

PENOBSCOT RIVER MERCURY STUDY

Chapter 8

Total and methyl mercury concentrations in mobile and surface sediments in the Upper Penobscot estuary

**Submitted to Judge John Woodcock
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1 SUMMARY

The objective of this chapter is to examine in detail the total mercury (Hg) and methyl Hg concentrations in the components of the large mobile sediment pool, and the underlying surface sediments, in geographic sub-areas of the Penobscot Estuary. These sub-areas included the main stem of the river, below Veazie Dam and to the southern end of Verona Island, the Marsh River in Mendall Marsh, the Orland River, and the Ft Point Cove area south of Verona Island. Sediment samples were classified first as either mobile or non-mobile (surface sediments). "Mobile" sediment samples were then further classified as unconsolidated mud, mix of unconsolidated mud and other material, sand with mud, or woodchips. Surface ("non-mobile") sediments were classified as consolidated mud; mixed mud, sand, shells, rocks; woodchips, mussels, mussels with rocks and other material; sand; sand with rocks, shells, woodchips, mussels; gravel or rocks, or scoured.

This sampling effort was confined to the contaminated areas of the Penobscot estuary, as it did not include areas above Veazie Dam. Both mobile and surface sediments were elevated in total Hg and methyl Hg.

Total Hg concentrations were more related to the type of sediment (mud, sand, etc.) than to geographic location. For example, muds tended to have the same total Hg concentration whether they were located in the upper or lower estuary, Mendall Marsh, or the Orland River, or whether the sample was from mobile or surface sediment. The exception was the Fort Point Cove area, where total Hg concentrations were lower than in the areas further north.

The characteristics in both mobile and surface sediments that were positively related to total Hg concentrations were % organic matter and % fines, demonstrating that transport of fine, organic and/or clay material is especially important in transport of total Hg within the system. The similarity of total Hg concentrations in the mobile pool and in surface sediments supports the concept of a system where total Hg concentrations are changing only slowly with time. This finding, and the large size of the contaminated mobile pool, have important implications for remediation efforts.

The average methyl Hg concentration in each class of sediment sample, including both mobile and non-mobile sediments, was directly related to the average total Hg concentration, with 3% of total Hg being methyl Hg. This was the same proportion seen in intertidal sediments. This was somewhat surprising as the mobile muds were more oxidized than the non-mobile, surface sediments (brown color as opposed to black). The large mobile pool of sediment is likely an important source of methyl Hg to biota.

2 INTRODUCTION

The hydrodynamic characteristics of the Upper Penobscot Estuary result in the existence of a large pool of mobile sediments that tend to remain trapped north of the southern tip of Verona Island (Chapter 7). The slow escape of these sediments to the south means that this pool, once contaminated, is only slowly being replaced with cleaner sediments. This is an important factor in determining natural attenuation of mercury (Hg) concentrations in particles in the upper estuary. The characteristics and movements of these mobile sediments are described in Chapter 7. This chapter examines patterns of total Hg and methyl Hg concentrations in these mobile sediments and compares them to patterns in the underlying (non-mobile) surface sediments.

One of the main objectives of this part of the Penobscot River Mercury Study (PRMS) was to determine if the mobile sediments were ‘cleaner’ (lower in Hg concentrations) than the underlying surface sediments. If so, it would help indicate how quickly the system is currently cleaning itself, through the mechanism of inputs of cleaner material from upstream or from the watershed.

In addition to classifying sediments as “mobile” and “non-mobile”, all samples were characterized as one of 10 categories: (1) unconsolidated mud, (2) consolidated mud, (3) mix of unconsolidated mud and other material, (4) mixed mud, sand, shells, rocks, woodchips, mussels, (5) mussels with rocks and other material, (6) sand with mud, (7) sand (8) sand with rocks, shells, woodchips, mussels, (9) gravel or rocks; or scoured, and (10) woodchips. Each sample was characterized analytically by measuring % fines, % organic matter, and total Hg concentration.

The Hg results were analyzed according to five major questions:

- 1 What was the distribution of Hg concentrations, grain sizes, and organic carbon content of samples within each class, and what was the average value of each of these for each class?
- 2 What factors were related to total Hg concentrations in these sediments?
- 3 Were total Hg concentrations related more to the location of sampling, or to type (class) of sediment?
- 4 Were total Hg concentrations different in mobile vs non-mobile sediments?
- 5 What were methyl Hg concentrations in the mobile and non-mobile sediment grab samples - were they related to total Hg concentrations, and how did they compare to other sediments that have been sampled closer to shorelines (intertidal sites)?

3 METHODS

The methods for collecting and processing the sediment samples are described in detail in Chapter 7 by Dr. W.R. Geyer. Briefly, grab samples were taken by a van Veen sampler. Subsamples, and subsamples of material in the top 3 cm were taken for analysis of grain size, organic carbon content (measured as loss on ignition) and total

Hg. A total of 264 samples were taken, and 77% of these (203) were analyzed for total Hg. Grain size and loss on ignition were measured at Woods Hole Oceanographic Institution, and total Hg was analyzed at Flett Research Ltd. by the same methods as used on all other PRMS samples

As soon as samples were brought into the boat, sediments were classified visually into one of 10 categories. Some of these classes are considered “mobile”. One of these classes is unconsolidated mud, which are identified by color, with brown indicating oxidation due to recent mixing with oxygenated water. Other mobile classes are unconsolidated mud mixed with other material, sand with mud and wood chips. All other classes were considered non-mobile, or surface sediments. Non-mobile, or consolidated mud, was identified by its black color. This is an indicator of black iron sulfide (FeS), which is only produced under conditions where sediment is undisturbed long enough to develop anoxic conditions.

- 1 unconsolidated mud
- 2 consolidated mud
- 3 mix of unconsolidated mud and other material
- 4 mixed mud, sand, shells, rocks, woodchips, mussels
- 5 mussels with rocks and other material
- 6 sand with mud
- 7 sand
- 8 sand with rocks, shells, woodchips, mussels
- 9 gravel or rocks; or scoured
- 10 woodchips

For the purposes of this report, “mobile” classes are color-coded blue: 1, 3, 7, and 10, with 6 being “somewhat mobile”. “Non-mobile” classes are color coded red: 2, 4, 5, 8, and 9. Some samples that were originally designated as “1” were removed from this category, because they were described as having unconsolidated sediment in the first 1-2 cm, overlying consolidated sediment just below, i.e., the upper 3 cm contained both unconsolidated and consolidated sediments. These were designated as “1.5”, and not included in many of the data analyses because of the mixed nature of the sample. The terms “mobile” and “non-mobile” were put in quotes here because these are not meant to be absolute terms, rather a best judgment, based on appearance just after collection and other characteristics of the sample.

3.1 Statistical Tests

An analysis of variance (ANOVA) was used to test whether the means of different characteristics (total Hg, % fines, etc.) of the classes were different or not. Studentized

range distribution was used to test for normal distribution. The Duncan test was used to see if the means of certain classes were grouped together. Tests in this group assume equality of variances across all levels of the grouping variable.

4 RESULTS

4.1 What was the distribution of Hg concentrations, grain sizes, and organic carbon content of samples within each class, and what was the average value of each of these for each class?

4.1.1 Total Hg concentrations

There were wide ranges of total Hg concentrations in samples within many of the classes, especially within class 2, the consolidated muds (Figure 8-1). Classes 6, 7, and 8 (sand and sand mixtures) tended to be in the low ranges of total Hg concentrations (Figure 8-1a and b). Classes 1, 2, and 3 (mud and mud mixtures) tended to be in the high ranges of total Hg concentrations. Class 10 (wood chips) was the highest. The mobile classes tended to have more uniform total Hg concentrations within each class (Figure 8-1a) than did the non-mobile classes (Figure 8-1b).

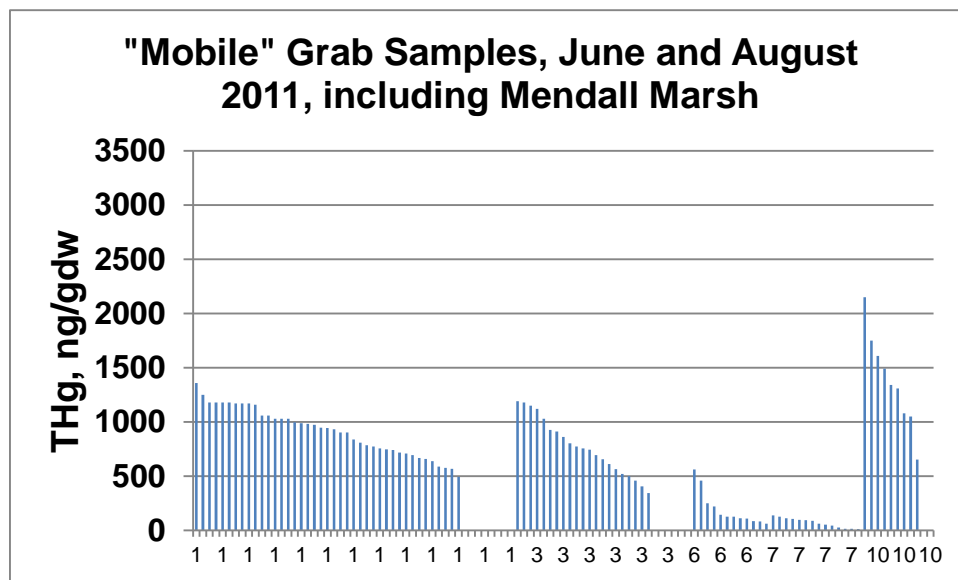


Figure 8-1a. Distribution of total Hg concentrations in grab samples collected in June and August 2011 and designated "mobile". Classes: 1 - unconsolidated mud, 3 - mix of unconsolidated mud and other material, 6 - sand with mud, 7 - sand, 10 - woodchips. Gaps in the graph indicate that a sample was taken in that category, but total Hg analysis was not done.

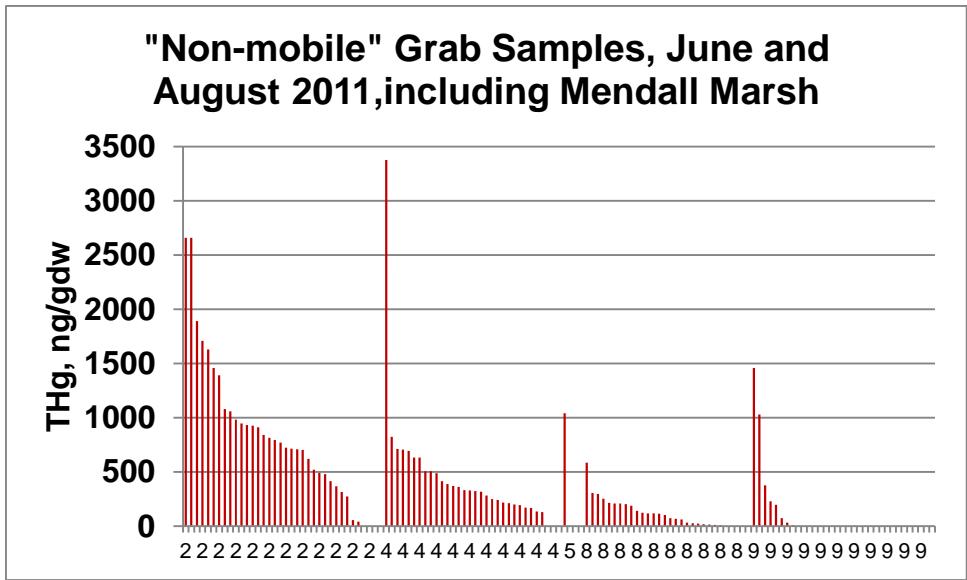


Figure 8-1b. Distribution of total Hg concentrations in grab samples collected in June and August 2011 and designated “non-mobile”. Classes: 2 - consolidated mud, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks and other material, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured. Gaps in the graph indicate that a sample was taken in that category, but total Hg analysis was not done.

The average values for total Hg (ng/g dry wt.) in each class showed wide differences among the classes (Figure 8-2). Also, the classes that were distinguished as “mobile” were not all like each other in terms of total Hg concentration, and the same was true of the classes that were distinguished as “non-mobile”. Thus, the characterization of mobility was not an indicator of total Hg (ng/g dry wt.) concentration.

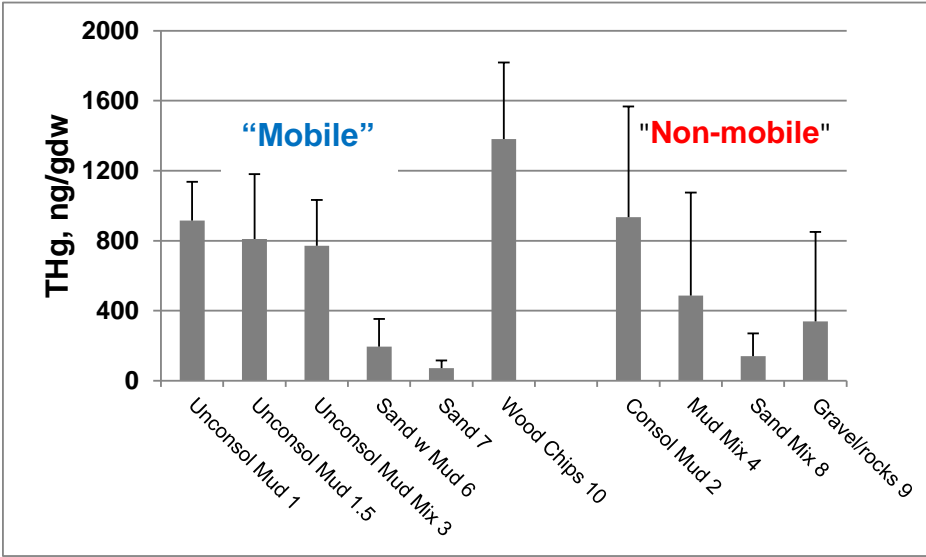


Figure 8-2. Average Hg concentrations in each class of grab sample, plus one standard deviation.

When the average values for total Hg were looked at in order of descending concentration, the wood chips were highest in total Hg concentration (Table 8-1). The muds were next highest, and sands and gravels were lowest in total Hg concentration.

