

MERCURY DYNAMICS IN SEDIMENTS OF TIVOLI SOUTH BAY, HUDSON RIVER, NY

A Report of the 1996 Tibor T. Polgar Fellowship Program

Linda M. Zelewski
Polgar Fellow

and

David E. Armstrong
Faculty Advisor

Water Chemistry Program
University of Wisconsin-Madison
Madison, WI 53706

Zelewski, L. M., and D. E. Armstrong. 1997. Mercury dynamics in sediments of Tivoli South Bay, Hudson River, NY. Section II: 30 pp. In W. C. Nieder and J. R. Waldman (Eds.). Final Reports of the Tibor T. Polgar Fellowship Program, 1996. Hudson River Foundation, New York.

ABSTRACT

Total mercury (Hg_T) concentrations in sediment cores from Tivoli South Bay, a freshwater tidal wetland in the Hudson River National Estuarine Research Reserve, were measured to evaluate the spatial variability of Hg_T deposition, and to establish a chronology of Hg_T flux over the past 50 years. Cores taken from the northern, middle, and southern sections of the bay had similar distribution patterns and absolute concentrations of Hg_T . This suggests a common source of Hg_T throughout the bay. The occurrence of non-anthropogenic Hg_T in the bay is estimated to be on the order of 100 ng $Hg\ g^{-1}$, or less. Sediment concentrations ranged from 190 to 1070 ng $Hg\ g^{-1}$, which are 2 to 10 times greater than the concentration estimated to be from non-anthropogenic sources. Hg_T deposition rates increased from 0.35 $\mu g\ Hg\ cm^{-2}\ yr^{-1}$ in 1950 to a maximum of 0.55 $\mu g\ Hg\ cm^{-2}\ yr^{-1}$ in the early 1970s. Deposition rates have steadily declined since the 1970s and are currently at 0.14 $\mu g\ Hg\ cm^{-2}\ yr^{-1}$. Deposition of Hg_T is driven by the high sedimentation rate ($0.86 \pm 0.15\ cm\ yr^{-1}$) of contaminated sediments in the bay. Direct atmospheric Hg_T deposition is on the order of 1 ng $Hg\ cm^{-2}\ yr^{-1}$ and accounts for less than 1 percent of Hg_T loading in the bay. The major source of monomethyl mercury (MMHg) in the bay is deposited sediment. A higher percentage of Hg_T is in the form of MMHg in near surface sediments. This fraction decreases with depth to a constant value, suggesting that as sediments are buried, MMHg is demethylated or transported to overlying surficial waters.

TABLE OF CONTENTS

ABSTRACT	II-3
LIST OF FIGURES	II-6
INTRODUCTION	II-7
METHODS	II-9
RESULTS	II-15
DISCUSSION	II-22
CONCLUSIONS	II-24
ACKNOWLEDGMENTS	II-26
REFERENCES	II-27

LIST OF FIGURES

Figure 1.	Sampling sites in Tivoli South Bay, Hudson River, NY	II-11
Figure 2.	Vertical distribution of Hg_T in sediments. Vertical bars indicate the thickness of the sediment layer analyzed	II-16
Figure 3.	Vertical distribution of MMHg in sediments. Vertical bars indicate the thickness of the sediment layer analyzed	II-17
Figure 4.	Vertical profile of filtrable MMHg in the pore water at TSB5/TSB6. The dashed line is the method detection limit of 0.091 ng/L. Vertical bars indicate the width of the sediment from which the porewater was drawn	II-19
Figure 5.	Distribution coefficients of MMHg	II-20
Figure 6.	Hg_T deposition in Tivoli South Bay.....	II-21
Figure 7.	Percent Hg_T as MMHg in sediments	II-25

INTRODUCTION

Interest in the cycling of mercury in aquatic systems has been prompted by the observation of high concentrations of mercury in game fish from lakes throughout the United States, Canada, and Sweden. Mercury-contaminated fish stocks can sometimes be linked to point sources of pollution, but mercury contaminated fish are frequently found in lakes remote from human disturbance (Lathrop et al. 1991). Atmospheric deposition is believed to be the principal source of mercury to these systems (Fitzgerald et al. 1991; Watras et al. 1994) and is estimated to have increased by a factor of two to five since preindustrial times based on peat core profiles (Benoit et al. 1994). Most of the mercury originating in atmospheric deposition is immobilized in soils and sediments (Mierle and Ingram 1991), however, changing biogeochemical conditions can cause metals to be released from sediments or mobilized in soil solutions and groundwater that supply lakes, streams and rivers.

The key process leading to bioaccumulation of mercury in fish is the methylation of inorganic mercury, Hg^{2+} , to monomethyl mercury, CH_3Hg^+ (MMHg). Mercury contamination has the potential to create detrimental health effects in aquatic organisms and humans because MMHg bioaccumulates in the food chain to toxic levels even where aqueous concentrations are very low. Mercury in atmospheric deposition is dominated by inorganic species (Fitzgerald et al. 1991), but 95% of the total mercury (Hg_T) found in piscivorous fish is present as MMHg (Bloom 1992). A broad range of MMHg concentrations in fish have been observed across lakes receiving similar loadings of Hg_T (Sorenson et al. 1990), indicating that MMHg production in lakes or in lake sediments is an important factor in determining the level to which mercury accumulates in fish.

Several investigations have shown that near-surface sediments are an important site of mercury methylation (Ramal et al. 1993; Gilmour et al. 1992; Korthals and Winfrey 1987; Callister and Winfrey 1986) and that sulfate reducing bacteria are important mediators of methylation in lacustrine and estuarine sediments (Gilmour et al. 1992; Gilmour and Henry 1991). Using concentrations of radiolabeled mercury orders of magnitude above normal environmental levels, these studies have been useful in determining which factors affect methylation and demethylation processes. Mercury methylation is favored in organic-rich sediments and in the presence of active microbial sulfate reduction, but is limited by high porewater sulfide concentrations which act to inhibit MMHg production in saline sediments (Compeau and Bartha 1987). In freshwater sediments, microbial reduction is often sulfate limited. Adding sulfate to lacustrine sediments has been shown to increase mercury methylation rates (Gilmour and Henry 1991). In the H₂SO₄-acidified basin of experimentally partitioned Little Rock Lake, WI, MMHg concentrations in lake water (Bloom et al. 1991) and fish (Wiener et al. 1990) increased relative to the control basin; however, it is not clear whether this was due to the increased acidity or sulfate.

Measurements of MMHg in sediment and porewater under normal environmental conditions are necessary to understand the dynamics of mercury cycling that lead to bioaccumulation of MMHg in aquatic organisms. Few measurements of MMHg in bulk sediment and porewater have been reported to date. Those studies directed at assessing the transport of MMHg across the sediment-water interface have focused on marine (Gagnon et al. 1996) and lacustrine (Benoit et al. 1996) sediments.

