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Mercury dynamics in Tivoli South Bay, a freshwater tidal mudflat wetland in the Hudson River

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Abstract. The accumulation of total mercury (Hg_T) and methylmercury (MeHg) was evaluated in sediments of Tivoli South Bay, a freshwater tidal mudflat wetland in the Hudson River National Estuarine Research Reserve system. Hg_T concentrations in sediment cores were measured to evaluate the spatial variability of Hg_T deposition, and to establish a chronology of Hg_T accumulation. Cores taken from the northern, middle, and southern sections of the bay had similar distribution patterns and concentrations of Hg_T, suggesting a common source of Hg_T throughout the bay. Sediment concentrations ranged from 190 to 1040 ng Hg g^{-1}, 2 to 10 times greater than concentrations expected in sediments from non-anthropogenic sources. Hg_T deposition rates were similar in different regions of the bay, and increased from 200 ng Hg cm^{-2} yr^{-1}in the 1930s to a maximum of 300 ng Hg cm^{-2} yr^{-1} in the 1960s. Deposition rates have steadily declined since the 1970s and are currently at 80 ng Hg cm^{-2} yr^{-1}. Transport of Hg_T by tidal waters from the Hudson River is likely the main source of Hg_T in the bay. Distribution patterns and absolute concentrations of MeHg in sediment cores were similar throughout the bay, with concentrations ranging from 0.43 to 2.95 ng g^{-1}. Maxima in MeHg concentration profiles occurred just below the sediment-water interface and at a depth of 30 cm. The maximum at 30 cm was coincident with maximum Hg_T concentrations. MeHg concentrations in suspended particulate matter (SPM) from the Hudson River suggest that MeHg in the bay could be derived from riverine SPM rather than formed *in situ.*

Introduction

Understanding mercury dynamics in freshwater tidal wetlands is important because wetlands have been identified as a significant source of methylmercury (MeHg), the predominant form of mercury bioaccumulated in fish (Bloom 1992). St. Louis et al. (1994) observed that yields of MeHg were 26 to 79 times higher from wetland portions of catchments than from purely upland areas in a Canadian boreal forest. A mass balance indicated that lakes and purely upland catchments were sites of MeHg retention or demethylation, while catchments with wetland areas were sites of net MeHg production. Babiarz et al. (1998) and Hurley et al. (1995) have observed similar increases in MeHg yield with wetland composition in watersheds in Wisconsin, U.S.A.

In addition to MeHg discharged from wetlands, precipitation and methylation of mercury in near-surface sediments are important sources of MeHg in aquatic systems. Deposition rates of MeHg in the northern hemisphere range from 0.39 mg ha^{-1} yr^{-1} in northwestern Ontario (St. Louis et al. 1994) to 4.0 mg ha^{-1} yr^{-1} in southern Sweden (Hultberg et al. 1994). The origin of MeHg in deposition is not known, but may be related to industrial activity (Rudd 1995) or formation in the atmosphere from dimethylmercury derived from coastal upwelling seawater (Fitzgerald & Mason 1995). Several investigations have shown that near-surface sediments are an important site of the methylation of inorganic mercury, Hg(II), to MeHg, CH_3HgX, where X is typically Cl or OH (Ramal et al. 1993; Gilmour et al. 1992; Korthals & Winfrey 1987; Callister & Winfrey 1986), and that sulfate reducing bacteria are important mediators of methylation in lacustrine and estuarine sediments (Gilmour et al. 1992; Gilmour & Henry 1991; Compeau & Bartha 1985). Mercury methylation is favored in organic matter-rich sediments and in the presence of active microbial sulfate reduction, but is limited by high pore water sulfide concentrations which act to inhibit MeHg production in saline sediments (Compeau & Bartha 1984). In freshwater sediments, microbial reduction is often sulfate limited, and adding sulfate to lacustrine sediments has been shown to increase mercury methylation rates (Gilmour & Henry 1991). Demethylation of MeHg occurs abiotically in lakes as a photodegradation process (Sellers et al. 1996), and microbially as a detoxification response to MeHg exposure (Tsai & Olson 1990).

The purpose of our investigation was to study the dynamics of MeHg and total mercury (Hg_T) in Tivoli South Bay, a freshwater tidal mudflat wetland in the Hudson River National Estuarine Reserve system. Fine-grained sediments control the transport and fate of contaminants in estuarine ecosystems, and shallow embayments and wetlands account for a disproportionate share of the accumulation of fine-grained sediments on an areal basis. Hg_T has a high affinity for particulate matter and is readily transported via suspended particulate matter and resuspended sediments. Sedimentation rates in protected areas such as Tivoli South Bay are significantly higher than in the main river channel, possibly allowing a large pool of mercury contaminated sediment to build up. Sulfate reduction has been shown to be a significant process in the bay (Gould & Findlay 1990; McCarron & Findlay 1988), suggesting that methylation of mercury may also be significant. In this study, we estimate the accumulation rate of Hg_T in the sediments of Tivoli South Bay, determine the spatial distribution of MeHg in the sediments, evaluate the partitioning of

MeHg between sediment and pore water, and assess the implications of this information for possible sources of Hg_T and MeHg in the bay. Our investigation benefits from intensive research conducted at this site over the years, and contributes to an understanding of biogeochemistry in the bay and the behavior of Hg in freshwater tidal wetlands.

