

# **PENOBSCOT RIVER MERCURY STUDY**

## **Chapter 6**

### **Estimates of recovery from mercury contamination in the Penobscot River Estuarine System by an assessment of sedimentation rates**

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## 1 SUMMARY

Sediment core dating using the bomb test fallout radionuclides  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  as 1963 event markers and the steady-state atmospherically delivered tracer radionuclide  $^{210}\text{Pb}_{\text{xs}}$ , ( $^{210}\text{Pb}_{\text{xs}} = \text{Excess-}^{210}\text{Pb} = \text{Total } ^{210}\text{Pb} - ^{226}\text{Ra}\text{-supported } ^{210}\text{Pb}$ ) revealed time-averaged sedimentation rates for each site. Mercury (Hg) profiles in the same sediment cores showed maxima at depths that can be attributed to a 1967 release date, and decreased to lower surface sediment Hg concentrations. Hg(o) values at different sites were quite similar, even though individual Hg profiles are, at times, quite heterogeneous. For example, while highest Hg(o) values were found in Penobscot River cores, mean (average) Hg(o) values decrease from Orland River > Penobscot River ~ Mendall Marsh > estuarine sites. However, Penobscot River, Orland River and Mendall Marsh cores are statistically not different (1 standard deviation [SD] of the mean value is given below), averaging about 600-700 nanograms per gram (ng/g), while estuarine sites cores are lower. Penobscot River:  $742 \pm 88$  ng/g; Mendall Marsh:  $639 \pm 75$  ng/g; Orland River:  $892 \pm 156$  ng/g; estuarine sites:  $513 \pm 53$  ng/g. Only six out of 24 Penobscot River cores have Hg(o) values  $\geq 1000$  ng/g, and only 1 out of 11 Mendall Marsh cores have Hg(o) values  $\geq 1000$  ng/g. Furthermore, only 1 out of 5 Orland River cores have Hg(o) values  $\geq 1000$  ng/g, and none of the 17 estuarine sites cores have Hg(o) values  $\geq 1000$  ng/g.

One could ask the question in what form Hg was deposited to the sediments. In agreement with the recent literature, one can assume that the carrier phases for Hg are sulfur (S) containing compounds (e.g., iron sulfides and thiols). However, these compounds are present at much higher concentrations than Hg, and thus, relationships between Hg and S cannot necessarily be expected. Indeed, no relationships have been found between Hg concentrations and concentrations of total organic carbon (TOC) or S in sediments, except for Hg values at the peak depth and immediately above and below. This strongly suggests that initial dispersal of Hg and deposition was aided by S in TOC, most likely from S and TOC compounds in co-occurring paper mill effluents. However, the dispersal and deposition of Hg in recent times is controlled by lateral processes, which redistributes Hg from sites with higher to sites with lower Hg concentrations in surface sediments, which also explains the slowing down of the decrease in Hg concentration in most surface sediments.

Sedimentation rates determined from radionuclide profiles agreed, within the errors of the measurements, with the assumption of a major Hg input into the Penobscot River in 1967. Thus, Hg peaks were also useful for sediment dating and sedimentation rate calculations. Apparent sedimentation rates calculated from event tracers Hg,  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$ , and steady state tracer  $^{210}\text{Pb}_{\text{xs}}$ , agree well. Since vertical sediment mixing is restricted to the upper 3 cm or so, historic input rates of radionuclides and Hg to a particular site are only minimally distorted by vertical mixing. The Hg profiles are more influenced by lateral processes, as evidenced by uneven tracer profiles that are likely reflecting lateral inputs of sediments and associated tracers.

Therefore, we are confident that radioactive dating of sediments established that one can take Hg profiles and interpret them as a temporal input record into sediments from a particular site. Average sedimentation rates from all 57 sediment cores, using either

$^{137}\text{Cs}$  (or  $^{239,240}\text{Pu}$ ) or Hg, are  $0.6 \pm 0.06$  cm/yr (1 SD of mean). Calculated average sedimentation rate (SR, cm/yr) for each core assuming constant SR over the length of the sediment core, are then used to reconstruct the input history of Hg to that site.

Hg tracer profiles reveal sharp peaks around this maximum Hg deposition event assumed to have occurred in 1967, strongly suggesting that initially, the apparent recovery after this Hg pulse input was quite fast. However, afterwards, in most cores, Hg decreased relatively more slowly with time (in cores where Hg concentrations were elevated), stayed constant, or even increased towards the present time (when Hg concentrations were generally lower), which strongly suggests input from redistribution of the Hg from sites with higher surface concentrations, Hg(o), to sites with lower Hg(o) concentrations. Therefore, the Hg profiles were divided into two sections: the first 21 years (1967-1988) with relatively fast recovery, and the recent 21 years (1988-2009), with a relatively slower recovery rate. The recent 21 years of input history was then given close attention to reveal 'apparent' Hg recovery rates. 'Apparent' is used here to indicate that evaluated recovery rates depend on assumptions and degree of extrapolation. Calculated apparent recovery half times ( $t_{1/2} = \ln 2/\alpha$ ) were calculated from an exponential ( $\text{Hg}(t) = \text{Hg}(t=21) * \exp(-\alpha * t)$ ) fit to the Hg concentration profiles over the past 21 years. Hg concentrations from the past 21 years (1988-2009) were then evaluated to reveal apparent recovery rates and apparent half times ( $t_{1/2}$ ). These calculations were first carried out assuming a recovery to near 0 ng/g Hg in surface sediments. When  $t_{1/2}$  are calculated assuming a non-zero asymptotic level ( $\text{Hg}(\infty)$ ) of 400 ng/g Hg, apparent recovery half times would appear to be faster, but the time scale to reach a certain target concentration of  $\text{Hg}(\infty)$  would be more similar to the  $\text{Hg}(\infty)$  approach, depending on what is assumed for  $\text{Hg}(\infty)$ .

Suitable Hg profiles would need to indicate that these coring sites have been in close communication with the system, and thus, can be taken as an indicator what the system as a whole has experienced in the last 21 years. For the recent 21 year time period, there is a large spread of  $t_{1/2}$  values at Penobscot River, but not as much at Mendall Marsh sites, in the cores that were deemed to be representative of the recovery of the Penobscot River 'system'. Mean values of  $t_{1/2}$  at Penobscot River were  $31 \pm 6$  years for 16 of our 24 cores, and  $22 \pm 3$  years in 9 out of 11 cores at Mendall Marsh (where semi-exponential decreases were observed). Eight out of 24 Penobscot River cores, and 2 out of 11 Mendall Marsh cores (with generally lower Hg concentrations) do not show any Hg decrease in the past 21 years (or even show Hg increases towards the surface), thus indicating that they were in much slower 'communication' with the rest of the system. In 12 out of 18 estuarine sites cores,  $t_{1/2}$  values range from 20 to 120 years (mean of  $78 \pm 13$  years). In 5 out of 18 estuarine sites cores (with lower Hg concentrations), Hg values actually increase towards the surface or stay constant. In 4 out of 5 Orland River cores,  $t_{1/2}$  values average  $77 \pm 21$  years. In the other Orland River core, Hg values slightly increased towards the surface. One can conclude that such sites with lower and/or Hg concentrations that increase towards the surface are sites, which are not in close communication with the rest of the system, and thus, are also not representative of that system as a whole. The Penobscot system, as a whole, however, clearly has recovered a great deal since the late 1960's. It appears then that

sedimentary Hg(o) values in cores that are deemed to be representative of the system as a whole are currently converging to values close to 600-700 ng/g.

Of course, calculated apparent half times of several decades do not mean that after that time, sediments have fully recovered. Estimated recovery times depend on what acceptable Hg(o) concentration one assumes. Regardless, one would have to assume several of these half times to estimate system recovery. For example, one can estimate that to get from Hg(o) of about 700 ng/g to a value of Hg( $\infty$ ) of about 50 ng/g at Mendall Marsh, it would take about 4 half lives of 21 y, or 84 years.

## 2 INTRODUCTION

The Penobscot River drains a watershed of approximately 19,350 km<sup>2</sup> and represents the second largest river system in New England. The lower Penobscot River is defined by a long narrow estuary (mean width, 0.75 km), and measurable tidal influence extends 35 km upriver to the city of Bangor. Point sources of mercury (Hg) pollution within the estuary include a recently (in the year of 2000) closed chlor-alkali production facility (HoltraChem) that operated from 1967, as well as several upriver paper mills. Sediment total Hg concentration upstream of the limit of tidal influence is of the order of 100 nanogram per gram (ng/g) dry weight (dry wt.) of sediment, comparable to that of other New England rivers (Morgan 1998). Surface-sediment total Hg concentrations in the Penobscot estuary have been previously reported to range between about 125 and 2750 ng/g (Merritt and Amirbahman 2007). The highest value that has been reported in the published literature is 230,000 ng/g, which is within the chlor-alkali plant discharge zone (Morgan 1998). The question arises as to how long it will take for these elevated concentrations to come down to an acceptable level, i.e., how long will it take for the Penobscot River Estuary system to 'recover' from Hg pollution. This Hg pollution has produced greatly elevated methyl Hg concentrations in wetlands and wildlife, threatening organism and ecosystem health. In order to assess recovery, an evaluation and comparison of sedimentation rates and deposition rates of Hg, calculated as the product of sedimentation rate and Hg concentration over the polluted riverine and estuarine system, was needed. The purpose of this study was therefore to assess recovery, using an approach whereby Hg concentrations and sedimentation rates were determined using the 1963 bomb fallout event markers <sup>137</sup>Cs and <sup>239,240</sup>Pu, and the atmospherically delivered steady-state marker Excess-<sup>210</sup>Pb ( $^{210}\text{Pb}_{\text{xs}} = \text{Total } ^{210}\text{Pb} - ^{226}\text{Ra}\text{-supported } ^{210}\text{Pb}$ ) in 57 sediment cores taken from the Hg polluted riverine – estuarine Penobscot system.

### 2.1 Materials and Methods

57 sediment cores that were collected in summer 2009 by Dr. Kevin Yeager (formerly at the University of Southern Mississippi [USM], and now at the University of Kentucky [UK]) from the Penobscot River estuarine system (Figure 6-1), cut into sections, and distributed to 3 labs at Texas A&M University, Galveston (TAMUG), USM/UK and Flett Research Ltd. While aliquots of these sections were kept and analyzed at USM/UK, samples were also sent to TAMUG and to Flett Research. This included aliquots of all sediment samples analyzed first for Hg at Flett Research, 840 sediment samples that were non-destructively gamma counted for <sup>137</sup>Cs and <sup>7</sup>Be, and further processed for <sup>210</sup>Pb analysis in each of the 3 labs. Furthermore, at TAMUG, 200 samples were processed and analyzed for plutonium, <sup>239,240</sup>Pu, 2000 samples for carbon (C) and nitrogen (N), and 240 samples for sulfur (S). In each lab, sediments were weighed, dried, and reweighed to determine porosity from the water content. After that, they were ground with mortar and pestle, homogenized, and then gamma counted for the determination of <sup>137</sup>Cs, as pulse input tracer for the bomb fallout deposition in 1963. After spiking with yield-tracer <sup>209</sup>Po, aliquots underwent a wet chemical digestion and separation procedure to quantify <sup>210</sup>Po as a measure of total <sup>210</sup>Pb in the sediments. Excess-<sup>210</sup>Pb ( $^{210}\text{Pb}_{\text{xs}} = \text{Total } ^{210}\text{Pb} - ^{226}\text{Ra}\text{-supported } ^{210}\text{Pb}$ ) was then used to

determine sedimentation rates, as described in Santschi et al. (1999). Furthermore, a separate aliquot was spiked with  $^{242}\text{Pu}$ , underwent a wet chemical digestion and separation procedure to quantify  $^{239,240}\text{Pu}$ , which is another pulse input tracer for the bomb fallout deposition in 1963. An advantage of Pu(IV) is that, contrary to  $^{137}\text{Cs}^+$ , it cannot be remobilized by  $\text{K}^+$  in salt water, and thus is a more reliable tracer for the 1963 bomb fallout event, especially in estuarine regions of the Penobscot River. Besides  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ,  $^{239,240}\text{Pu}$ , total organic carbon (TOC) and S were also determined according to procedures given in Santschi et al. (2001).

Results from all the three laboratories (USM/UK, TAMUG and Flett Research) were then combined in this report. All Hg samples were determined by Flett according to procedures given in <http://www.flettresearch.ca/Webdoc2.htm>.  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$  in cores determined in Flett Research were processed according to <http://www.flettresearch.ca/index.htm>, and those determined at USM/UK according to Yeager et al. (2004). The radiochemical results have also undergone interlab calibration and reported values compare favorably.

Details of procedures: In general, dried sediment samples of about 10 g size were used for non-destructive gamma counting in a low-background, high-efficiency high-purity Germanium (HPGe) well detector, followed by wet chemical extraction procedures and alpha counting for individual radionuclides. All 57 samples were thus first gamma counted and then processed for wet chemical/alpha counting analyses for Pu and Pb isotopes.

The sequence of steps followed was as follows:

- gamma counting of samples for about one day to obtain results for  $^{210}\text{Pb}$  (46 keV),  $^{234}\text{Th}$  (63 keV),  $^{226}\text{Ra}$  (352 keV, only approximate),  $^7\text{Be}$  (478 keV),  $^{137}\text{Cs}$  (662 keV),
- $^{210}\text{Pb}$  analysis (in all 3 labs) by wet chemistry followed by alpha counting for 1-2 days,
- $^{239,240}\text{Pu}$  analysis of a subset of samples (200 samples only) at TAMUG by wet chemistry (about 8 days) followed by alpha counting for 1-2 days.

Sedimentation rates, SR, were calculated from the Pu and Cs peaks using their 1963 peak concentration, as the ratio of the depth of maximum activity concentration and time (2009-1963=46 years). SRs were also calculated from the steady state tracer  $^{210}\text{Pb}_{\text{xs}}$  using the slope of an exponential model to the  $^{210}\text{Pb}_{\text{xs}}$  activities (vs. depth) below the mixed layer, as  $\text{SR} = \lambda/\text{slope}$ , with  $\lambda = \text{decay rate of } ^{210}\text{Pb} = \ln 2/22.1 \text{ years} = 0.03 \text{ yr}^{-1}$ , and slope in  $\text{cm}^{-1}$ . Alternatively, sediment accumulation rates were also calculated also from the  $^{210}\text{Pb}_{\text{xs}}$  profiles vs. cumulative mass depth ( $\text{g cm}^{-2}$ ).

Hg recovery rates were then estimated from an assessment of how fast Hg was decreasing from its peak Hg concentration (Hg(max)) to the surface concentration (Hg(o)), either by taking that ratio, or by using the sections of the Hg profiles in the dated sediments to determine Hg inputs as a function of time.

Apparent recovery half time calculation: Apparent recovery half times ( $t_{1/2} = \ln^2/\alpha$ ) were calculated from an exponential fit to the Hg concentration profiles (Hg(t)) over the past 21 years (Hg(t=21)), as  $Hg(t) = Hg(t=21) \exp(-\alpha*t) + Hg(\infty)$ , with  $Hg(\infty)$  = asymptotic level of either 0 or 400 ng/g ( $t_{1/2}^*$ ).

### 3 RESULTS

Analysis of profiles of radionuclides, Hg, TOC, and S, were carried out to determine recovery rates of Hg in the Penobscot River estuarine system, which is dominated, to a large extent, by lateral transport processes (Figure 6- 2).

Considering this caveat, rates of sediment mixing, sediment accumulation, Hg accumulation and inventories, as well as accumulation and inventories of radionuclides, were determined and evaluated for their usefulness to assess Hg recovery in the riverine-estuarine system. Results for all 57 cores are given in Table 6-1 and Appendix 1 ('Summary Inventory\_Sed Rate\_Hg Summary\_UK TAMUG FLETT').

$^{210}\text{Pb}_{\text{xs}}$  profiles, determined from  $^{210}\text{Po}$  analyses, were then used to calculate sedimentation rates from the exponential portion of the profile below the surface layers in the historical layer (eq. 1)

$$\ln(^{210}\text{Pb}_{\text{xs}} / ^{210}\text{Pb}_{\text{xs}}^0) = -\lambda z/S = -\lambda z_m/S_a \quad (\text{Robbins et al. 1978}) \quad (1)$$

With:

$z$ =depth (cm);

$t$ =time;

$\lambda$ =decay constant =  $0.03 \text{ yr}^{-1}$ ;

$^{210}\text{Pb}_{\text{xs}} = ^{210}\text{Pb} - ^{226}\text{Ra}$ ;

$^{226}\text{Ra} = ^{222}\text{Rn}$ ;

$^{210}\text{Po} = ^{210}\text{Pb}$  (for alpha counting);

$t = z/S = z_m/SR_a$ ;

$z_m$  = cumulative mass depth in  $\text{g cm}^{-2}$ ;

$SR_a$  = sediment accumulation rate in  $\text{g cm}^{-2} \text{ yr}^{-1}$ .

A list of sedimentation rates, calculated from event (pulse input) and steady state tracer radionuclides, are given in Table 6-1.

Selected profiles of porosity and particle concentration are depicted in Figure 6-3, and  $^7\text{Be}$  in Figure 6-4, in order to assess extent of surface sediment mixing. The large variability of porosity and particle concentrations as a function of depth, together with the shallow penetration of  $^7\text{Be}$ , supports the assumption that vertical mixing in the sediments is very limited, as further discussed below.

Vertical mixing of sedimentary particles can broaden and displace peaks to greater depths, and might need to be taken into consideration for sedimentation rate estimation and Hg profile interpretation (Santschi et al. 1999, 2001). Such effects can be estimated

from  $^7\text{Be}$  profiles, peak broadening of tracers, or level of 'smoothness' of porosity profiles.