Our study was aimed at understanding the dynamics of both MMHg and Hg_T in

Tivoli South Bay sediments. Tivoli South Bay is a freshwater tidal wetland in the Hudson River National Estuarine Reserve. The Hudson River watershed is a critical water resource, and the results of this study will be a starting point for addressing the potential for mercury contamination in drinking water, fish, and shellfish in the estuary. Prior research on the geochemistry of mercury in Hudson River estuarine sediment by Stevenson et al. (1986) suggested that the main source of mercury to Tivoli South Bay was atmospheric deposition. The sedimentary environment of Tivoli South Bay is spatially heterogeneous (Benoit et al. 1996), and therefore requires that more cores be collected to evaluate the spatial variability and to establish a chronology of Hg_T flux to sediments in the bay. Evidence that sulfate reduction is a significant process in the bay (Gould and Findlay 1990; McCarron and Findlay 1988) suggests that methylation of Hg_T may also be a significant process. Measurements of MMHg concentrations in bay sediments are needed to assess the extent of MMHg in the bay and the potential for bioaccumulation of MMHg in the food chain. The goals of this study are to estimate the fluxes of Hg_T to the sediments of Tivoli South Bay over the past 50 years, to evaluate the spatial distribution of MMHg in the sediments, and to determine the partitioning of MMHg between sediment and porewater.

METHODS

STUDY SITE

Tivoli South Bay is a freshwater tidal wetland, covering approximately 113 ha. 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 across the causeway, which represents 3 percent of the original interface. The tidal prism, however, remains close to historical values. Tidal flow comprises approximately 90 percent of the annual water budget for the bay (Lickus and 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 km² and includes a broad range of land use and land cover categories (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 (Goldhammer and Findlay 1988; Findlay et al. 1990). The sedimentation rate for the bay, as calculated by Benoit et al. (1996) using ²¹⁰Pb dating techniques, ranges from 0.62 to 0.98 cm y⁻¹ over the past 40 years.

SAMPLE COLLECTION

A total of six cores was collected along a north-south transect (Fig. 1) in Tivoli South Bay on May 17, 1996. Two cores were taken from the northern (TSB1, TSB2) middle (TSB3, TSB4) and southern (TSB5, TSB6) parts of the bay at high tide by a snorkeller using 2.25 inch I.D. acrylic core tubes. Cores TSB2, TSB4 and TSB6 were taken as duplicates of TSB1, TSB3 and TSB5, respectively. Cores were taken to shore and immediately sectioned every 2 cm to a depth of 8 cm, and every 4 cm below that

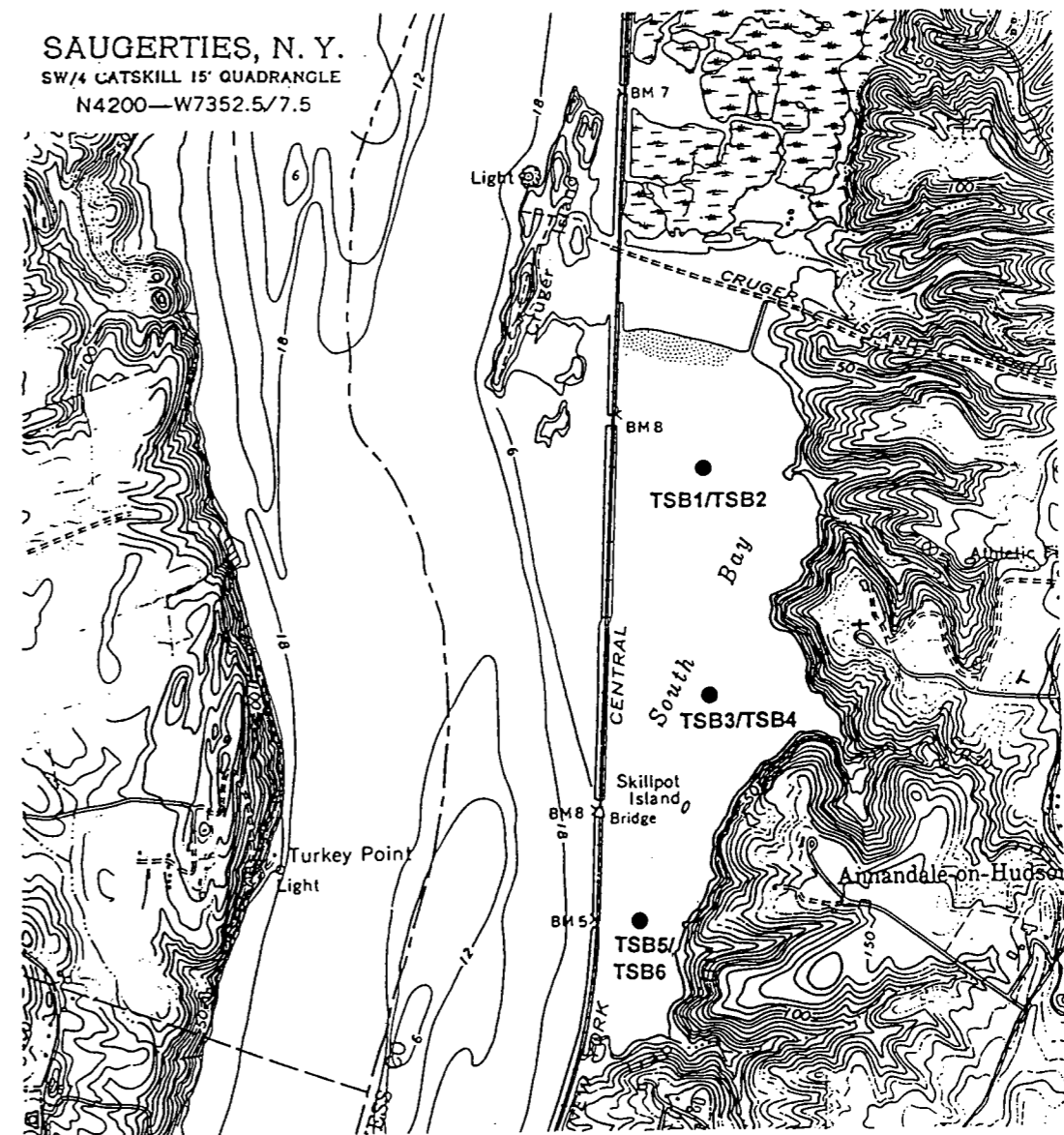


Figure 1. Sampling sites in Tivoli South Bay, Hudson River, NY

depth. Core sections were transferred to pre-weighed, acid-cleaned polyethylene jars, frozen, and shipped to the University of Wisconsin-Madison Water Chemistry Laboratory for chemical analysis. Clean techniques established in our laboratory (Hurley et al. 1996), similar to techniques developed for sampling lead in the mid-1970s (Patterson and Settle 1976), were used during all stages of sample collection and handling.

Samples of unfiltered surface water and particulate matter were collected from the Hudson River near bridge BM 5 on May 17, 1996 as the tide was coming in. All surface water samples were collected using a peristaltic pump outfitted with acid-cleaned Teflon™ sampling line and silicone pumphead tubing. Samples of unfiltered water were collected in Teflon™ 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™ filter cartridges. The filters are rated by their manufacturer, 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 suspended particulate matter (SPM) analysis were collected on 0.8 µm Nucleopore™ filters. Unfiltered water samples for MMHg 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.

In the southern region of the bay, near site TSB5/TSB6, a Teflon™ close interval membrane equilibrium sampler (peeper), fitted with a 0.22 µm polyvinylidene difluoride filter was installed to collect porewater samples. The design of the peeper allows 20 mL

porewater 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 porewater samples to Teflon™ 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*) fruits 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 porewater samples were obtained at these depths.

