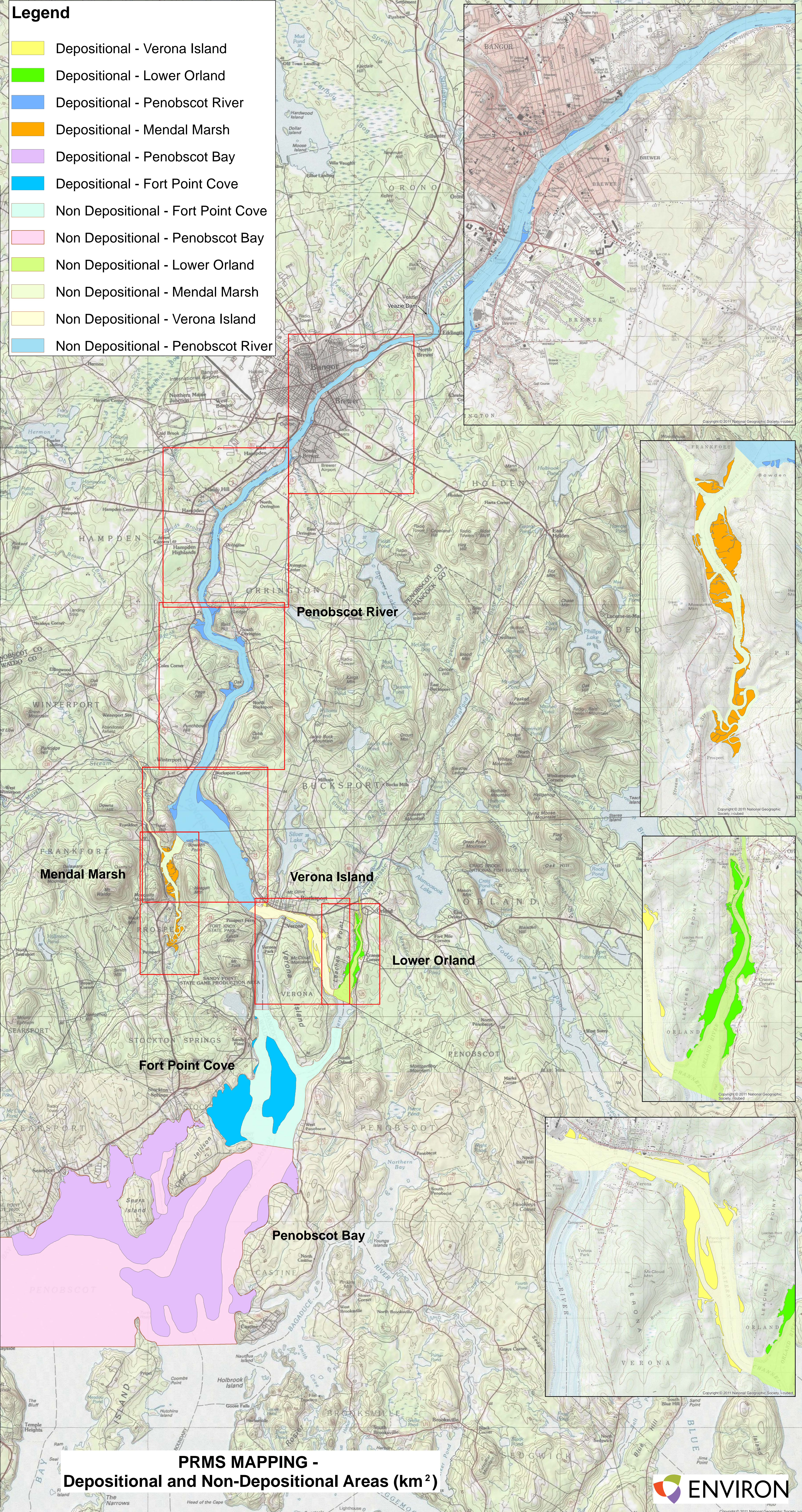
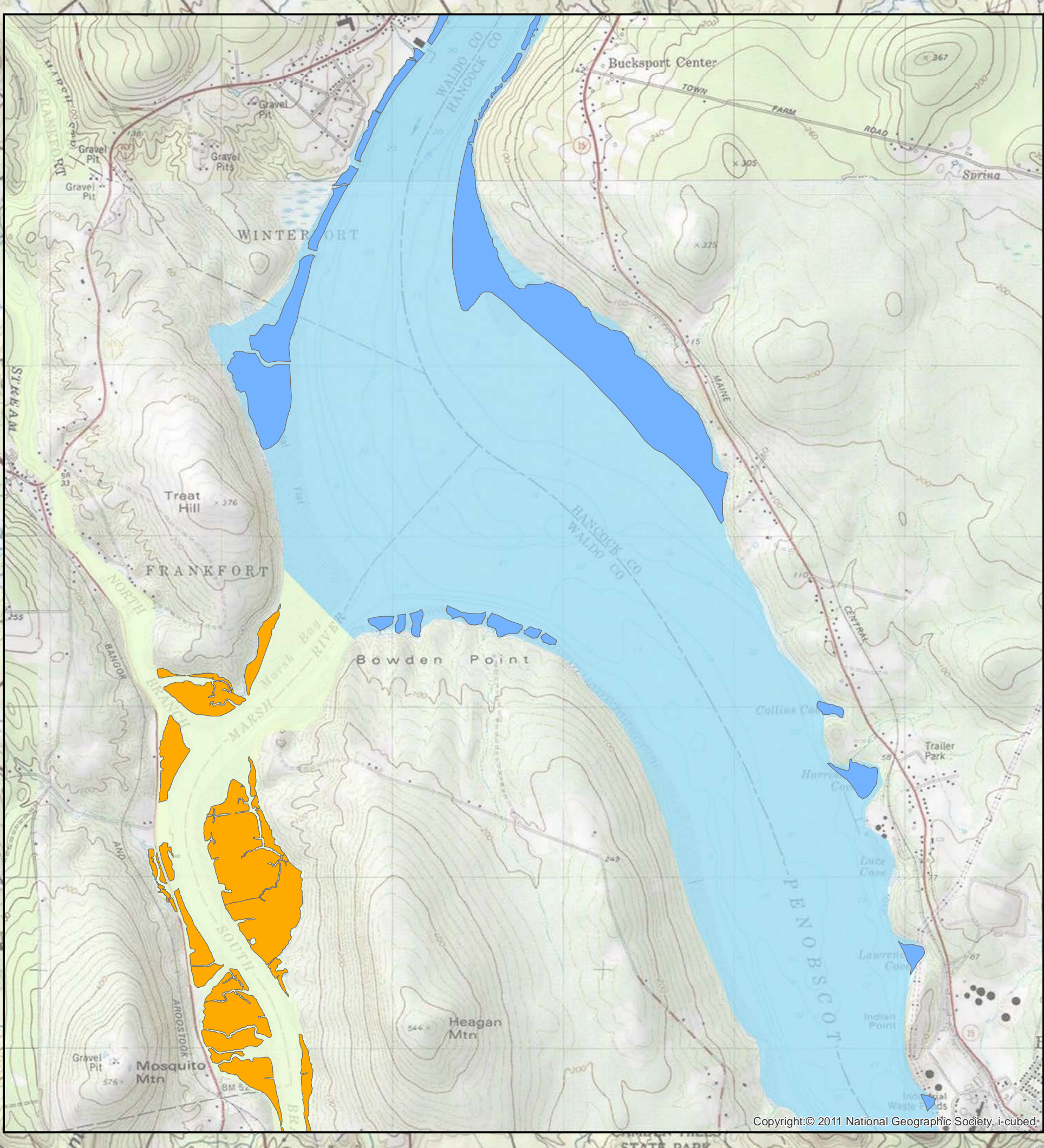