Sediment mixing rates can be estimated from shape and depth of  $^7\text{Be}$  penetration into surface sediments (Figure 6-4), as follows:

$$[^7\text{Be}(z)] = [^7\text{Be}(0)] \exp(-(\lambda/D_b)^{1/2} z), \quad (2)$$

With:

$\lambda$  = decay rate of  $^7\text{Be} = 4.77 \text{ yr}^{-1}$ ,  
 $D_b$  = particle mixing rate ( $\text{cm}^2 \text{ yr}^{-1}$ ),  
 and  $z$  = depth (cm).

In 2 out of 6 cores (MM7A and MM8A)  $^7\text{Be}$  penetration depths,  $z_m$ , were about 3 cm (see Figure 6-4), while in 4 out of 6 cores  $^7\text{Be}$  was only detectable in the upper 1 cm. In the remainder of sediment cores,  $^7\text{Be}$  activity concentrations were below detection limits, mostly due to radioactive decay during longer storage times. Maximum values of  $D_b$  ranged from 3-6  $\text{cm}^2/\text{y}$  ( $\sim 10^{-7} \text{ cm}^2/\text{s}$ ), which is rather low. Similar estimates can be obtained from the analysis of  $^{137}\text{Cs}$  or  $^{239,240}\text{Pu}$  peaks. Those few  $^7\text{Be}$  profiles shown in Figure 6-4 indicate relatively shallow mixing close to the surface, which agrees with the relatively uneven ('ragged') porosity profiles that indicate also a layering of accumulating sediments (example is shown in Figure 6-3). Our low estimates  $D_b$  and low  $Z_m$  are consistent with the relatively high variability in porosity and particle concentration profiles, which indicate that mixed layers must be rather shallow, mostly in the range of 1-2cm, in agreement with the  $^7\text{Be}$  profiles.  $^7\text{Be}$  inventories were determined as 1-2  $\text{dpm}/\text{cm}^2$ , which is within the expected range from atmospheric fallout

Furthermore, sediment mixing can also be estimated from the full-width at half maximum, FWHM, of the Hg peak =  $3.3 \cdot \text{sqrt}(D_b \cdot \Delta t)$  (Robbins et al. 1978) (3)

With:

$\Delta t$  = time within a mixed layer,  
 $D_b$  = particle mixing rate ( $\text{cm}^2 \text{ yr}^{-1}$ ),  
 FWHM = 5-10cm

This results in  $D_b = \leq 0.2 \text{ cm}^2/\text{y}$  for the time,  $\Delta t$ , Hg would reside in a mixed layer of 3 cm (assuming an average SR of 0.6  $\text{cm}/\text{y}$ ), i.e.,  $\Delta t$  of  $\sim 5\text{y}$ . This value of  $D_b$  is even lower than the estimate from  $^7\text{Be}$ , but confirms our assumption of negligible sediment mixing. Deeper  $^{210}\text{Pb}_{\text{xs}}$  mixed layers are not inconsistent with this interpretation, as these can also be produced by lateral processes, which are deemed important (see discussion). Thus, we conclude that sedimentation rate and Hg profile interpretations are not greatly affected by vertical sediment mixing.



## 4 DISCUSSION

As seen from Hg tracer profiles, they reveal sharp peaks around this 1967 input event. Examples are given in Figures 6-5 to 6-10. The existence of sharp Hg peaks at depth in the sediments strongly suggests that, at a given sampling site, initial apparent recovery after this pulse input was quite fast. However, afterwards, in most cores, Hg decreased relatively more slowly with time (in cores where Hg concentrations were elevated), stayed constant, or even increased towards the present time (when Hg concentrations were generally lower), strongly suggesting input from redistribution of the Hg from sites with higher surface concentrations, Hg(o), to sites with lower Hg(o) concentrations.

Hg was thus rapidly deposited and incorporated into all sediments, showing little evidence of remobilization or mixing. Even though it can be expected from the chemistry of Hg that Hg is tightly bound to sulfides and thiols in the environment, there is no correlation between Hg, total S or particulate organic carbon (POC) content (Figures 6-11 to 6-12). It appears that the likely carrier phases for Hg, S containing compounds (e.g., iron sulfides and thiols), are present at much higher concentrations than Hg, and thus, no relationships between Hg and S were found. However, Hg concentrations at peak depth and immediately above and below do show significant relationships to POC. This suggests that initial dispersal of Hg and deposition was aided by S in TOC, most likely from S and TOC compounds in co-occurring paper mill effluents. However, later present-day dispersal and deposition of Hg are controlled mainly by lateral processes, which is in agreement with the interpretation of the Hg profiles.

An overview of SR obtained from the deposition of sediments by Hg (1967 peak)  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  (1963 peak), and  $^{210}\text{Pb}_{\text{xs}}$  (evaluating steady state profile below mixed layer) are depicted in Figures 6-13 and 6-14. Sediment core dating using the 1963 event marker for maximum  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$  bomb test fallout, and the steady-state tracer  $^{210}\text{Pb}_{\text{xs}}$  agreed, within the errors of the measurements, with sedimentation rates calculated using the assumption of a major Hg input into the Penobscot River in 1967 (see Figures 6-5 to 6-10, and Figures 6-15 and 6-16). Thus, Hg peaks can also be used for sediment dating and sedimentation rate calculations. As can also be seen by Figures 6-13 to 6-16, apparent sedimentation rates calculated from event tracers Hg,  $^{137}\text{Cs}$  and  $^{239,240}\text{Pu}$ , and steady state tracer  $^{210}\text{Pb}_{\text{xs}}$ , agree well. Examples for this agreement are displayed in Figures 6-15 and 6-16. Since vertical sediment mixing is restricted to the upper 3cm or so, historic input rates of radionuclides and Hg are only minimally distorted by vertical mixing. However, uneven tracer profiles are likely reflecting lateral inputs of sediments and associated tracers.

It is important to realize that there is no contradiction with Rocky Geyer's statement (Chapter 7) that we are dealing here with "the more energetic parts of the estuary with an annual 'disturbance thickness' varying between ~1 cm (in quiescent areas) and perhaps 20 cm (e.g., in the intense trapping zone near Bucksport), superimposed on an overall net deposition of roughly 2 mm/yr (or whatever the local sea-level rise is)". Our averaged sedimentation rate is about 6 mm/yr. However, one does not find a thick resuspension layer of more than a few cm in thickness. One way to think about this is that, on one hand, Dr. Kevin Yeager sampled prospective sediment accumulation zones and not 'sediment slushing zones', and on the other hand, that sediment accumulation

is likely happening as an 'accretionary' process, whereby unconsolidated surface sediment can easily be disturbed by currents, but underlying sediment that is slowly hardening and accreting can no longer easily be resuspended and/or mixed.

It was furthermore very important to have data on Pu profiles for dating these sediments, especially for the estuarine sediments (see Figures 6-7 and 6-9). While the  $^{137}\text{Cs}$  profile shows either no peak or a double peak, Pu consistently peaked at one singular depth, which is also near the depth where Hg shows a peak. The reason why  $^{137}\text{Cs}$  in estuarine sediments can be an unreliable indicator of sedimentation rates is that adsorbed  $\text{Cs}^+$  can be displaced by the  $\text{K}^+$  from seawater.

One can conclude from sediment profile analysis of porosity,  $^7\text{Be}$ ,  $^{210}\text{Pb}_{\text{xs}}$ , and other radionuclides that 1) vertical mixing is restricted to a layer of 3 cm or less; 2) radionuclide profiles reflect inputs from horizontal inputs more than from vertical mixing, explaining irregularities in sediment profiles that are often observed; 3) the agreement between different radionuclides is best for  $\text{Hg}/^{137}\text{Cs}/^{239,240}\text{Pu}$ , and can be more variable for  $^{210}\text{Pb}_{\text{xs}}$  (see Figures 6-10 and 6-16).

Therefore, radioactive dating of sediments established that one can take Hg profiles and interpret them as a time input record into sediments from a particular site. Average sedimentation rates from all 57 sediment cores, using either  $^{137}\text{Cs}$  (or  $^{239,240}\text{Pu}$ ) or Hg, are  $0.6 \pm 0.06$  cm/yr (1 SD of mean). Calculated average SR (cm/y) for each core, assuming constant SR over the length of the sediment core, were then used to reconstruct the input history of Hg to that site.

Areas with higher SRs have higher  $^{137}\text{Cs}$  inventories, as they contain  $^{137}\text{Cs}$  not only from direct fallout (about 10 dpm/cm<sup>2</sup> for the Penobscot River estuary system, estimated from the recorded fallout of  $^{90}\text{Sr}$  to New York City, and assuming a ratio of  $^{137}\text{Cs}/^{90}\text{Sr}$  of 1.5), but also from erosion of drainage basin soils and river bank sediments.  $^{137}\text{Cs}$  inventories, when compared to those expected from bomb fallout (Table 6-1), can be taken as indicators of sediment focusing or erosion for that coring site. The ratios of measured  $^{137}\text{Cs}$  inventory to  $^{137}\text{Cs}$  inventory estimated from average expected fallout, range from  $<1$  to  $>10$ , indicating both sediment erosion ( $<1$ ) and sediment focusing ( $>1$ ) effects in different sediment cores. This information on the tendency of a particular site to focus  $^{137}\text{Cs}$  could then be applied to Hg as well.

Apparent recovery times can be calculated in a number of different ways (Figure 6-17), using analyses of Hg peak spreading, a vertical mixed layer approach, or a recovery index ( $\text{Hg}(\text{o})/\text{Hg}(\text{max})$  ratio) approach. However, all these approaches suffer from assumptions of steady state, vertical transport only (i.e., no horizontal inputs), and constancy of recovery rates. Such assumptions were deemed less realistic, as discussed below. Thus, another, and as it turned out, the most appropriate, approach, that was then adopted, was by simply using the last 21 years of the Hg profiles in the 57 sediment cores (Figure 6-18). As discussed further below, this was accomplished by using the calculated average SR) (cm/y) to calculate the time of deposition of Hg (Figures 6-5 to 6-10).

The striking observation from assessing these Hg profiles is that Hg in most sediment cores shows a sharp peak over about the lower half of the profile, and a much slower change in the upper profile. The time period since assumed Hg release date is 42 years (=2009-1967). Therefore, the profiles were then analyzed in these two separate sections. When plotting Hg concentrations vs. the time of deposition for the first 21 years (1967-1988) it shows a fairly narrow Hg peak, which indicates an initially fairly fast recovery. The recent 21 years (1988-2009), however, shows often a considerably slower recovery, as deduced from the more modest Hg concentration changes. The recent 21 years of input history was then given close attention to deduce apparent Hg recovery rates. Apparent recovery half times ( $t_{1/2} = \ln 2/\alpha$ ) were thus calculated from an exponential fit, i.e., eq. 1, to the Hg concentration profiles over the past 21 years.

$$\text{Hg}(t) = \text{Hg}(t=21) * \exp(-\alpha * t) \quad (4)$$

Hg concentrations from the past 21 years (1988-2009) plotted vs. the time of deposition are given in Figures 6-19 and 6-20.

Suitable Hg profiles would need to indicate that these coring sites have been in close communication with the system, and thus, can be taken as an indicator what the system as a whole has experienced in the last 21 years. For the recent 21 year time period, there is a large spread of  $t_{1/2}$  values at Penobscot River, but not as much at Mendall Marsh sites, in the cores that were deemed to be representative of the recovery of the Penobscot River 'system'. Mean values of  $t_{1/2}$  at Penobscot River were  $31 \pm 6$  years for 16 of our 24 cores, and  $22 \pm 3$  years in 9 out of 11 cores at Mendall Marsh (where semi-exponential decreases were observed). Eight out of 24 Penobscot River cores, and 2 out of 11 Mendall Marsh cores (with generally lower Hg concentrations) do not show any Hg decrease in the past 21 years (or even show Hg increases towards the surface), thus indicating that they were in much slower 'communication' with the rest of the system. In 12 out of 18 estuarine sites cores,  $t_{1/2}$  values range from 20 to 120 years (mean of  $78 \pm 13$  years). In 5 out of 18 estuarine sites cores (with lower Hg concentrations), Hg values actually increase towards the surface or stay constant. In 4 out of 5 Orland River cores,  $t_{1/2}$  values average  $77 \pm 21$  years. In the remainder (1) of the Orland River cores, Hg values either stay constant, or increase towards the surface. One can conclude that such sites with lower and/or Hg concentrations that increase towards the surface are sites, which are not in close communication with the rest of the system, and thus, are also not representative of that system as a whole. The Penobscot system, as a whole, however, clearly has recovered a great deal since the late 1960's. It appears then that sedimentary Hg(o) values in cores that are deemed to be representative of the system as a whole are currently converging to values close to 600-700 ng/g.

Apparent recovery half times ( $t_{1/2} = \ln 2/\alpha$ ) could also be calculated from an exponential fit to the Hg concentration profiles over the past 21 years, assuming a non-zero asymptotic level ( $\text{Hg}(\infty)$ ).

$$\text{Hg}(t) = \text{Hg}(t=21) * \exp(-\alpha * t) + \text{Hg}(\infty) \quad (5)$$

If one were to assume an asymptotic level ( $Hg(\infty)$ ) of 400 ng/g Hg, apparent recovery half times would be different. For example, at Mendall Marsh, the average apparent recovery half times from 8 out of 11 sediment cores where Hg is decreasing semi-exponentially, would be  $12.5 \pm 1.5$  years instead of  $21 \pm 3$  years (using the  $H(t=21)$  recovery half time method, eq. 4).

However, it would take different amounts of time to reach a certain target concentration of  $Hg(\infty)$ , and also depend on what is assumed for  $Hg(\infty)$ , as can be seen from the following example. Assuming  $Hg(t) = 700$  ng/g, and  $t_{1/2}$  of 12.5 y for  $Hg(\infty) = 400$  ng/g, and 21 y for  $Hg(\infty) = 0$ . Using the method in eq. 5, after 3 half lives of 12.5 y for  $Hg(\infty) = 400$  ng/g, i.e., 38 y, one would expect to reach 440 ng/g. However, using the method in eq. 4, after only 1 half life of 21 y for  $Hg(\infty) = 0$  ng/g, one would get already below that target concentration, i.e., to 350 ng/g. Thus, using the estimates from the 2 methods, it would take about 21-38 y for Mendall Marsh to get to about 400 ng/g, depending on the assumptions. To get to  $Hg(\infty)$  of about 50 ng/g, however, it would be expected to take about 4 half lives of 21 y, or 84 years to get from 700 ng/g to 44 ng/g.

Even though sediment profiles are quite heterogeneous, average  $Hg(o)$  concentrations in the top 1 cm of sediments are not so dissimilar. For example, while the highest  $Hg(o)$  values are found in Penobscot River cores, mean (average)  $Hg(o)$  values decrease from Orland River > Penobscot River ~ Mendall Marsh > estuarine sites. While Penobscot River, Orland River and Mendall Marsh cores are statistically not different (1 SD of mean value is given below), averaging about 600-700 ng/g, the mean value of ER cores is slightly lower. Penobscot River:  $742 \pm 88$  ng/g; Mendall Marsh:  $639 \pm 75$  ng/g; Orland River:  $892 \pm 156$  ng/g; estuarine sites:  $513 \pm 53$  ng/g. Only six out of 24 Penobscot River cores have  $Hg(o)$  values  $\geq 1000$  ng/g, and only 1 out of 11 Mendall Marsh cores have  $Hg(o)$  values  $\geq 1000$  ng/g. Furthermore, only 1 out of 5 Orland River cores have  $Hg(o)$  values  $\geq 1000$  ng/g, and none of the 17 estuarine sites cores have  $Hg(o)$  values  $\geq 1000$  ng/g, with 1000 ng/g arbitrarily taken for comparison purposes only.

When taking the ratio of surface concentrations of Hg ( $Hg(o)$ ), to the maximum Hg concentration,  $Hg(max)$ , this ratio, which can be taken as a proxy for a recovery index, inversely correlates with SR, as shown in Figure 6-21. This inverse correlation can be taken as an indicator for the speed of recovery at the sites with higher S values, i.e., faster recovery at places with higher sedimentation rates. Furthermore, this recovery index is also inversely related to  $Hg(max)$ , consistent with the conclusion that more contaminated sites recover faster (Figure 6-23), especially when the 3 most contaminated sites near-HoltraChem sites are excluded from the correlations. More contaminated areas, as indicated by their  $Hg(max)$  values, have lower  $Hg(o)/Hg(max)$  values (Figure 6-23). Sites with lower  $Hg(o)/Hg(max)$  values also have higher SRs (and thus, recover more rapidly), as shown in Figures 6-21 and 6-22.

Inverse correlations of  $Hg(o)/Hg(max)$  with SR (Figure 6-21), and direct correlations of SR with inventories of Hg (Figure 6-24), indicate that sites with higher SR tend to dilute Hg and lead to faster recovery times, i.e., sites with higher Hg inventories generally seem to recover faster than those with lower Hg inventories. Average peak Hg concentrations,  $Hg(max)$  decrease in the order Penobscot River > Mendall Marsh > Orland River > estuarine sites, i.e.,  $8000 > 3260 > 3200 > 1060$  ng/g. Average recovery indices,

Hg(o)/Hg(max), are lowest for Penobscot River and Mendall Marsh sites, i.e., 0.28, higher for Orland River (0.45), and highest for estuarine sites (0.58). Thus, the upper regions of the contaminated Penobscot River sites are the most contaminated and recover the fastest in terms of recovery rate, and the lower regions of Penobscot River/Estuary are the least contaminated and are recovering at the slowest rate. However, Hg(o) values are presently still higher upstream (Penobscot River) than downstream the river (estuarine sites).

Furthermore, inventories of Hg (Figure 6-24), as well as those of the different radionuclides (Figure 6-25) are also proportional to SR, leading to correlations among the inventories of radionuclides, and those of Hg (Figure 6-26). Conceptually, the redistribution process of Hg across the estuary includes Hg at sites with higher Hg concentrations that are decreasing semi-exponentially and faster, while Hg at sites with lower Hg concentrations stay more constant or increase slowly towards a common concentration, leading to a homogenization of Hg surface concentrations but not inventories across the Hg contaminated river-estuarine system (system recovery phase).