Study site

Tivoli South Bay is a freshwater tidal mudflat wetland, covering approximately 1.13 km^2. It is located along the east shoreline of the Hudson River, approximately 160 km north of lower Manhattan. A freight and passenger railway right-of-way, constructed in 1851, separates the bay from the river with an embankment approximately 30 to 60 m wide and 3 m above mean sea level. Tidal exchange between the river and the bay is restricted to three bridge openings (60 m), however, the tidal prism remains close to historical values. Tidal flow comprises approximately 90 percent of the annual water budget for the bay (Lickus & Barten 1990). The average tidal range is 1.2 m, and large areas of mudflats are exposed at lowest tides. The principal source of non-tidal surface water to South Bay is the Saw Kill which has a drainage area of 68 km^2 and includes a broad range of land use and land cover types (e.g., forest, wetland, cropland, transportation, residential, and commercial). The physical alteration of the bay, combined with shallow waters and an invasion of a dense seasonal stand of water chestnut (*Trapa natans*), may have caused the wetland to begin to act as a more efficient sediment trap (Findlay et al. 1990; Goldhammer & Findlay 1988). The sedimentation rate for the bay, as calculated by Benoit et al. (1999) using ^{210}Pb dating techniques has ranged from 0.62 to 1.92 cm y^{-1}, depending on location, over the past 50 years.

Methods

Six sediment cores were collected along a north-south transect (Figure 1) in Tivoli South Bay on May 17, 1996 for mercury analysis. Duplicate cores (50 cm) were taken from the northern (TSB1, TSB2), middle (TSB3, TSB4), and southern (TSB5, TSB6) parts of the bay on a rising tide by a snorkeller using 2.25 inch I.D. acrylic core tubes. Cores were taken to shore and immediately sectioned every 2 cm to a depth of 8 cm, and every 4 cm below that depth. Core sections were transferred to pre-weighed, acid-cleaned polyethylene jars, frozen, and shipped back to the laboratory for chemical analysis. Clean

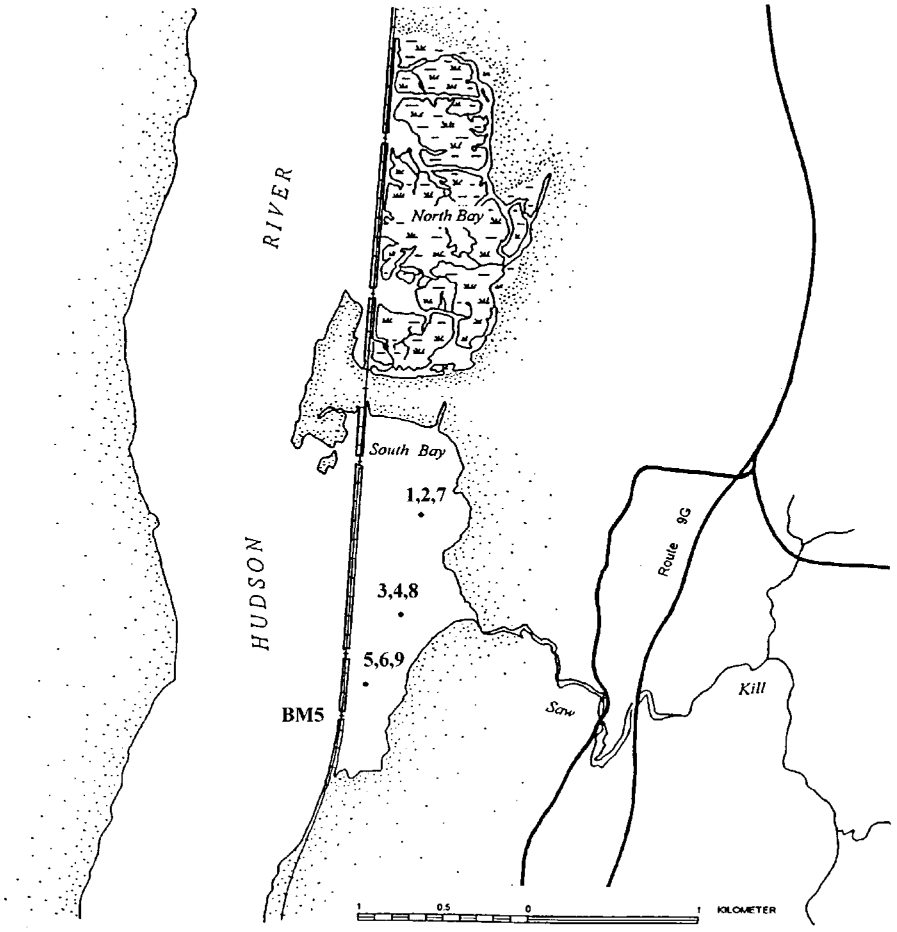

Figure 1. Tivoli South Bay, Hudson River, NY (42°01′ N, 73°55.5′ W).

techniques established in our laboratory (Hurley et al. 1996), similar to techniques developed for sampling lead in the mid-1970s (Patterson & Settle 1976), were used during all stages of sample collection and handling. One additional core was collected at each location (TS7-9) to evaluate sedimentation rates by means of ^{137}Cs dating. Cores were collected in 12.5 cm I.D. PVC core tubes that had been pre-sectioned into a series of rings, then reassembled into a cylinder by wrapping with waterproof plastic tape. After collection, cores were sectioned immediately at 1 cm intervals to a depth of 5 cm, every 2 cm from 5 to 15 cm, and every 3 cm thereafter. These cores were also used by Benoit et al. (1999) to evaluate sedimentation rates in the bay. The ^{137}Cs activity in cores TS7-9 was measured by non-destructive gamma spectroscopy. Our cores TS7-9 are identical to those in Benoit (1999), but cores designated TS1-6 are different in the two studies.