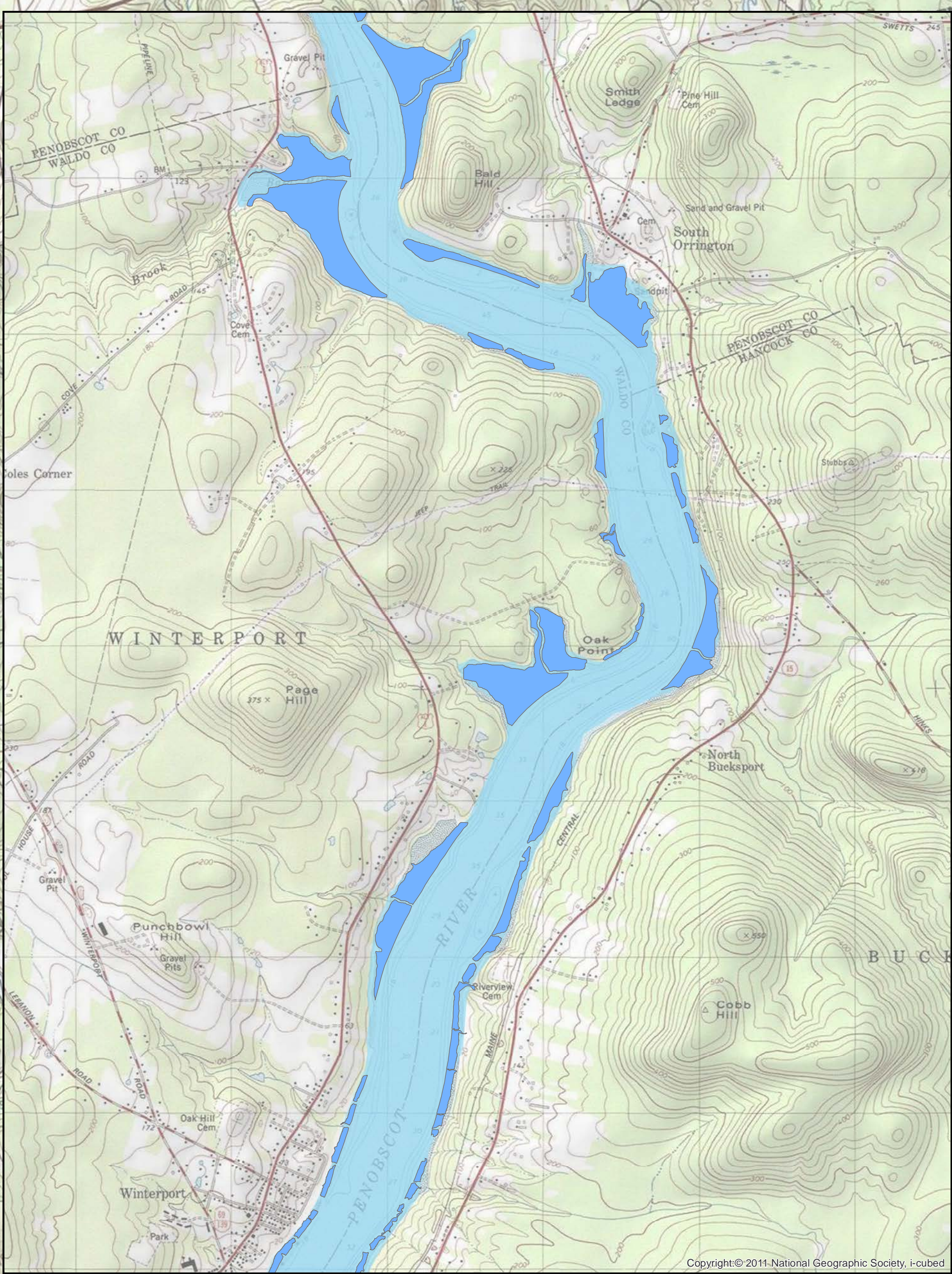