## 5 MAJOR CONCLUSIONS

1. Mean surface sediment (top 1 cm) Hg concentration [Hg(o)] values from Penobscot River, Orland River and Mendall Marsh cores were statistically not different (1 SD of mean value is given below), averaging about 600-700 ng/g. Penobscot River:  $742 \pm 88$  ng/g; Mendall Marsh:  $639 \pm 75$  ng/g; Orland River:  $892 \pm 156$  ng/g; estuarine sites:  $513 \pm 53$  ng/g.
2. Only six out of 24 Penobscot River cores had Hg(o) values  $\geq 1000$  ng/g in the top cm, and only 1 out of 11 Mendall Marsh cores had Hg(o) values  $\geq 1000$  ng/g. Furthermore, only 1 out of 5 Orland River cores had Hg(o) values  $\geq 1000$  ng/g, and none of the 17 estuarine sites cores had Hg(o) values  $\geq 1000$  ng/g.
3. Areas with higher sedimentation rates had higher  $^{137}\text{Cs}$  inventories, as they contain  $^{137}\text{Cs}$  not only from direct fallout (about 10 dpm/cm<sup>2</sup> for the Penobscot River estuary system, estimated from the recorded fallout of  $^{90}\text{Sr}$  to New York City, and assuming a ratio of  $^{137}\text{Cs}/^{90}\text{Sr}$  of 1.5), but also from erosion in the drainage basin and of river banks.
4.  $^{137}\text{Cs}$  inventories, when compared to those expected from bomb fallout, can be taken as indicators of sediment focusing or erosion for that coring site. Measured to calculated  $^{137}\text{Cs}$  inventory ratios ranged from  $<1$  to  $>10$ .
5. Areas with higher sedimentation rates did not necessarily have higher Hg inventories, contrary to  $^{137}\text{Cs}$ , as  $^{137}\text{Cs}$  inventories can be enhanced from whole drainage basin inputs, whereas those of Hg can only be increased from resuspended river mudflats and other temporary sediment sources.
6. Radioactive dating of sediments established that one can take Hg profiles and interpret them as a time input record into sediments from a particular site. Average sedimentation rates from all 57 sediment cores, using either  $^{137}\text{Cs}$  (or  $^{239,240}\text{Pu}$ ) or Hg, are  $0.6 \pm 0.06$  cm/yr (1 SD of mean).  $^{239,240}\text{Pu}$  peak-derived sedimentation rates are more reliable in estuarine sediments than those derived from  $^{137}\text{Cs}$  because of the well-known

partial desorption of adsorbed  $\text{Cs}^+$  due to competition with more abundant  $\text{K}^+$ . Calculated average SR) (cm/y) for each core assuming constant SR over the length of the sediment core, were then used to reconstruct the input history of Hg to that site.

7. Hg profiles revealed sharp peaks around the time of maximum Hg deposition event assumed to have occurred in 1967, strongly suggesting that initial apparent recovery after this pulse input was quite fast. In most sediment cores, however, in more recently deposited sediments layers, Hg decreased relatively more slowly with time (in cores where Hg concentrations were elevated), stayed constant, or even increased towards the present time (when Hg concentrations were generally lower), strongly suggesting input from redistribution of the Hg from sites with higher surface concentrations, Hg(o), to sites with lower Hg(o) concentrations.

8. Inverse correlation of Hg(o)/Hg(max) with sSR and direct correlation of SR with inventories of Hg, indicates that sites with higher SR tend to dilute Hg and lead to faster recovery times, and also, that sites with higher Hg inventories generally seem to recover faster than those with lower Hg inventories. Average surface Hg concentrations, Hg(o), decreased in the order Penobscot River>Mendall Marsh>Orland River>estuarine sites. Average recovery indices, Hg(o)/Hg(max), were lowest for Penobscot River and Mendall Marsh sites, i.e., 0.28, higher for Orland River (0.45), and highest for estuarine sites (0.58). Thus, the upper regions of the contaminated Penobscot River sites were the most contaminated and have recovered the fastest, and the lower regions of Penobscot River/Estuary were the least contaminated and are recovering at the slowest rate.

9. When Hg profiles were divided into two sections: the first 21 years (1967-1988) showed a relatively fast recovery, and the recent 21 years (1988-2009) showed a relatively slower recovery rate. The recent 21 years of input history was then used to estimate Hg recovery rates. Apparent recovery half times ( $t_{1/2} = \ln 2/\alpha$ ) calculated from an exponential ( $\text{Hg}(t) = \text{Hg}(t=21) \cdot \exp(-\alpha \cdot t)$ ) fit to the Hg concentration profiles over the past 21 years indicate  $t_{1/2}$  values of 20 to over 100 years.

10. Suitable Hg profiles would need to indicate that these coring sites have been in close communication with the system, and thus, can be taken as an indicator what the system as a whole has experienced in the last 21 years. There was a large spread of apparent recovery half times ( $t_{1/2}$ ) at Penobscot River, but not at Mendall Marsh sites, in cores that were deemed to be suitable for calculating apparent recovery of the system. Mean values of  $t_{1/2}$ , calculated from cores with a semi-exponential decrease in Hg concentrations, were  $31 \pm 6$  years at Penobscot River,  $22 \pm 3$  years at Mendall Marsh,  $78 \pm 13$  years at ER, and  $77 \pm 21$  years at Orland River. In a substantial number of cores, Hg actually stayed relatively constant or increased from low concentrations towards the surface. One can conclude that such sites with lower and/or Hg concentrations that increase towards the surface are sites, which are not in close communication with the rest of the system, and thus, are also not representative of that system as a whole. The Penobscot system, as a whole, however, clearly has recovered a great deal since the late 1960's. It appears then that sedimentary Hg(o) values in cores that are deemed to be representative of the system as a whole are currently converging to values close to 600-700 ng/g.

11. Apparent recovery half times ( $t_{1/2} = \ln 2/\alpha$ ) could also be calculated from an exponential fit to the Hg concentration profiles over the past 21 years, assuming a non-zero asymptotic level ( $C_{\infty}$ ), e.g.,  $Hg(t) = Hg(t=21) \cdot \exp(-\alpha \cdot t) + Hg(\infty)$ . Assuming an asymptotic level ( $Hg(\infty)$ ) of 400 ng/g Hg, it would take about the same amount of time to reach a certain target concentration of  $Hg(\infty)$ , and depend on what is assumed for  $Hg(\infty)$ , as can be seen from the following example, where we assume  $Hg(0) = 700$  ng/g, and  $t_{1/2}$  of 12.5 y for  $Hg(\infty) = 400$  ng/g, and 21 y for  $Hg(\infty) = 0$ . After 3 half lives of 12.5 y for  $Hg(\infty) = 400$  ng/g, i.e., 38 y, we would expect then to reach 440 ng/g. After 1 half life of 21 y for  $Hg(\infty) = 0$  ng/g, we would get already below that target level, i.e., to 350 ng/g. Thus, it could take about 21-38 y for Mendall Marsh to get to about 400 ng/g, depending on the assumptions. To get to  $Hg(\infty)$  of about 50 ng/g, however, it would be expected to take about 4 half lives of 21 y, or 84 years to get from 700 ng/g to 44 ng/g.

12. Locations with higher sedimentation rates recover faster, as is evident from the inverse relationship between a 'recovery index', i.e., the ratio of surface concentrations of Hg ( $Hg(o)$ ) to maximum Hg concentrations ( $Hg(max)$ ), taken as an indicator for the speed of recovery, and the SR. More contaminated areas with higher  $Hg(o)/Hg(max)$  values generally had lower SR, and also, recover more slowly. Areas with higher SR tended to have lower  $Hg(o)/Hg(max)$  values, indicating faster recovery.

13. Calculated apparent half times of several decades do not mean that after that time, sediments have fully recovered, as they should be taken only as an indicator of the time scale of 'depuration' in the whole system. Estimated recovery times depend on what one assumes to be an acceptable future  $Hg(o)$ , i.e.,  $Hg(\infty)$ , concentration. As is shown here, one would have to take several of these half times to get down to acceptable levels of Hg, as the redistribution process across the river-estuarine region would depend on the slowest overall process, which is redistribution of Hg across the whole estuary. Conceptually, this redistribution process of Hg across the whole estuary can be imagined as follows: Hg at sites with higher Hg concentrations was initially decreasing exponentially and faster (pulse attenuation phase), while Hg at sites with lower Hg concentrations are still increasing towards a common concentration, leading to a homogenization of all surface  $Hg(o)$  concentrations (but not inventories) across the Hg contaminated river-estuarine system, and possibly, an even slower system recovery (system recovery phase). Extrapolated apparent  $t_{1/2}$  values should thus be taken with a level of caution.

## 6 REFERENCES

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# Figures

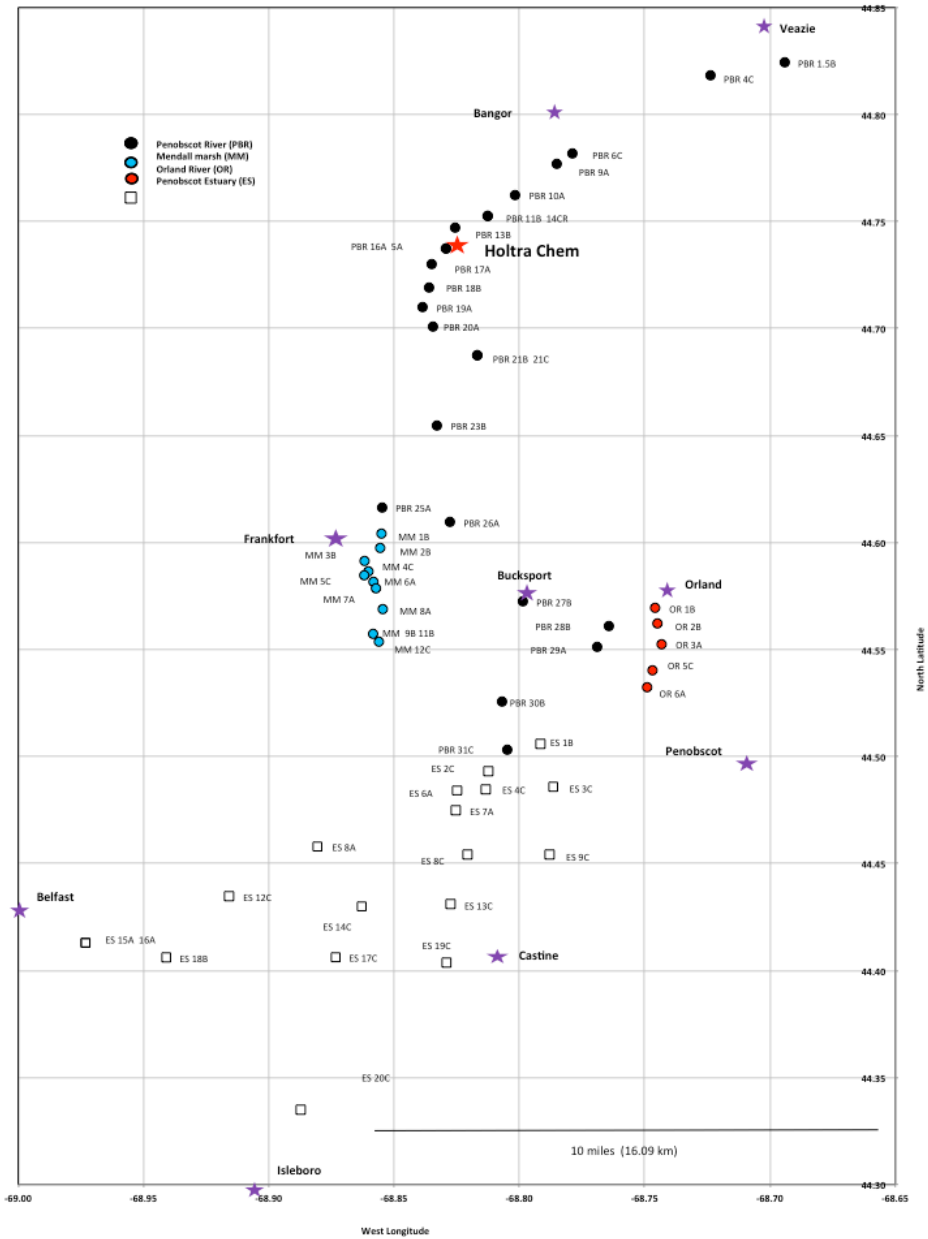


Figure 6-1. Map of sediment coring sites. PBR = upstream Penobscot River sites, MM = Mendall Marsh sites, ES = estuarine sites, OR = Orland River sites.

## Vertical vs. lateral Transport

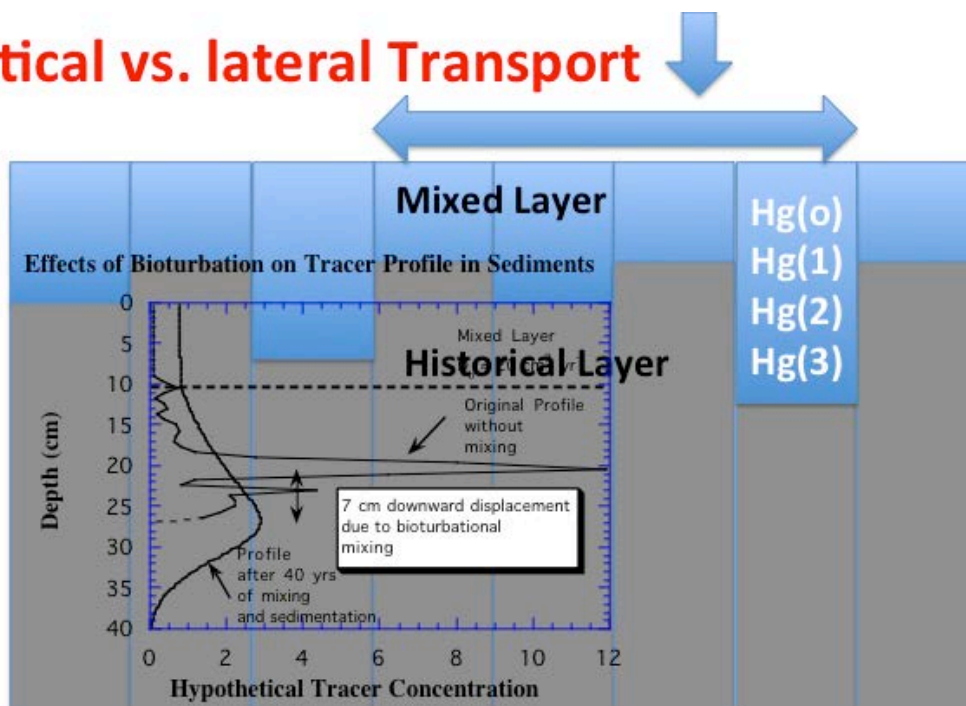


Figure 6-2. Because of fairly limited extent of vertical mixing of surface sediments, peaks of event (and steady-state) tracers are not distorted as much as is indicated by the example in this figure, allowing for generally more reliable dating using radioactive tracers as well as Hg peaks, except for horizontally transport events (e.g., floods, causing river bank erosion and redeposition). Pockets with higher Hg concentrations at the sediment surface (Hg(o)) can continuously 'bleed' Hg and other contaminants into areas with lower Hg(o) concentrations during events where sediment erosion and resuspension is coupled to lateral transport, thereby homogenizing Hg(o) concentrations in the river-estuarine system and moving Hg to downstream areas. As the slowest of the coupled transport processes, horizontal transport and redistribution of Hg is currently responsible for 'recovery' of the Hg in the Penobscot River – estuarine system.

## Porosity Profiles

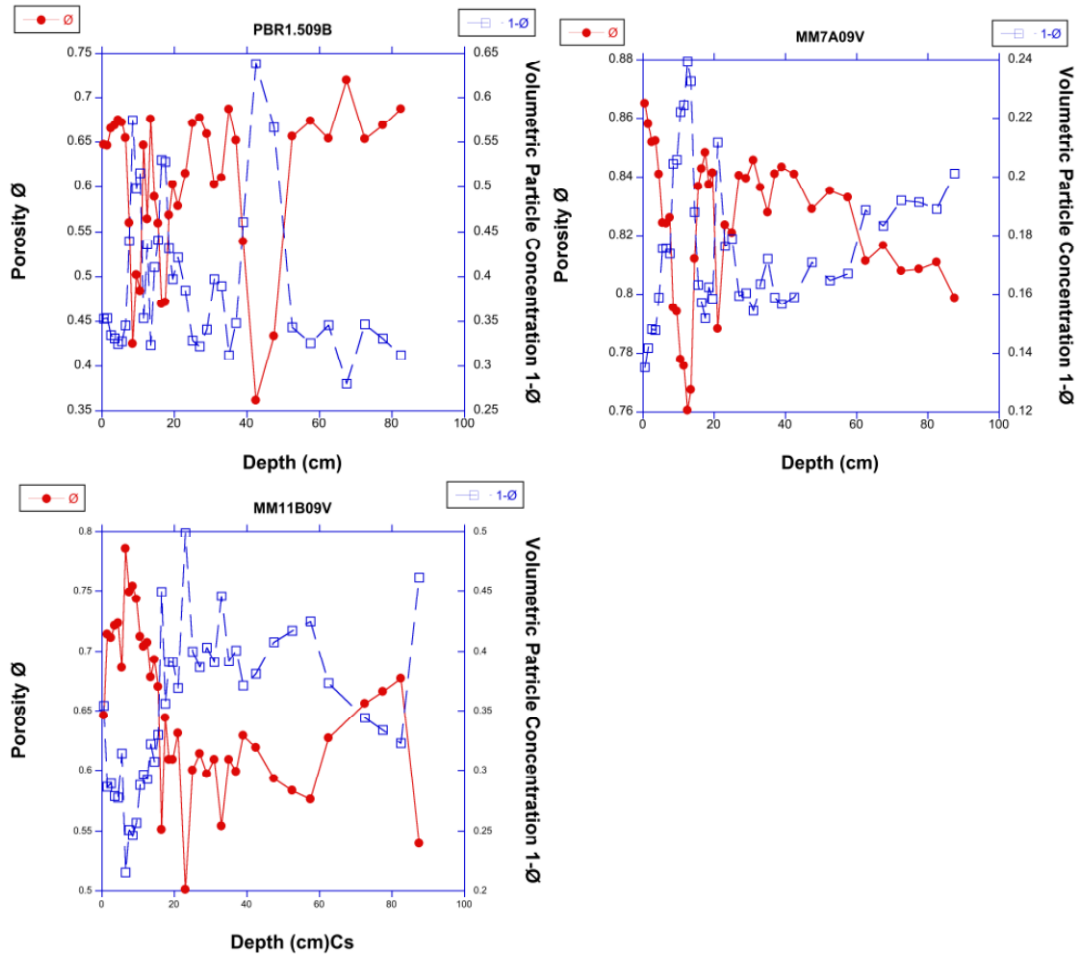


Figure 6-3. Typical porosity and particle concentration profiles indicate that sediments are highly layered and that vertical mixing is likely restricted to just a few cm at most.