SAMPLE ANALYSIS

Core sections were freeze-dried and re-weighed to calculate sediment bulk density. All sediment analyses were performed on freeze-dried, homogenized core sections. All samples were analyzed under clean room conditions.

Hg_T concentrations were measured by cold vapor atomic fluorescence spectrophotometry (CVAFS), following reduction with stannous chloride to form Hg⁰ (Fitzgerald and Gill 1979; Bloom and Crecelius 1983). The detection limit, calculated as three times the standard deviation of the blank, was 0.022 ng Hg. The analytical method involves preconcentrating Hg⁰ 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. All digested sediment samples were analyzed in duplicate. Differences between values expressed as a percent 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, $1470 \pm 70 \text{ ng g}^{-1}$) gave $1420 \pm 120 \text{ ng g}^{-1}$ ($n = 6$). Surface water and particulate samples were analyzed in triplicate.

Samples for MMHg analysis were treated with sulfuric acid and potassium chloride to convert all forms of MMHg to monomethyl mercury chloride (MMHgCl), and distilled to separate MMHgCl from associated organic matter (Horvat et al. 1993). MMHgCl was ethylated, chromatographically separated from other mercury forms, pyrolyzed to Hg^0 , and detected by CVAFS (Horvat et al. 1993). The detection limit was 5.1 pg MMHg. All MMHg concentrations in this text are reported as the mass of Hg that is in the form of MMHg. In most cases, values for sediments and porewaters represent a single determination. One section from core 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 MMHg concentration of $0.27 \pm 0.10 \text{ ng g}^{-1}$ ($n = 3$). This is comparable to published values of 0.348 ± 0.028 , 0.384 ± 0.043 , and $0.506 \pm 0.100 \text{ ng g}^{-1}$ from other laboratories (Horvat et al. 1993). To evaluate whether inorganic Hg 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

MMHg concentration of $2.59 \pm 0.03 \text{ ng g}^{-1}$, as compared to an unspiked concentration of $2.73 \pm 0.23 \text{ ng g}^{-1}$. Spikes of MMHg standard were added to some samples to determine distillation recovery. The average recovery of MMHg spikes in sediment samples was 98 ± 14 percent ($n = 8$). Recovery of an unfiltered surface water sample was 86 percent. Reported MMHg concentrations were not corrected to compensate for distillation recoveries.

RESULTS

The vertical distribution of Hg_T in the solid phase of the six sediment cores is shown in Fig. 2. Concentrations ranged from 190 to 1070 ng g^{-1} . All six cores had similar Hg_T concentration profiles. Concentrations were lowest near the surface, increased to a subsurface maximum approximately 28 cm below the sediment-water interface, and then dropped slightly. The subsurface maxima in the cores taken from the north region of the bay, as compared to cores taken from the middle and southern sections of the bay, are shifted slightly toward the surface. The vertical distribution of MMHg in the three sediment cores from different locations is shown in Fig. 3. Concentrations ranged from 0.43 to 2.95 ng g^{-1} . Distribution patterns and absolute concentrations of MMHg in the cores were very similar. Maxima occurred approximately 2 and 30 cm below the sediment-water interface, and minima at approximately 12 and 40 cm.

The concentration of Hg_T in unfiltered surface water was $4.77 \pm 0.11 \text{ ng L}^{-1}$, of which $2.80 \pm 0.57 \text{ ng L}^{-1}$ was associated with particulate matter. An SPM concentration of $22.9 \pm 0.8 \text{ mg L}^{-1}$ (dry weight) was measured and used to calculate a concentration of Hg_T in suspended particulate matter of 119 ng g^{-1} . The concentration of MMHg in

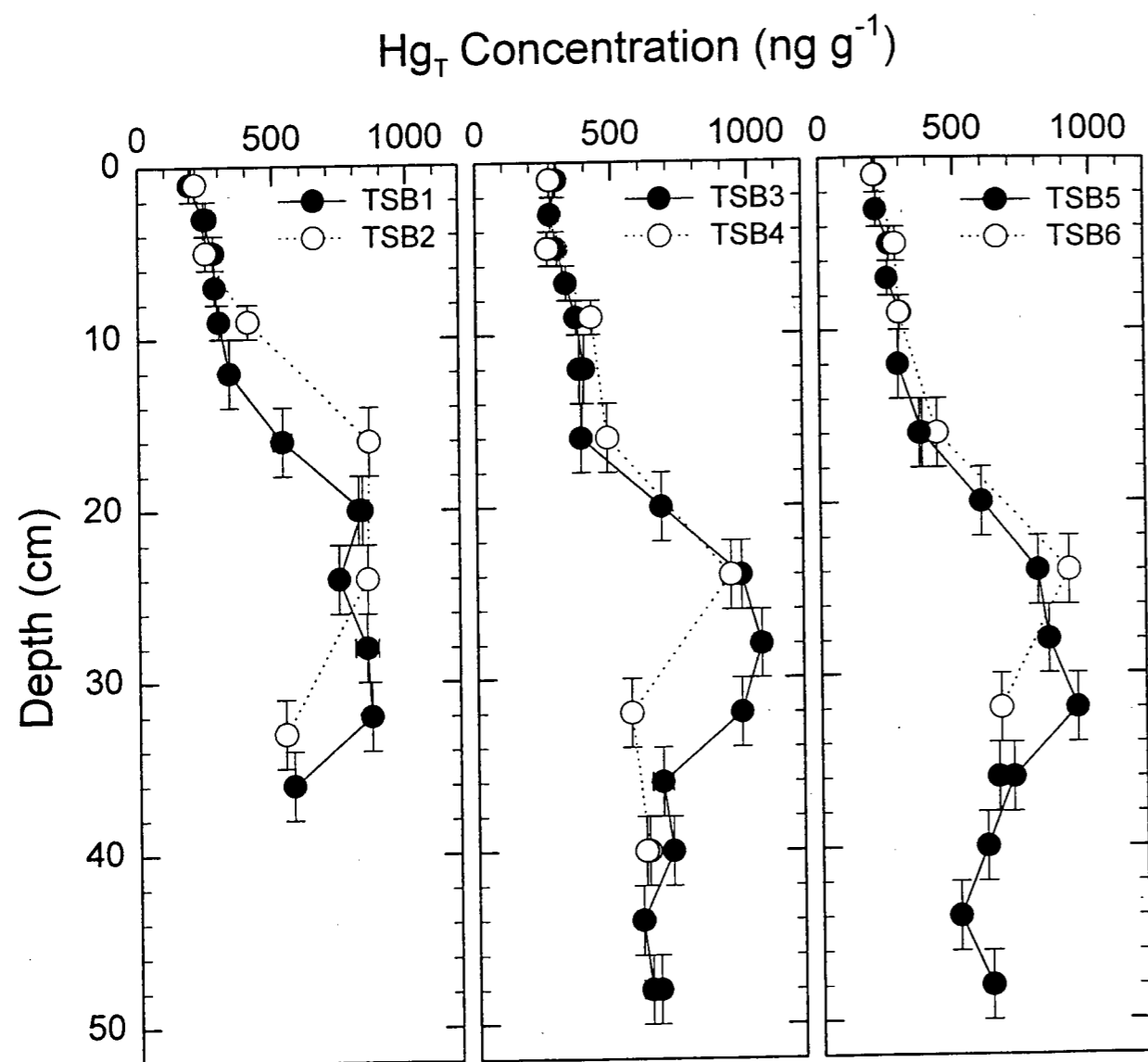


Figure 2. Vertical distribution of Hg_T in sediments. Vertical bars indicate the thickness of the sediment layer analyzed.