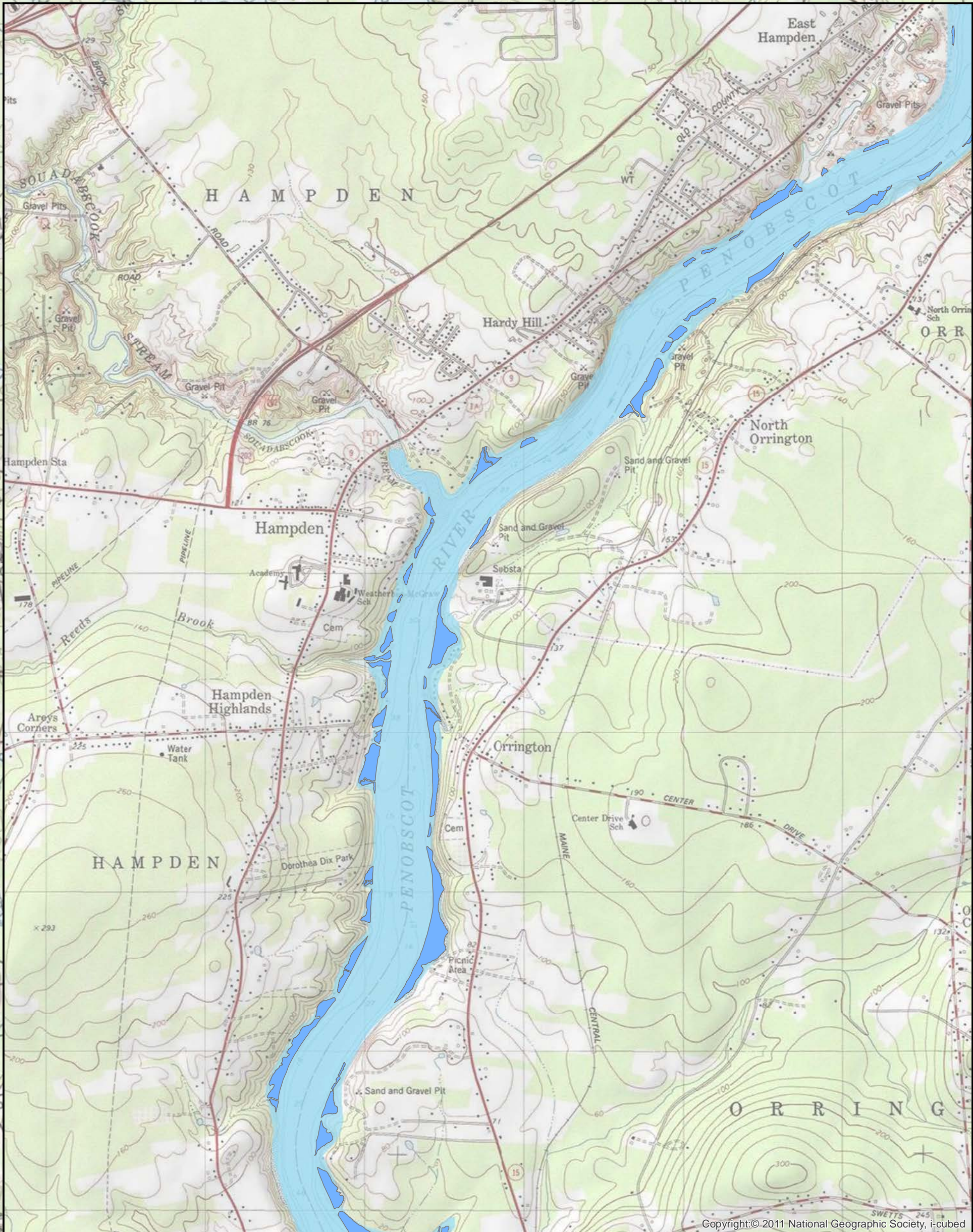
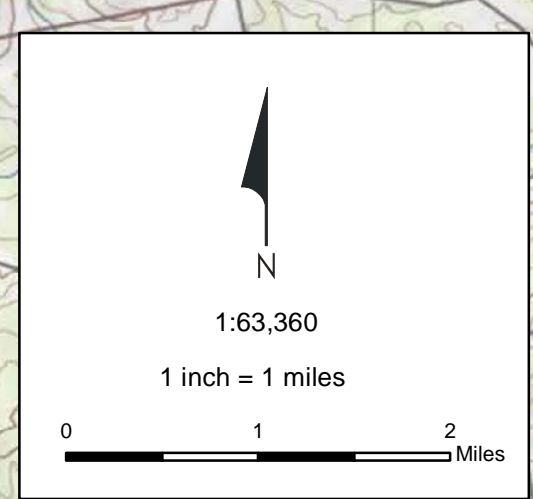