**Sediment mixing rates from <sup>7</sup>Be penetration:**

$$[{}^7\text{Be}(z)] = [{}^7\text{Be}(0)] \exp(-(\lambda/D_b)^{1/2} z)$$

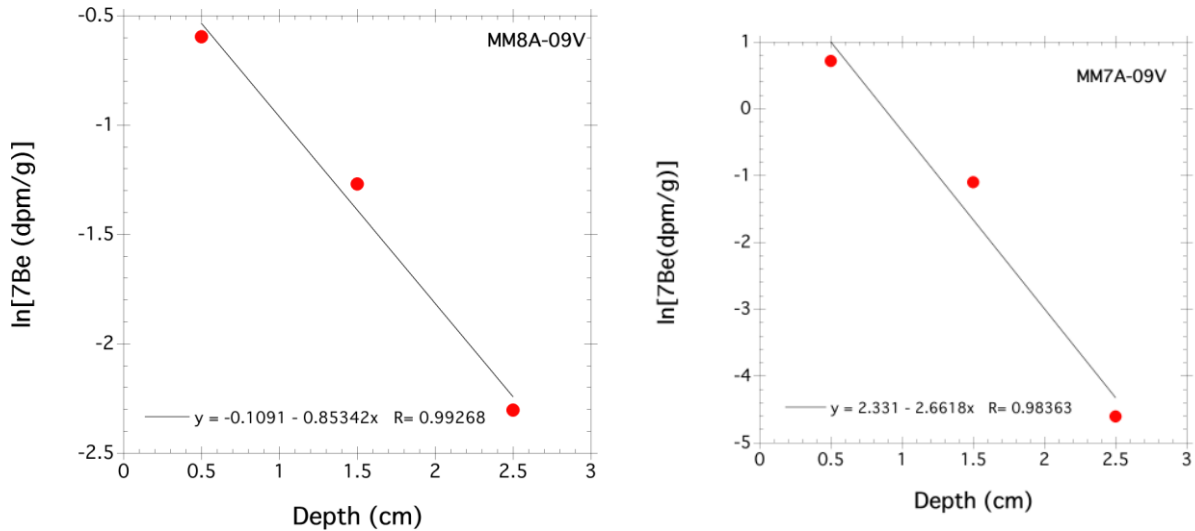


Figure 6-4. Sediment mixing rates can be calculated from the penetration of atmospherically delivered and short-lived <sup>7</sup>Be (t<sub>1/2</sub> of 53 days) into surface sediments according to  $[{}^7\text{Be}(z)] = [{}^7\text{Be}(0)] \exp(-(\lambda/D_b)^{1/2} z)$ . In 2 out of 6 cores (MM7A and MM8A) we found <sup>7</sup>Be penetration depths of 2 cm, in 4 out of 6 cores we found <sup>7</sup>Be to be present in only the upper 1 cm. In the remainder of the cores, we found <sup>7</sup>Be to be below the detection limit. Thus, the maximum particle mixing rate is 3-6 cm<sup>2</sup>/y (~10<sup>-7</sup> cm<sup>2</sup>/s), which is rather low for surface sediments. Inventories of <sup>7</sup>Be are 1-2 dpm/cm<sup>2</sup>, which is within expected range from atmospheric fallout.

# MM 8A 09V

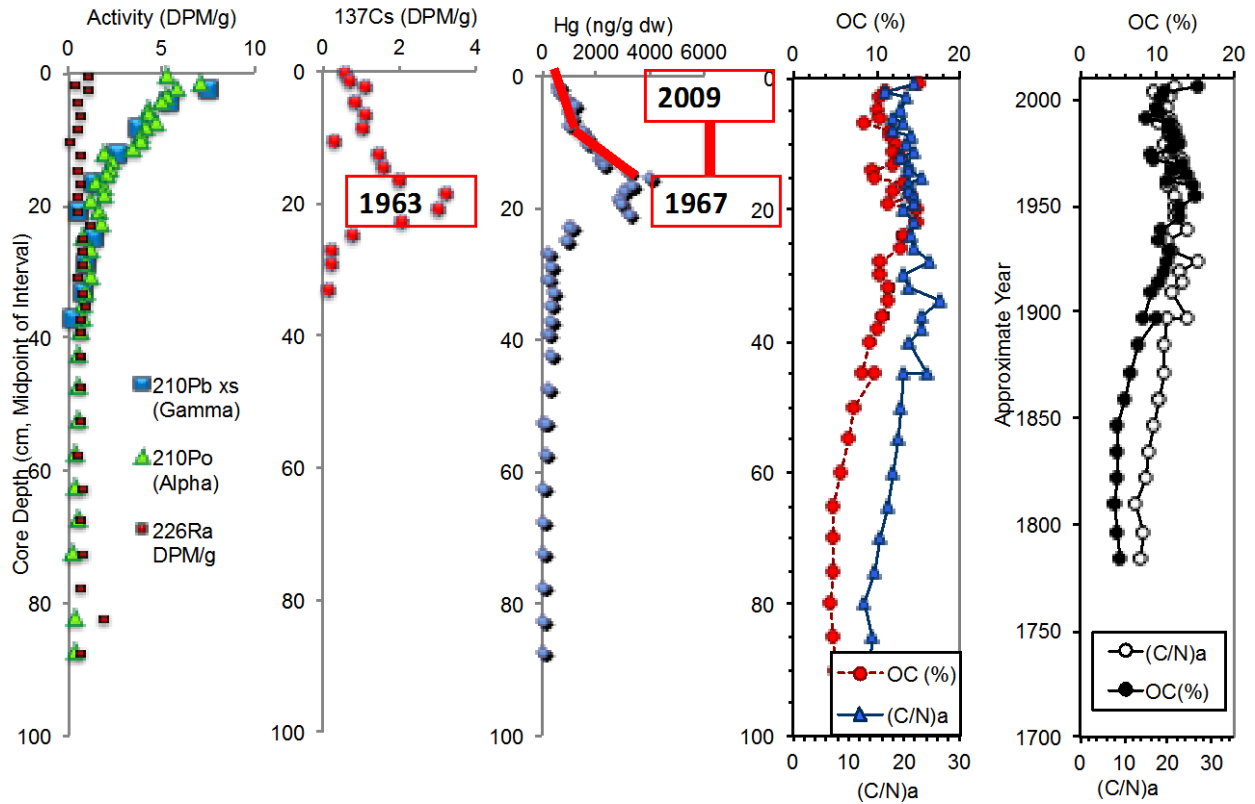


Figure 6-5. Comparison of profiles of different radionuclides and Hg, organic carbon, OC, and C/N ratios. Radionuclides include  $^{210}\text{Pb}_{\text{xs}}$  by gamma and alpha (for which  $^{210}\text{Po}$ , determined by alpha counting, is a proxy),  $^{226}\text{Ra}$  as an indicator for supported  $^{210}\text{Pb}$ , and atmospherically delivered  $^{137}\text{Cs}$ . Peak concentrations of  $^{137}\text{Cs}$  occurred in 1963, and those of Hg are assumed to be in 1967. Typically, Hg drop-off after peak concentration of Hg is faster than in recent times. OC and C/N ratios indicate here higher organic carbon (OC) and organic carbon to nitrogen (C/N) ratios in recent times, likely indicating higher terrestrial erosional OC inputs in recent times. Notes: dpm = disintegration per minute (activity unit);  $^{210}\text{Pb}_{\text{xs}} = \text{excess-}^{210}\text{Pb} = ^{210}\text{Pb} (\text{total}) - ^{210}\text{Pb} (\text{supported by } ^{226}\text{Ra} \text{ decay})$ ;  $^{210}\text{Pb}$  can be determined by non-destructive gamma counting or by alpha counting after chemical separation (see methods section).

# MM 1B 09V

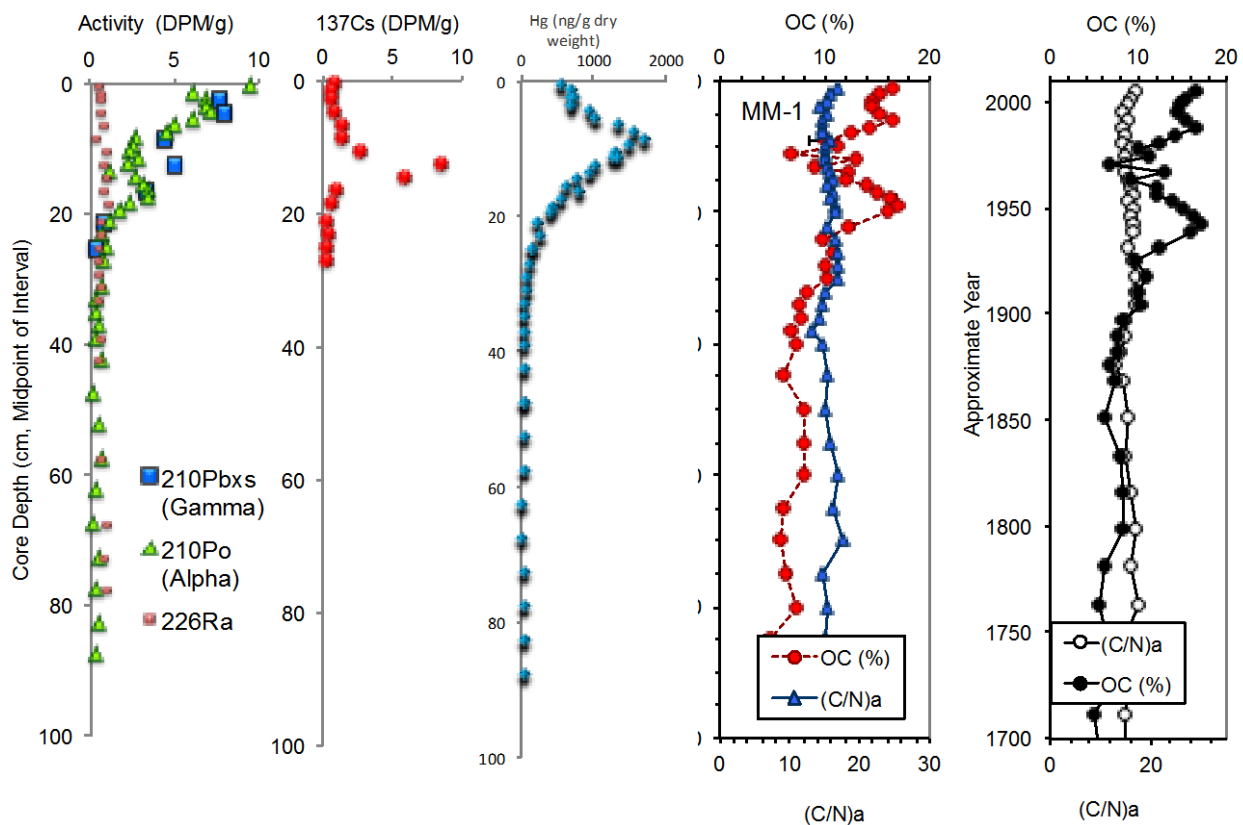


Figure 6-6. Comparison of profiles of different radionuclides and Hg, organic carbon (OC) and carbon to nitrogen ratio (C/N). Radionuclides include  $^{210}\text{Pb}_{\text{xs}}$  by gamma and alpha (for which  $^{210}\text{Po}$ , determined by alpha counting, is a proxy),  $^{226}\text{Ra}$  as an indicator for supported  $^{210}\text{Pb}$ , and atmospherically delivered  $^{137}\text{Cs}$ . Peak concentrations of  $^{137}\text{Cs}$  occurred in 1963, and those of Hg are assumed to be in 1967.

## PBR 1.5B 09V

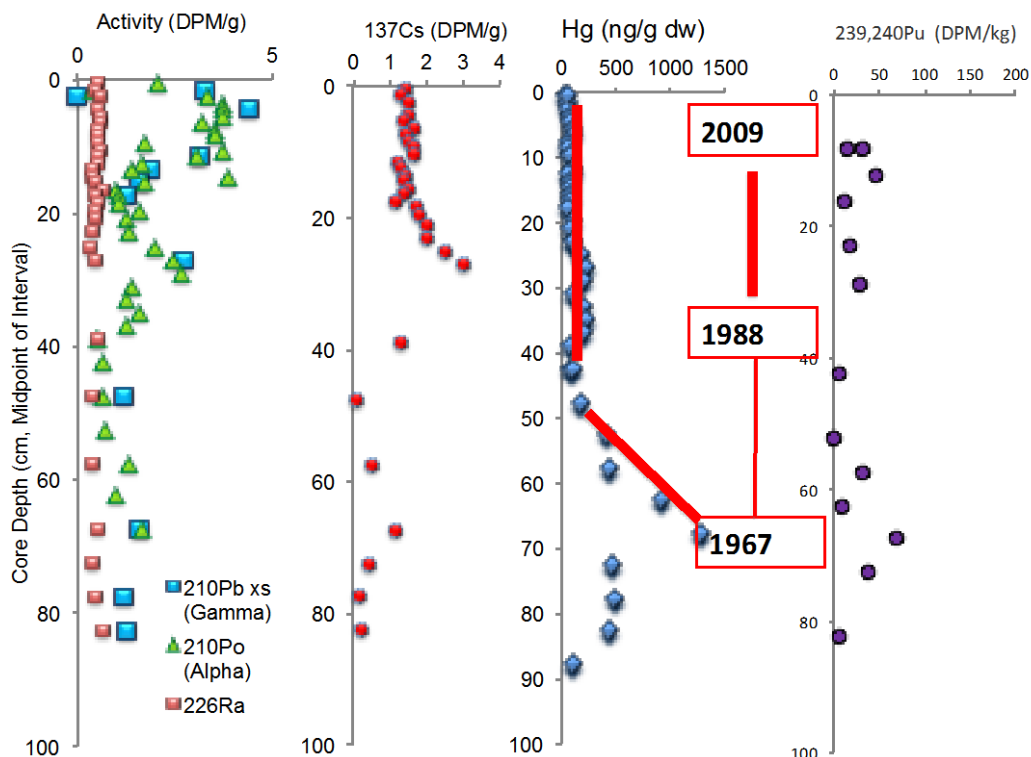


Figure 6-7. Comparison of profiles of different radionuclides and Hg, OC and C/N. Radionuclides include  $^{210}\text{Pb}_{\text{xs}}$  by gamma and alpha (for which  $^{210}\text{Po}$ , determined by alpha counting, is a proxy),  $^{226}\text{Ra}$  as an indicator for supported  $^{210}\text{Pb}$ , and atmospherically delivered  $^{137}\text{Cs}$ . Peak concentrations of  $^{137}\text{Cs}$  occurred in 1963, and those of Hg are assumed to be in 1967. Typically, Hg drop-off after peak concentration of Hg is faster than in recent times. Occurrence of  $^{210}\text{Pb}_{\text{xs}}$  between 20 and 30 cm depth likely indicates inputs from lateral inputs of sediments with higher  $^{210}\text{Pb}_{\text{xs}}$  concentrations at those times. This example demonstrates, too, that it is important to have multiple methods to determine sedimentation rates (SR).

**Comparison of Methods for determining Sedimentation Rates**  
**Core PBR 17A TAMUG**

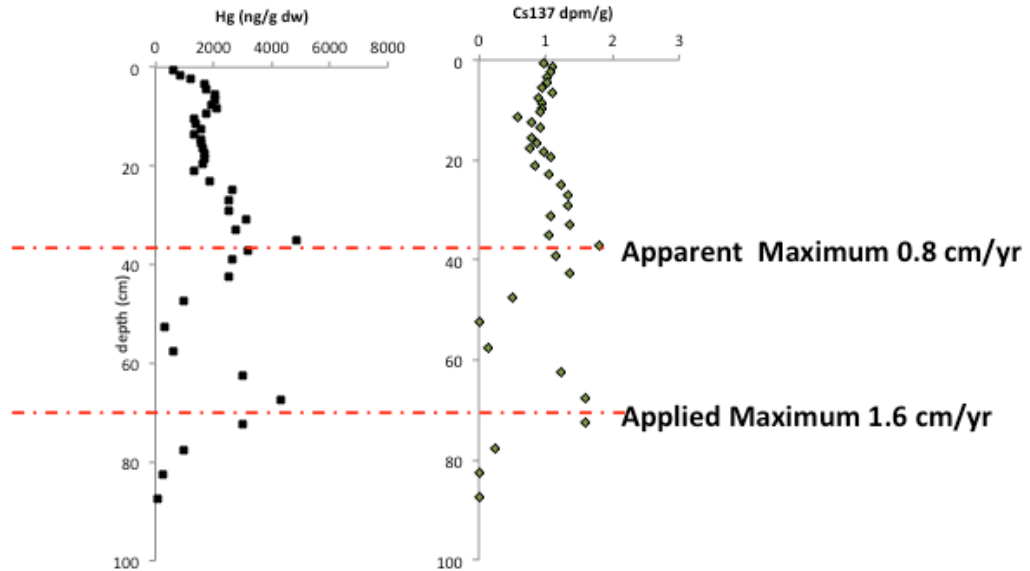


Figure 6-8. Core Penobscot River17A shows a comparison of Methods for determining sedimentation rates (SR) using the maximum concentrations of Hg and <sup>137</sup>Cs when profiles look more complicated. Since <sup>137</sup>Cs shows two different maxima, the lower one is assumed to be due to peak fallout in 1963, while the upper one is likely due to a later river bank or soil erosional event transporting more recent material into this site. This example demonstrates, too, that it is most important to have multiple methods to determine sedimentation rates.