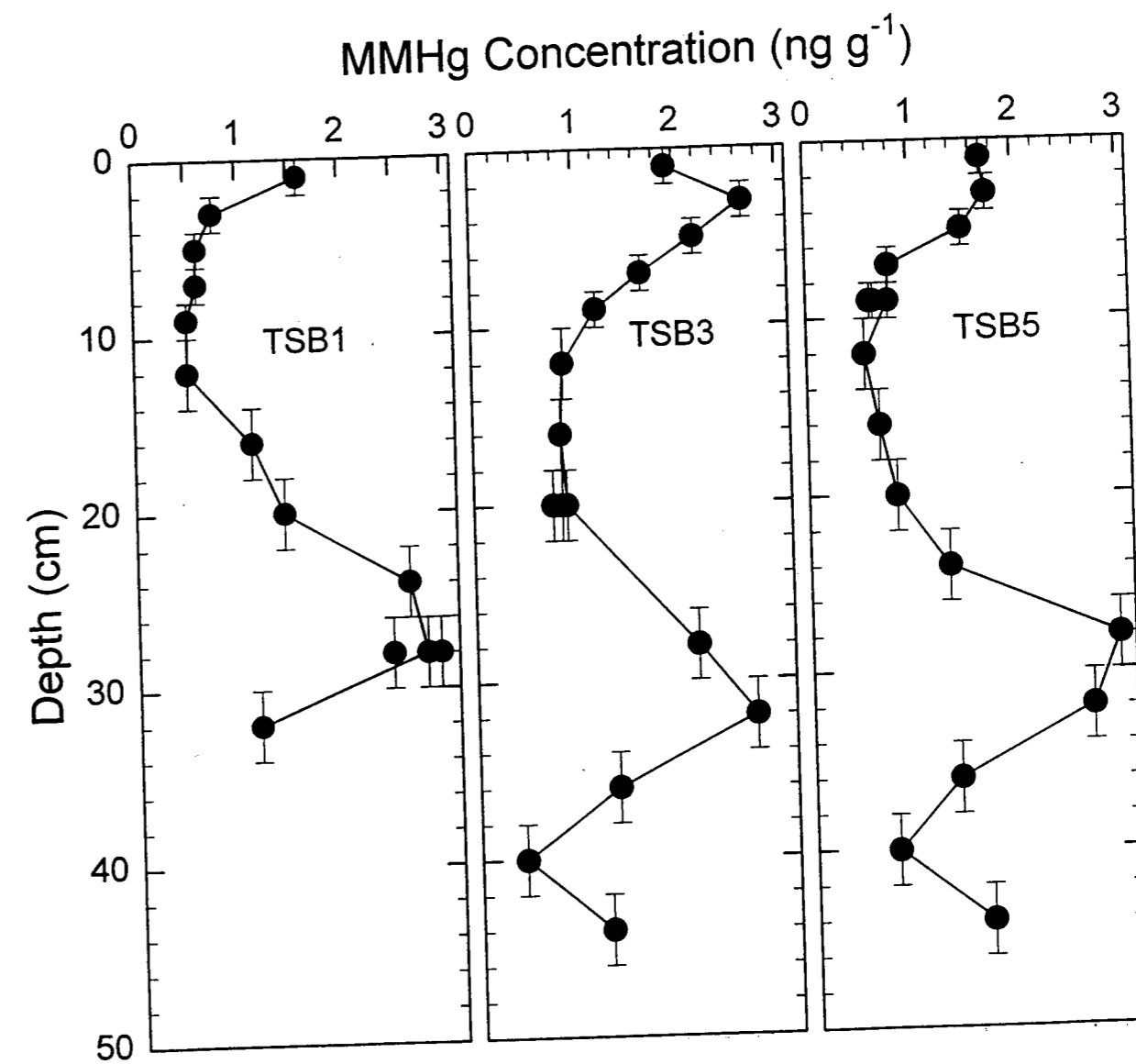


Figure 3. Vertical distribution of MMHg in sediments. Vertical bars indicate the thickness of the sediment layer analyzed.

unfiltered surface water was $0.0877 \pm 0.0210 \text{ ng L}^{-1}$, of which $0.0334 \pm 0.0010 \text{ ng L}^{-1}$ was associated with particulate matter. The concentration of MMHg in suspended particulate matter was 1.46 ng g^{-1} . Concentrations of MMHg in porewaters ranged from 0.17 to 0.55 ng L^{-1} (Fig. 4). There was no discernable trend in concentration with depth.

The partitioning of MMHg between sediment and porewater can be expressed as a distribution coefficient, K_D , which relates the MMHg concentration in the sediment or SPM, C_s (ng kg^{-1}), to the aqueous concentration, C_w (ng L^{-1}).

$$K_D = C_s / C_w$$

Log K_D values are shown in Fig. 5. Concentrations of MMHg in sediments and SPM are similar, however, concentrations of MMHg in porewater are 10 times greater than the concentration in surface water. These differences in partitioning are reflected in the K_D values. The K_D in the Hudson River is 10 times greater than the average K_D in the sediments.

Hg_T deposition rates for the bay were calculated using bay-wide average sediment Hg_T concentrations and an average sedimentation rate of 0.86 cm yr^{-1} (Benoit et al. 1996). In order to compensate for compaction of the sediment, depth in the core was expressed as cumulative dry mass in which 1 cm of sediment is equivalent to 0.7 g cm^{-2} (Benoit et al. 1996). Hg_T deposition rates increased from $0.35 \mu\text{g Hg cm}^{-2} \text{ yr}^{-1}$ in 1950 to a maximum of $0.55 \mu\text{g Hg cm}^{-2} \text{ yr}^{-1}$ in the early 1970s (Fig. 6). Deposition rates have steadily declined since the 1970s and are currently at about $0.14 \mu\text{g Hg cm}^{-2} \text{ yr}^{-1}$.