Samples of unfiltered surface water and particulate matter were collected from the Hudson River near the southern-most bridge (42°00′43″ N, 73°55′39″ W) on May 17, 1996 during the in-coming tide. All surface water samples were collected using a peristaltic pump outfitted with acid-cleaned Teflon^{TM} sampling line and silicone pumphead tubing. Samples of unfiltered water were collected in Teflon^{TM} bottles that had been cleaned in hot, concentrated nitric acid. Particulate matter for Hg analysis was collected on quartz fiber filters housed in acid-clean Teflon^{TM} filter cartridges. The filters are rated by Whatman Scientific to retain particles larger than 2.2 μm in diameter when liquid is the filtered medium. Prior to sampling, the quartz fiber filters were ashed at 450 °C to volatilize any Hg associated with them. Samples for SPM analysis were collected on 0.8 μm Nucleopore^{TM} filters. Unfiltered water samples for MeHg analysis, and all particulate matter samples were frozen and shipped back to the laboratory for analysis. Unfiltered water samples for Hg_T analysis were acidified to 1 percent with trace metal grade HCl in the field.

A Teflon^{TM} close interval membrane equilibrium sampler (peeper), fitted with a 0.22 μm pore size polyvinylidine difluoride filter was installed near site TSB5/TSB6 to collect pore water samples. The design of the peeper, similar to that introduced by Hesslein (1976), allows 20 mL pore water samples to be collected at 1 cm intervals from 0 to 12 cm below the sediment-water interface. Both the peeper and filter were cleaned in hot nitric acid prior to installation. The peeper was deployed August 30, 1996 and removed on September 20, 1996. An acid-cleaned polyethylene syringe was used to transfer pore water samples to Teflon^{TM} vials that had been cleaned in hot, concentrated nitric acid. Samples were frozen, and shipped back to the laboratory for analysis. Water chestnut (*Trapa natans*) seeds ruptured the filter membrane at depths of 6 to 7, 7 to 8, and 10 to 11 cm below the sediment water interface; consequently, no pore water samples were obtained at these depths.

Core sections were freeze-dried and re-weighed to calculate sediment bulk density. All sediment analyses were performed on freeze-dried, homogenized core sections. The organic matter content of sediments was estimated by weight from loss on ignition (LOI) at 450 °C.

All samples were analyzed for Hg_T and MeHg under clean room conditions. Hg_T concentrations were measured by cold vapor atomic fluorescence spectrophotometry (CVAFS), following reduction with stannous chloride to form Hg^0 (Bloom 1989; Bloom & Crecelius 1983; Fitzgerald & Gill 1979). The detection limit, calculated as three times the standard deviation of the blank, was 22 pg Hg. The analytical method involves preconcentrating Hg^0 onto a gold trap prior to detection, and therefore, detection limits expressed in units of concentration depend on the original mass or volume of a sample. All of the samples analyzed were above the limit of detection. Prior to analysis, sediment samples (100 mg) were digested with nitric (5 mL) and sulfuric (2 mL) acid, and unfiltered water samples and suspended particulate matter samples were oxidized with bromine monochloride (Hurley et al. 1994). All digested sediment samples were analyzed in duplicate. Differences between duplicates expressed as a fraction of the average value were less than 13 percent. In addition, duplicate sediment samples were taken from sections of TSB1 and TSB3, digested, and analyzed. Differences between core subsamples were less than 8 percent. Analysis of Standard Reference Material 2704 (Buffalo River sediment, reported $Hg_T = 1470 \pm 70$ ng g^{-1}) gave measured values of 1420 ± 120 ng g^{-1} ($N = 6$). Surface water and particulate matter samples were analyzed in triplicate.

Water and sediment samples for MeHg analysis were treated with sulfuric acid and potassium chloride to convert all forms of MeHg to methylmercury chloride (MeHgCl), and distilled to separate MeHgCl from associated organic matter. MeHgCl was ethylated, chromatographically separated from other mercury forms, pyrolized to Hg^0, and detected by CVAFS (Horvat et al. 1993a; Horvat et al. 1993b). The analytical detection limit was 2.4 ± 0.4 pg MeHg ($N = 6$). All MeHg concentrations are reported on a mass of Hg basis. In most cases, values for sediments and pore waters represent a single determination. One section from each of cores TSB1, TSB3, and TSB5 was subsampled in triplicate. Coefficients of variation for core subsamples were less than 14 percent. In lieu of a standard reference material, all of which are biological tissue samples, the NRCC standard MESS-1 (sediment from the Miramichi River estuary that is certified for Hg_T) was analyzed and found to contain a MeHg concentration of 0.27 ± 0.10 ng g^{-1} ($N = 3$). This is comparable to published values of 0.348 ± 0.028, 0.384 ± 0.043, and 0.506 ± 0.100 ng g^{-1} from other laboratories (Horvat et al. 1993a). To evaluate whether inorganic Hg(II) was methylated during the distillation process, subsamples from one of the core sections were spiked with 100 ng of Hg_T standard. The spiked samples had an average MeHg concentration of 2.59 ± 0.03 ng g^{-1}, as compared to an unspiked concentration of 2.73 ± 0.23 ng g^{-1}. Spikes of MeHg standard were added to some samples to determine distillation recovery. The average recovery of MeHg spikes in sediment samples was 98 ± 14 percent ($N = 8$). Recovery of an unfiltered, spiked, surface water sample was 86 percent. Reported MeHg concentrations were not corrected to compensate for distillation recoveries.