4%Relative Std Deviation between Methods of determining Sedimentation Rates

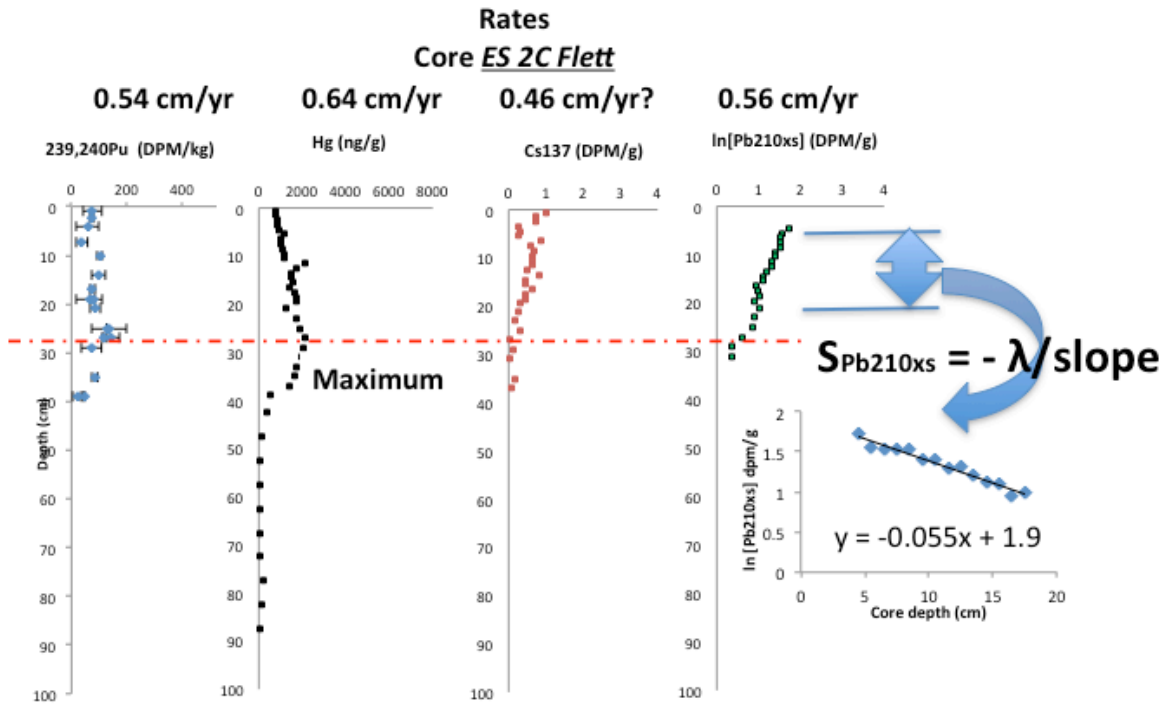


Figure 6-9. Core ES2C profiles show a comparison of sedimentation rate determinations using the maximum concentrations of Hg, and atmospherically delivered <sup>239,240</sup>Pu and <sup>137</sup>Cs. These three parameters should occur at the same depth, but <sup>137</sup>Cs maximum occurs at the surface, most likely due to the well-known remobilization of <sup>137</sup>Cs due to K+ in saltwater. This demonstrates that <sup>239,240</sup>Pu, whose peak is occurring at similar depths as that of Hg, is a more reliable indicator for sedimentation than <sup>137</sup>Cs in saltwater. The steady-state profile of <sup>210</sup>Pb<sub>xs</sub>, which can be linearized by plotting ln[<sup>210</sup>Pb<sub>xs</sub>] vs depth, is indicating similar sedimentation rates as those of the pulse input tracers <sup>137</sup>Cs and Hg..

Comparison of Methods for determining Sedimentation Rates  
Core *OR 6B USM*

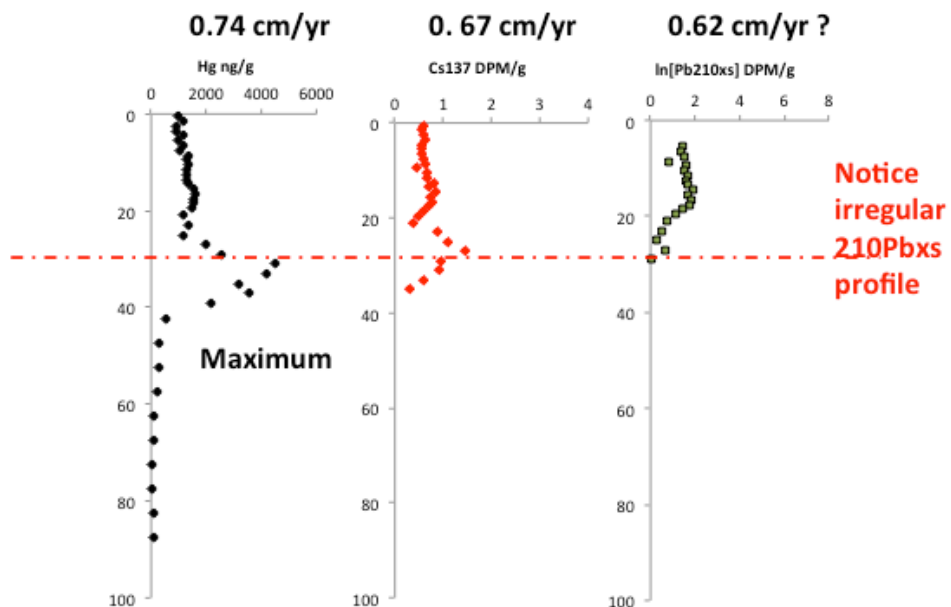


Figure 6-10. Example for a case where the profile of  $^{210}\text{Pb}_{\text{xs}}$  is not suitable to derive sedimentation rates (SR), but Hg and  $^{137}\text{Cs}$  are. This example demonstrates, too, it is most important to have multiple methods to determine sedimentation rates.

## Importance of OC or S for Hg?

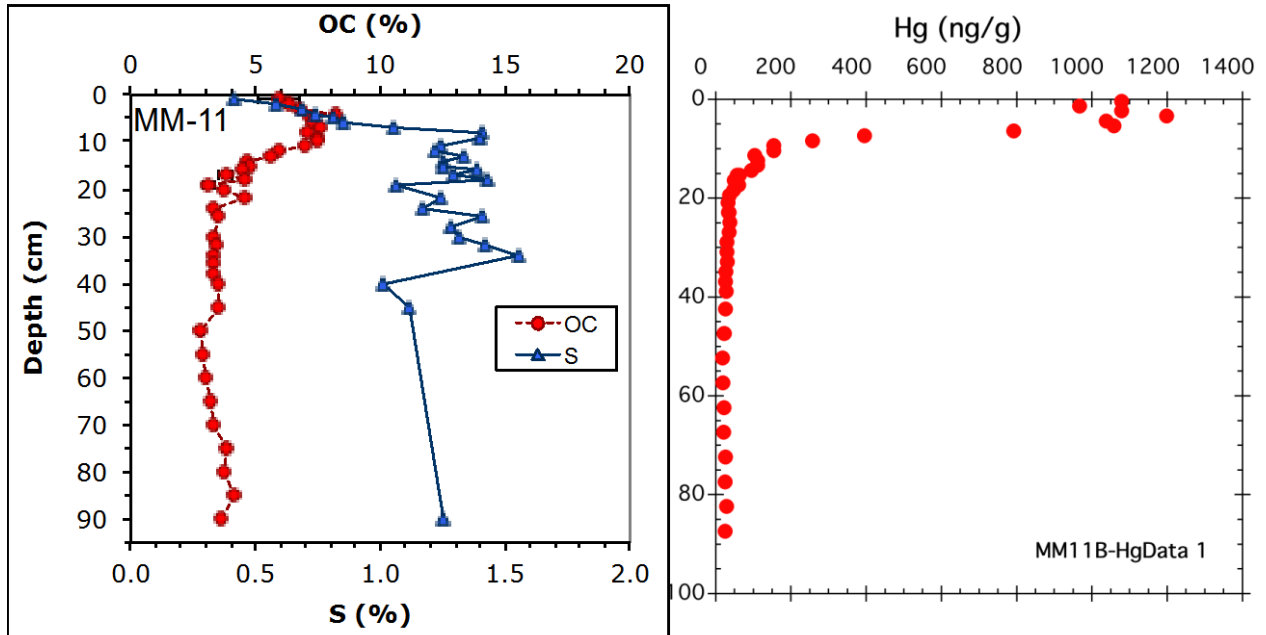


Figure 6-11. Typical profiles of Hg, organic carbon (OC) and total sulfur (S), demonstrating the lack of correlation between Hg and OC or S, due to the large excess concentration of OC (mM/g) and S (10s of  $\mu\text{M/g}$ ) vs Hg (nM/g).

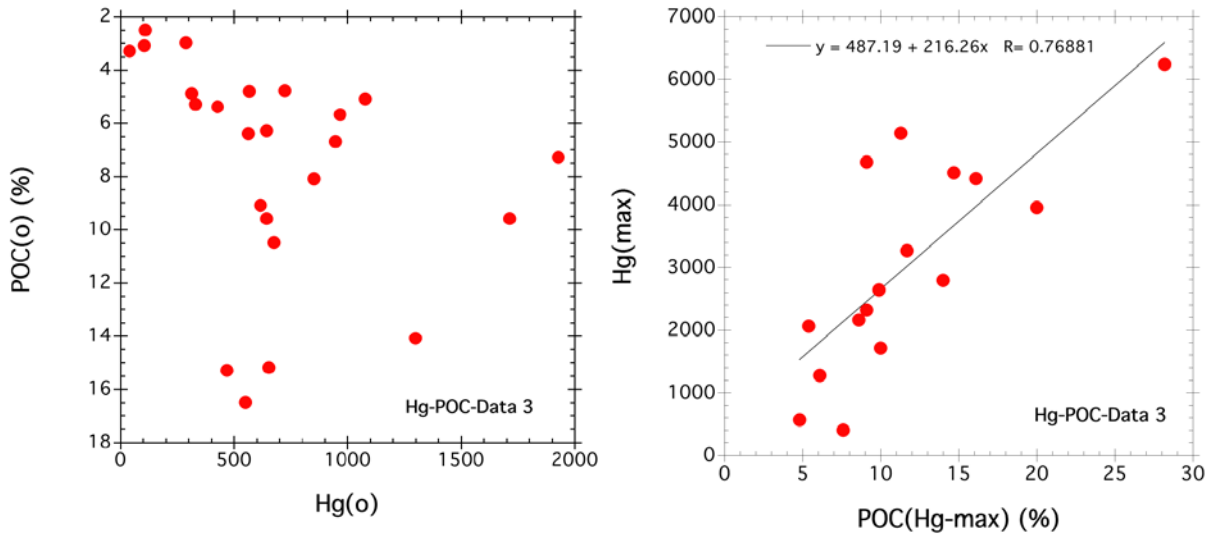


Figure 6-12. When correlating Hg concentrations with organic carbon (OC) concentrations, there is no significant relationship between Hg and OC. However, there is a significant correlation between Hg and OC at and around the Hg peak concentration.

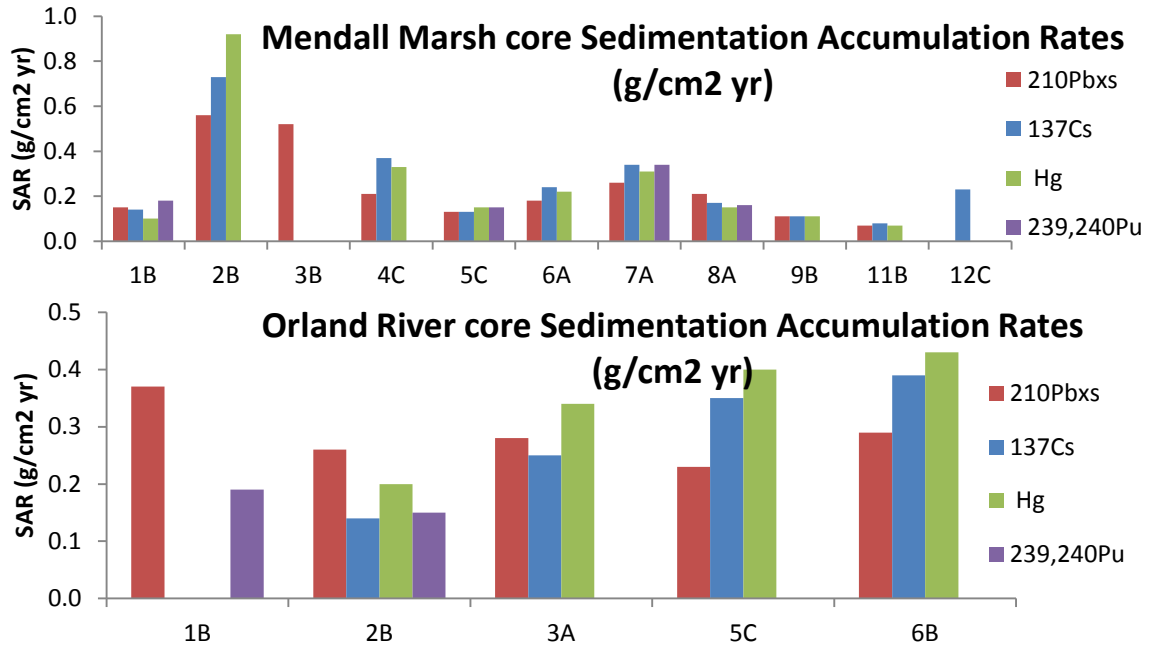


Figure 6-13. Overview of sediment accumulation rates (SAR) at MM (Mendall Marsh) and OR (Orland River) sites.

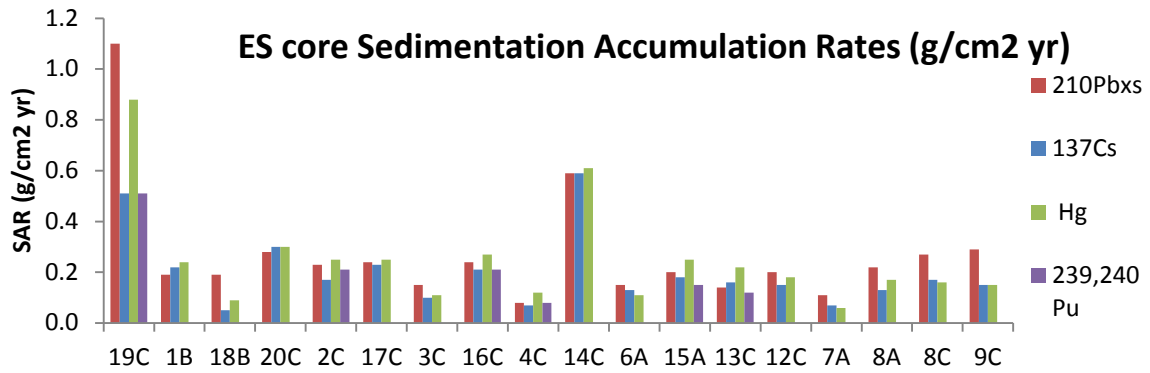
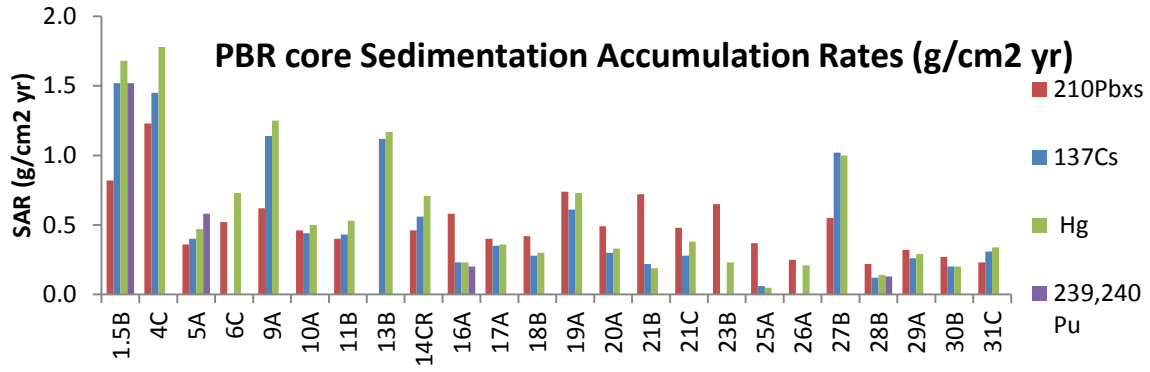


Figure 6-14. Overview of sediment accumulation rates (SAR) at PBR (Penobscot River) and ES (Estuary) sites.