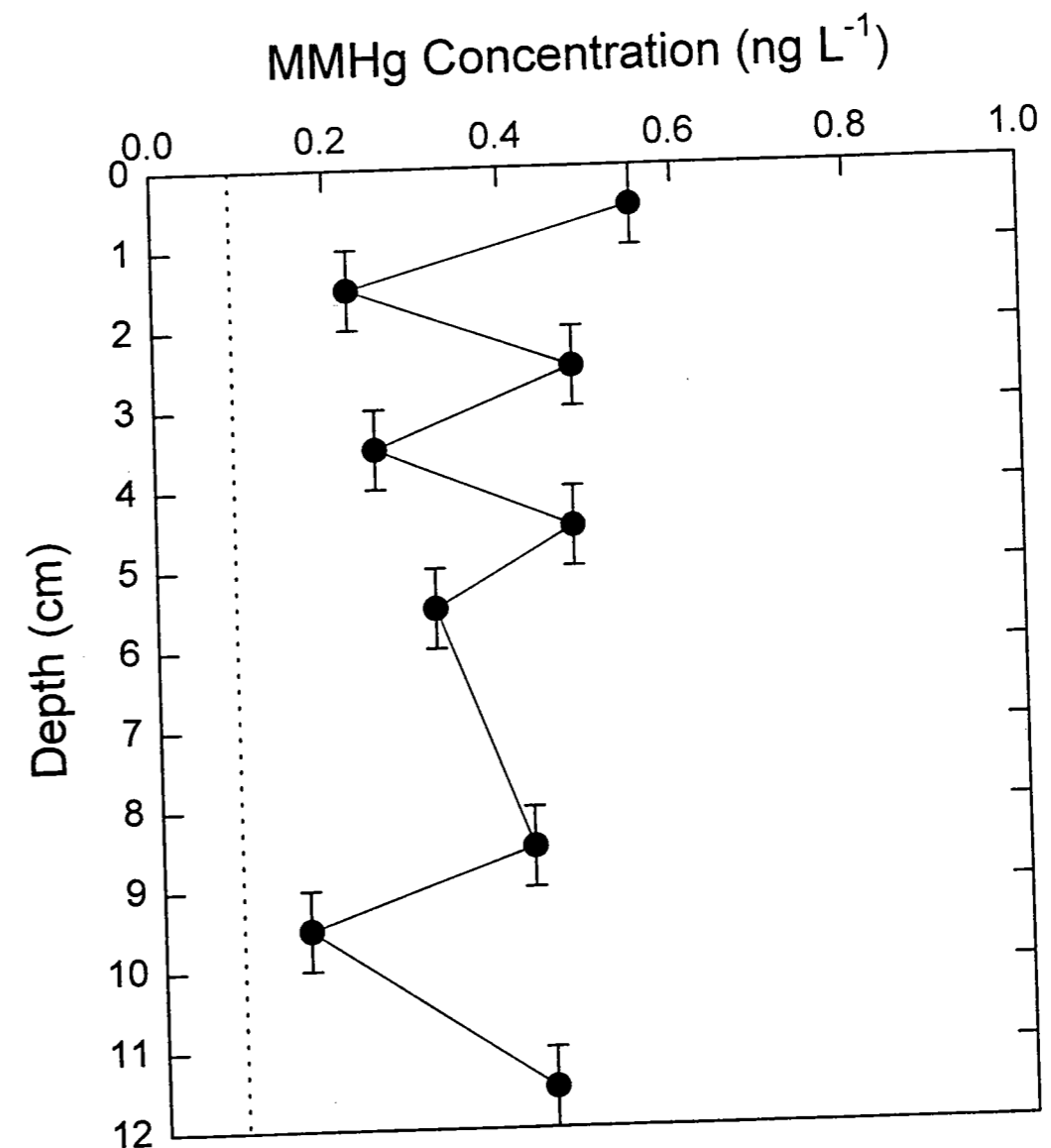


Figure 4. Vertical profile of filtrable MMHg in the porewater at TSB5/TSB6. The dashed line is the method detection limit of 0.091 ng L^{-1} . Vertical bars indicate the width of the sediment from which the porewater was drawn.

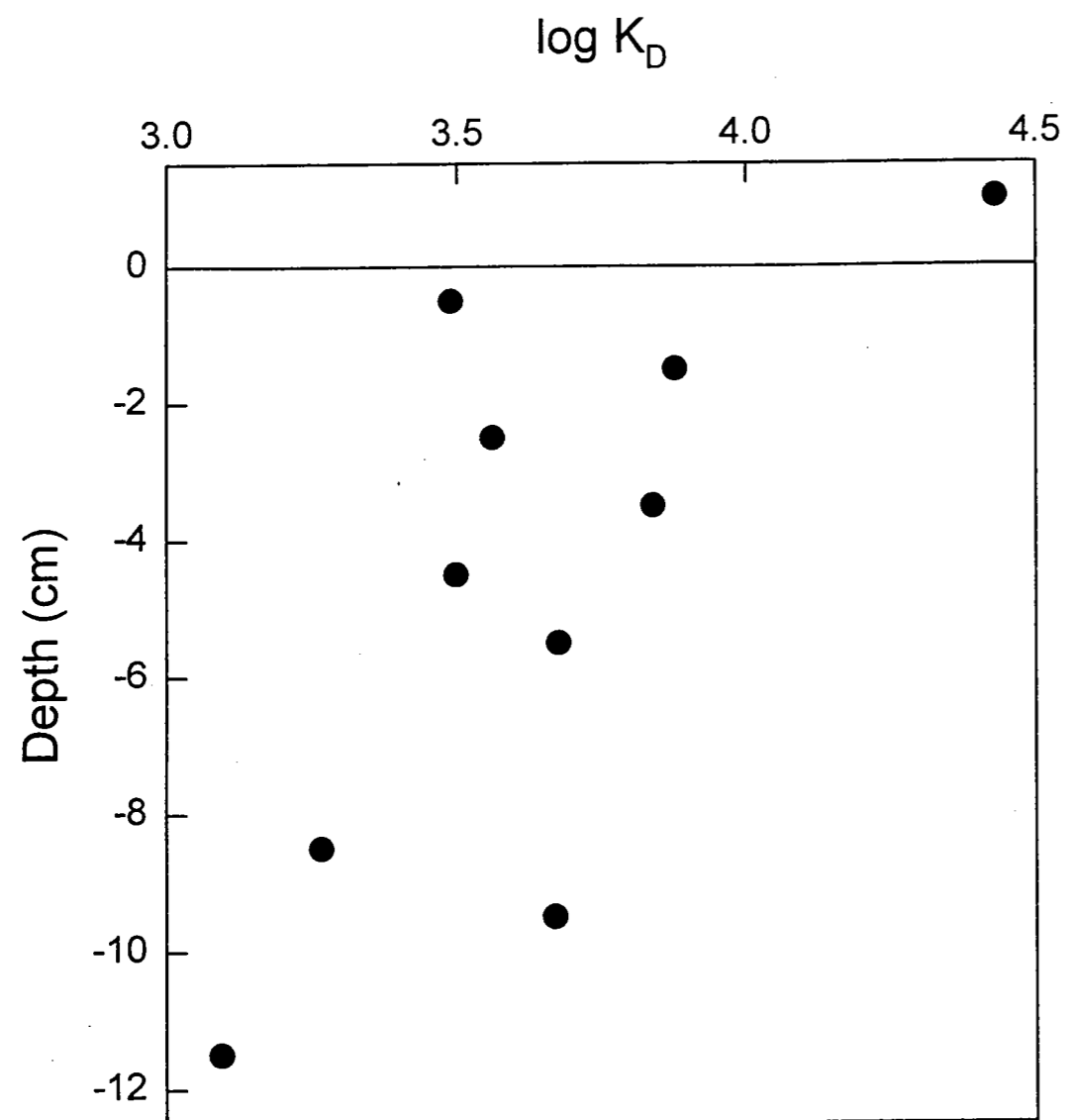


Figure 5. Distribution coefficients of MMHg.