Figure 23-10. Concentrations of total Hg in the “new mud” (i.e. unconsolidated fine grained material) in the mobile sediment pool, and “old muds”, which is fine grained material in the surface sediments of long term depositional areas. BO = Brewer to Orrington reach, OB3&5 = sites 3 and 5 in Orrington to Bucksport reach, PR n of OB2 = Penobscot River north of site OB2, PR FF = Penobscot River at Frankfort Flats, mm = Mendall Marsh, PR nr Bksprt = Penobscot River near Bucksport, EC,n OR = east channel of Verona Island north of the Orland River, WC= west channel of Verona Island, FtPc = Fort Point Cove

Figure 23-11. Sites of long term sediment deposition in the Penobscot estuary

Legend

- Depositional - Verona Island
- Depositional - Lower Orland
- Depositional - Penobscot River
- Depositional - Mendal Marsh
- Depositional - Penobscot Bay
- Depositional - Fort Point Cove
- Non Depositional - Fort Point Cove
- Non Depositional - Penobscot Bay
- Non Depositional - Lower Orland
- Non Depositional - Mendal Marsh
- Non Depositional - Verona Island
- Non Depositional - Penobscot River



**PRMS MAPPING -
Depositional and Non-Depositional Areas (km²)**



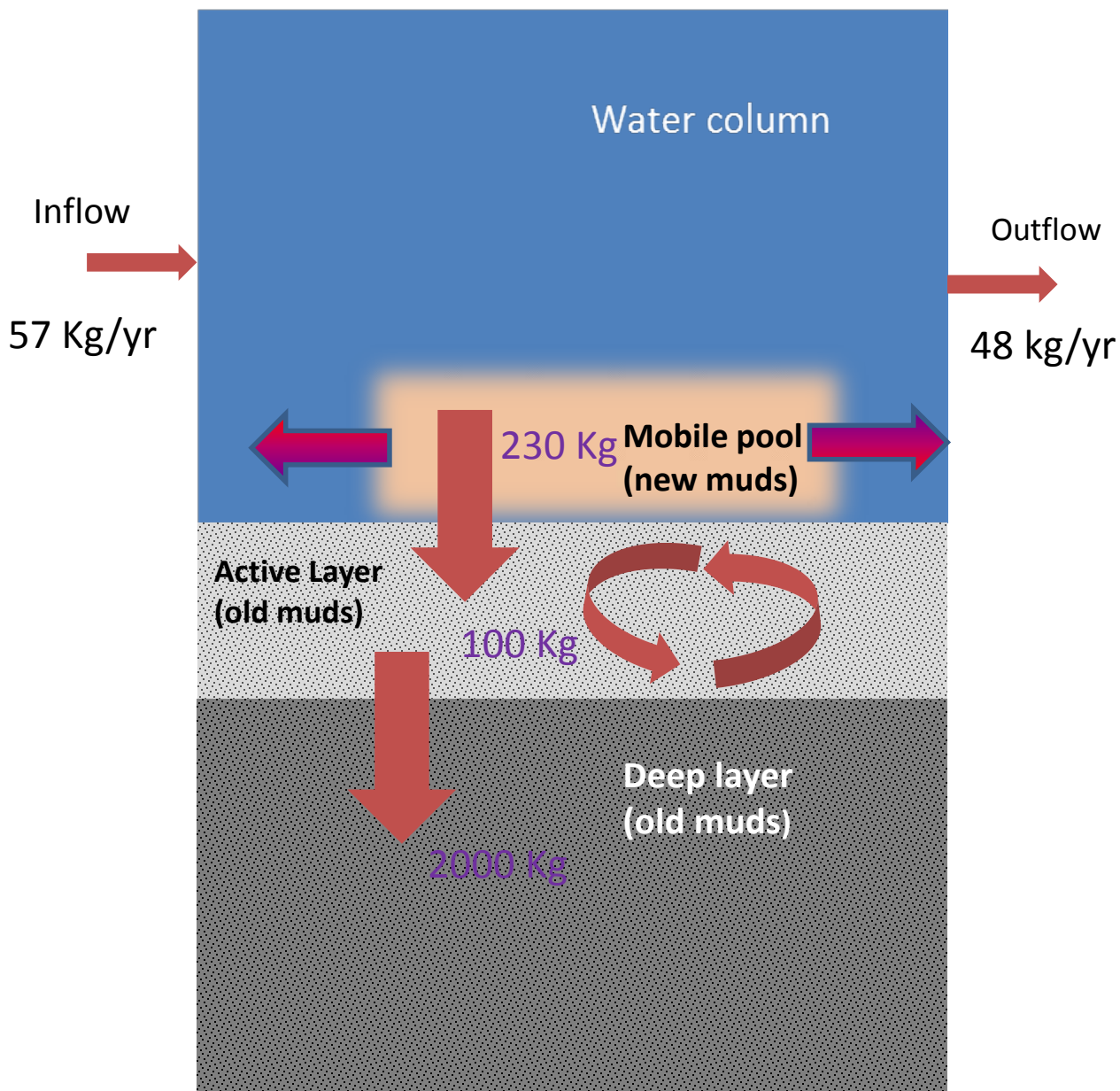
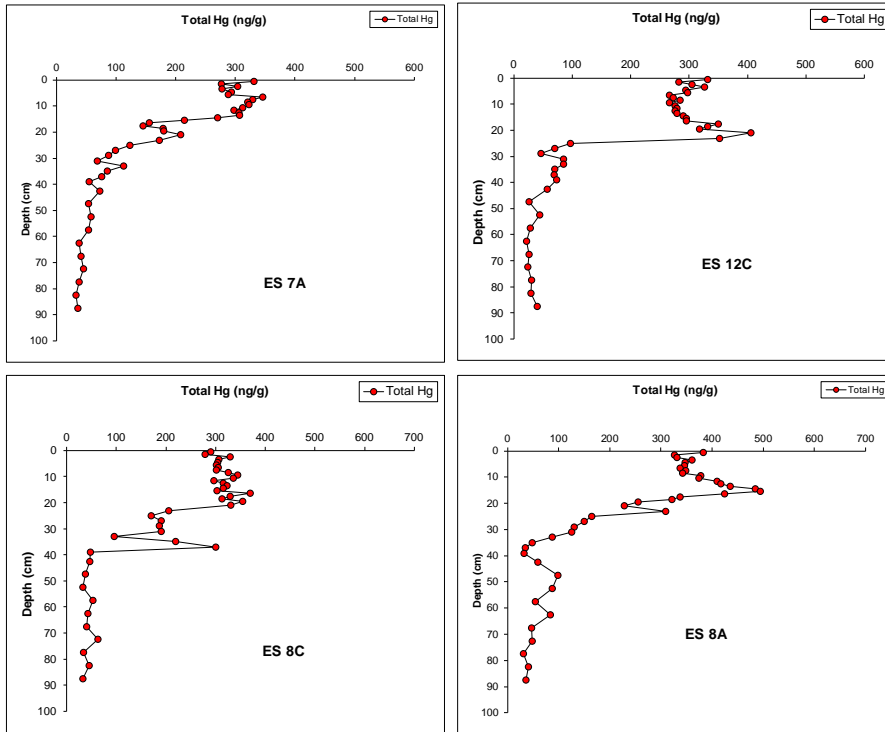