Results and discussion

Distribution and accumulation of Hg_T in sediments

Distribution patterns and absolute concentrations of Hg_T were very similar in duplicate cores, and in cores taken from different regions of the bay (Figure 2). Concentrations were lowest in near surface sediments, increased to a subsurface maximum about 30 cm below the sediment-water interface, and then dropped slightly. The subsurface maxima in the cores taken from the northern region of the bay, as compared to cores taken from the middle and southern sections of the bay, are shifted slightly toward the surface. Concentrations ranged from 190 ng g^{-1} in near surface sediments to a maximum of 1040 ng g^{-1}. Cores were not long enough to reach sediments representing pre-industrial times. The current, relatively low concentration in riverine SPM (119 ng Hg g^{-1}) combined with a trend of declining Hg_T in recently deposited sediments suggests that the level of non-anthropogenic mercury in the bay sediments is on the order of 100 ng g^{-1} or less. Hg_T concentrations in bay sediments were not correlated with percent organic matter.

Hg_T deposition rates in bottom sediments were calculated using the average Hg_T concentration in each region of the bay and sedimentation rates calculated from ^{137}Cs profiles (Figure 3). The peak of the ^{137}Cs distribution is assumed to be 1963, the year of the atmospheric weapons test ban treaty (Ritchie & McHenry 1990). The relative sharpness of the 1963 maximum peaks in cores TS8 and TS9 indicates that sediments have not undergone extensive mixing. In contrast, the broader peak in core TS7 suggests that some mixing may have occurred. In order to compensate for compaction of the sediment and differences in bulk density for purposes of calculating sedimentation rates, depth in the sediment cores was expressed as cumulative dry mass. On average, 1 cm of sediment is equivalent to 0.60 g cm^{-2} in cores TSB1 and TSB2, 0.44 g cm^{-2} in cores TSB3 and TSB4, and 0.45 g cm^{-2} in cores TSB5 and TSB6. Calculated linear sedimentation rates based on ^{137}Cs were 0.59, 0.68, and 0.77 cm yr^{-1} in the northern, middle, and southern areas of the bay, respectively. These are average values for the period of time from the test ban (1963) to the time the cores were collected (1996). The ^{137}Cs-based sediment accumulation rates fall within the range of values, 0.62 to 1.92 cm yr^{-1}, reported by Benoit et al. (1999) for Tivoli South Bay using a combination of ^{210}Pb and ^{137}Cs analyses. Cores in the current study were all collected from mudflat locations, while Benoit and coworkers sampled a broader range of depositional environments, including channels. Hg_T deposition rates were similar in the northern, middle, and southern regions of the bay (Figure 4). Hg_T mass deposition rates increased from 200 ng Hg cm^{-2} yr^{-1} in the 1930s to a maximum of 300 ng Hg cm^{-2} yr^{-1} in the 1960s. The peak in

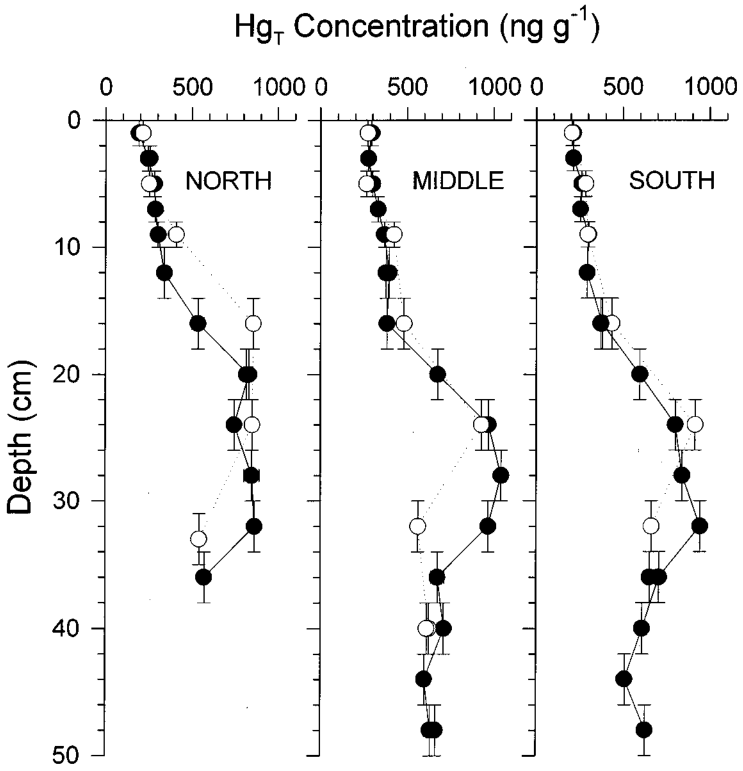

Figure 2. Vertical distribution of Hg_T in Tivoli South Bay sediments. Solid circle represent cores TSB1, TSB3, and TSB5. Open circles represent TSB2, TSB4, and TSB6. Vertical bars indicate the thickness of the sediment layer analyzed.

Hg_T deposition corresponds to a maximum in annual usage of mercury in the U.S. between 1950 and 1984 (Steinnes 1990). Deposition rates have steadily declined since the 1970s and are currently at about 80 ng Hg cm^{-2} yr^{-1}.

The similarity in Hg_T deposition rates among the regions of Tivoli South Bay is consistent with a common source of Hg_Tthroughout the bay. In a study of heavy metal (Pb, Cu, and Zn) deposition, Benoit et al. (1999) observed that distribution patterns and absolute concentrations of Pb, Cu, and Zn among cores at different locations in the bay were highly variable. Although metal distribution patterns varied from core to core, a relatively constant ratio was maintained between metals in individual cores, suggesting a common source of the three metals at any one site. The Hudson River and the Saw Kill were hypothesized to be the disparate sources of metals. If sediments from the bay are derived from different sources, similar Hg_T deposition rates suggest that Hg_T in the bay could be derived from direct atmospheric deposition, or from