Table 8-1: Average THg concentrations in each class of grab sample.				
		Total Hg ng/g dry wt.		
Class	n	Average	Standard Deviation	% Standard Deviation
Wood Chips 10	9	1381	437	32%
Consol Mud 2	32	934	632	68%
Unconsol Mud 1	41	916	220	24%
Unconsol Mud 1.5	11	810	371	46%
Unconsol Mud Mix 3	21	772	261	34%
Mud Mix 4	29	487	589	121%
Gravel/rocks 9	7	340	510	150%
Sand w Mud 6	12	195	159	81%
Sand Mix 8	25	141	130	92%
Sand 7	14	71	44	62%

ANOVA was performed on log-transformed data, to see if the means of total Hg concentrations of each class were significantly different from each other. Log transformation was done in order to have a more normal distribution of data within each class. The means of classes 1, 1.5, 2, 3, (these are all consolidated or unconsolidated muds) and 10 (wood chips) were not significantly differently from each other.

To simplify the comparisons, a Duncan test was used to group classes according to similarity of means. Using this approach, Classes 1, 1.5, 2, 3, and 10 were grouped together, 4, 6, and 9 were grouped together, and 7 and 8 (sand and sand mixture) were each in their own group.

4.1.2 Mercury per gram carbon

Because Hg is tightly bound to the sulfhydryl groups of organic matter, it is useful to examine Hg concentrations per gram of carbon, in addition to the previous analysis of Hg per gram dry wt. of material.

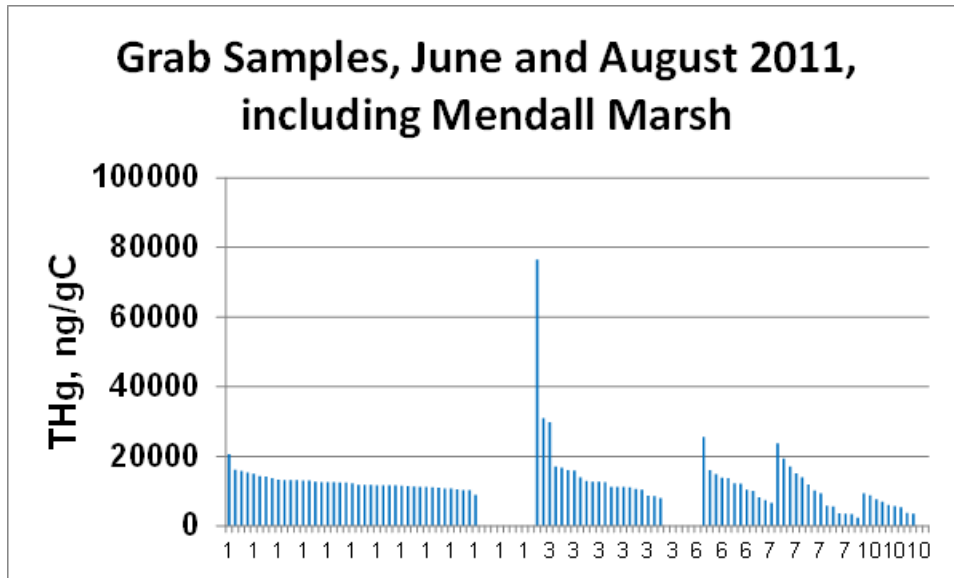


Figure 8-3a. Distribution of total Hg concentrations, per gram carbon, in grab samples collected in June and August 2011 and designated “mobile”. Classes: 1 - unconsolidated mud, 3 - mix of unconsolidated mud and other material, 6 - sand with mud, 7 - sand, 10 - woodchips. Gaps in the graph indicate that a sample was taken in that category, but total Hg analysis was not done.

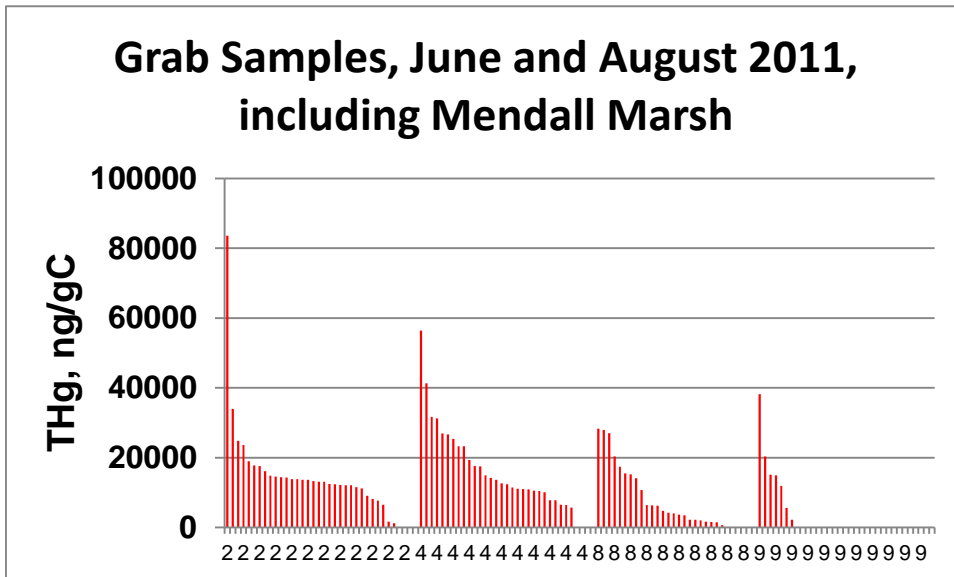


Figure 8-3b. Distribution of total Hg concentrations, per gram carbon, in grab samples collected in June and August 2011 and designated “non-mobile”. Classes: 2 - consolidated mud, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured. Gaps in the graph indicate that a sample was taken in that category, but total Hg analysis was not done.

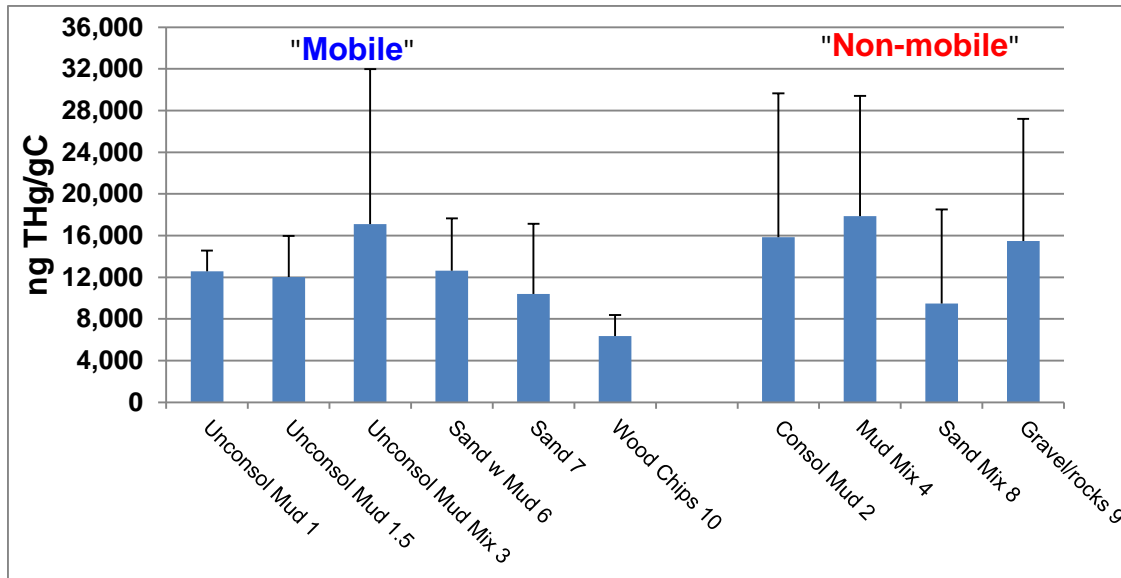


Figure 8-4. Average Hg concentrations, per gram carbon, in each class of grab sample, plus one standard deviation.

Table 8-2: Total Hg concentrations, per gram carbon in classes of grab samples. Classes are listed in descending order.

Class	n	THg ng/g C Average	Standard Deviation	% Standard Deviation
Mud Mix 4	29	17,900	11,600	65%
Unconsol Mud Mix 3	21	17,100	14,900	87%
Consol Mud 2	32	15,800	13,800	87%
Gravel/rocks 9	7	15,500	11,700	76%
Sand w Mud 6	12	12,600	5,040	40%
Unconsol Mud 1	41	12,600	2,010	16%
Unconsol Mud 1.5	11	12,000	3,940	33%
Sand 7	14	10,400	6,740	65%
Sand Mix 8	25	9,480	9,040	95%
Wood Chips 10	9	6,350	2,040	32%

Normalizing Hg to per gram carbon resulted in means that were less different from each other than concentrations of Hg per gram dry wt., as expected from the affinity of Hg(II) for sulfhydryl groups in organic molecules (e.g., Haitzer et al. 2002; Kim et al. 2013).

The Duncan test for grouping of classes showed only two groups. One group was made up of the two lowest classes 8 (sand mix) and 10 (wood chips). All other classes were grouped together. While the Duncan test resulted in only two groups for the classes with respect to total Hg ng/g C, there were 4 groups based on total Hg/g dry wt., indicating that expression of concentrations as ng total Hg per gram C resulted in more homogenous values for the classes.

The % standard deviations were calculated to provide an estimate of homogeneity within each class. The most homogeneous classes in terms of Hg concentrations per gram dry wt. were the mobile muds (1, 1.5, 3) and wood chips (10). For % fines, the most homogeneous were the muds (1, 1.5 and 2). For percent loss on ignition (% LOI), it was the muds (1, 1.5, 2) and wood chips (10). For Hg per unit of carbon, it was the mobile muds (1 and 1.5) and wood chips. Expressing the Hg concentration as total Hg ng/g C dry wt. reduced the range of data within some classes, as indicated by the % standard deviations, Tables 8-1 and 8-2. These classes were the mud mixture (4), the gravel/rocks (9), the sand with mud (6), and sand (7), and were the classes with low values of organic content (%LOI, Table 8-4). In classes with the higher organic content (wood chips (10), consolidated mud (2), unconsolidated mud (1), and unconsolidated mud mixtures (3), the ranges as indicated by the % standard deviation were greater when total Hg was expressed as total Hg/g C.

4.1.3 Percent fines

“Fines” are defined as particles that pass through a 63 µm filter, following digestion to remove organic material. There was a wide range of % fines within each class, but the muds (classes 1, 1.5, 2, and 3) tended to have higher % fines than the sands and gravel classes (6, 7, 8, and 9). The mixed mud (class 4) and wood chips (class 10) had a fairly even distribution of % fines, (Figure 8-3a and b). The mobile grab samples (Figure 8-3a) tended to have higher % fines than the non-mobile samples (Figure 8-3b).

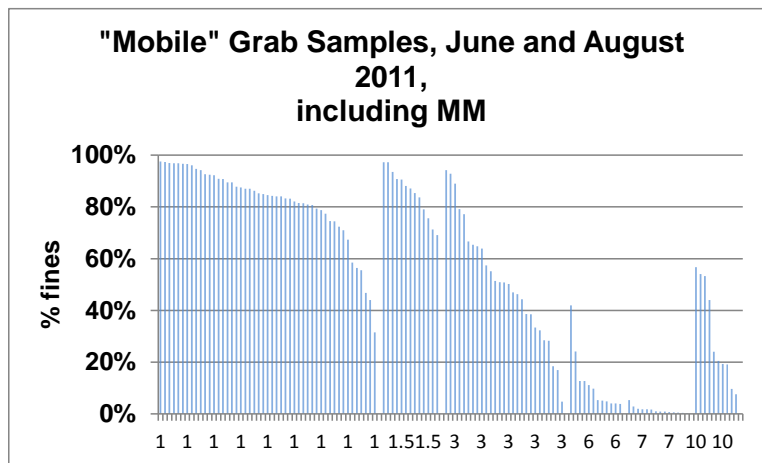


Figure 8-3a. Distribution of % fines in grab samples collected in June and August 2011 and designated “mobile”. Classes: 1 - unconsolidated mud, 3 - mix of unconsolidated mud and anything else, 6 - sand with mud, 7 - sand, 10 - woodchips.

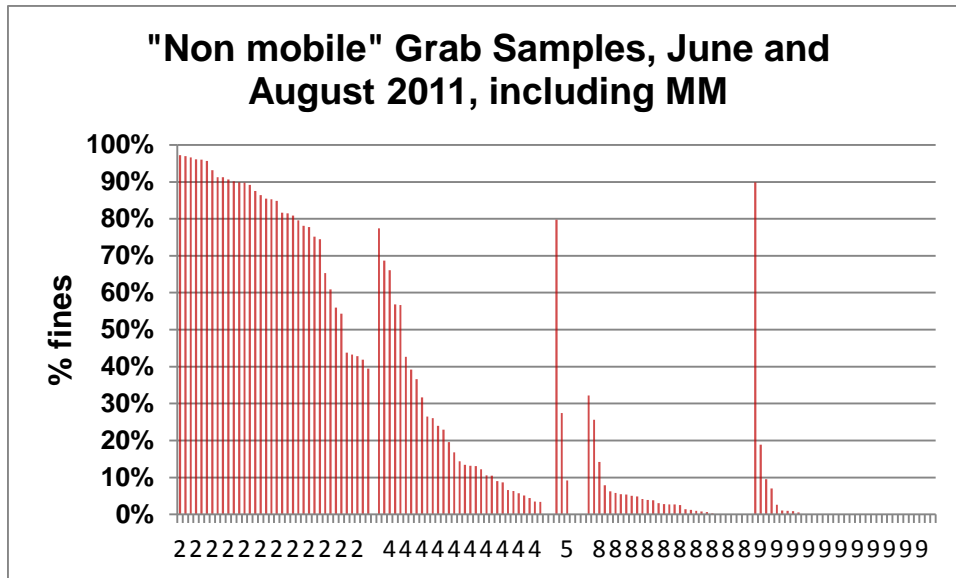


Figure 8-3b. Distribution of % fines in grab samples collected in June and August 2011 and designated “non-mobile”. Classes: 2 - consolidated mud, and anything else, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured. MM = Mendall Marsh.