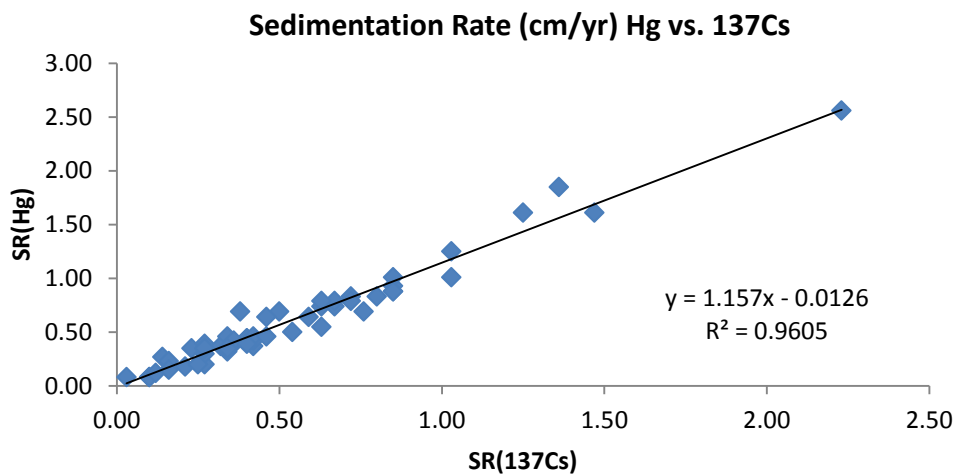
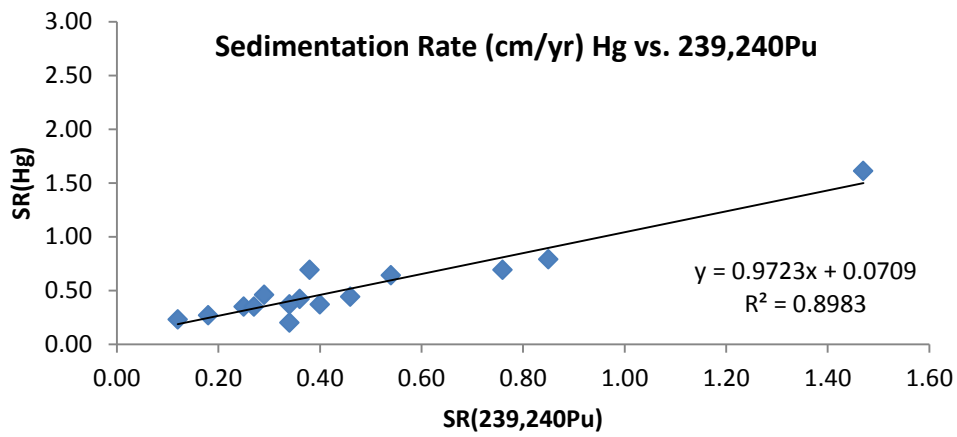
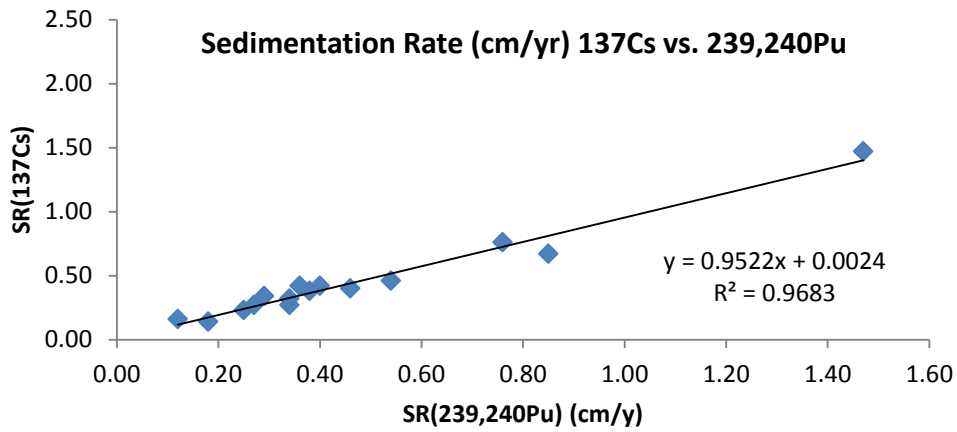


Figure 6-15. Correlation of sedimentation rates, SR, for different methods.

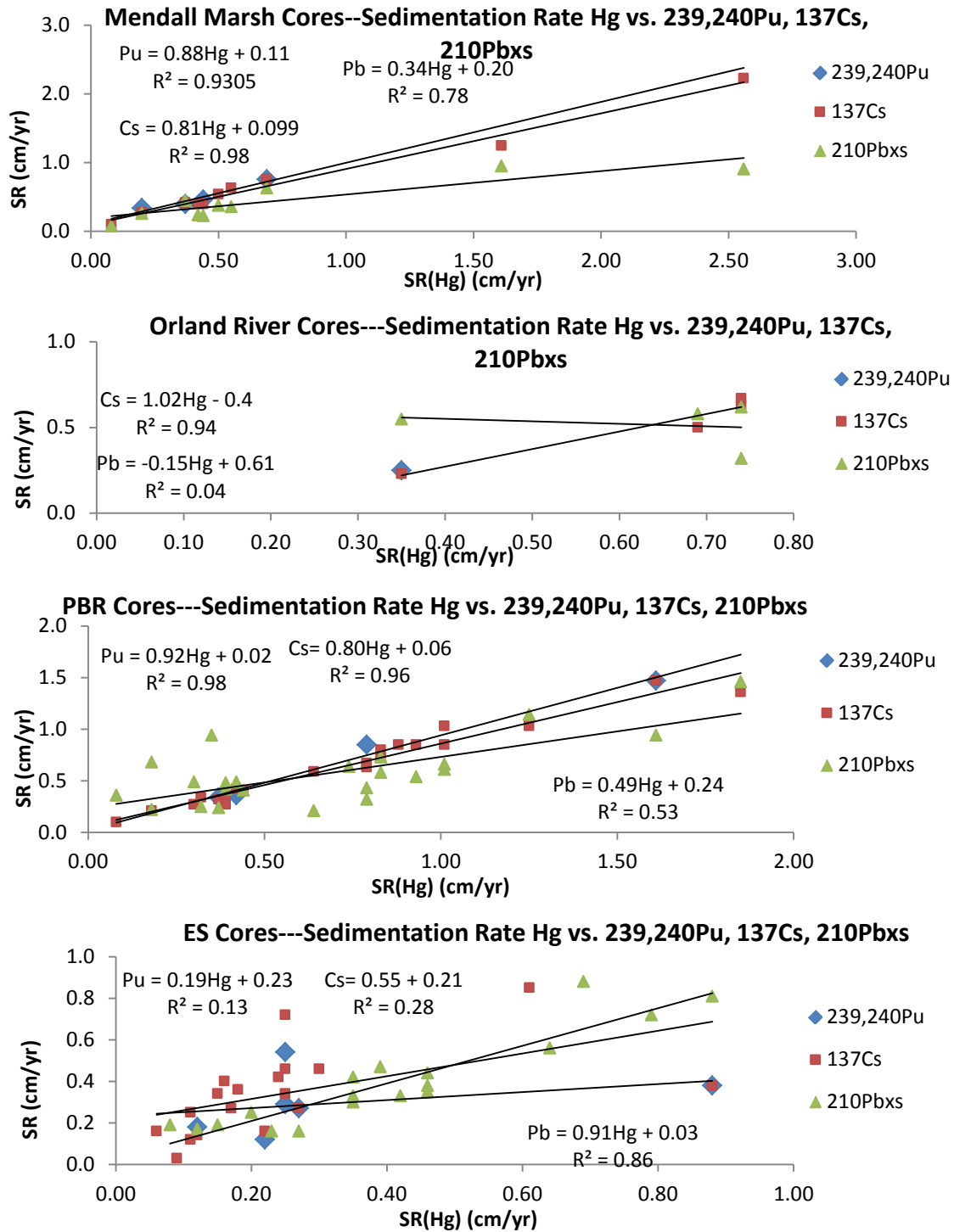


Figure 6-16. Correlation of sedimentation rates, SR, for different methods and individual sites.



## How to get recovery (half-)times, T1/2?

- **1) Vertical Profile approach:** taken from semi-exponential decrease towards the surface of Hg concentration profiles of dated sediment cores with shallow mixed layer depth  $Z_m$ , as  $Hg(z) = Hg(\max)\exp(-at)$ ,  $a = \ln 2 / T_{1/2}$ .  
→ 4-5y near peak region, at near-surface region it is 10-20y at MM, longer (~20-30y) at all other sites.
- **2) Vertical mixed layer model:** assumes a tracer transit or mixing (1/e) time through the mixed layer of depth  $Z_m$ , as  $T_{1/2} = \ln 2 * Z_m / SR$ , with SR=sed. rate.  
→ 1-10y
- **3) Recovery Index, RI:**  $T_{1/2} = \ln 2 * \Delta T / \ln[RI]$ , using A 'recovery index',  $RI = [(Hg(\max))/Hg(o)]$ , and  $\Delta T = 42y$  → 20-200y
- **4) Exponential fit to Hg from past 21 years**

Figure 6-17. Comparison of different approaches for determining half-times for recovery.

## Approach for recovery times assessment

- Calculated **average sedimentation rate ( $S$ , cm/y)** assuming constant  $S$ , are used to calculate the time of deposition of Hg.
- **Hg from past 21 years** (= (2009-1967)/2, **slow recovery period**; the last 21 years is well below the peak depth, in a region where the system is recovering only slowly) is **plotted vs the time of deposition**

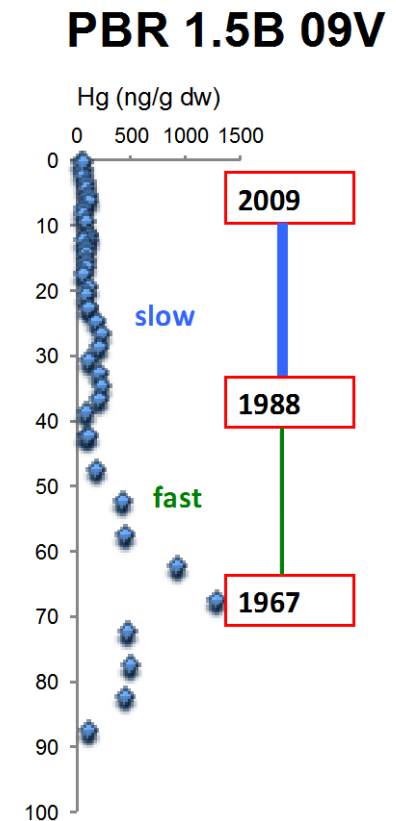
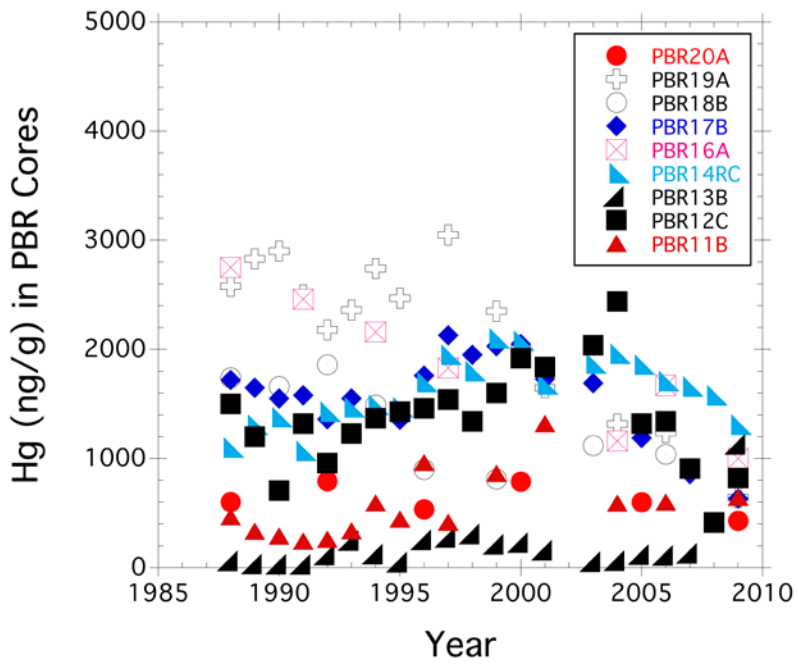
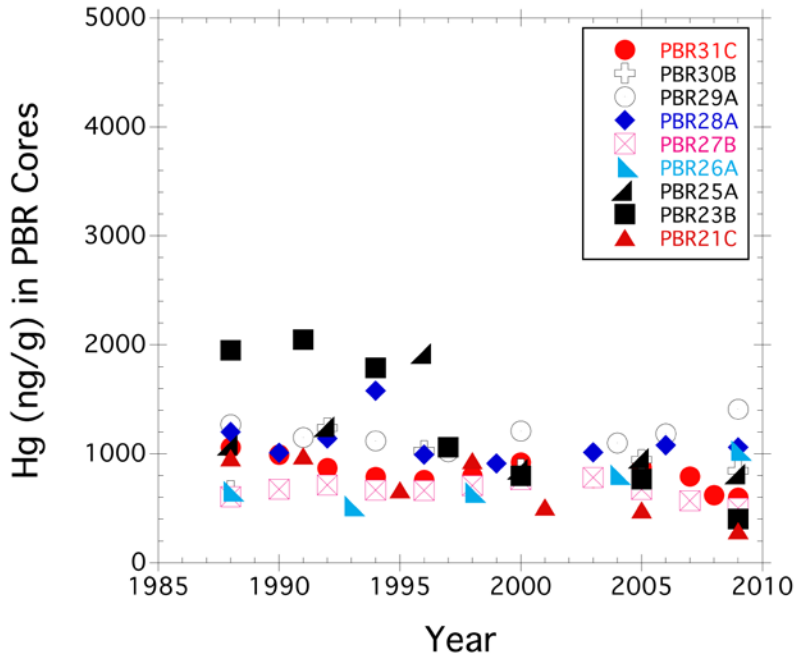
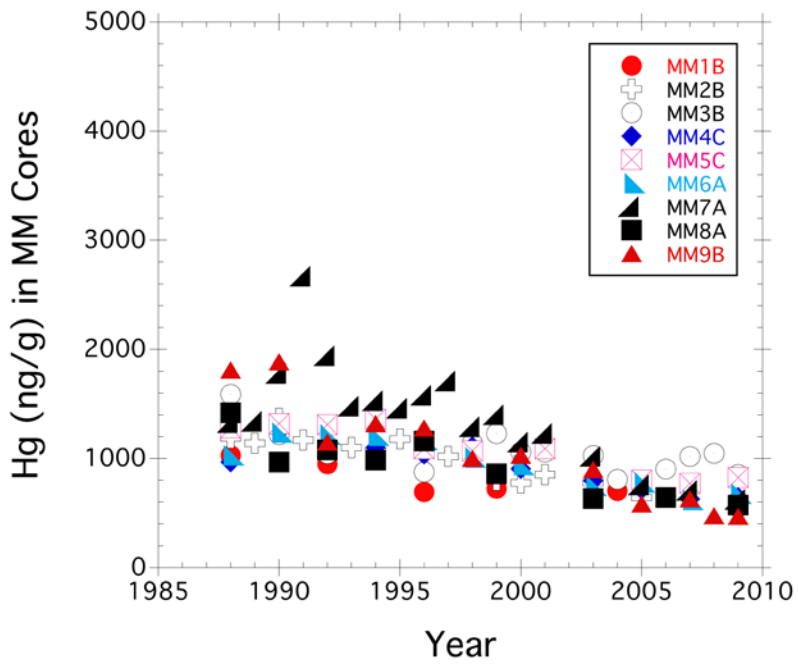
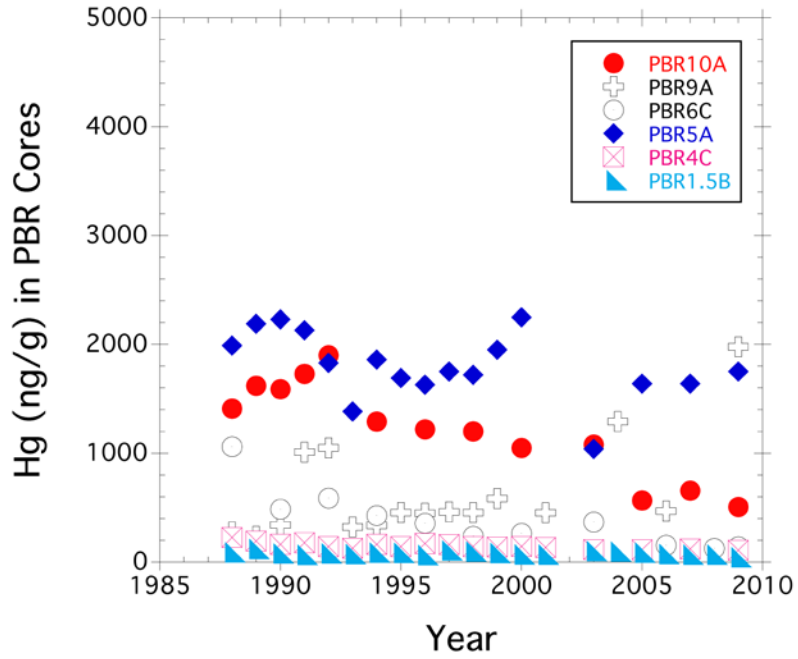
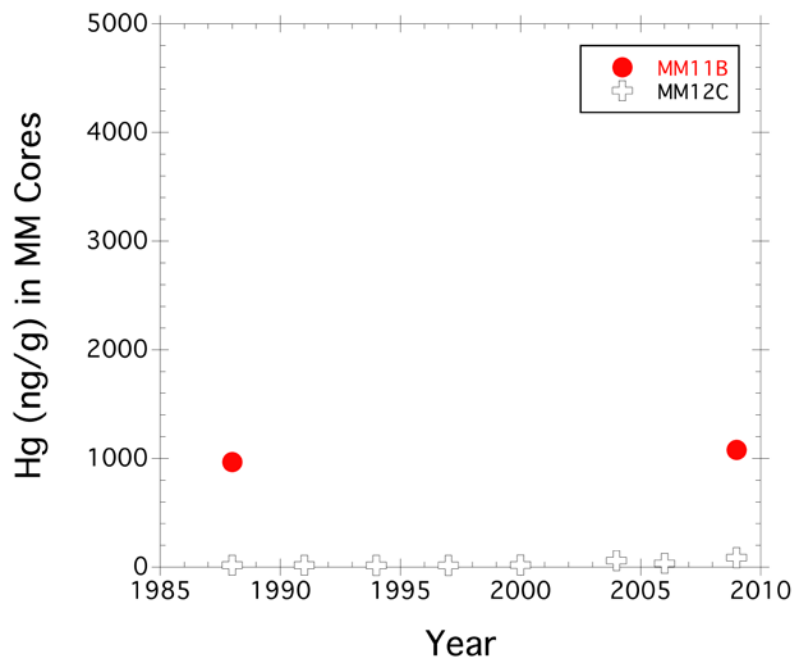
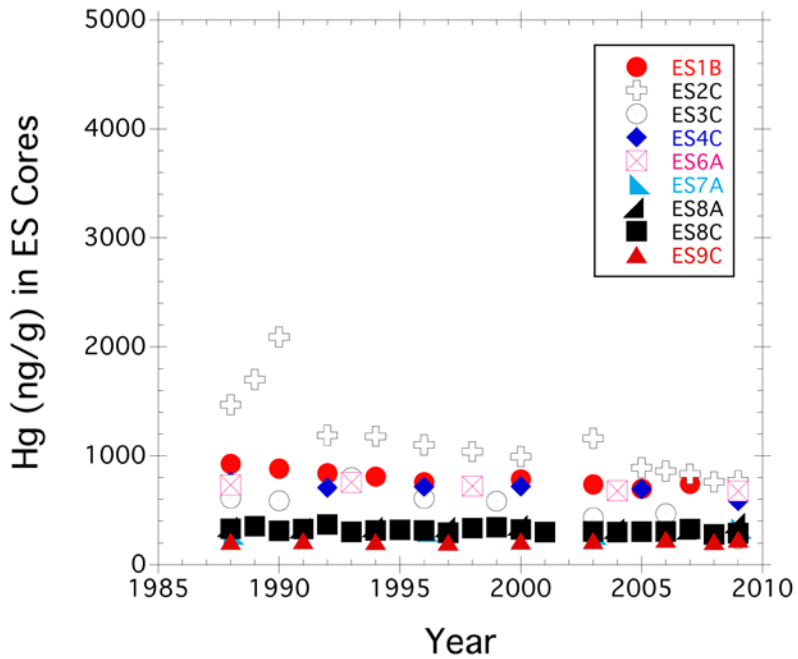