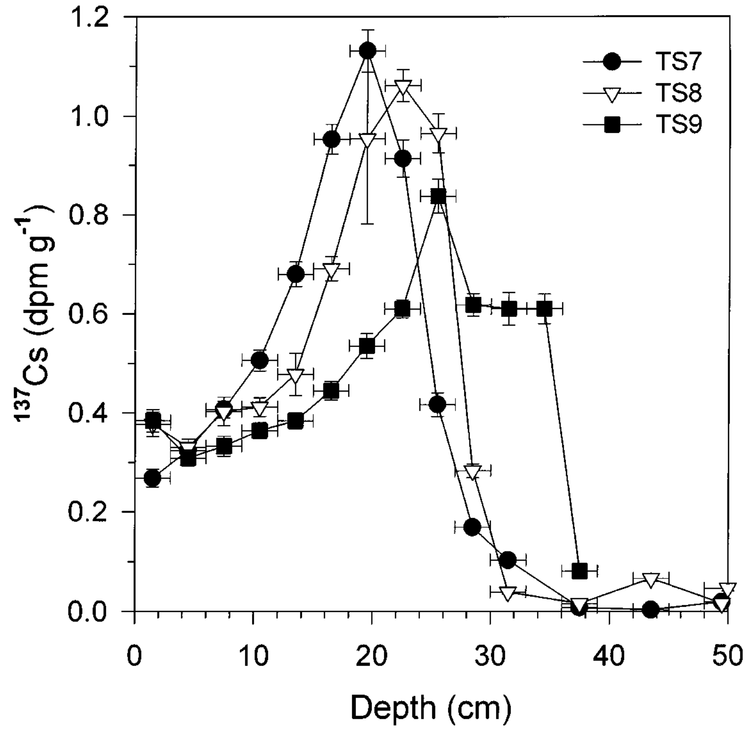

Figure 3. Activity of ^{137}Cs versus depth of core. Horizontal bars indicate the thickness of each section, while vertical bars are uncertainties (±1 standard deviation) based on counting statistics. ^{137}Cs ages are calculated from the depth of maximal activity, which corresponds to the year 1963.

large, watershed-scale events that would equally impact the Saw Kill and the Hudson River. Conversely, given the limited number of sediment cores and the predominance of the Hudson River in the water budget of the bay, similar deposition rates may be due to loading of riverine particulate matter from the Hudson River.

Direct atmospheric deposition is one source of Hg_T that would result in uniform Hg_T deposition throughout the bay (Stevenson et al. 1986). Atmospheric deposition rates of Hg_T vary regionally and temporally, depending on the extent of industrialization, but are on the order of 1 ng cm^{-2} yr^{-1}. Reported atmospheric mercury deposition rates are 1.0 ng cm^{-2} yr^{-1} in northern Wisconsin (Fitzgerald et al. 1991), 1 to 3.8 ng cm^{-2} yr^{-1} in northeastern Minnesota (Benoit et al. 1994), and 1 to 2 ng cm^{-2} yr^{-1} in Maryland (Mason et al. 1997). However, Hg_T deposition in the sediments of the bay is a factor of 100 times the atmospheric Hg_T deposition rate, indicating that

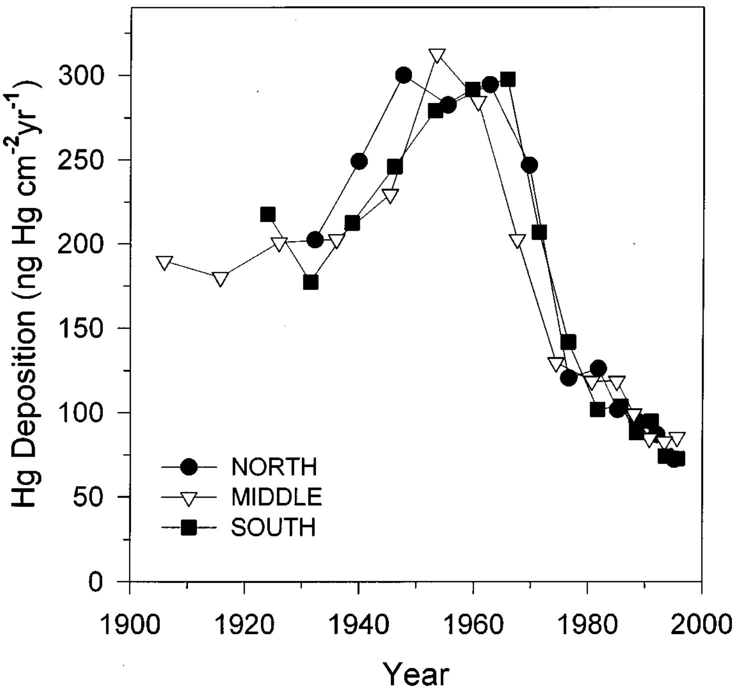

Figure 4. Hg_T deposition in sediments of Tivoli South Bay.

direct atmospheric deposition to the surface of the bay is not the major source of Hg_T in Tivoli South Bay.

The depositional flux of Hg_T into bay sediments is driven by the high sedimentation rate in the bay combined with relatively high levels of Hg_T in SPM. Besides direct atmospheric deposition, the Hg_T in bay sediments could be derived from three general sources: natural weathering processes, atmospheric deposition onto the watershed, and other sources of Hg_T introduced from the Hudson River or the Saw Kill. Natural weathering is unable to account for the Hg_T temporal distribution pattern in the sediment cores. Hg_T derived solely from natural weathering processes would result in a relatively constant Hg_T deposition rate in the bay over the past 80 years, with Hg_T concentrations in sediments comparable to pre-industrial Hg_T soil concentrations.