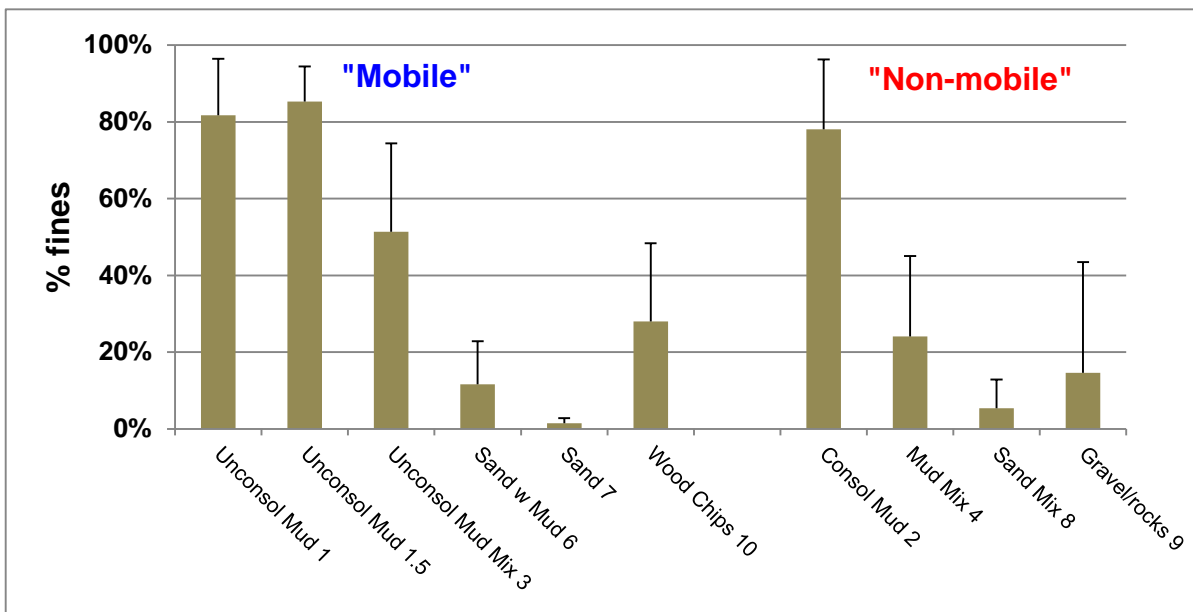


Figure 8-4. Average % fines in each class of grab sample, plus one standard deviation.

The average values of % fines for each class ranged from a high of 85% to a low of 1.5% (Figure 8-4; Table 8-3). From the Duncan Test, the pure mud classes (1, 1.5, and 2) were grouped together, with means ranging from 78% to 85% fines. The unconsolidated mud mixture (3) was in its own group. Classes 10, 4, 9, and 6 were grouped together. Classes 7 and 8 were in the fourth and lowest % fines group.

Table 8-3: Percent fines in sediments of different classes.				
Class	n	% fines		
		Average	Standard Deviation	% Standard Deviation
Unconsol Mud 1.5	11	85%	9%	11%
Unconsol Mud 1	50	82%	15%	18%
Consol Mud 2	33	78%	18%	23%
Unconsol Mud Mix 3	23	51%	23%	45%
Wood Chips 10	9	28%	20%	73%
Mud Mix 4	29	24%	21%	87%
Gravel/rocks 9	7	15%	29%	198%
Sand w Mud 6	12	12%	11%	96%
Sand Mix 8	25	5%	8%	141%
Sand 7	14	1%	1%	89%

4.1.4 Percent Loss on Ignition (%LOI)

Most classes showed a fairly wide range of % LOI (Figure 8-5a). The most homogeneous class was the unconsolidated muds, with a range of 8% - 22%.

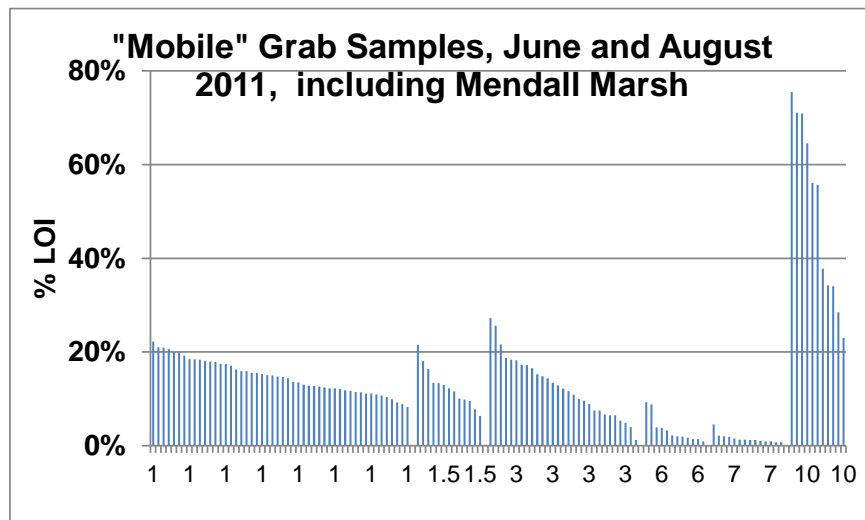


Figure 8-5a. Distribution of % LOI each class of grab sample designated "mobile". Classes: 1 - unconsolidated mud, 3 - mix of unconsolidated mud and anything else, 6 - sand with mud, 7 - sand, 10 - woodchips.

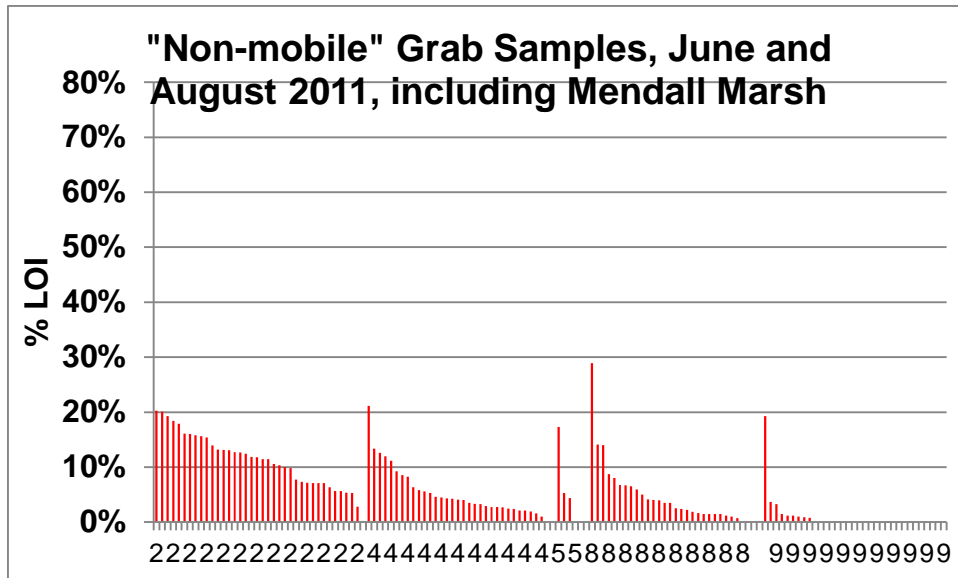


Figure 8-5b. Distribution of % LOI in each class of grab sample designated “non-mobile”. Classes: 2 - consolidated mud, and anything else, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured.

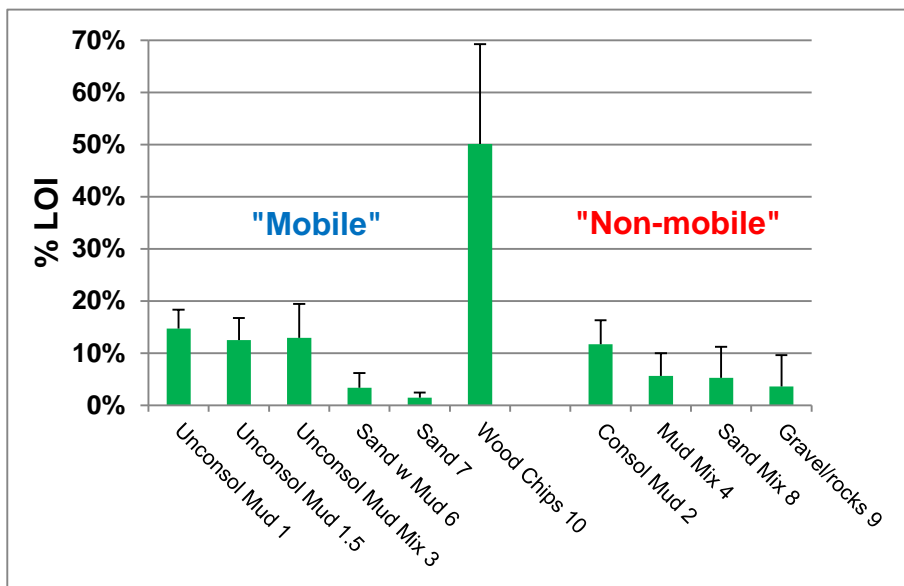


Figure 8-6. Average % LOI in each class of grab sample, plus one standard deviation.

Table 8-4: Average % LOI (loss on ignition) in each class of grab sample, plus one standard deviation.

Class	n	%LOI		% Standard Deviation
		Average	Standard Deviation	
Wood Chips 10	9	50%	19%	38%
Unconsol Mud 1	41	15%	4%	24%
Unconsol Mud Mix 3	21	13%	6%	50%
Unconsol Mud 1.5	11	13%	4%	33%
Consol Mud 2	32	12%	5%	39%
Mud Mix 4	29	6%	4%	78%
Sand Mix 8	25	5%	6%	112%
Gravel/rocks 9	7	4%	6%	164%
Sand w Mud 6	12	3%	3%	83%
Sand 7	14	2%	1%	65%

Wood chips had by far the greatest % LOI, and were in a group by themselves. The next highest group included all the mud classes (1, 3, 1.5, and 2), both consolidated and unconsolidated. All these groups had very similar % LOI, between 12 and 15% (Table 8-4). The third group included all the low % LOI classes - the mud and sand mixtures (4 and 8) and the gravel and sand classes (9, 6, and 7).

4.1.5 Summary

All of the mud classes (1, 1.5, 2, and 3) had average total Hg concentrations between 770 and 930 ng/g dry wt. The only class with higher total Hg was the wood chips (10). The sand (7) and sand mixtures (6, 8) had the lowest average total Hg concentrations, and the heterogeneous mix (4) and gravel (9) classes were intermediate (430-490 ng/g dry wt.). Total Hg ng/g C dry wt. values were higher in the non-mobile muds and gravel, and in the mobile mud mixture class: the lowest values were in sands and wood chips. % fines and % LOI were high in the mud classes, and low in the sands and sand mixtures, and in the consolidated mud mixtures.

4.2 What factors were related to total Hg concentration?

In this section the data are examined to see if different Hg concentrations were related to % fines or % LOI. Percent fines is a measurement based on of the sizes of the inorganic particles in the sediment, and includes both clay and fine to medium size silt. Clay has negatively charged surfaces that bind cations. Hg can also be bound, even more tightly, to sulfhydryl moieties in organic molecules. Therefore, there is an expectation that sediments with either high clay content or high organic content will

have higher total Hg concentrations. This was examined in the Penobscot grab sample data set by comparing total Hg concentrations to % LOI, which is a direct measure of organic content, and to % fines.

It should be noted that % fines is often correlated with % LOI, and this was the case for the Penobscot samples (Figure 8-7). This is true even though % fines are measured on sediment from which the organic material has been removed. The common association between % LOI and % fines is simply that organic particles in aquatic system tend to be fine, and so are deposited in the same low energy environments as are fine mineral particles.

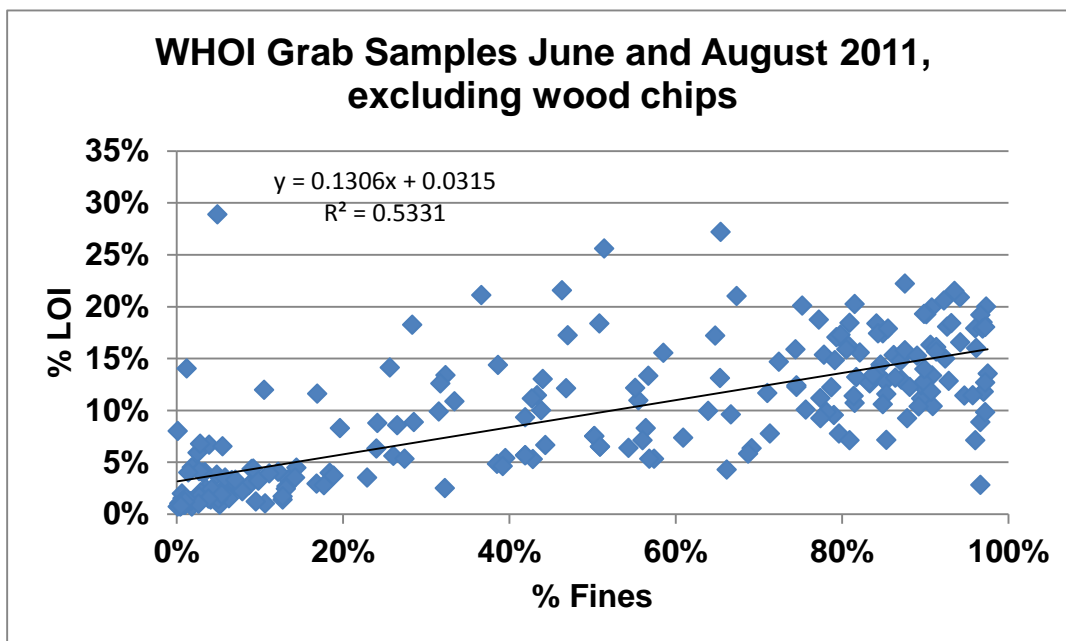


Figure 8-7. %LOI vs % fines in all grab samples except wood chips (wood chips were excluded because they are quite different in composition from all other sample types, and have very high % LOI and very low % fines). Regression was significant at $P < 0.001$.

4.2.1 % Fines

Total Hg concentrations were plotted against % fines for all samples, and with different classes represented by different symbols (Figure 8-8). This showed that most samples showed a trend of higher total Hg with higher % fines, but that wood chips fell clearly outside this trend (Figure 8-8). Another observation is that samples in class 2 (consolidated muds, blue +’s) had an unusually large range of total Hg concentrations over a fairly small range of % fines, at the higher % fines levels (Figure 8-8).