Figure 23-12. Conceptual diagram of the mobile sediment pool feeding surface sediments. Also shown are the inventories of Hg in the mobile sediment pool, the active layer where methyl Hg is formed, and the deep layer of sediments, as compared to annual inflows and outflows of Hg from the upper estuary. The details of inflows and outflows are given in Figure 23-3.

A



B

Figure 23-13. Depth profiles of total Hg concentration in a transect of cores located in Penobscot Bay south of Fort Point (b), showing very low total Hg concentrations at depths below about 30 cm below the sediment-water interface.

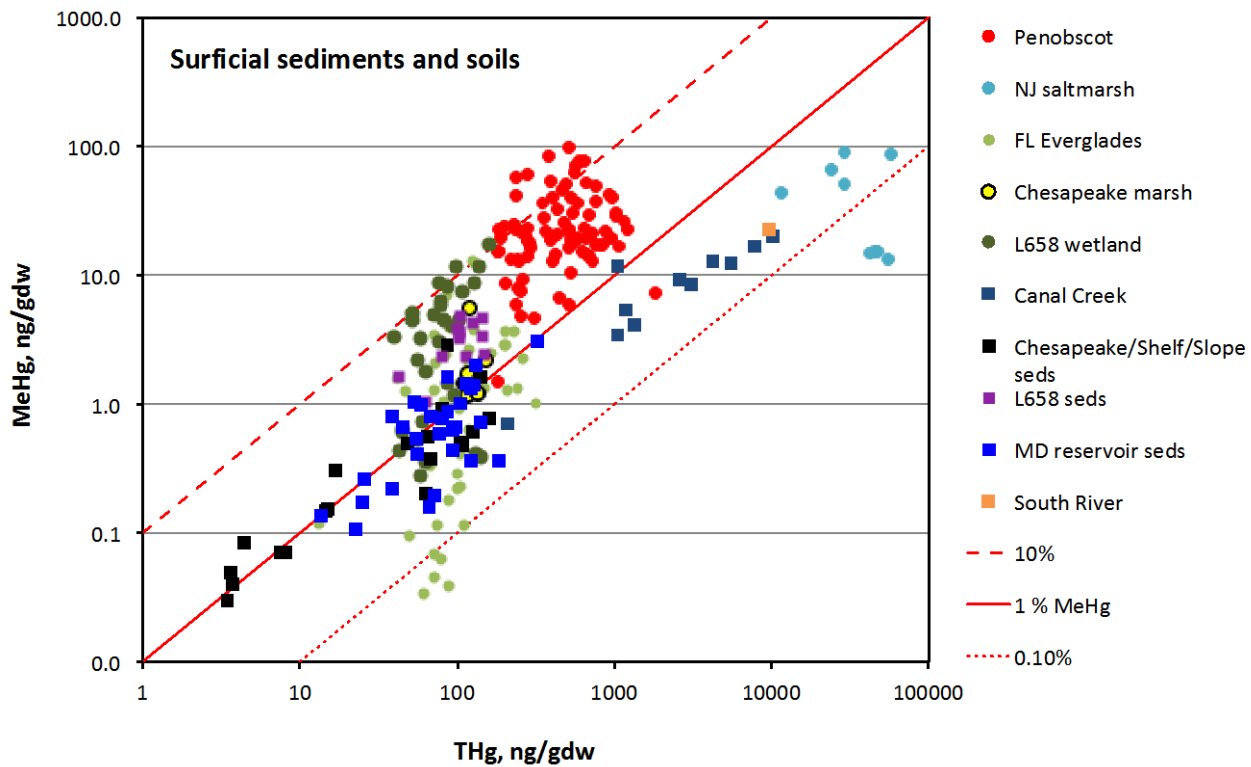