A simple relation is not expected between atmospheric loading of trace metals to watersheds and metal burdens in the bottom sediments of water bodies receiving sediment from the watershed. For example, strong retention of metals by contributing watersheds or inefficient scavenging in the water column can lead to low metal levels in downstream sediments, while sediment focusing or substantial release by the watershed can cause elevated levels. In spite of these complications, the amount of Hg_T supplied from the watershed can be estimated by comparison to a related tracer or through mass balance calculations. ^{210}Pb, which is delivered in constant amounts from the atmosphere and has no contaminant sources, provides a benchmark tracer against which to compare other metals having similar behavior (Kada & Heit 1992). Benoit et al. (1999) showed that ^{210}Pb inventories in Tivoli South Bay sediments were consistent in magnitude with amounts expected from direct atmospheric delivery alone, at least within a factor of three. Therefore, it is unlikely that the 100-fold elevation of mercury observed in these sediments can be explained through some combination of atmospheric delivery to the watershed and post-depositional processes.

Simple mass balance calculations confirm results indicated by the tracer approach. Reported watershed retention efficiencies are 92 to 96% in Sweden (Lindqvist et al. 1991), 70 to 90% in Ontario (Mierle & Ingraham 1991), and $>$90% in the Chesapeake Bay watershed (Mason et al. 1997). A Hg_T deposition rate of 2 ng cm^{-2} yr^{-1}, combined with a watershed retention rate of 90%, would result in 136 g Hg_T yr^{-1} released into Tivoli South Bay from the Saw Kill watershed. If this load were evenly distributed over the bay, it would account for 12 ng Hg_T cm^{-2} yr^{-1}. A similar calculation can be made to estimate the input of Hg_T from the Hudson River watershed. In this case, we make the assumption that Hg_T is associated with riverine particulate material. An atmospheric Hg_T deposition rate of 2 ng cm^{-2} yr^{-1} and a watershed retention rate of 90% would result in 7×10^4 g Hg_T yr^{-1} released into the Hudson River. Yearly fluvial sediment loading to the Hudson estuary is 7×10^{11} g (Bero & Gibbs 1990), of which 4×10^9 g is deposited in Tivoli South Bay. If we assume that the fraction of Hg_T deposited in Tivoli South Bay is proportional to the fraction of sediment deposited (0.6%), then 400 g Hg_T yr^{-1} is deposited in the bay. This would account for a deposition rate of 36 ng Hg_T cm^{-2} yr^{-1}. Thus, atmospheric deposition of Hg_T to the Hudson and Saw Kill watersheds contributes to Hg_T loading in the bay, but cannot account for peak depositional rates of 300 ng Hg_T cm^{-2} yr^{-1} in the 1960s nor the current deposition of 80 ng Hg_T cm^{-2} yr^{-1}.

Having ruled out weathering, direct atmospheric delivery, and atmospheric deposition to contributing watersheds as major sources of Hg_T to TSB, it appears that high levels in sediments must have come mainly from point and nonpoint sources of pollution. For the Hudson, we are aware of no basin-wide inventory of Hg pollution, but there has been widespread use of metals for industrial and consumer purposes. There are two known past point sources of anthropogenic mercury to the Hudson River, both of which are currently Superfund sites. (The Superfund Program was established in 1980 to locate, investigate, and clean up the worst hazardous waste sites in the United States.) When the Mercury Refining Company in Albany, NY (located 80 km upstream of Tivoli South Bay) became a Superfund site in the early 1970s, pools of Hg^0 were present on the property, and the Hercules Paint Company in Glen Falls, NY (located 160 km upstream of Tivoli South Bay) was cited for discharging raw pigment (mercury was commonly used as a fungicide in paints) into the Hudson River (R. Sloan, New York Department of Environmental Conservation, pers. comm.). The decline of Hg_T deposition in Tivoli South Bay since the early 1970s corresponds to a general improvement in water quality of the Hudson River that has been attributed to legislation aimed at controlling pollution at the source by reducing or banning direct discharge of point-source pollutants into the river (Ayres & Rod 1986; Bonavist 1981).

The watershed of the Saw Kill includes extensive orchards. Heavy applications (sometimes biweekly) of pesticides in apple orchards were common throughout the Hudson Valley from the 1950s through the late 1970s. (Then, Integrated Pest Management reduced the quantity and potency of agricultural chemicals.) Although a quantitative assessment can not be made, agricultural chemicals, used intensively during the period of peak accumulation of Hg_T in Tivoli South Bay sediments, may have been a significant contributor of Hg_T to the bay.

In view of the historical pattern and uniform deposition among the three segments of the bay, we believe that transport of Hg_T by tidal waters from the Hudson River has been the major source of Hg_T in the bay or that Hg levels on sediments of the Hudson River and Saw Kill have been nearly equal over time. Hg_T concentration profiles are similar to those of other trace metals in the bay. Hg_T profiles resemble the distribution of Pb, Cu, and Zn in cores TS1, TS-B, and TS-C of Benoit et al. (1999) in that concentrations reach a broad sub-surface maximum and decline towards the surface. The depth of the maxima do not coincide and this may be due to different temporal input functions for Hg_T compared to the other metals or to postdepositional redistribution of metals such as Zn and Cu under redox gradients in the sediments.