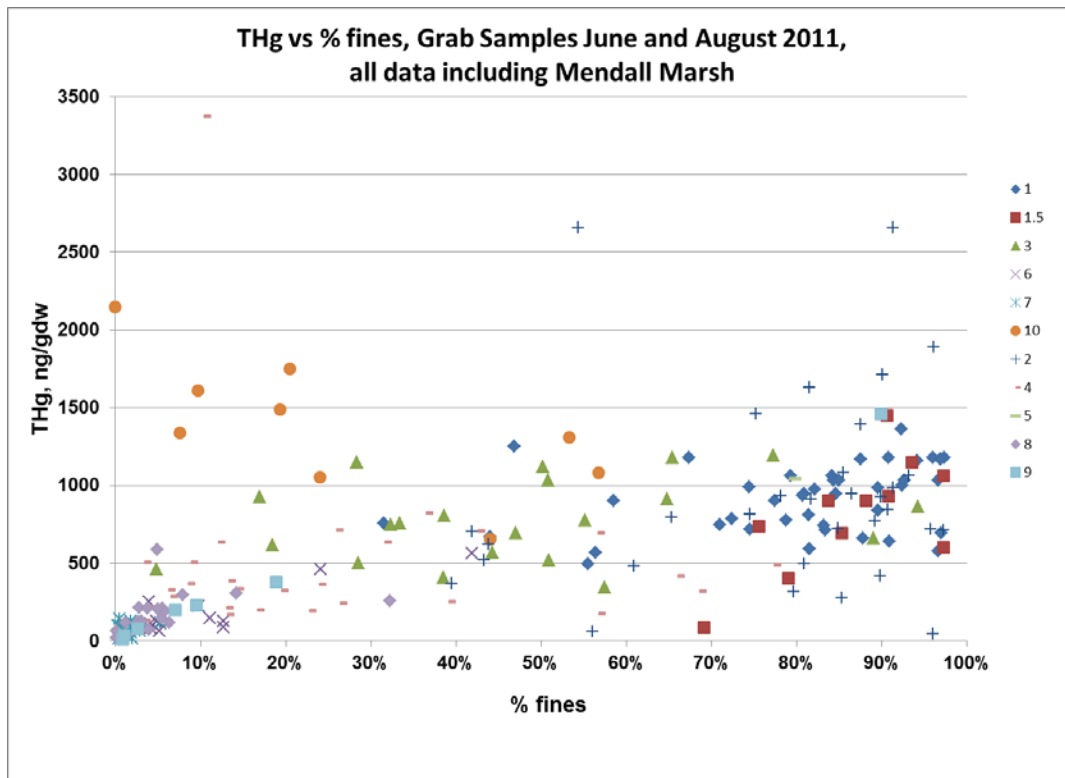


Figure 8-8. Total Hg plotted against % fines for all samples. Classes: 1 - unconsolidated mud, 1.5 - unconsolidated mud overlying consolidated mud, 2 - consolidated mud, 3 - mix of unconsolidated mud and anything else, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks etc., 6 - sand with mud, 7 - sand, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured, 10 - woodchips.

Because wood chips were clearly different from other classes, being composed entirely of organic material that would have no relationship to size of particles, wood chips were excluded from the regression of the larger data set. When this class was excluded, there was a significant linear relationship between total Hg and % fines for individual samples (Figure 8-9).

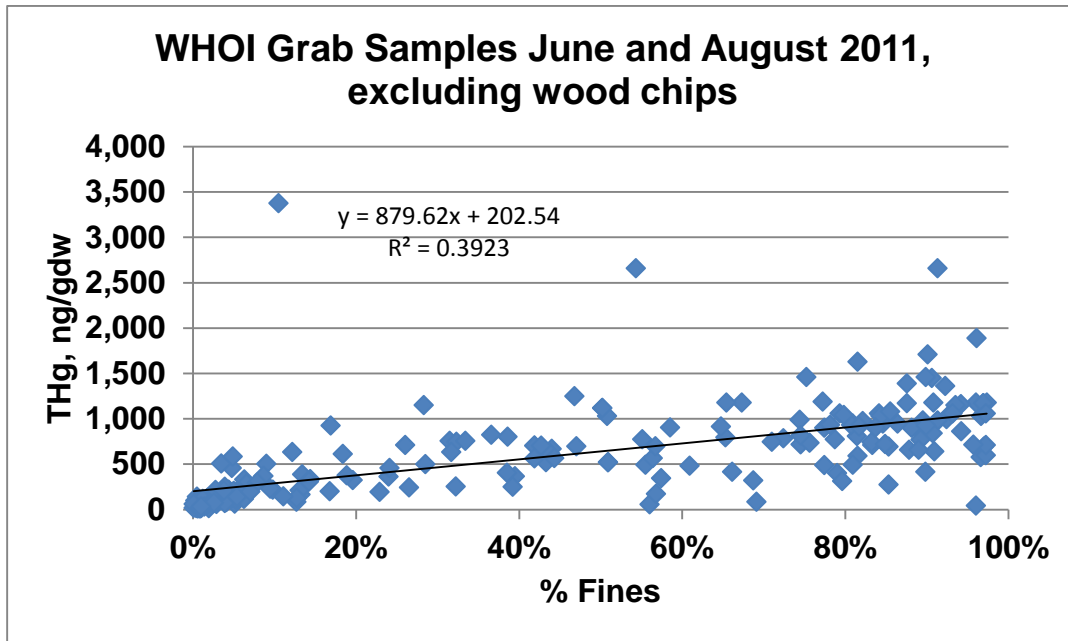


Figure 8-9. Total Hg concentrations plotted against % fines for all samples, excluding wood chips. Regression was significant at $P < 0.001$

In addition to finding a very good relationship between total Hg concentration and % fines in individual samples (Figure 8-9), the average total Hg concentration in each class (Table 8-1) showed a very good relationship with average % fines (Table 8-3) if wood chips are excluded (Figure 8-10).

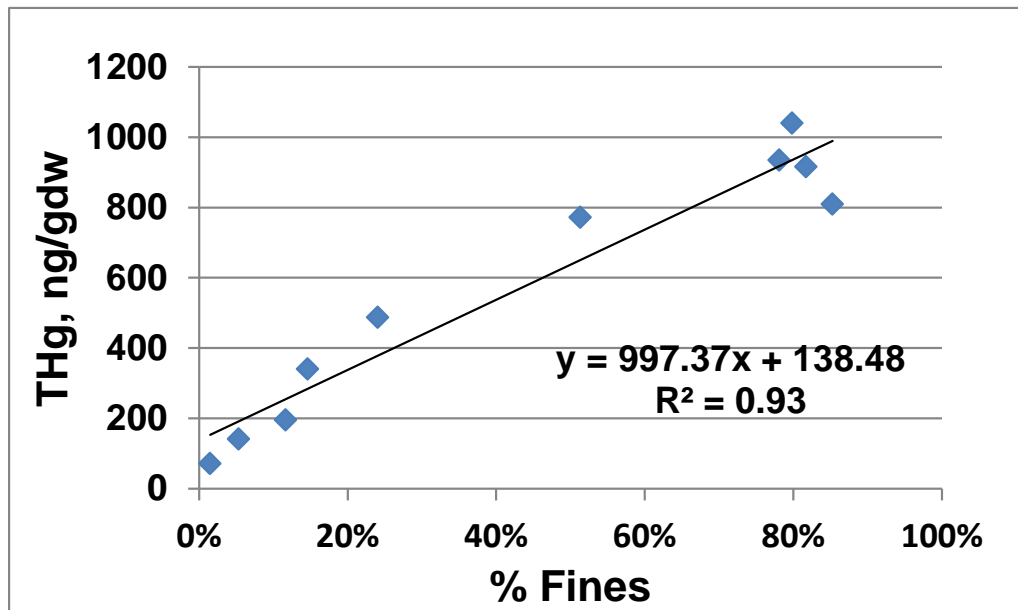


Figure 8-10. Average total Hg concentration for each class, plotted against average % fines for each class, excluding wood chips.

4.2.2 Detailed grain size measurements

In addition to % fines done on most of the 263 samples taken, 191 samples also had a full suite of grain size measurements. Size distribution was determined by sieving, separating particle sizes into 11 size ranges, between $\phi = -4$ (>16 mm) and $\phi = 5$ ($< 44 \mu$).

This detailed size fraction analysis showed that THg concentrations were higher in samples with greater abundance of particles $< 44 \mu$ (Figure 8-11). This fraction includes both medium to fine silt, and clay. The next size larger ($44-63 \mu$) also contains silt (coarse silt), but it had no correlation with total Hg concentration, suggesting that the correlation in the smallest size range was due to the clay, not the silt. Similar to the $\phi = 4.5$ particles, the $\phi = 4$ particles also showed no correlation with total Hg concentration (Figure 8-11). All larger particles showed a tendency for higher abundance in samples with lower total Hg concentrations.

In this detailed grain size scheme, the two smallest fractions together are the same as the “% fines” fraction used in the general analysis above. The interesting result from looking at these sizes separately is that only the finest size showed a positive correlation with total Hg. The smallest fraction is the only one that contains clay particles, and clay particles have a negatively charged surface, which attracts positively charged ions, including metals. They also are coated with an organic layer that would have an affinity for Hg(II).

It should be remembered that the particle size measurements are carried out on samples that have been digested to remove organic matter, while the total Hg analyses are done on whole samples. Thus, the higher total Hg concentrations are found in samples that have higher abundance of the finest size clay particles, but in the whole sample, the Hg could be attached either to the clay itself, or to organic molecules that form a film on the surface of the clay particles. The total Hg could be also attached primarily to organic molecules in fine organic particles that tend to deposit in the same places as clays and fine silts. In either case, it is important to note that total Hg is associated more strongly with fine particles than with any other size, and this has implications for Hg transport.

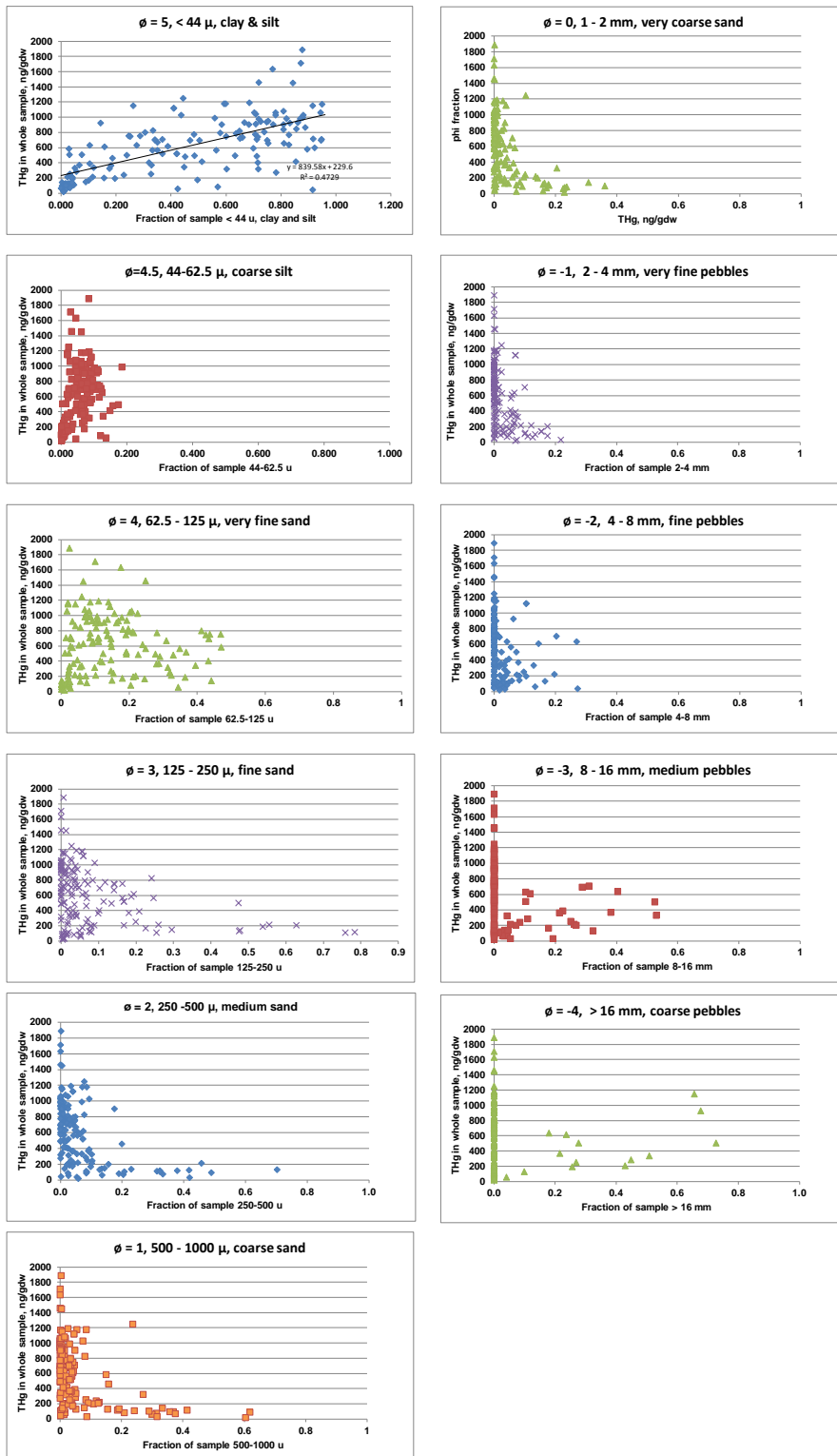


Figure 8-11. Abundance of each grain size fraction in samples of different Hg concentrations. Hg concentrations were measured on whole sediment, and grain size fractions were measured on a separate aliquot of the same sample.

4.2.3 Percent Loss on Ignition

% LOI is a measure of organic content. This measurement is expected to correlate well with total Hg because Hg(II) binds more tightly to sulfhydryl groups that are present in naturally occurring organic molecules than to any other naturally occurring materials in aquatic systems (e.g., Haitzer et al.2002, Drexel et al. 2002).

There was a significant relationship between total Hg concentrations and % LOI (Figure 8-12). Wood chips were not included in this figure because they have very different composition than the sediment samples. The relationship with % LOI was stronger than with % fines (Figure 8-9).