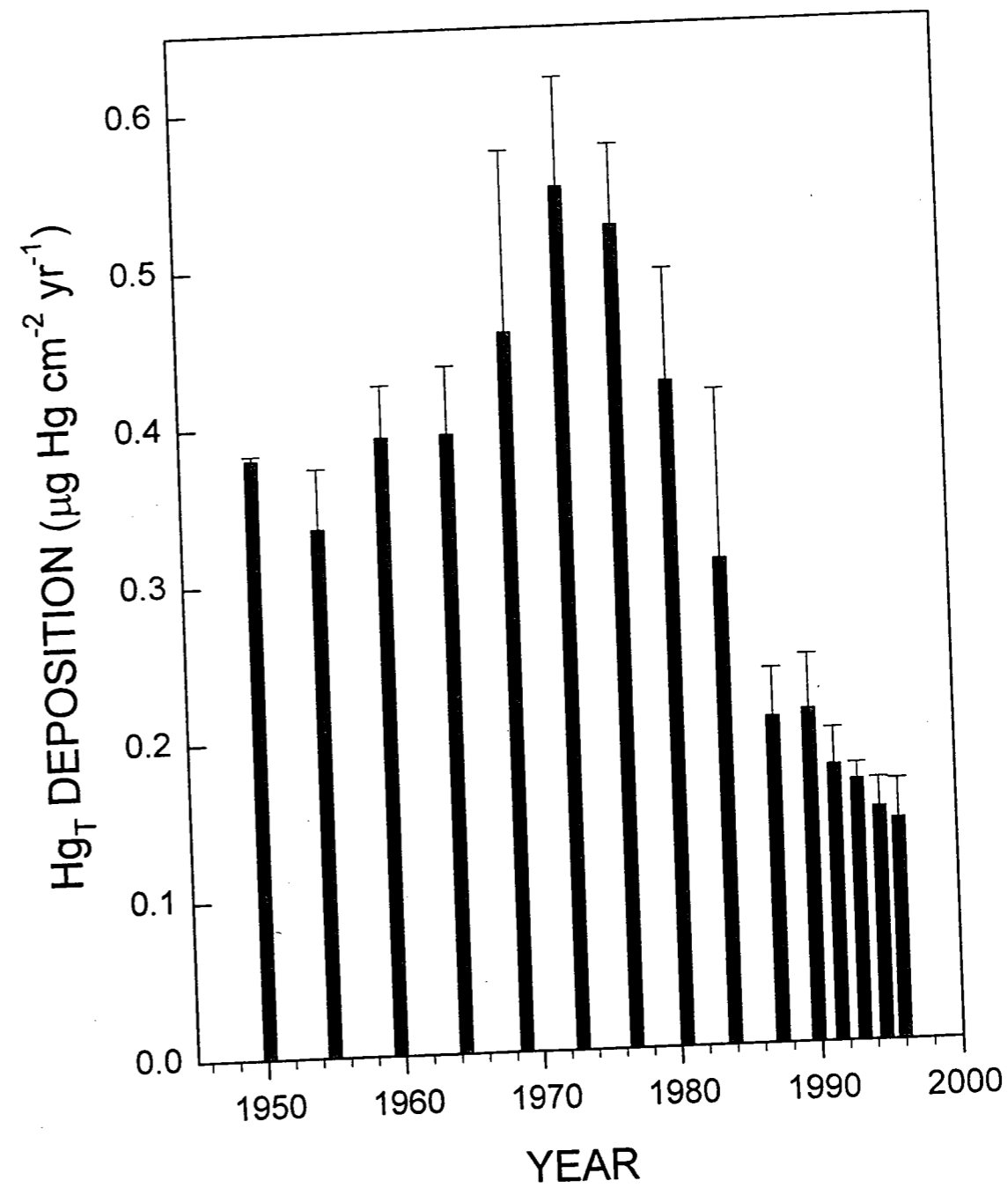


Figure 6. Hg_T deposition in Tivoli South Bay.

DISCUSSION

Distribution patterns and absolute concentrations of Hg_T in all six cores were very similar suggesting a common source of mercury to the bay. Direct atmospheric deposition is a source of Hg_T that would result in uniform deposition throughout the bay, however, atmospheric deposition of Hg_T is a small fraction of Hg_T deposited in the bay. Atmospheric deposition rates vary regionally and temporally, depending on the extent of industrialization, but are on the order of $1 \text{ ng cm}^{-2} \text{ yr}^{-1}$. Atmospheric mercury deposition rates of 0.6 to $1.4 \text{ ng cm}^{-2} \text{ yr}^{-1}$ have been reported in Denmark and southern Sweden (Jensen and Iverfeldt 1994), $1.0 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in northern Wisconsin (Fitzgerald et al. 1991), and 1 to $3.8 \text{ ng cm}^{-2} \text{ yr}^{-1}$ in northeastern Minnesota (Benoit et al. 1994). Hg_T deposition in the bay is a factor of 100 times the atmospheric Hg_T deposition rate, which rules out the possibility that direct atmospheric deposition plays a major role in the mass balance of Tivoli South Bay.

Deposition of Hg_T is driven by the high sedimentation rate in the bay. Cores were not long enough to reach sediments representing pre-industrial times. Declining Hg_T concentrations of recently deposited sediments and a concentration of 119 ng Hg g^{-1} in SPM suggest, however, that the occurrence of non-anthropogenic mercury in the bay is on the order of 100 ng g^{-1} or less. A sediment concentration of 100 ng g^{-1} corresponds to a Hg_T deposition rate of $0.06 \mu\text{g cm}^{-2} \text{ yr}^{-1}$. Hg_T deposition exceeding $0.06 \mu\text{g cm}^{-2} \text{ yr}^{-1}$ is likely due to anthropogenic inputs. There are two known sources of anthropogenic mercury inputs to the Hudson River, both of which are superfund sites. The Mercury Refining Company in Albany, NY, is located on a tributary creek, 4 miles upstream from the Hudson River. The company recycles mercury from batteries, and had pools of Hg^0

on its property at the time it became a superfund site in the early 1970s (Ron Sloan, New York Department of Environmental Conservation, personal communication). The Hercules Paint Company in Glen Falls, NY, located 50 miles north of Albany, was cited for discharging raw pigment (mercury was commonly used as a fungicide in paints) into the Hudson River (Ron Sloan, New York Department of Environmental Conservation, personal communication). A dam at Fort Edwards, NY provided the first impoundment of water downstream from the Hercules Paint Company. In the summer of 1973, the dam was damaged, and accumulated sediments were flushed downstream. Bopp et al. (1982) observed a maximum in chlorinated hydrocarbon concentrations in Hudson River sediments that they attributed to removal of the dam. Removal of the dam corresponds to peak Hg_T deposition in the bay, but there is insufficient evidence to create a definite link between these events. Peak Hg_T deposition in the bay also corresponds to passage of the Clean Water Act of 1972. Deposition has declined since the early 1970s, which corresponds to a general improvement in water quality that resulted from passage and implementation of this important piece of environmental legislation.

The similarity in Hg_T sediment profiles contrasts with a study that found disparate levels of Pb, Cu and Zn in northern and southern regions of the bay (Benoit et al. 1996). Metal concentrations were highly correlated at individual sites, which led the authors to hypothesize that metals in the northern region of the bay were derived primarily from tidal exchange with the Hudson River, and metals in the southern region were derived primarily from Saw Kill inflow. If sediments from the bay are derived from different sources, similar Hg_T deposition rates suggest that large, watershed-scale events that would equally impact the Saw Kill and the Hudson River are the source of Hg_T to Tivoli

South Bay.