Figure 23-14. Concentrations of methyl Hg and % methyl Hg in pore waters at different locations showing the very high concentrations of methyl Hg and % methyl Hg in Mendall Marsh (see Chapter 11).

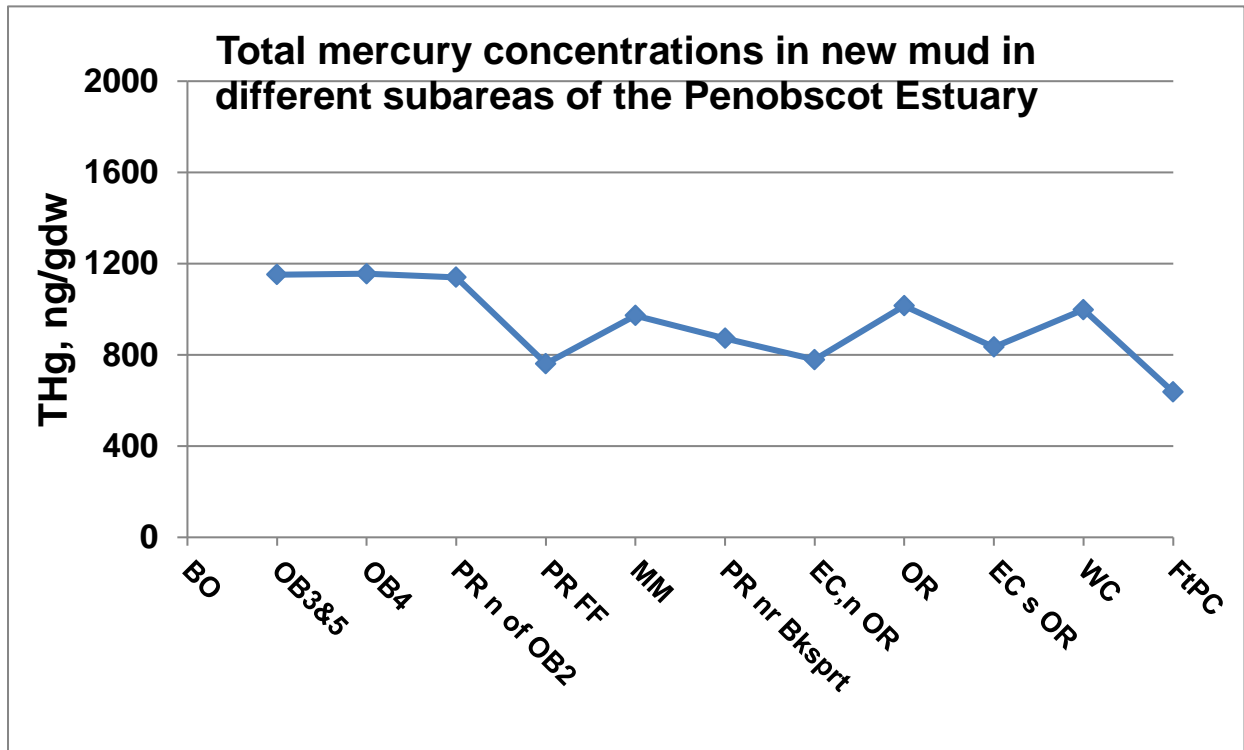
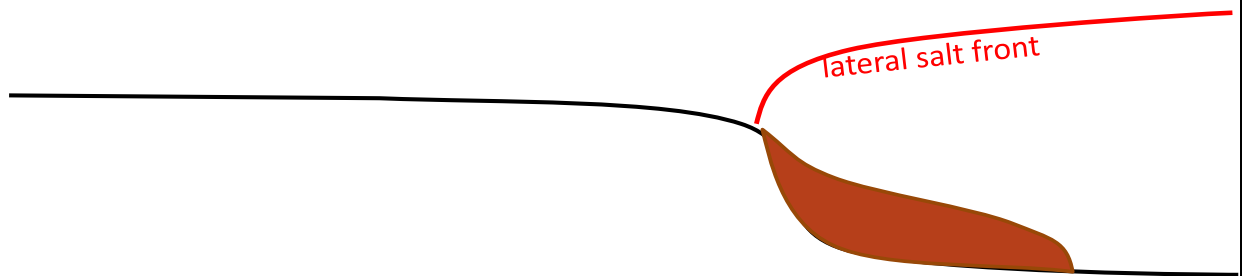


Figure 23-15. Concentrations of total Hg in new muds, a constituent of the mobile sediment pool, at various locations in the upper estuary of the Penobscot (OB = Orrington to Bucksport reach, PR = Penobscot River, FF = Frankfort Flats, MM = Mendall Marsh, Bksprt = Bucksport, EC = East Channel of Verona Island, OR = Orland River, WC = West Channel of Verona Island, FtPC = Fort Point Cove).