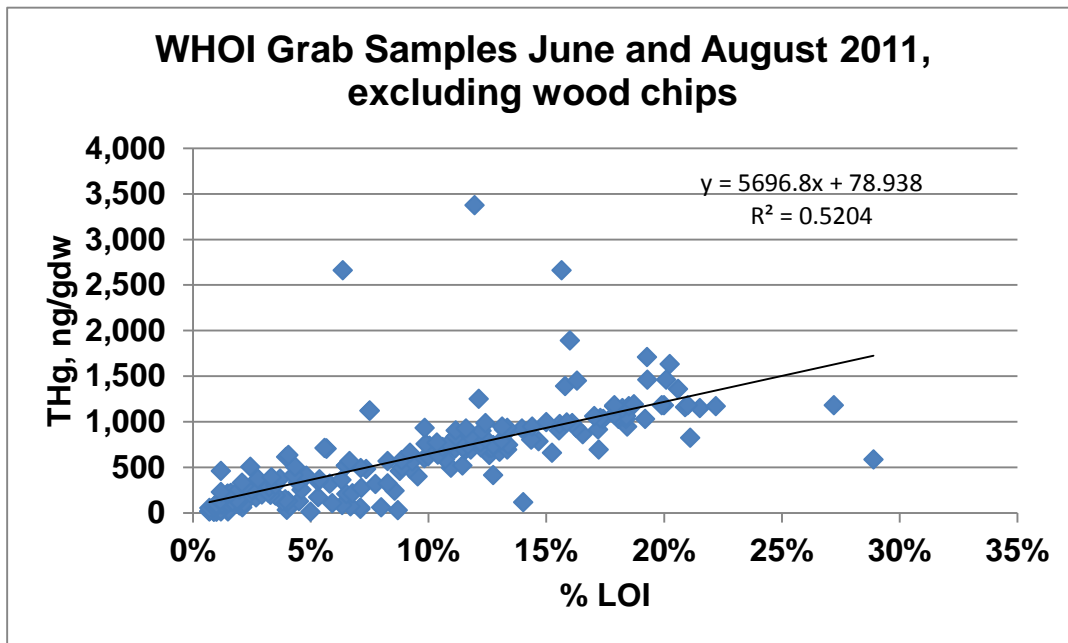


Figure 8-12. Total Hg vs Loss on Ignition in all grab samples except wood chips. Regression was significant at $P < 0.001$

When the averages for each class were used (Table 8-1), there was an even clearer relationship between total Hg and % LOI (Figure 8-13).

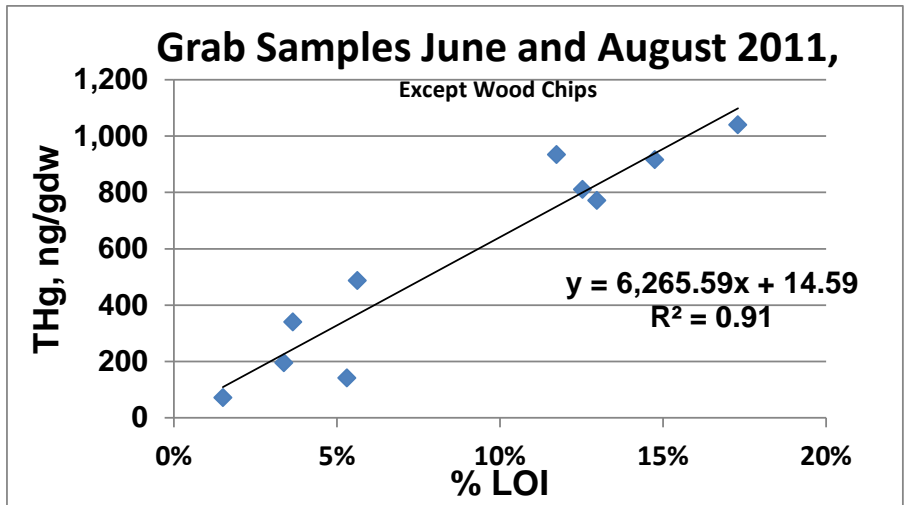


Figure 8-13. Average total Hg concentrations vs average % LOI in each class of grab sample, except wood chips.

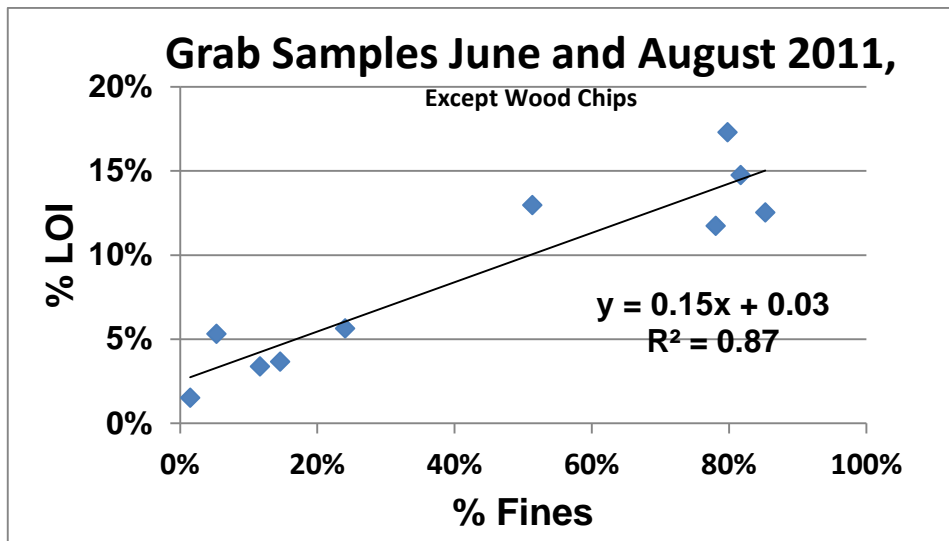


Figure 8-14. % LOI vs % fines each class of grab sample, except wood chips.

It is worthwhile to note that the relationship between average total Hg and average % LOI in each class (Figure 8-13) is similar to the relationship between total Hg and % fines (Figure 8-11), because % LOI and % fines are related to each other (Figure 8-14). The stronger relationship of total Hg with % LOI than with fines suggests that this factor is a more dominant determinant.

4.2.4 Summary

Total Hg concentrations were significantly related to both % fines and to % LOI. The average values for total Hg in each class were strongly related to the average values for

% fines or for % LOI in each class. Thus, the type of sediment, whether mud or sand, was an important determinant in total Hg concentration.

4.3 Were total Hg concentrations related more to location, or to type (class) of sediment?

This question can be paraphrased as “What matters more - the type of sediment, or where it was?” Three types of site location-related factors were examined: north to south distribution, depth of water at sampling site, and local geographic sub-area.

4.3.1 North to south

When the total Hg concentration results are viewed in a generally north to south order, there was no pattern for total Hg ng/g dry wt. (Figure 8-15a), or for total Hg normalized to organic C (Figure 8-15b), in the main stem of the Penobscot River, from near Brewer to Fort Point Cove. There was a lack of samples with total Hg higher than 750 ng/g dry wt., or 15000 ng/g C dry wt., in the Ft. Point Cove area.

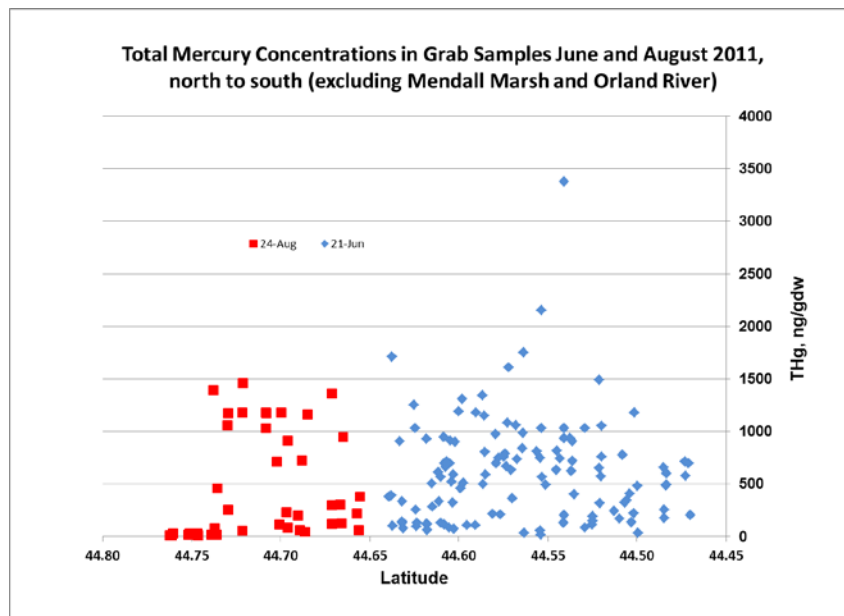


Figure 8-15a. Concentrations of total Hg in sediment samples from the main stem of the Penobscot River from Brewer to Fort Point Cove, plotted on a north to south gradient.

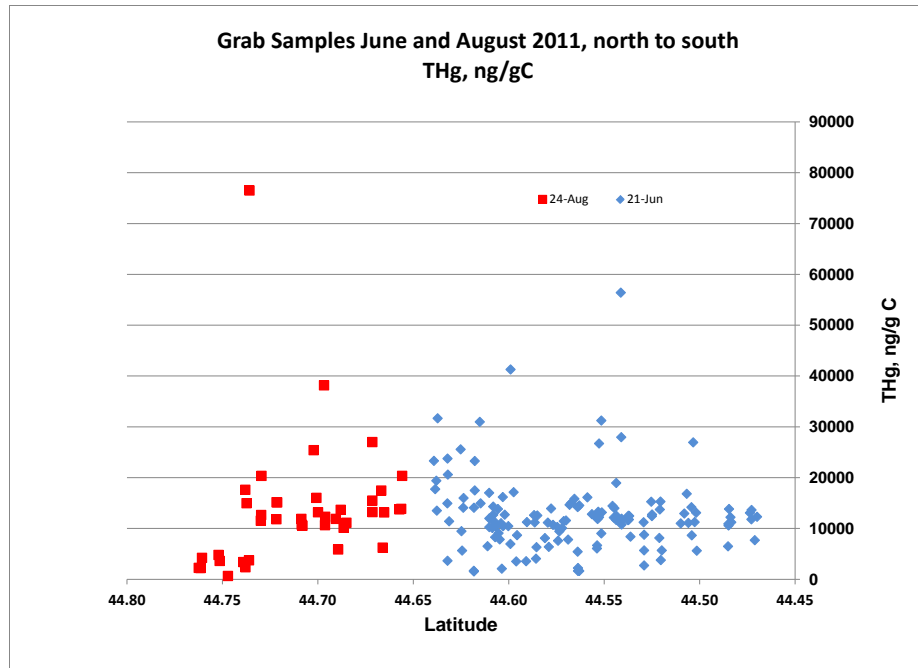


Figure 8-15b. The north to south pattern of concentrations of total Hg per unit of carbon (estimated using % LOI measurements and assuming 50% of the LOI was due to carbon).

4.3.2 Depth

There was no pattern of total Hg concentration with depth of water at the sampling site (Figure 8-16a and b). There was a slightly greater range of total Hg concentrations (total Hg ng/g dry wt.) in samples from depths less than 20 m (Figure 8-16a), but there were also a greater number of samples taken at these depths, so it is difficult to draw a conclusion from this. It does seem safe to say that depth was not a major determinant of total Hg concentration.

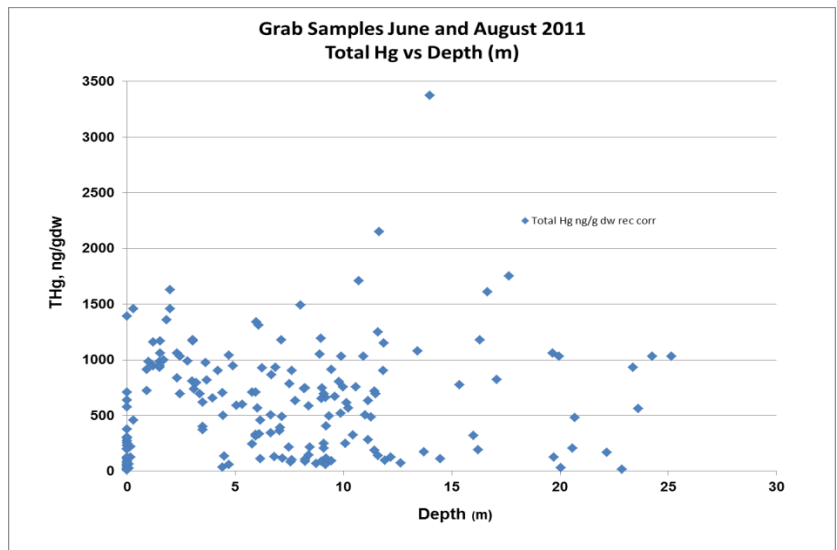


Figure 8-16a. Concentrations of total Hg in grab sediment samples plotted against depth of water at the sampling site.

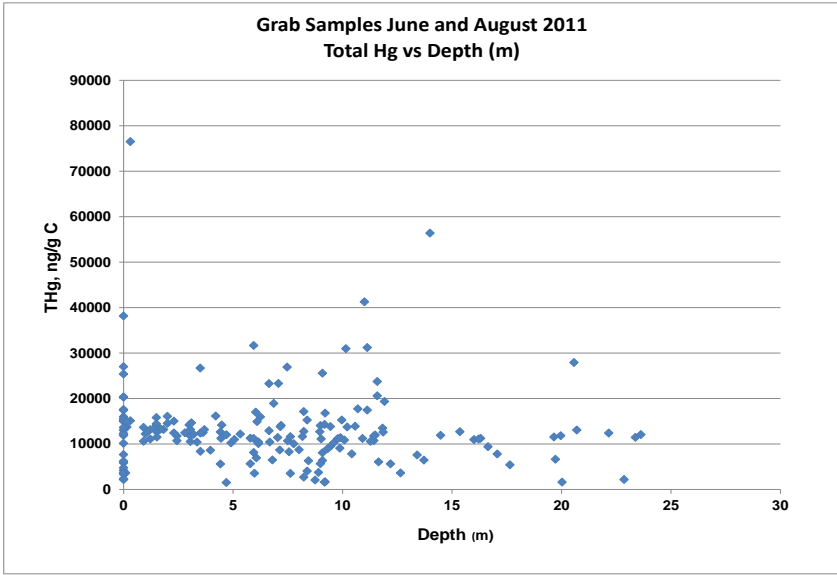


Figure 8-16b. Hg concentrations per gram carbon vs depth in the main stem of the Penobscot River.