Distribution of MeHg in sediments and pore water

The vertical distribution of MeHg in sediment cores taken from the northern, middle, and southern sections of the bay is shown in Figure 5. Distribution patterns and absolute concentrations of MeHg were very similar in all three cores. Concentrations ranged from 0.43 to 2.95 ng g^{-1}. Maxima in the MeHg concentration profiles occurred just below the sediment-water interface and at a depth of about 30 cm. The MeHg concentration maximum at 30 cm is

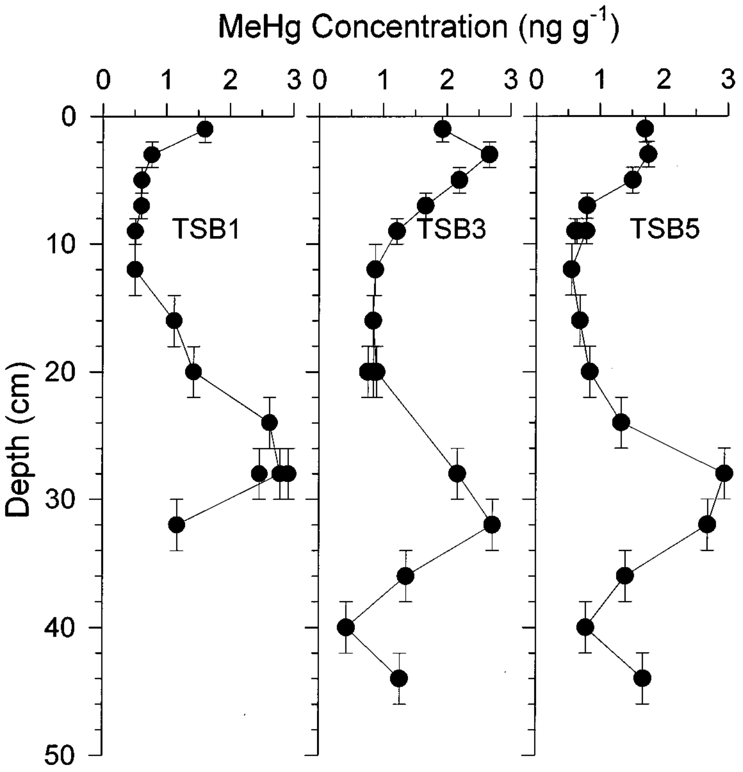

Figure 5. Vertical distribution of MeHg in Tivoli South Bay sediments. Vertical bars indicate the thickness of the sediment layer analyzed.

coincident with maximum Hg_T concentrations. However, near surface MeHg concentration maximum coincide with the lowest Hg_T concentration. Sediment samples spiked with Hg_T showed no evidence of inorganic methylation during the distillation process suggesting that MeHg concentrations observed are real sediment concentrations, and not artifacts of the distillation process. MeHg concentrations were not correlated with Hg_T or percent organic matter. The concentration of MeHg in SPM from the Hudson River was 1.46 ± 0.07 ng g^{-1}. This value is the mean of three samples collected off the southernmost bridge on May 17, 1996 during an in-coming tide, and may not be representative of yearly average concentrations. However, it does fall within the surficial sediment range of 1.5 to 2 ng g^{-1}, which suggests that MeHg in Tivoli South Bay could be derived from riverine SPM rather than formation in situ. In a study of the Chesapeake Bay, Mason et al. (1997) also observed results that indicated MeHg was generated in the watershed and transported to the bay via river runoff.

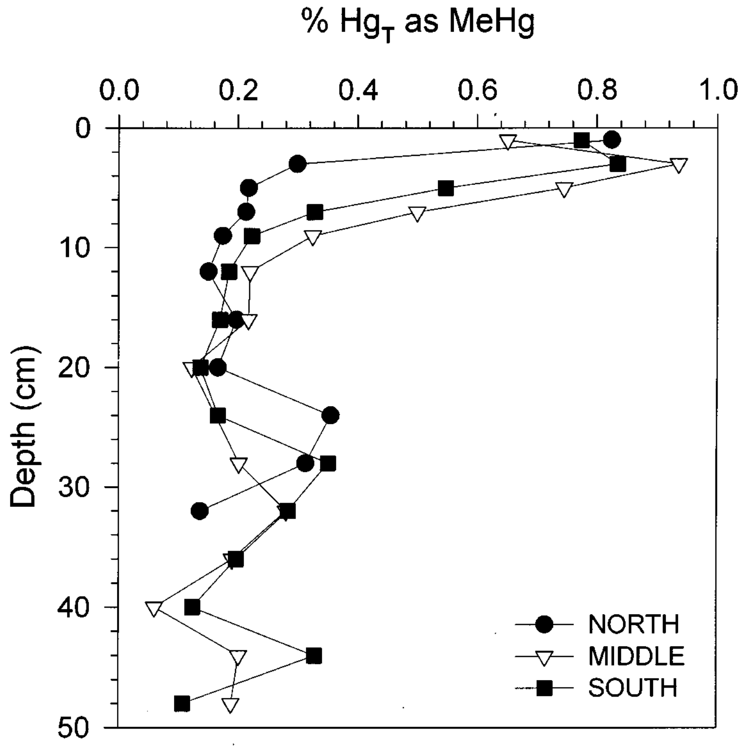

Figure 6. Fraction of Hg$_T$ present as MeHg in Tivoli South Bay sediments.

Concentrations of MeHg in bay sediments are a result of the concentration of MeHg in freshly deposited sediments, methylation and demethylation rates in the sediments, and the transport of dissolved MeHg in pore water to overlying surface waters. The fraction of Hg$_T$ that occurs as MeHg is greatest, 0.9 percent, in the top 4 cm of sediment, declines to 0.2 percent at 10 cm, and remains fairly constant throughout the rest of the core (Figure 6). The decreasing fraction of Hg$_T$ as MeHg with depth in the sediments combined with the possibility that all MeHg could be derived from riverine SPM suggests that net demethylation of MeHg is occurring. Elevated MeHg concentrations in near surface sediments have previously been attributed to higher net methylation rates due to the availability of more labile carbon (Korthals & Winfrey 1987; Callister & Winfrey 1985). The fraction of Hg$_T$ as MeHg in Tivoli South Bay sediments is comparable to values observed in other lacustrine and estuarine sediments (Table 1).