Trapping in side embayments

early flood tide— sediment remobilized in channel



high tide— sediment carried into side embayment

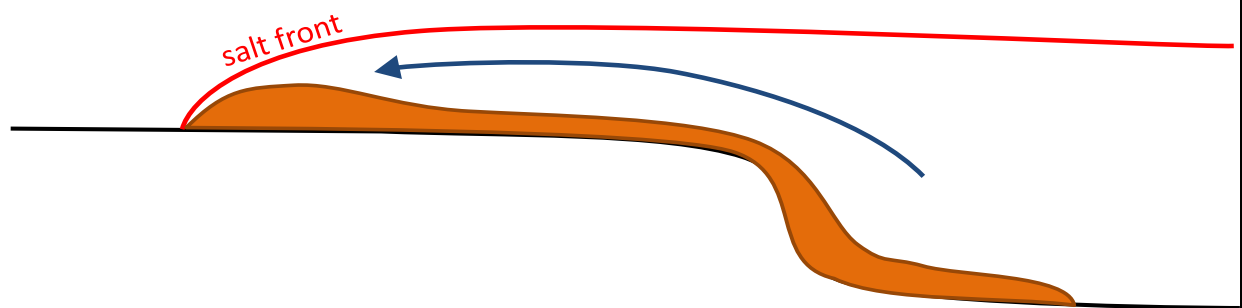


Figure 23-16. Conceptual diagram of mobile sediments being trapped at the salt front in the main stem of the river (upper panel), followed by movement into “side embayments” (such as Mendall Marsh and the lower Orland River) during high tides (bottom panel).

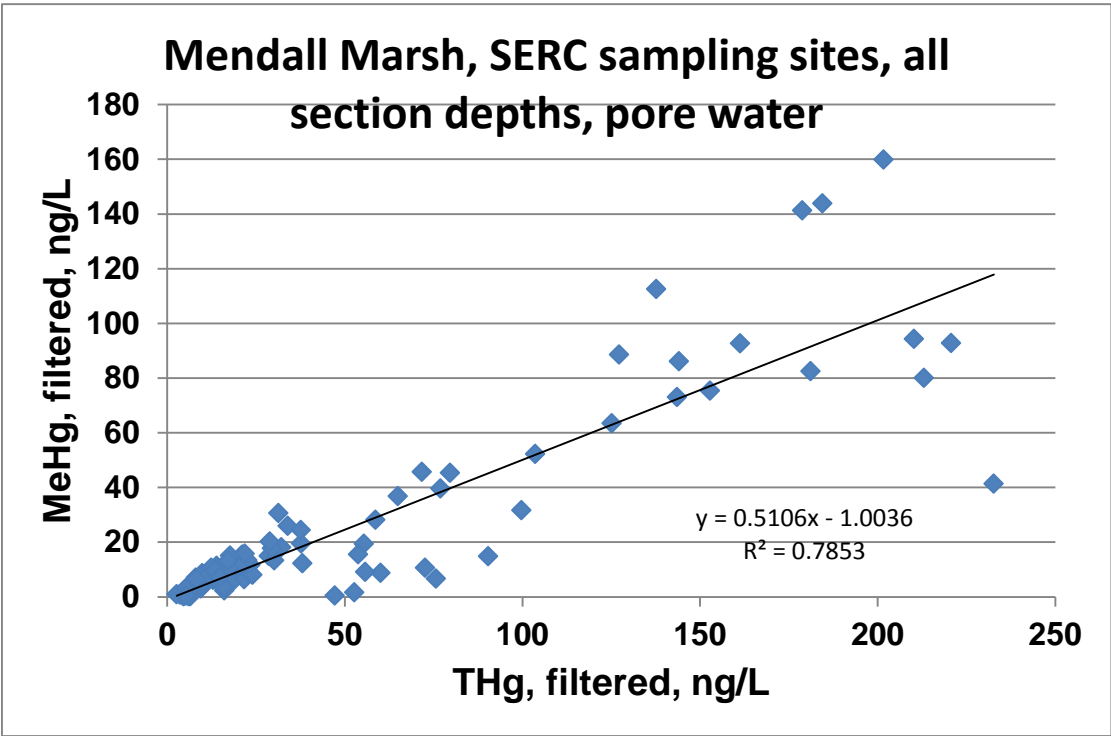


Figure 23-17. Concentrations of methyl Hg as a function of total Hg in the porewaters of the Mendall Marsh platform (original data presentation in Chapter 11).