4.3.3 Local geographic area

Was the type (class) of sediment, or the geographic area, a more important factor in predicting Hg concentrations? The sampling area was divided into 12 local sub-areas, and ordered roughly north to south (Table 8-5). The east and west channels around Verona Island, and the Orland River are all at about the same latitude.

Sub-area	Latitude range	Description
BO	44.77 to 44.74	south of I-395 bridge, Brewer to north of HoltraChem, includes BO1,5,3,2,4
OB3&5	44.74 to 44.69	HoltraChem site to Mill Creek, includes OB5 and OB3 at south end of segment
OB4	44.69 to 44.66	Mill Creek to south of OB4
PR n of OB2	44.64 to 44.62	near Winterport
PR FF	44.62 to 44.60	Frankfort Flats area, north of inlet to Mendall Marsh, includes OB2 and OB1
MM	44.60 to 44.56	Mendall Marsh
PR n of Bucksport	44.60 to 44.57	Penobscot River near Bucksport, south of Mendall Marsh, to where channel divides north of Verona Island.
EC, n OR	44.57 to 44.54	East Channel around Verona Island, north of Orland River, includes ES11, ES2
OR	44.56 to 44.54	Orland River, includes ES5, ES6
EC, s OR	44.54 to 44.50	East Channel around Verona Island, south of Orland River, includes ES13
WC	44.56 to 44.50	West Channel around Verona Island, includes ES15
FtPC	44.49 to 44.47	Fort Point Cove, includes ES12, ES03, ES14

The class of sediment appeared to be more important than the geographic area in determining the total Hg concentration (Figure 8-17a). For example, the lines for the four mud classes (1, 1.5, 2, and 3) were uniformly above the lines for the other classes, regardless of geographic position within the system. Lines for other classes also remained in approximately the same relative positions throughout the system, with some slight overlapping (Figure 8-17a). The sand (7) and sand mixtures (6 and 8) were all low in total Hg, and the heterogeneous mix (4) samples were intermediate in total Hg, throughout the system.

When Hg concentrations were calculated per gram of carbon, the only class that showed “crossing of lines” of the class averages from one area to another was the sand mixture (8), a “non-mobile” class (Figure 8-17b).

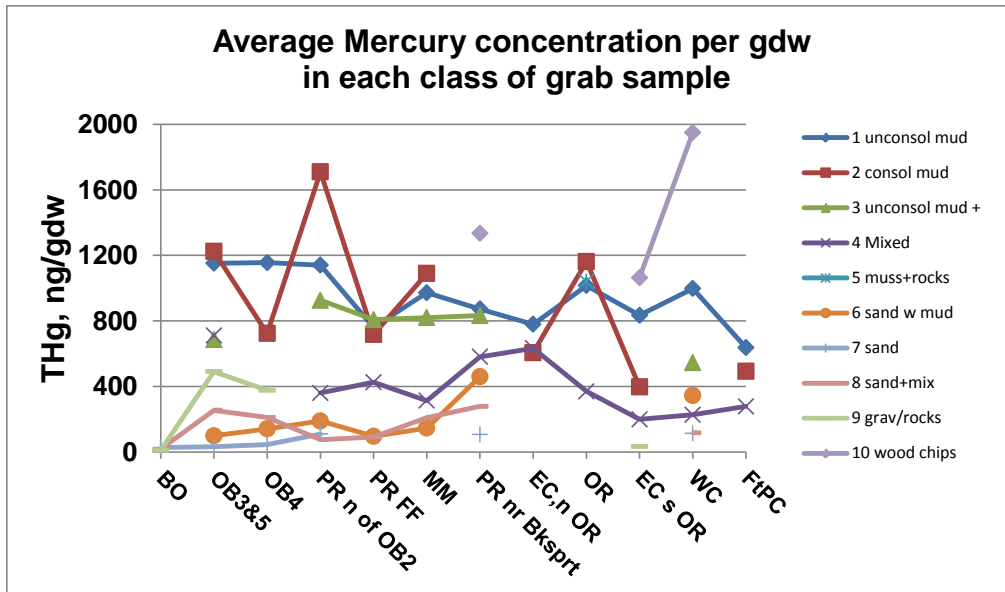


Figure 8-17a. Average total Hg concentration in each class of sediment, for each of the 12 geographic sub-areas, ordered north to south. Classes: 1 - unconsolidated mud, 1.5 - unconsolidated mud overlying consolidated mud, 2 - consolidated mud, 3 - mix of unconsolidated mud and anything else, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks etc., 6 - sand with mud, 7 - sand, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured, 10 - woodchips.

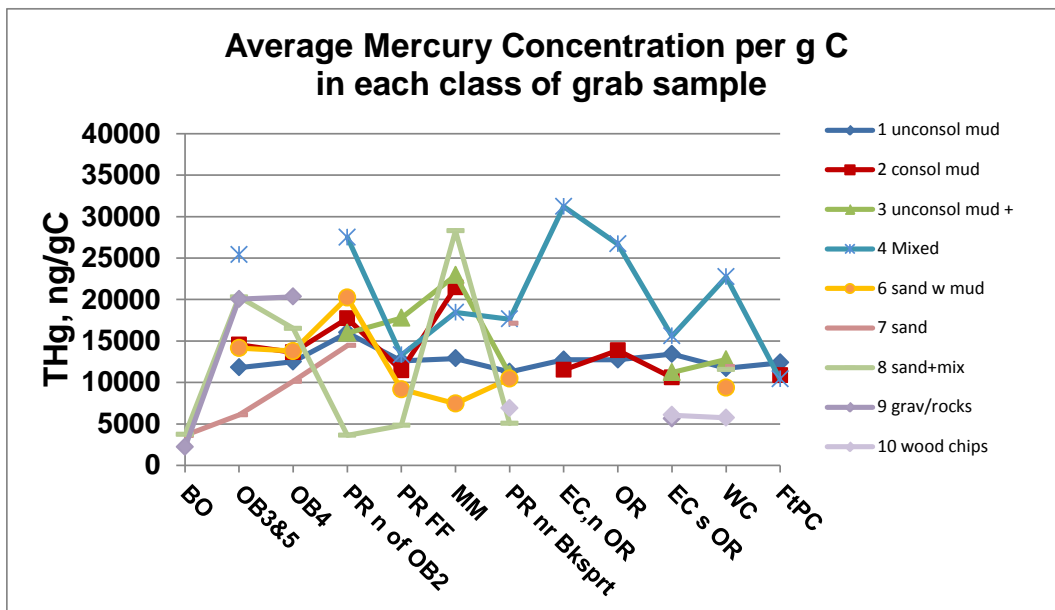


Figure 8-17b. Average total Hg concentration in each class of sediment, for each of the 12 geographic sub-areas, ordered north to south. Classes: 1 - unconsolidated mud, 1.5 - unconsolidated mud overlying consolidated mud, 2 - consolidated mud, 3 - mix of unconsolidated mud and anything else, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks etc., 6 - sand with mud, 7 - sand, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured, 10 - woodchips.

The best data set for examining possible geographic trends in total Hg concentrations was the data set for “muds” (1 and 2), because mud samples were found throughout the system, giving the best geographic coverage (many of the other classes were only sampled in 7 or fewer of the 12 sub-areas). Thus, the same type of sediment could be compared from one subarea to another, eliminating the difficulties that arise when trying to compare sediments of different types.

When only “muds” were compared, the general picture of total Hg distribution throughout the upper estuary was similar, whether looking at “mobile”muds (1) or “non-mobile” muds (2) (Figure 8-18a & b). With concentrations expressed on a dry wt. basis, there was a slight trend of lower concentrations from north to south (Figure 8-18a). Also, the non-mobile samples showed greater differences in total Hg concentrations from one sub area to another (Figure 8-18a). When expressed per unit of carbon, however (Figure 8-18b), there was no north to south trend and subareas were very similar to each other.

The geographic coverage of sand samples was not as good as for muds, but the samples available did not show a north to south trend, whether expressed on a dry wt. basis (Figure 8-19a), or as per unit of carbon (Figure 8-19b).

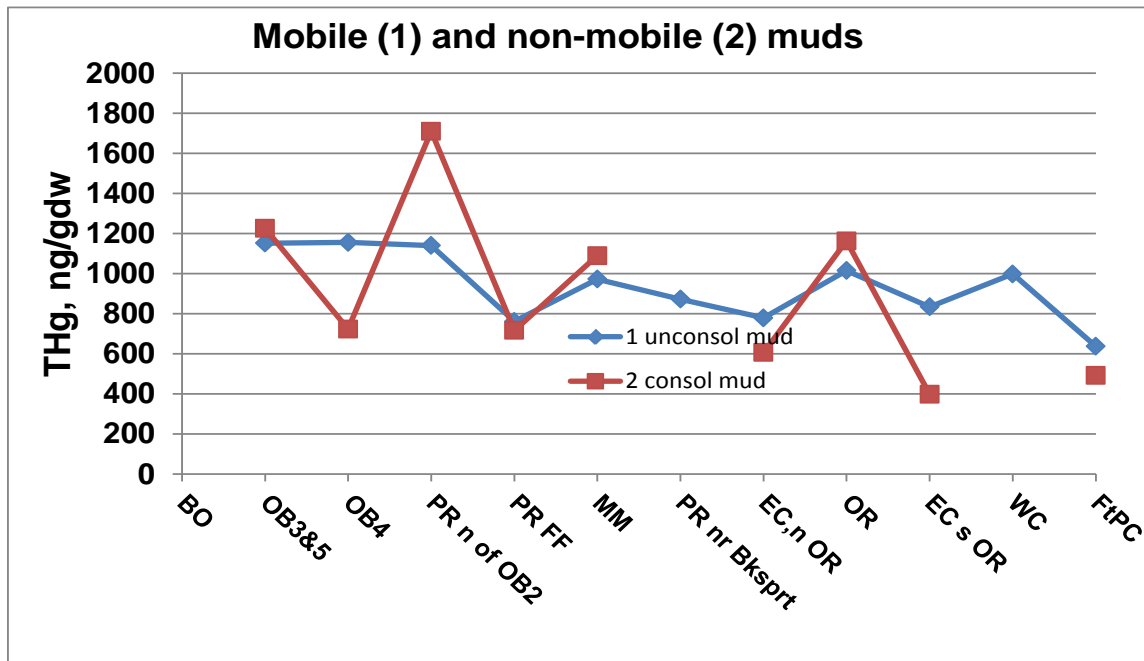


Figure 8-18a. Average total Hg concentration in “mobile and “non-mobile” classes of muds (1 and 2), for each geographic sub-area, ordered north to south.

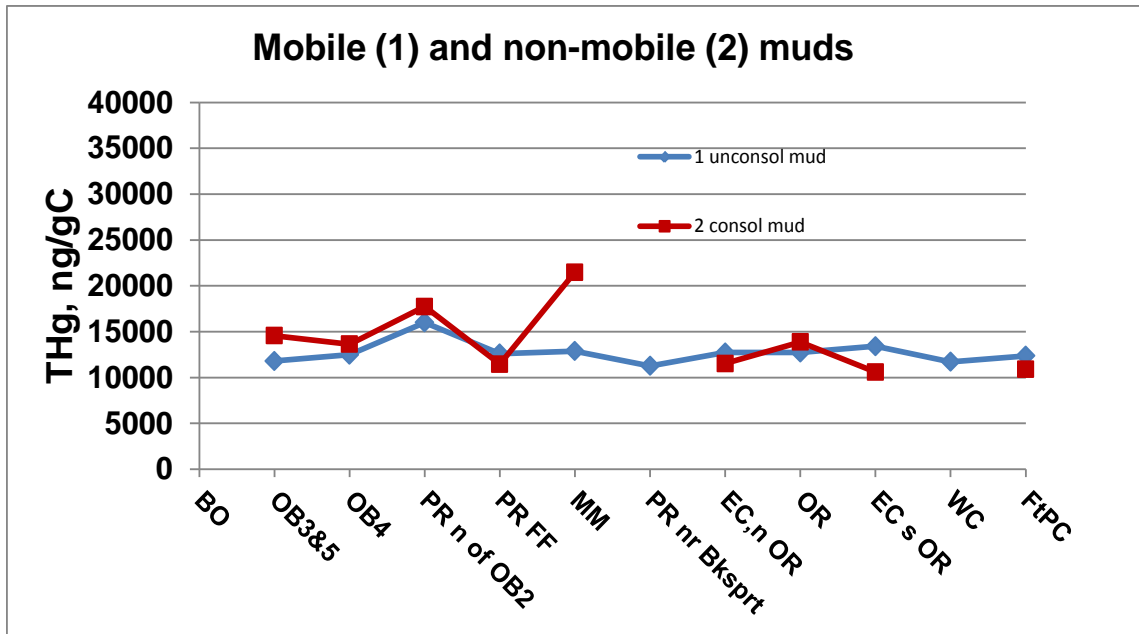


Figure 8-18b. Average total Hg concentration per unit carbon in “mobile and “non-mobile” classes of muds (1 and 2), for each geographic sub-area, ordered north to south.