Figure 6-18. Principle of the adopted approach for determining apparent recovery half times from exponential fit to Hg profile from the past 21 years.







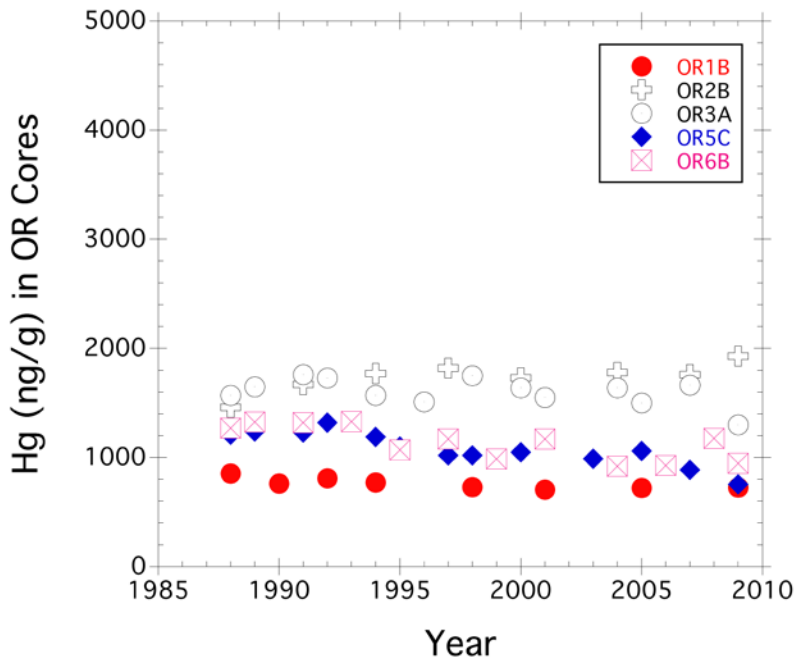
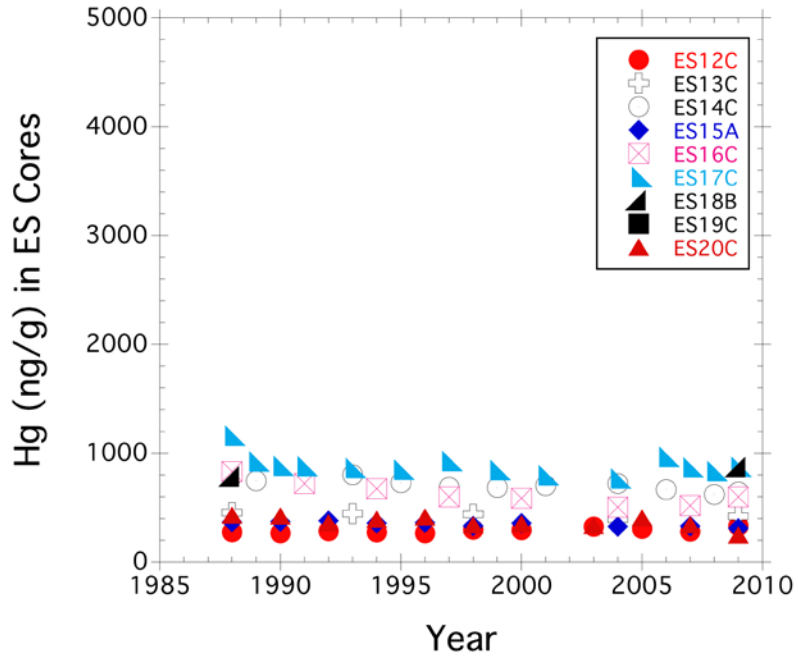


Figure 6-19. Hg concentrations in the last 21 years (1988 until 2009) for Penobscot River, Orland River, Mendall Marsh and estuarine sites sediment cores.

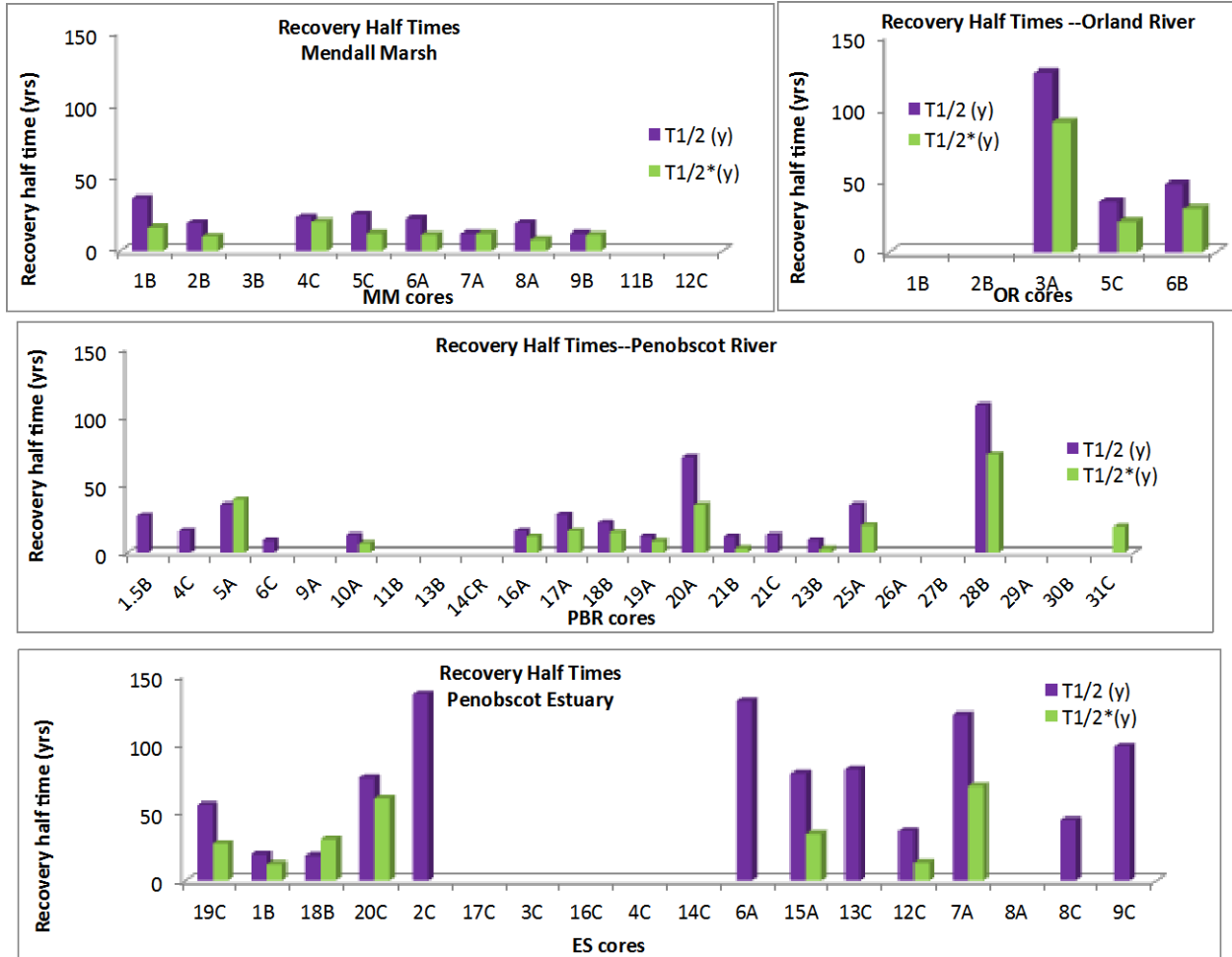


Figure 6-20. Apparent recovery half times for the last 21 years (1988 until 2009) for Penobscot River, Orland River, Mendall Marsh and estuarine sites sediment cores.

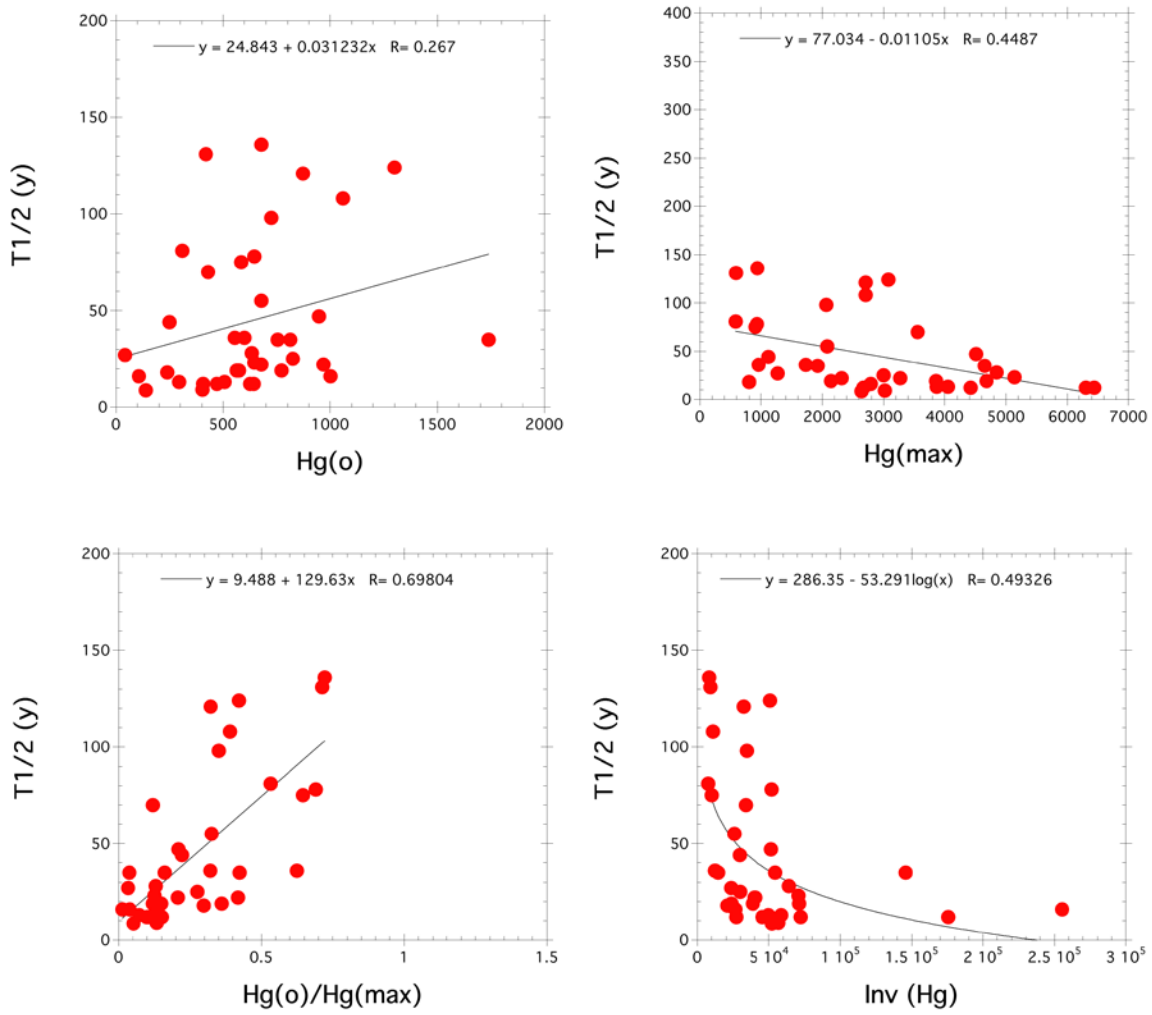


Figure 6-21. Correlation between the recovery index,  $Hg(o)/Hg(max)$  vs. Sedimentation rate, SR, determined by Hg, indicating faster recovery at sites with higher sedimentation rates. R-values above  $R=0.35$  indicate a significance level of 99 percent ( $p$  of 0.01) or better.



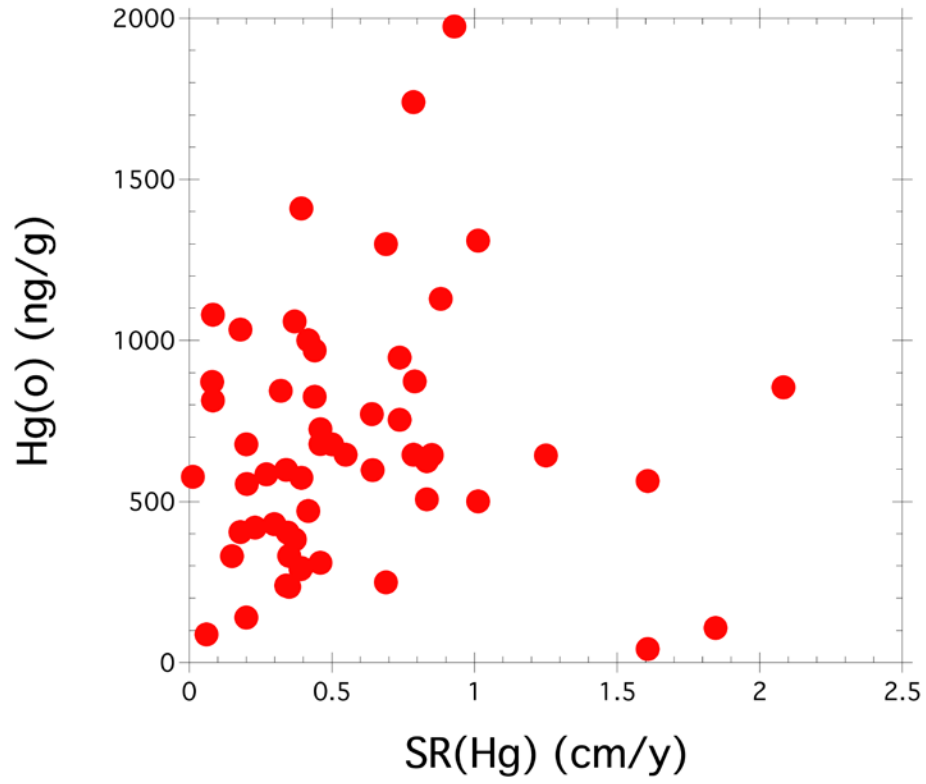


Figure 6-22. No correlation for Hg(o) vs. SR is evident.