Concentrations of MeHg in pore waters ranged from 0.17 to 0.55 ng L^{-1} (Table 2). Concentrations are above the analytical detection limit of 0.12 ng L^{-1}; however, the atypical profile suggests that concentrations are likely at

Table 1. Concentrations of Hg_T and % MeHg in lacustrine and estuarine sediments. In most cases, values represent a range. Single values are means. Percent Hg_T as MeHg is generally less than 1% in both lacustrine and estuarine sediments.

Location	% MeHg	Hg_T (ng g^{-1})	Reference
Hudson River, NY	0.06–0.94	190–1,040	This study
Lakes in Norfolk, U.K.	0.057–0.125	1,120–36,900	Croston et al. 1996
Yare River, U.K.	$<$1–7	400–32,900	Bubb et al. 1993
Lake Onondaga, NY	0.021–0.45	1,080–49,500	Henry et al. 1993
Quabbin Reservoir, MA	0.1–16.3	10–30	Gilmour et al. 1992
Patuxent Estuary	0.1–0.5	60–160	Benoit et al. 1998
Estuaries in Florida	0.77	1–219	Kannan et al. 1998
Scheldt Estuary	0.7	144–1,192	Muhaya et al. 1997
St. Lawrence Estuary	$<$1	40–9,500	Gagnon et al. 1996
Mersey Estuary, U.K.	0.46	50–5,310	Bartlet & Craig 1981
Estuaries in southeastern U.S.A.	$<$0.01–0.07	80–570	Andren & Harriss 1973

or below the field detection limit which we were unable to determine as part of our analysis. MeHg concentrations in pore water should therefore be considered an upper limit of pore water concentrations. The partitioning of MeHg between sediment and pore water can be expressed as a partition coefficient, K_D, which relates the MeHg concentration in the sediment or SPM, C_S (ng kg^{-1}), to the aqueous concentration, C_W (ng L^{-1}).

$$K_D = C_S/C_W$$

The K_D in the Hudson River sample is 10 times greater than the average K_D in Tivoli Bay sediments (Table 2). Concentrations of MeHg in sediments and riverine SPM are similar; however, concentrations of MeHg in pore water are 10 times greater than the concentration in surface water. High MeHg concentrations are usually associated with anoxic conditions which favor MeHg production in sediment and water (Regnell & Tunlid 1991; Compeau & Bartha 1984) and the partitioning of MeHg into the aqueous phase (Regnell 1994). Regnell has shown in microcosm studies that MeHg is released from sediments during anoxia, and that the release is redox controlled by iron and manganese chemistry. MeHg pore water concentrations reaching 10 ng L^{-1} were observed by Gagnon et al. (1996) in organic matter-rich marine sediments in the Saguenay Fjord and St. Lawrence estuary; however, oxic surficial sediments contained virtually no MeHg, suggesting that the oxic layer served as a geochemical barrier to its diffusion to overlying surface waters. MeHg transfer to overlying surface waters could still occur by advection or bioturbation. In addition, benthic organisms may assimilate MeHg

Table 2. Filterable MeHg concentrations and particle-water partition coefficients, K_D, in the Hudson River and in pore water from the southern section of Tivoli South Bay.

Sample source	Depth (cm)	MeHg concentration Water (ng L^{-1})	 Sediment or SPM (ng g^{-1})	K_D (L kg^{-1})
Hudson River		0.054	1.50	2.7×10^4
Pore water	0–1	0.55	1.70	3.1×10^3
	1–2	0.23	1.75	7.6×10^3
	2–3	0.48	1.75	3.6×10^3
	3–4	0.25	1.51	6.9×10^3
	4–5	0.48	1.51	3.2×10^3
	5–6	0.32	0.80	4.7×10^3
	8–9	0.43	0.80	1.9×10^3
	9–10	0.17	0.79	4.7×10^3
	11–12	0.45	0.79	1.2×10^3

directly from the underlying anoxic sediments and serve as transport vectors of MeHg into the food web.

Conclusions

Sediments deposited from the Hudson River are believed to be the major source of Hg_T in Tivoli South Bay. Hg_T deposition rates among regions of the bay were similar, which is consistent with a single source of Hg_T. Hg_T mass deposition rates increased from 200 ng Hg_T cm^{-2} yr^{-1} in the 1930s to a maximum of 300 ng Hg_T cm^{-2} yr^{-1} in the 1960s. Deposition rates have declined since the 1970s and are at a 90 year low of 80 ng Hg cm^{-2} yr^{-1}. Atmospheric deposition rates are on the order of 1 ng Hg_T cm^{-2} yr^{-1}; therefore, direct deposition onto the bay is only a small fraction of Hg_T deposition in the bay. Atmospheric deposition of Hg_T onto the watershed and transport into the bay by river runoff is estimated to contribute 40 to 50 ng Hg_T cm^{-2} yr^{-1}. Atmospheric deposition cannot account for the high depositional rates observed between 1930 and 1970 and the rapid decline in the 1970s and 1980s. Peak depositional rates observed prior to 1970 are most likely due to Hg_T contaminated sediments. Other trace metals have similar concentration profiles (Benoit et al. 1999) in the bay, consistent with the transport of anthropogenically impacted sediments. Sediments deposited from the Hudson River may also be the major source of MeHg in the bay. The concentration of MeHg in riverine SPM was 1.5 ng g^{-1}, measured as the tide was coming in. This value falls within the surficial sediment range of 1.5 to 2 ng g^{-1} in the bay. The fraction of Hg_T that occurs as MeHg declines from 0.9 percent in surficial sediments to 0.2 percent at 10 cm, and remains fairly constant throughout the rest of the cores. This suggests that net demethylation or post depositional migration to the water column is occurring in near surface sediments.

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