The concentrations of MMHg in bay sediments is a result of the concentration of MMHg in freshly deposited sediments, methylation and demethylation rates in the sediments, and the transport of dissolved MMHg in porewater to overlying surface waters. Maxima in MMHg concentration profiles occur near the surface and at 30 cm below the sediment-water interface. Percent Hg_T as MMHg is plotted as a function of depth in Fig. 6. Percent MMHg reaches a maximum value of 0.8 percent near the surface, declines to 0.2 percent at 10 cm and remains fairly constant throughout the rest of the cores. Lack of a peak corresponding to the MMHg concentration peak at 30 cm is attributed to the high concentration of Hg_T at the same depth. The concentration of MMHg in SPM is 1.5 ng g^{-1} which falls within the surficial sediment range of 1.5 to 2 ng g^{-1} , suggesting the primary source of MMHg in Tivoli South Bay is deposited sediments. A higher percent of Hg_T occurs as MMHg in near surface sediments, and as sediments are buried, there is a net decrease in the fraction of Hg_T as MMHg. Concentrations of MMHg in porewaters are 10 times greater than overlying surface waters, and as porewaters are flushed either through diffusion, advection or bioturbation, MMHg may be transferred to overlying surface waters. In addition to this process, decreasing fractions of Hg_T as MMHg with depth in the sediments indicates that net demethylation of MMHg may be occurring in Tivoli South Bay sediments.

CONCLUSIONS

1. Hg_T and MMHg core profiles were very similar which implies there is a single common source of Hg_T to Tivoli South Bay. Since Hg_T deposition is a factor of 100 times

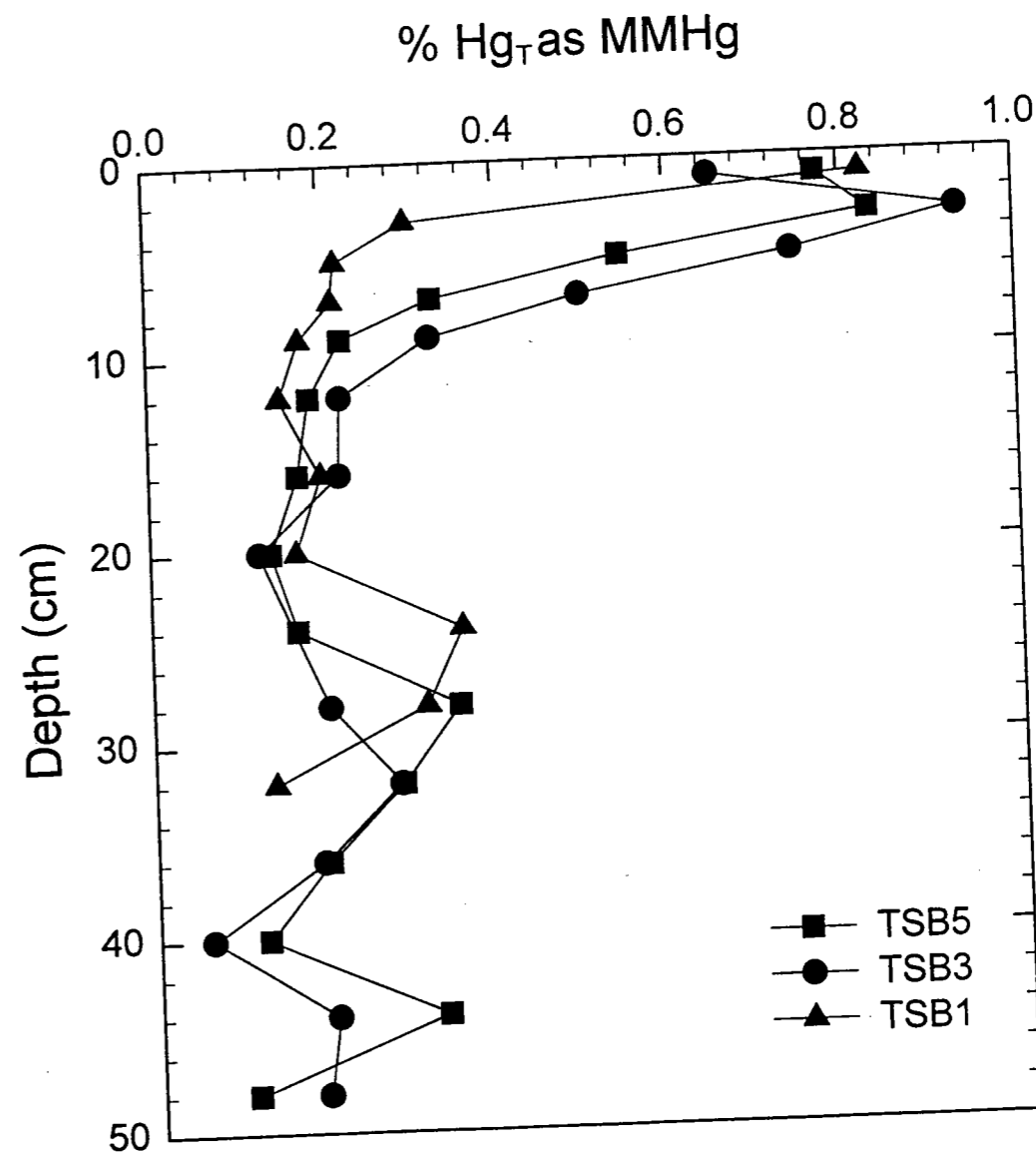


Figure 7. Percent Hg_T as MMHg in sediments.

greater than atmospheric Hg_T deposition, direct atmospheric deposition cannot be that source.

2. A maximum deposition rate of $0.55 \mu g Hg cm^{-2} yr^{-1}$ occurred in the bay in the early 1970s. Deposition rates have been declining since the 1970s and are at a 50 year low of $0.14 \mu g Hg cm^{-2} yr^{-1}$. The decline of Hg_T deposition corresponds to passage and implementation of the Clean Water Act of 1972.
3. Deposited sediments are the major source of MMHg to Tivoli South Bay. As sediments are buried, some of the MMHg appears to be lost either by demethylation or by transport to overlying surficial waters.

ACKNOWLEDGMENTS

I would like to thank the New York State Department of Environmental Conservation and the Hudson River Foundation for making this research possible. I would also like to thank Chuck Nieder, Gaboury Benoit, Susan Conrad, and Dennis Mildner for assistance with the field sampling; and Dave Armstrong and Russ Herrin for their thoughtful comments and suggestions regarding all aspects of mercury research and this report.