**Most contaminated sites recover faster (i.e., have lower Hg(o)/Hg(max) values**

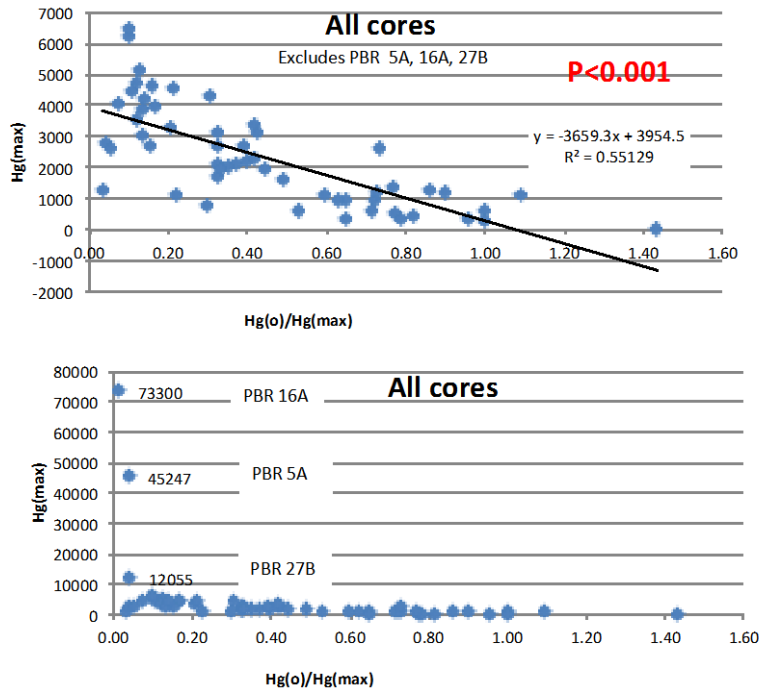


Figure 6-23. Shows that more contaminated sites (with higher Hg(max) concentrations) recover faster (i.e., have lower Hg(o)/Hg(max) ratios). This is mainly evident when excluding the core data from the sites near Holtrachem, i.e., PBR5A, 16A, 27B.

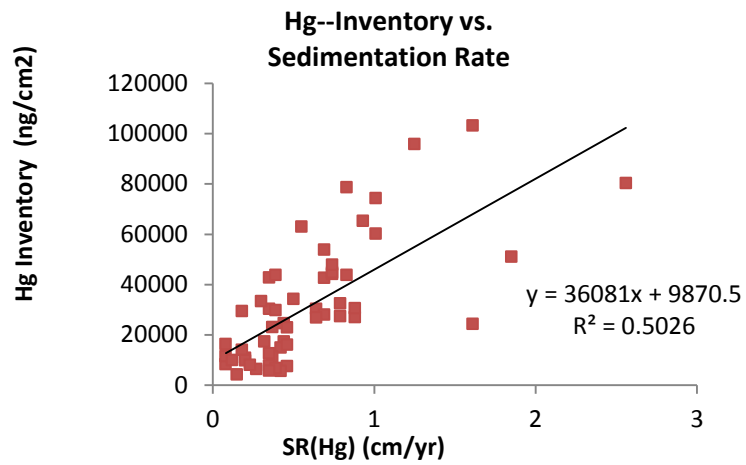
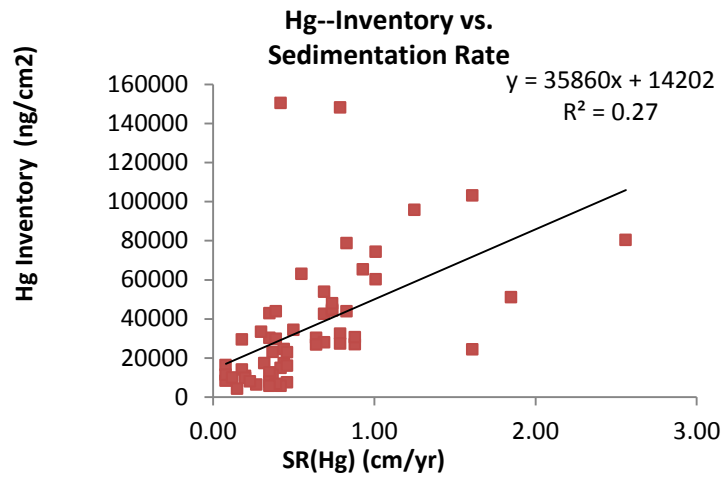


Figure 6-24. Correlations between sedimentation rates, SR, and Hg inventories. Top: all core data; Bottom: excluding sites close to HoltraChem (PBR5A, 16A, 27B). The close correlation (B) indicates that Hg inventories are generally proportional to SR, except for sites close to the point source of HoltraChem.

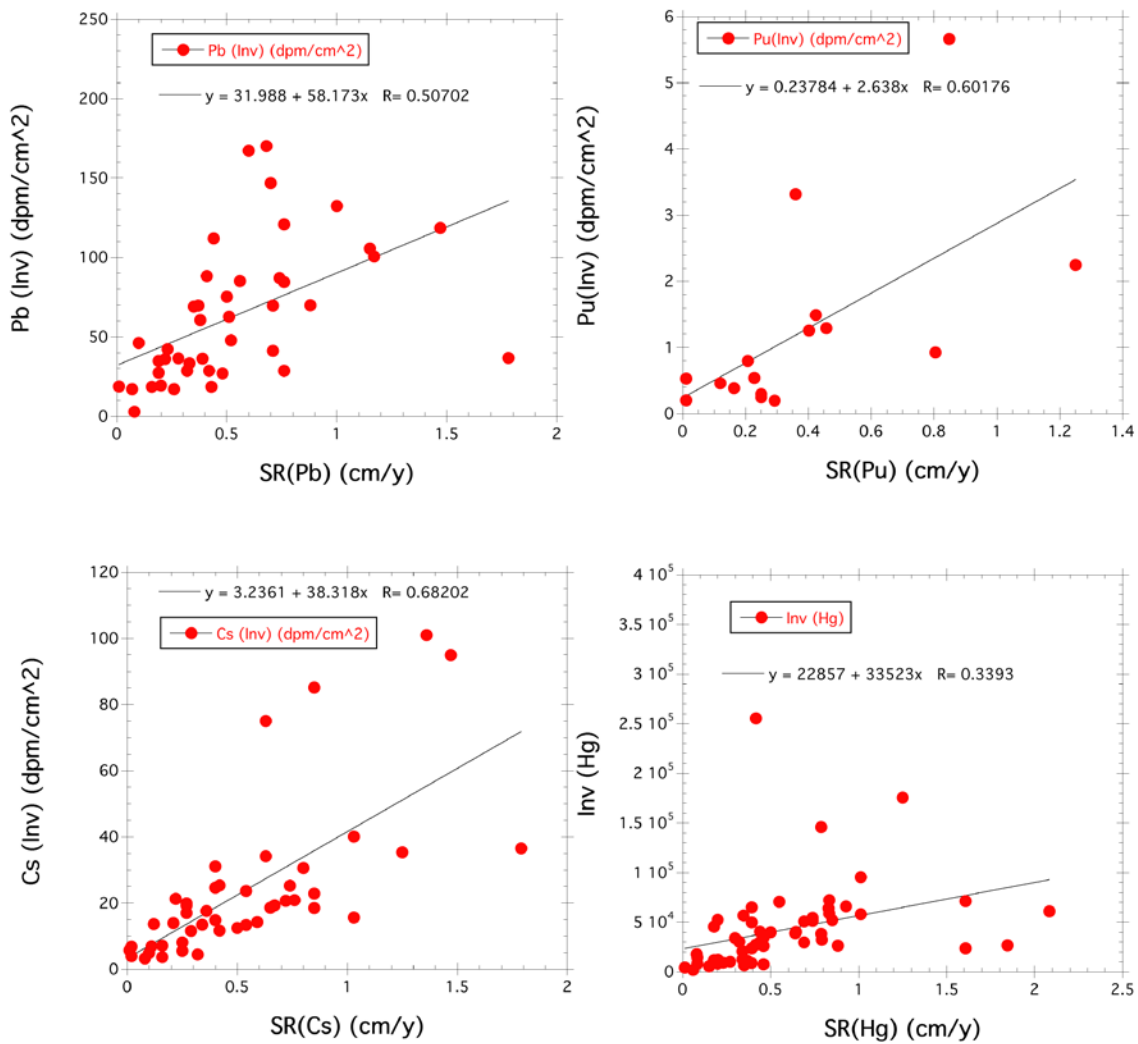


Figure 6-25. Correlations between sedimentation rates, SR, and inventories of Pu, Cs, Pb, and Hg, indicating that their inventories are generally proportional to SR, except for Hg at sites close to the point source of HoltraChem (PBR5A, 16A, 27B).

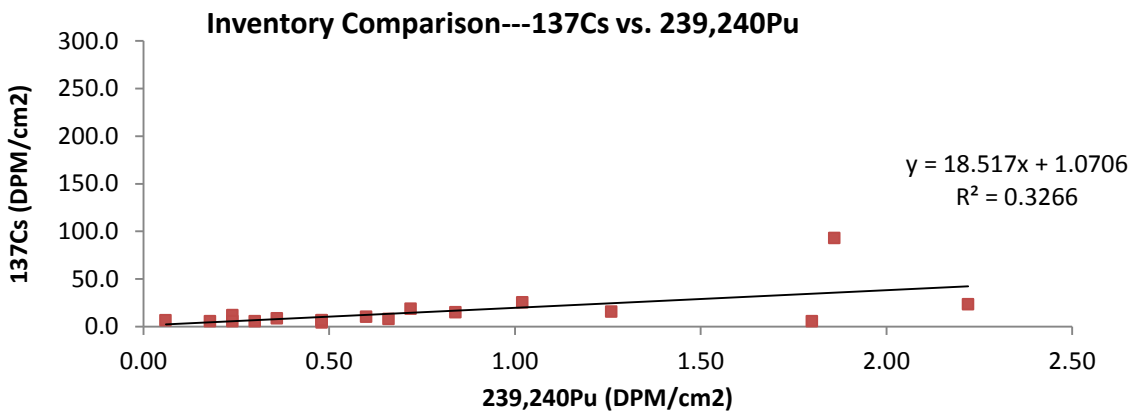
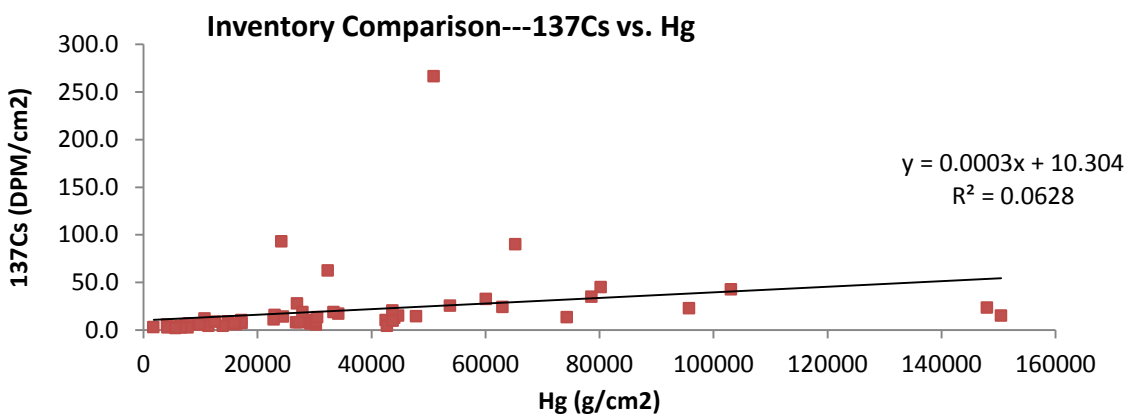
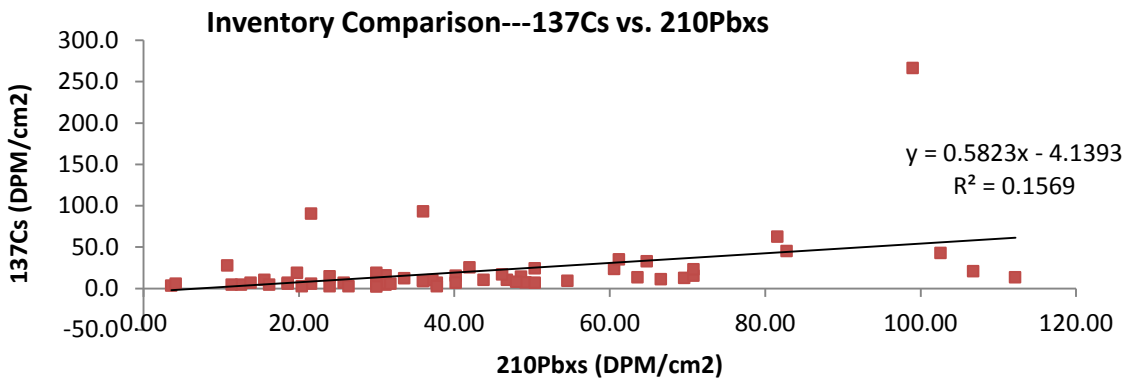


Figure 6-26. Correlations between inventories of Cs, Pu, Pb and Hg at different sites.

**Table 6-1: Summary of recovery parameters**

Core	t <sub>1/2</sub> (y)	t <sub>1/2</sub> * (y)	Hg <sub>(o)</sub> ng/g	Hg <sub>(max)</sub> ng/g	Hg <sub>(o)</sub> /Hg <sub>(max)</sub>	Sed Rate** Hg (cm/yr)	Inv Hg (ng/cm <sup>2</sup> )
<b>Mendall marsh</b>							
MM_01B_09V	26	16	555	1730	0.321	0.20	10754
MM_02B_09V	19	10	564	4680	0.121	1.61	103098
MM_03B_09V	39		855	3290	0.260	2.56	80264
MM_04C_09V	23	20	646	5140	0.126	0.55	62996
MM_05C_09V	25	12	826	3000	0.275	0.44	17218
MM_06A_09V	22	11	678	3270	0.207	0.50	34219
MM_07A_09V	15	12	626	6310	0.099	0.69	53799
MM_08A_09V	18	8	574	3860	0.149	0.37	23039
MM_09B_09V	11	11	471	4420	0.107	0.42	14850
MM_11B_09V			1080	1200	0.900	0.08	8189
MM_12C_09V			88	88.2	0.998		1781
<b>Penobscot River</b>							
PBR_01.5B_09V	50		42	1270	0.033	1.61	24231
PBR_04C_09V	26		108	2790	0.039	1.85	50947
PBR_05A_09V	54	39	1750	46300	0.038	0.79	148014
PBR_06C_09V	8		140	2640	0.053	0.74	47856
PBR_09A_09V			1975	1976.5	1.204	0.93	65244
PBR_10A_09V	13	7	507	3870	0.131	0.83	43719
PBR_11B_09V			646	1960	0.330	0.79	32389
PBR_13B_09V			1130	1310	0.863	0.88	26975
PBR_14CR_09V			1310	4260	0.308	1.01	60105
PBR_16A_09V	16		1001	73300	0.014	0.42	150451
PBR_17A_09V	28	16	634	4850	0.131	0.83	78639
PBR_18B_09V	23	15	969	2320	0.418	0.44	24507
PBR_19A_09V	12	8	643	6440	0.100	1.25	95720
PBR_20A_09V	47	35	430	3560	0.121	0.30	33352
PBR_21B_09V	12	3	406	2670	0.152	0.18	29310
PBR_21C_09V	13		294	4050	0.073	0.39	29796
PBR_23B_09V	9	3	404	3020	0.134	0.35	42730
PBR_25A_09V	35	20	814	1920	0.424	0.08	16258
PBR_26A_09V			1034	1340	0.772	0.18	13941
PBR_27B_09V			501	10193	0.049	1.01	74268
PBR_28B_09V	106	72	1060	2710	0.391	0.37	11261
PBR_29A_09V			1410	3390	0.416	0.39	43753
PBR_30B_09V			844	1670	0.505	0.32	17238
PBR_31C_09V	41	19	598	4240	0.141	0.64	30224

Core	t <sub>1/2</sub> (y)	t <sub>1/2</sub> * (y)	Hg <sub>(o)</sub> ng/g	Hg <sub>(max)</sub> ng/g	Hg <sub>(o)</sub> /Hg <sub>(max)</sub>	Sed Rate*	
						Hg (cm/yr)	Inv Hg (ng/cm <sup>2</sup> )
<b>Penobscot Estuary</b>							
ES_01B_09V	56	12	679	2080	0.326	0.46	15953
ES_02C_09V	19		772	2140	0.361	0.64	26792
ES_03C_09V	2		239	803	0.298	0.12	9936
ES_04C_09V	76		585	905	0.646	0.27	6372
ES_06A_09V	140		678	939	0.722	0.20	9779
ES_07A_09V	117	69	331	346		0.15	4232
ES_08A_09V			383	495	0.774	0.35	7772
ES_08C_09V	117		290	370	0.784	0.39	6663
ES_09C_09V			236	365	0.647	0.35	5650
ES_12C_09V			332	406	0.818	0.42	5597
ES_13C_09V	132		420	589	0.713	0.23	7983
ES_14C_09V	79		645	934	0.691	0.88	30529
ES_15A_09V	74	34	310	583	0.532	0.46	7491
ES_16C_09V	37		599	959	0.625	0.35	12548
ES_17C_09V	123		873	2710	0.322	0.79	27304
ES_18B_09V		30	872	1200	0.727	0.08	11416
ES_19C_09V		27	249	1120	0.222	0.69	27901
ES_20C_09V	45	60	725	2060	0.352	0.46	22902
<b>Orland River</b>							
OR_01B_09V	100		577	577	1.000		4190
OR_02B_09V			1930	2640	0.731	0.35	30262
OR_03A_09V	125	90	1300	3080	0.422	0.69	42534
OR_05C_09V	35	21	754	4650	0.162	0.74	44048
OR_06B_09V	48	30	947	4510	0.210	0.74	44713

\*) Apparent recovery half times (t<sub>1/2</sub> = ln2/α) were calculated from an exponential fit to the Hg concentration profiles (Hg(t)) over the past 21 years (Hg(t=21)), as Hg(t) = Hg(t=21) exp(-α\*t) + Hg(∞), with Hg(∞) = asymptotic level of either 0 or 400 ng/g (t<sub>1/2</sub>\*).

\*\*) for a list of sedimentation rates derived from <sup>137</sup>Cs, <sup>239,240</sup>Pu, and <sup>210</sup>Pb<sub>xs</sub>, see chapter 5.