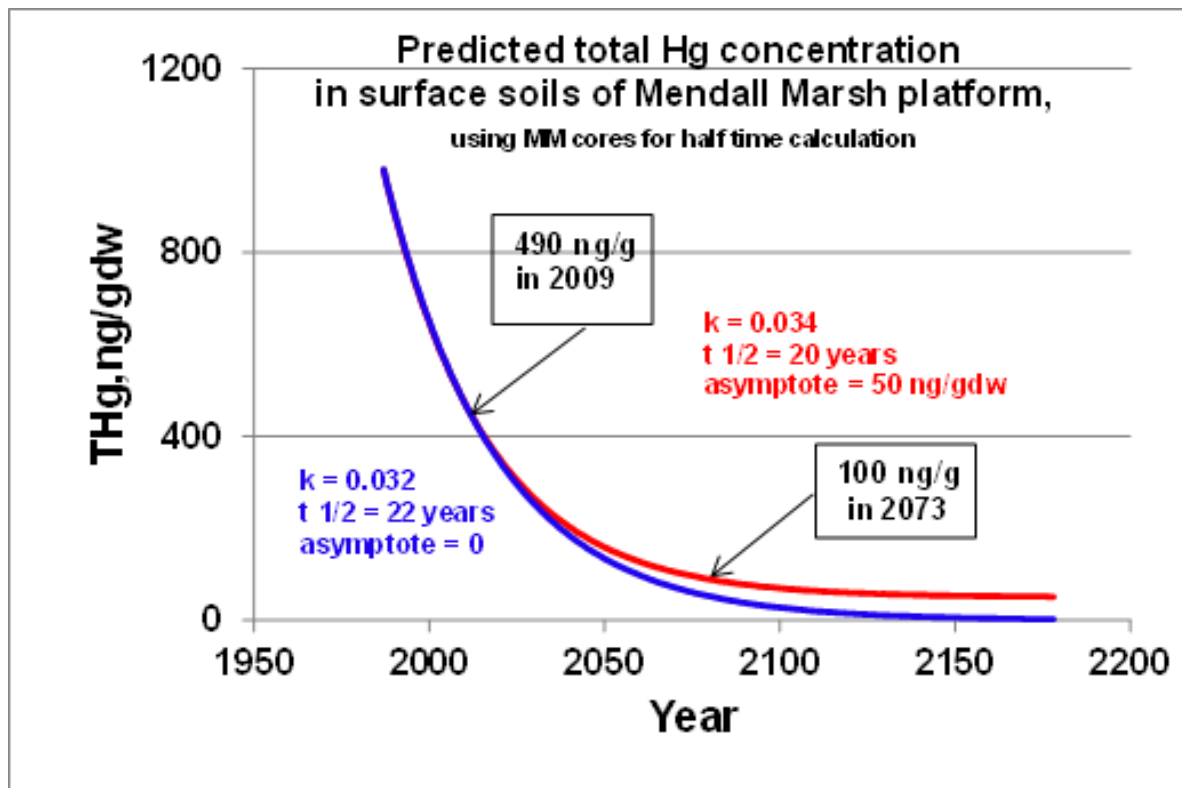


Figure 23-18. Predicted natural attenuation of total Hg concentrations in soils of the Mendall Marsh platform. The blue line is from the core data, using an expected asymptote of zero; the red line is adjusted to fit the past time period of 21 years of data, but also to fit an eventual background concentration of 50 ng/g dry wt.

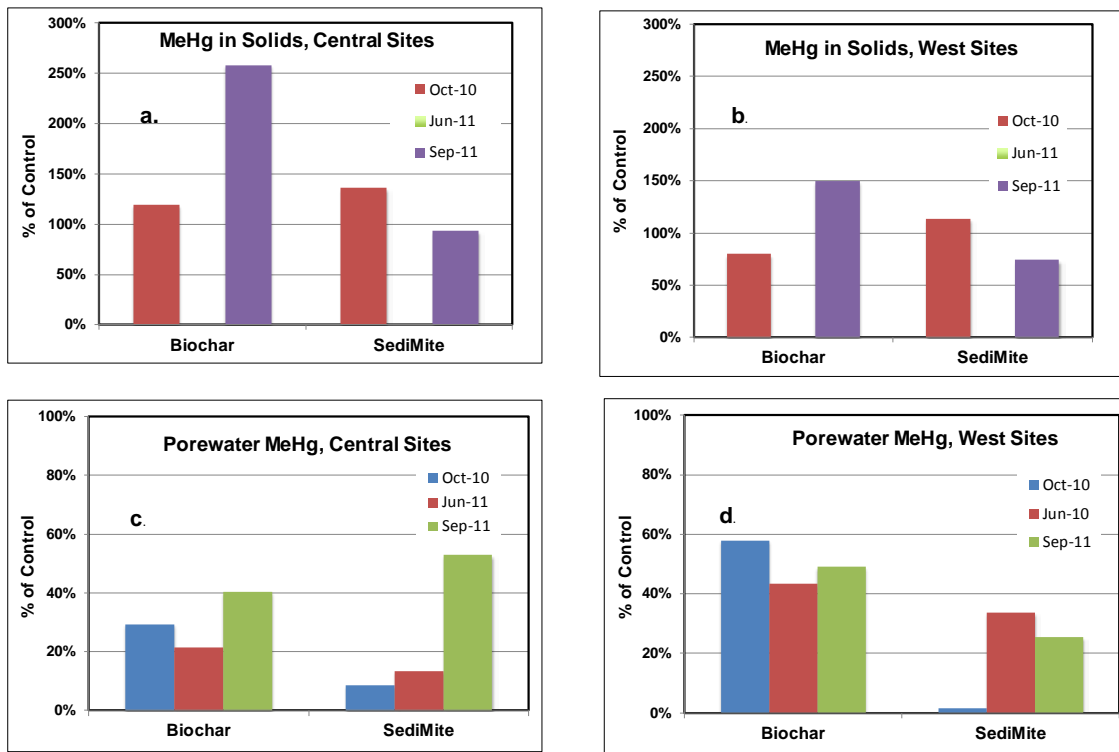


Figure 23-19. Methyl Hg concentrations in solids (a & b) and pore waters (c & d) at two sites in control, biochar treated and SediMite treated 1m² plots on the Mendall Marsh platform.