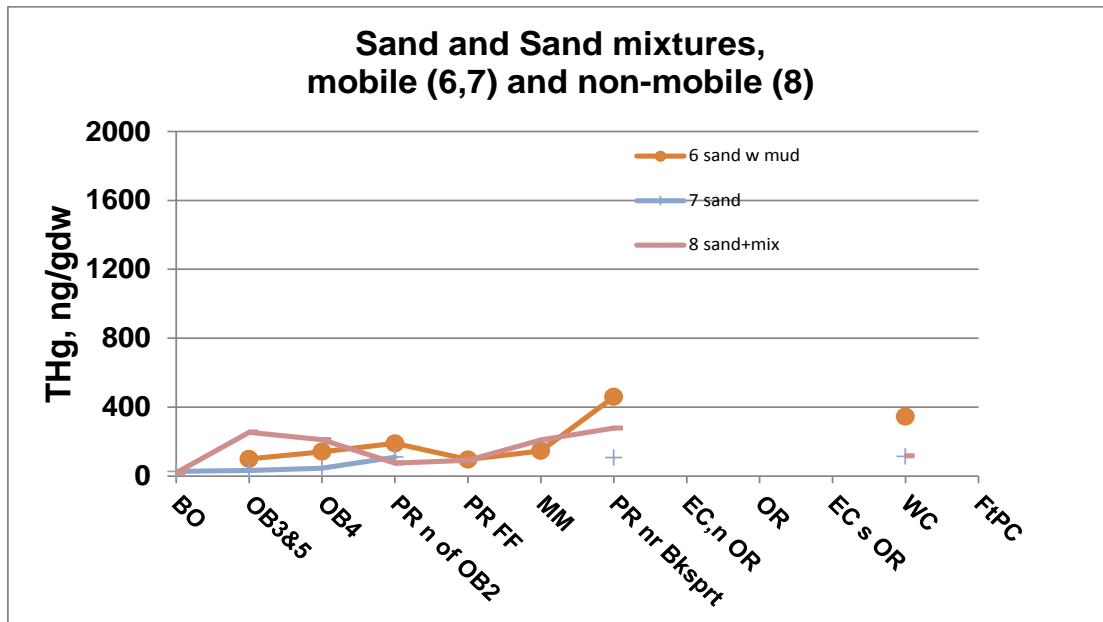


Figure 8-19a. Total Hg concentrations in “mobile” and “non-mobile” sand and sand mixtures. Mobile classes: 6 - sand with mud, 7 - sand. Non-mobile class: 8 - sand with rocks, shells, woodchips, mussels.

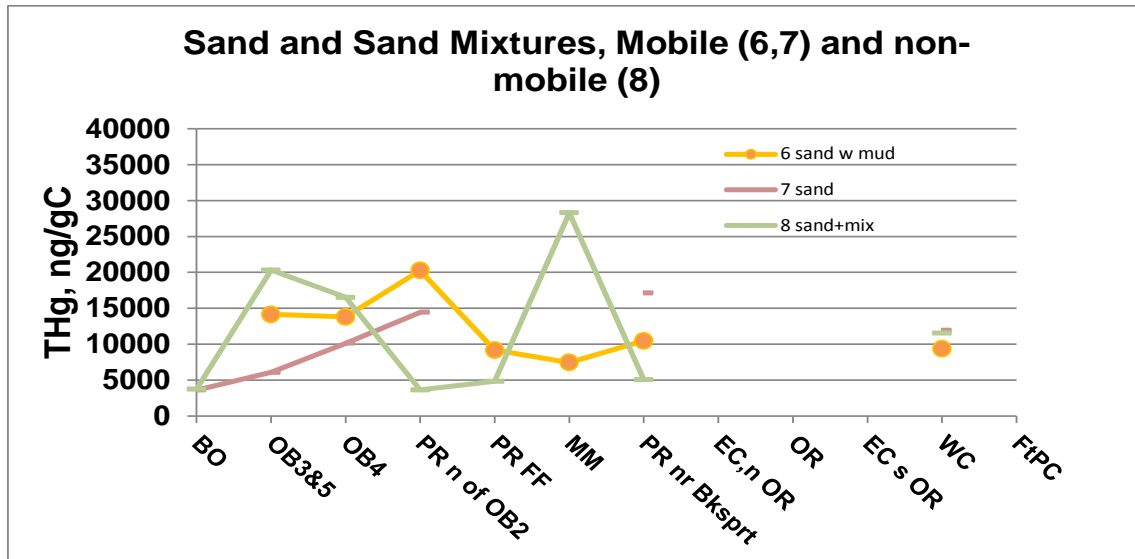


Figure 8-19b. Total Hg concentrations per unit of carbon in “mobile” and “non-mobile” sand and sand mixtures. Mobile classes: 6 - sand with mud, 7 - sand. Non-mobile class: 8 - sand with rocks, shells, woodchips, mussels.

4.3.4 Summary

In answer to the question “Were total Hg concentrations related more to location, or to type (class) of sediment?”, the sediment type was clearly more important than the location of the sample in determining the total Hg concentration on a dry wt. basis. The lack of importance of location was true for depth, north to south distribution, and local sub-area. With respect to local sub-area, the patterns were less clear, but no particular sub-area showed consistently higher or lower values for all the classes.

The wide differences in total Hg concentrations in different types of sediment means that care needs to be taken in looking at geographic patterns, i.e., it is best to compare sediments of the same type when doing comparisons from one place to another. In this data set, the mud samples were the most complete in terms of geographic coverage, and they showed very little difference in total Hg concentrations in the different subareas of this study. This is likely the result of hydrodynamic conditions in the estuary, which promote strong daily tidal movements of water, which result in mixing of mobile sediments prior to their settling in depositional areas. It should be noted that all the areas in this data set are within the part of the Penobscot identified as contaminated in the Phase I report, and do not include as wide a geographic range as in the Phase I report.

4.4 Were total Hg concentrations different in “mobile” vs “non-mobile” sediments?

To calculate the averages for mobile and non-mobile samples, all individual results were used, i.e., not the averages already calculated for each class in the previous section. The reasoning for this was that the sampling was done at random, and therefore the

types of samples collected should be somewhat reflective of the abundance of those types in the sampling area.

The average value of total THg ng/g dry wt. was higher for the “mobile” samples than for the “non-mobile” samples (Table 8-6a). This was a significant difference (P = 0.007, using a 2 sample t-test on log transformed data). This difference could be explained by the fact that the average values for % fines and % LOI were higher in the “mobile” samples (Tables 8-6a and 8-6b). These characteristics are both associated with higher Hg concentrations, and thus could explain the higher total Hg concentrations on a per gram dry wt. basis.

When Hg concentrations were expressed as total Hg per gram of carbon, there was no significant difference between the means of the mobile and non-mobile sample groups (using the same t-test referred to above).

Table 8-6a: Average total Hg and % fines in grab samples of different types. Averages are for all samples collected in June and August, 2011.							
Class	n	Total Hg, ng/g dry wt.			% fines		
		Average	Std Dev	% Std Dev	Average	Std Dev	% Std Dev
All Mobile samples*	108	731	444	61%	55%	34%	62%
All non-mobile samples*	94	544	598	110%	37%	35%	95%

Table 8-6b: Average % LOI and average concentrations of total Hg per gram of carbon in each class of grab sample.							
Class	n	%LOI			Total Hg, ng/g C		
		Average	Std Dev	% Std Dev	Average	Std Dev	% Std Dev
	202						
All Mobile samples*	108	15%	14%	94%	12800	7900	62%
All non-mobile samples*	94	8%	6%	78%	15000	12000	80%

For each geographic sub-area, the average total Hg concentration in “mobile” sediments was either similar to or greater than the corresponding average for “non-mobile” sediments (Table 8-7, Figure 8-20).

	Mobile total Hg ng/g dry wt.	Non-mobile, total Hg ng/g dry wt.
BO	27	17
OB3&5	576	672
OB4	632	324
PR n of OB2	458	626
PR FF	660	367
MM	921	927
PR n of Bucksport	895	429
EC, n OR	737	612
OR	994	1032
EC s OR	851	238
WC	804	567
FtPC	628	370

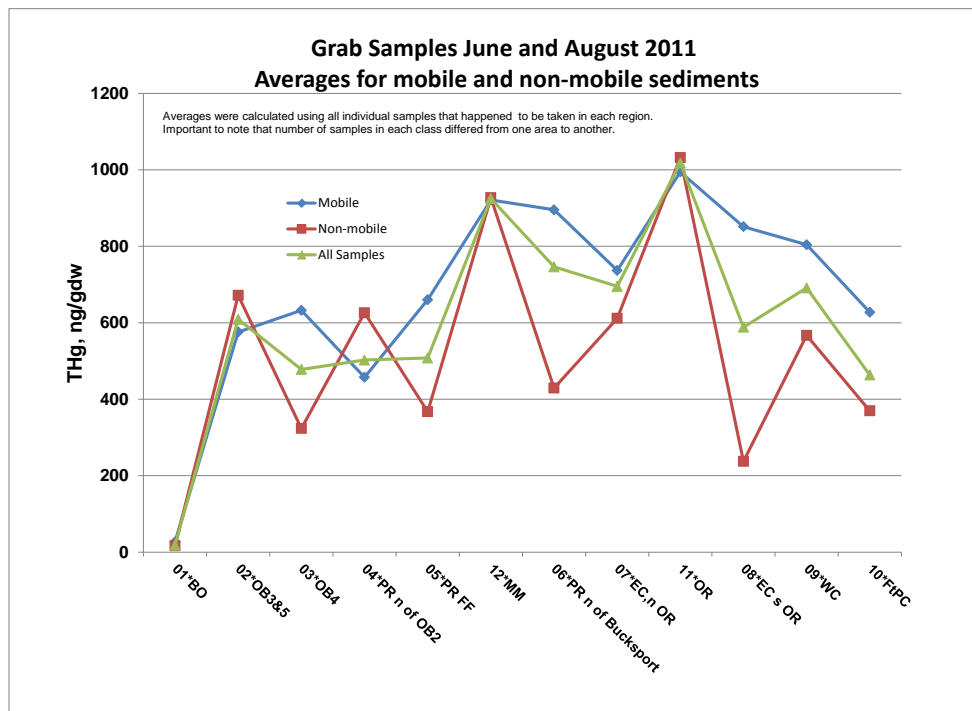


Figure 8-20. Average total Hg concentrations in mobile and non-mobile sediments, for each geographic sub-area, ordered roughly north to south.

There were some significant differences in mean mobile sediment total Hg concentrations, per gram dry wt., in the different geographic sub-areas, but the Duncan test did not identify any subgroups, and the Tukey pairwise test found only one pairwise difference, so overall there was not sufficient statistical evidence to say that total Hg concentrations in the mobile samples were different from one geographic area to another. In contrast, non-mobile samples were significantly different from one area to another, both for total Hg/g dry wt. (Figure 8-20) and for total Hg ng/g C (data not shown).

The “mobile” and “non-mobile” categories are large groups, made up of several subcategories or classes of sediments. The “mobile” classes were unconsolidated mud, unconsolidated mud mixtures, sand with mud, sand and wood chips (Figure 8-21), while the “non-mobile” classes were consolidated mud, mixed mud, mussels, sand with mud, sand with rocks, and gravel or rocks. These smaller classes have widely different total Hg concentrations (Table 8-1), and so the more general groupings into “mobile” and “non-mobile” categories in each sub-area (Table 8-7, Figure 8-20) could be affected by chance, i.e., how many of each type of sediment class, such as mud or sand, happened to be sampled in each geographic area. In the “mobile” category, mud and wood chips were high in total Hg, while sand and sand/mud mixtures were low (Figure 8-21). In the “non-mobile” category, only the consolidated muds were in the highest range (Figure 8-22).

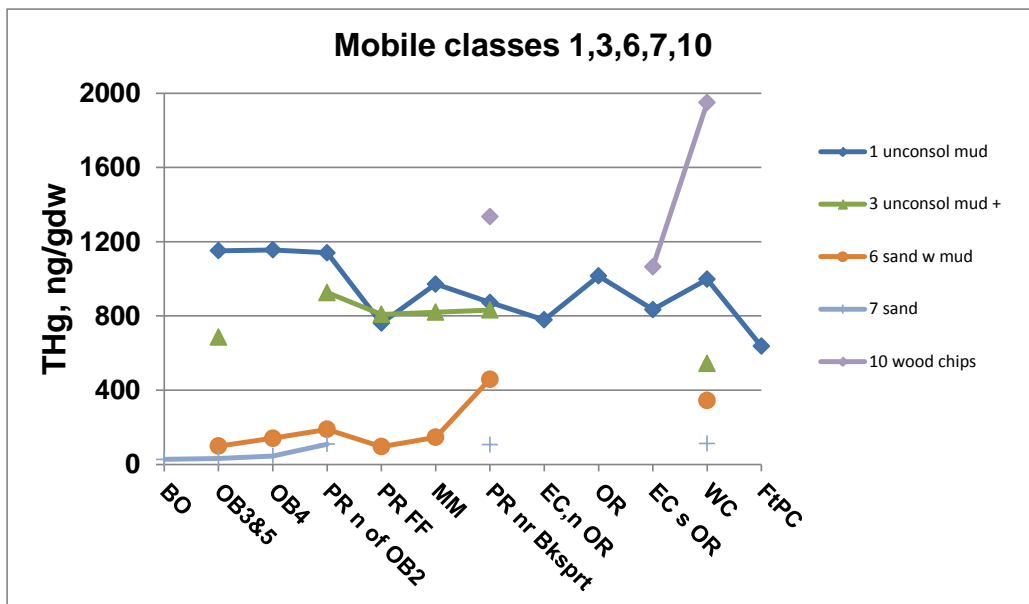


Figure 8-21. Total Hg concentrations in the “mobile” classes of sediments: 1 - unconsolidated mud, 1.5 - unconsolidated mud overlying consolidated mud, 3 - mix of unconsolidated mud and anything else, 6 - sand with mud, 7 - sand, 10 - woodchips.

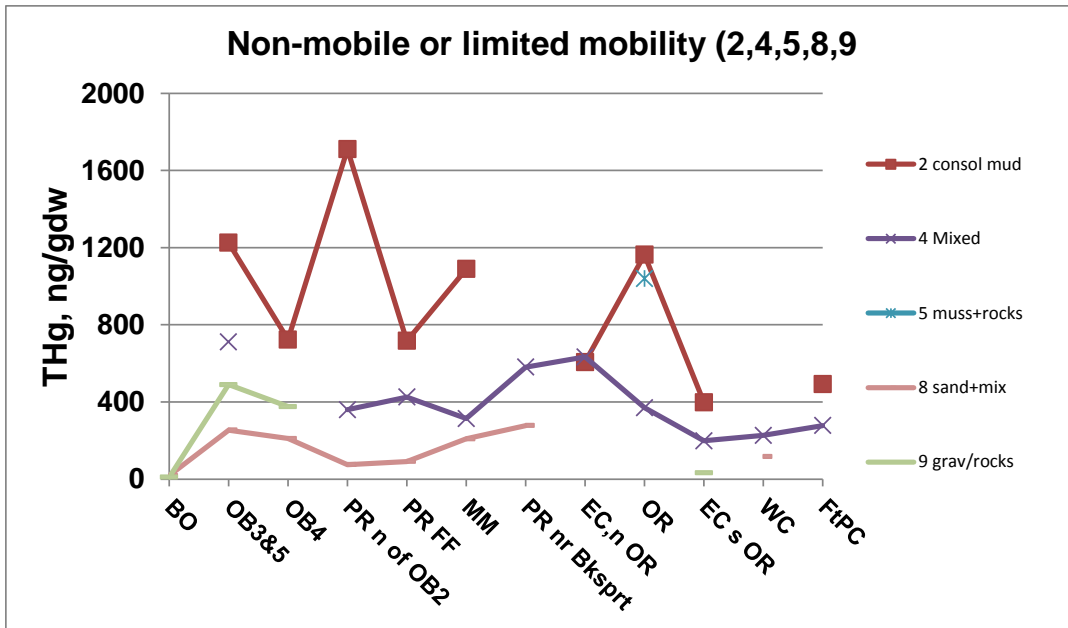


Figure 8-22. Total Hg concentrations in the “non-mobile” classes of sediments: 2 - consolidated mud, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks etc., 6 - sand with mud, 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured.

4.4.1 Summary

The mean concentration of total Hg ng/g dry wt. in mobile sediments was significantly higher than the mean in non-mobile sediments, but there was no significant difference for total Hg expressed as per gram of carbon. The difference on a per gram dry wt. basis could be because of differences in the prevalence of types of sediments in the mobile category as compared to the non-mobile category. By either measurement, the data indicated that the mobile sediments were either higher in total Hg than surface, non-mobile sediments, or similar in total Hg. Thus, the mobile pool cannot be viewed as made up of cleaner sediments than the consolidated surface sediments. Another important point is that in mobile samples, there was a wide variety of types of sediments, depending on the site, and so the mobile “pool” should not be visualized as one big mixed pool, but rather made up of smaller pools of different types of material.

4.5 What were methyl Hg concentrations in the mobile and non-mobile sediment grab samples - were they related to total Hg concentrations, and how did they compare to other sediments that have been sampled closer to shorelines (intertidal sites)?

Approximately half of the samples that were analyzed for total Hg were also analyzed for methyl Hg (117 out of 205). The range of average methyl Hg concentrations in the different classes of samples (0.5 to 45 ng/g dry wt., Table 8-8) was similar to that found previously in intertidal sediment sites (see “Copy of Sediment_Hg_data_IIIIIIIVVVI from Drew Feb 10_09 edited CK Dec 2012.xlsx]All Data sorted by Site, N to S”).

Table 8-8: Methyl Hg concentrations and % methyl Hg in different classes of mobile and non-mobile grab samples, 0-3 cm. %LOI and total Hg concentrations, which were measured on a larger number of samples, are included for comparison. “Mobile” classes were: 1 - unconsolidated mud, 3 - mix of unconsolidated mud and other material, 6 - sand with mud, 7 - sand, 10 - woodchips. “Non-mobile” classes were: 2 - consolidated mud, 4 - mixed mud, sand, shells, rocks, woodchips, mussels, 5 - mussels with rocks and other material 8 - sand with rocks, shells, woodchips, mussels, 9 - gravel or rocks; or scoured.

		n	Methyl Hg, ng/g dry wt., Average	Methyl Hg, ng/g dry wt. Std Dev	% Methyl Hg, Average	Class	n	% LOI Average	Total Hg ng/g dry wt. Average
Mobile									
Unconsolidated mud	1	22	19.9	7.6	2.3%	1	41	14.7%	916
Unconsolidated over consolidated	1.5	6	16.1	4.3	1.7%	1.5	11	12.5%	810
Mud mixture	3	10	23.1	15.0	2.7%	3	21	13.0%	772
Sand with mud	6	6	2.5	1.7	2.2%	6	12	3.4%	195
Sand	7	10	0.5	0.5	1.0%	7	14	1.5%	71
Wood chips	10	6	45.0	39.2	3.2%	10	9	50.1%	1381
Non-mobile									
Consolidated mud	2	27	16.9	10.1	2.1%	2	32	11.7%	934
Mud mixture	4	11	7.7	7.7	1.8%	4	29	5.6%	487
Sand mixture	8	12	5.1	8.6	2.1%	8	25	5.3%	141
Gravel, rocks	9	3	7.1	11.8	1.1%	9	7	3.6%	340

The muds, whether mobile or non-mobile (classes 1, 1.5, 3 and 2) had higher methyl Hg concentrations than the sands or gravels (7, 8, 9). Wood chips had the highest methyl Hg concentration, which was due to the high total Hg concentration (average of 1380 ng/g dry wt.), paired with a % methyl Hg at the high end of these classes (3.2 %, Table 8-8).

Methyl Hg was positively related to total Hg in both the mobile and non-mobile samples (Figure 8-23). All of the regressions were significant at the $p < 0.005$ level.

These methyl Hg measurements were done near the end of the Phase II study, and there was not an opportunity take fresh samples for measurement of methylation activity. The average percentage of total Hg that was methyl Hg (2%) suggests that methylation was occurring in both mobile and non-mobile sediments. % methyl Hg is a

good indicator of methylation activity, and the range of % methyl Hg found in these samples is similar to or greater than in continental shelf sediments where methylation has been measured (Hollweg et al. 2010). Methylation is generally thought to occur most readily in anoxic environments (e.g., Rudd 1995; Ullrich et al. 2001). Mobile sediments are frequently suspended in the oxic water column, where methylation should be minimal (Whalin et al. 2007). Also, the mobile mud samples were colored brown and therefore did not contain reduced FeS, as did the black, non-mobile consolidated muds, but on average the % methyl Hg was 3%. Wood chips had the highest average % methyl Hg. A possible explanation is the brown muds and the wood chips could contain microzones that are anoxic.

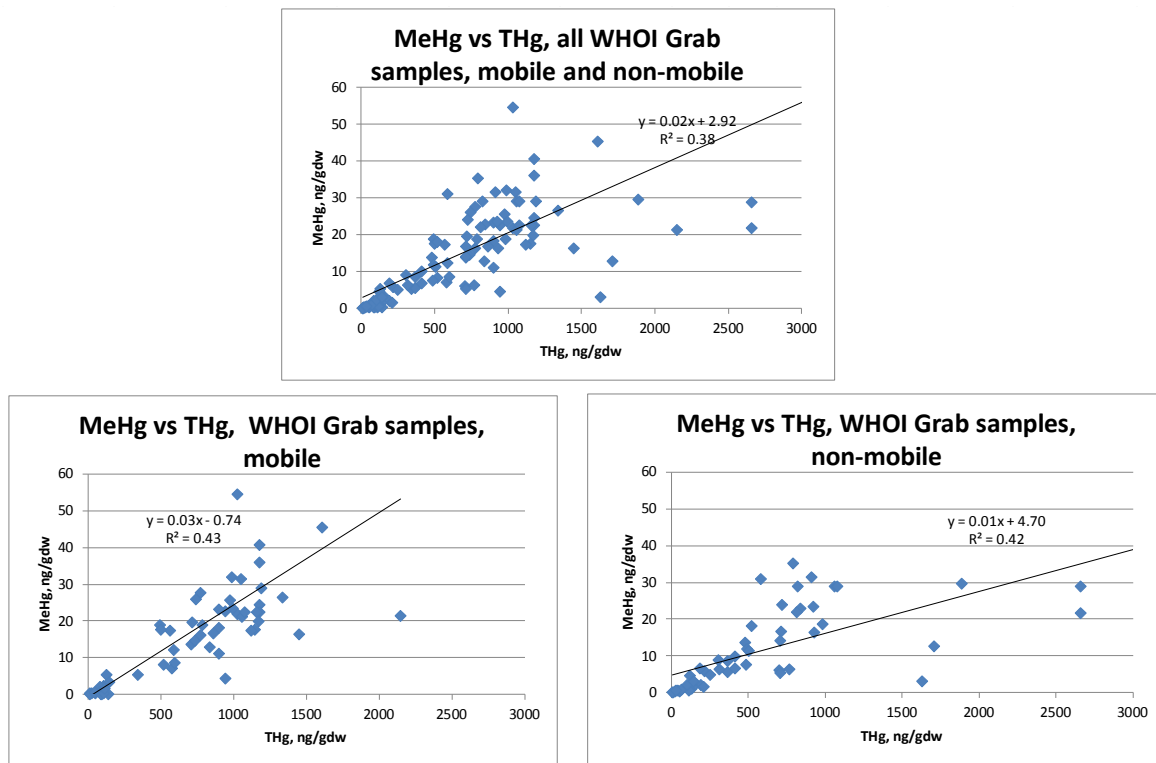


Figure 8-23. Methyl Hg vs total Hg in grab samples. All regressions were significant at the $p < 0.005$ level.

The class averages showed a better relationship between methyl Hg and total Hg (Figure 8-24), as in other data sets for these grab samples. The slope of this relationship was .03, indicating an average % methyl Hg of 3%. This is the same slope as found for the average methyl Hg vs average total Hg in the intertidal sites (Figure 1-3a in Chapter 1).

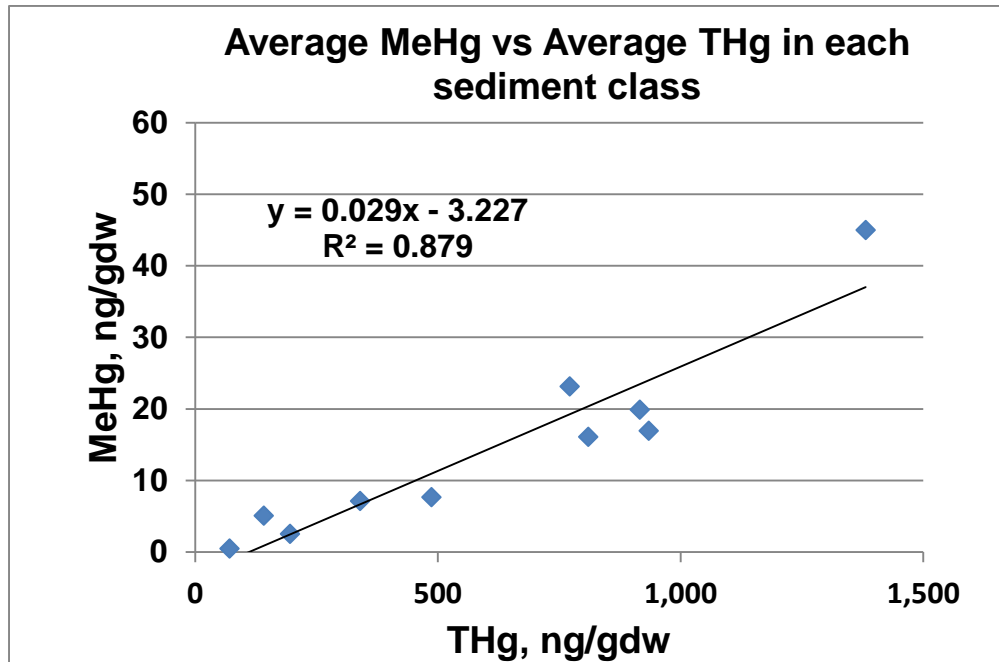


Figure 8-24. The average methyl Hg concentration in each sediment grab sample class vs the average total Hg concentration in each class.

4.5.1 Summary

Methyl Hg was detectable in most sediment grab samples, including “mobile” samples that are frequently suspended in the water column. Methyl Hg was positively correlated with total Hg, with average of 3% of total Hg present as methyl Hg. This % methyl Hg was similar to intertidal sediments. Methyl Hg in the mobile pool could be an important source of methyl Hg to biota, in addition to the methyl Hg in surface sediments already identified.

5 IMPLICATIONS

- The similarity of total Hg concentrations in mobile and non-mobile surface sediments supports the slow recovery rates discussed in other chapters. An inherent property of mobile sediments is that they are more often in the water column and subject to mixing. In contrast, radioisotope measurements in cores (Chapter 6) showed that there was very little mixing in surface sediments. Since an important source of sediment to depositional areas is presumably from the mobile pool, concentrations of Hg in non-mobile sediments are a historical record of what was in the mobile pool in the past. The surface sediment samples in this data set were the upper 3 cm, which on average contains 6 years of sediment accumulation. We found that concentrations in the mobile and surface sediments were very similar. This means that concentrations in the mobile pool must not have been changing rapidly enough in the past 6 years to be detected in the comparison of Hg concentrations in the mobile and non-mobile sediments. This agrees with the core data showing an approximately 34 year half time for

recovery of total Hg concentrations in the sediments (Chapter 6), and the hydrodynamic data showing that movement of particles from the upper estuary to the lower estuary below Verona Island is inhibited by the salt front near the southern end of Verona Island (Chapter 7)

- The large differences in total Hg concentrations among different classes of sediments shows that the type of sediment is an important factor in interpreting differences in total Hg concentrations from one site to another. Thus geographic patterns in total Hg contamination will be clearest when sediments of the same type, e.g., all mud samples, are used in the data analysis. In this study, data on muds showed very little difference in Hg concentrations from one area to another, in the part of the estuary below Veazie Dam and above Fort Point Cove. This is probably due to the strong tidal mixing throughout the estuary.
- The association of total Hg with the finest particles means that movement of these particles are important in determining the lateral movement and deposition patterns of total Hg in the upper estuary. Also, in any remediation procedure in which contaminated sediments are trapped and removed, the trapping of these finest particles needs to be considered as part of the engineering design.
- Normalizing Hg concentrations to carbon did not reduce the range of Hg concentrations found in individual samples within each class of sediments. However, the average values for total Hg, % fines, and % LOI showed very consistent relationships, i.e., sediment classes that were higher on average in % LOI or % fines were also high in average total Hg, and vice versa. Thus there are general characteristics of sands and muds that are useful in predicting Hg concentrations within the upper Penobscot Estuary. These would not be expected to generalize to areas where there is less Hg contamination.
- The similarity of the relationship between methyl Hg and total Hg in the grab samples and the intertidal sites shows that the sediments of the Penobscot estuary have remarkably similar characteristics with respect to methylation.
- Methyl Hg in the mobile pool should be considered a source of methyl Hg for biota, in addition to the methyl Hg in surface sediments already identified as a source.

6 ACKNOWLEDGEMENTS

This work could not have been done without the efforts and expertise of Dr. Rocky Geyer, Dr. David Ralston, and their crew from Woods Hole Oceanographic Institution. They designed and carried out the sampling program, collected all the samples, classified them, and did the grain size analyses and organic matter measurements. Mercury analyses were done by Flett Research, Ltd. and Dianne Kopec helped with the statistical analyses.

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