REFERENCES

- Benoit, G., E.X. Wang, W.C. Nieder, M. Levandowsky and V. Breslin. 1996. Sources and history of heavy metal contamination in the sediments of Tivoli South Bay, Hudson River, NY. Submitted to Estuaries.
- Benoit, J.M., W.F. Fitzgerald and A.W.H. Damman. 1994. Historical atmospheric mercury deposition in the mid-continental United States as recorded in an ombrotrophic peat bog. Pages 187-202. In C.J. Watras and J.W. Huckabee, editors. Mercury Pollution: Integration and Synthesis, Lewis Publishers, Chelsea, MI.
- Benoit, J.M., J.P. Hurley, C.L. Babiartz, A.W. Andren, and D.P. Krabbenhoft. 1996. Methyl mercury exchange across the sediment-water interface in Palette Lake: a hypolimnion mass-balance approach. Submitted to Canadian Journal of Fisheries and Aquatic Sciences.
- Bloom, N.S. 1989. Determination of picogram levels of methyl mercury by aqueous phase ethylation, followed by cryogenic gas chromatography with cold vapor atomic fluorescence detection. Canadian Journal of Fisheries and Aquatic Sciences 46: 1131-1140.
- Bloom, N.S. 1992. On the chemical form of mercury in edible fish and marine invertebrate tissue. Canadian Journal of Fisheries and Aquatic Sciences 49: 1010-1017.
- Bloom, N.S. and E.A. Crecelius. 1983. Determination of mercury in seawater at sub-nanogram per liter levels. Marine Chemistry 14: 49-59.
- Bloom, N.S., C.J. Watras, and J.P. Hurley. 1991. Impact of acidification on the Methyl mercury cycling of remote seepage lakes. Water Air and Soil Pollution 56: 477-491.
- Bopp, R.F., H.J. Simpson, C.R. Olsen, R.M. Trier, and N. Kostyk. 1982. Chlorinated hydrocarbons and radionuclide chronologies in sediments of the Hudson River and estuary, New York. Environmental Science and Technology 16: 666-676.
- Compeau, G.C. and R. Bartha. 1987. Sulfate-reducing bacteria: principal methylators of mercury in anoxic marine sediment. Applied Environmental Microbiology 50: 261.
- Findlay, S., K. Howe, and H.K. Austin. 1990. Comparison of detritus dynamics in two tidal freshwater wetlands. Ecology 71: 288-295.

- Fitzgerald, W.F. and G.A. Gill. 1979. Subnanogram determination of mercury by two stage gold amalgamation and gas phase detection applied to atmospheric analysis. *Analytical Chemistry* 51: 1714-1720.
- Fitzgerald, W.F., R.P. Mason, and G.M. Vandal. 1991. Atmospheric cycling and air-water exchange of mercury over mid-continental lacustrine regions. *Water Air and Soil Pollution* 56: 745-767.
- Gagnon, C., E. Pelletier, A. Mucci, and W.F. Fitzgerald. 1996. Diagenetic behavior of methyl mercury in organic-rich coastal sediments. *Limnology and Oceanography* 43: 428-434.
- Gilmour, C.C. and E.A. Henry. 1991. Mercury methylation in aquatic systems affected by acid deposition. *Environmental Pollution* 71: 131.
- Gilmour, C.C., E.A. Henry, and R. Mitchell. 1992. Sulfate stimulation of mercury methylation in freshwater sediments. *Environmental Science and Technology* 26: 2281-2287.
- Goldhammer A. and S. Findlay. 1988. Estimation of suspended material flux between a *Trapa natans* stand and the Hudson River estuary. Section VIII: 46 pp. In J.R. Waldman and E. A. Blair (eds.), Polgar Fellowship Reports of the Hudson River National Estuarine Research Reserve Program, 1987. Hudson River Foundation, NY.
- Gould, K.I. and S. Findlay. 1991. Changes in interstitial water chemistry along a salinity gradient. Section II: 33 pp. In E. A. Blair and J.R. Waldman (eds.), Final reports of the Tibor T. Polgar Fellowship Program, 1990. Hudson River Foundation, NY.
- Horvat, M., N.S. Bloom, and L. Liang. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part I. Sediments. *Analytica Chimica Acta* 281: 135-152.
- Horvat, M., N.S. Bloom, and L. Liang. 1993. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II. Water. *Analytica Chimica Acta* 282: 153-168.
- Hurley, J.P., M.M. Shafer, S.E. Cowell, D.E. Armstrong, J.T. Overdier, and P.E. Hughes. Trace metal assessment of Lake Michigan tributaries using low-level techniques. *Environmental Science and Technology* 30: 2093-2098.
- Jensen, A. and A. Iverfeldt. 1994. Atmospheric bulk deposition of mercury to the southern Baltic Sea area. Pp. 221-230. In C.J. Watras and J.W. Huckabee (eds.) *Mercury Pollution: Integration and Synthesis*, Lewis Publishers, Chelsea, MI.

- Korthals E.T. and M.R. Winfrey. 1987. Seasonal and spatial variations in mercury methylation and demethylation in an oligotrophic lake. *Applied Environmental Microbiology* 53: 2397-2404.
- Lathrop, R.C., P.W. Rasmussen, and D.K. Knauer. 1991. Mercury concentrations in walleyes from Wisconsin (USA) lakes. *Water Air and Soil Pollution* 56: 295-307.
- Lickus, M. R. and P. Barten. 1991. Hydrology of a tidal freshwater marsh in the Hudson River Estuary. Section I: 45 pp. In E. A. Blair and J.R. Waldman (eds.). Final reports of the T. Polgar Fellowship Program, 1990. Hudson River Foundation, New York, New York.
- McCarron, E. and S. Findlay. 1989. Sediment metabolism at Tivoli South Bay and a *Vallisneria* bed in the Hudson River. Section I: 24 pp. In J.R. Waldman and E. A. Blair (eds.), Polgar Fellowship Reports of the Hudson River National Estuarine Research Reserve Program, 1988. Hudson River Foundation, NY.
- Mierle, G. and R. Ingram. 1991. The role of humic substances in the mobilization of mercury from watersheds. *Water Air and Soil Pollution* 56: 349-357.
- Patterson, C.C. and D.M. Settle. 1976. The reduction of orders of magnitude of error in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection, handling, and analysis. Pages 321-351. In P.D. Lefleur, editor. *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis*, Spec Publ. 422., U.S. Natl. Inst. of Stand. and Technol., Gaithersburg, MD.
- Rada, R.G., D.E. Powell, and J.G. Wiener. 1993. Whole-lake burdens and spacial distribution of mercury in surficial sediments in Wisconsin seepage lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 50: 865-873.
- Ramlal, P.S., C.A. Kelly, J.W.M. Rudd, and A. Furutani. 1993. Sites of methyl mercury production in remote Canadian shield lakes. *Canadian Journal of Fisheries and Aquatic Sciences* 50: 972-979.
- Sorenson, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber, and G.R. Rapp, Jr. 1990. Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environmental Science and Technology* 24: 1716-1727.
- Stevenson, K.A., R. Armstrong, and W.R. Schell. 1986. Chronological determination of mercury, lead and cadmium in two Hudson River freshwater tidal marshes. Section VIII: 27 pp. In J.C. Cooper (ed.), Polgar Fellowship Reports of the Hudson River National Estuarine Sanctuary Program, 1985. Hudson River Foundation, NY.

Watras, C.J., N.S. Bloom, R.J.M. Hudson, S. Gherini, R. Munson, S.A. Claas, K.A. Morrison, J. Hurley, J.G. Wiener, W.F. Fitzgerald, R. Mason, G. Vandal, D. Powell, R. Rada, L. Rislov, M. Winfrey, J. Elder, D. Krabbenhoft, A.W. Andren, C. Babiarez, D.B. Porcella, and J.W. Huckabee. 1994. Sources and fates of mercury and methyl mercury in Wisconsin lakes. Pages 153-177. In C.J. Watras and J.W. Huckabee, editors. Mercury Pollution: Integration and Synthesis, Lewis Publishers, Chelsea, MI.

Wiener, J.G., W.F. Fitzgerald, C.J. Watras, and R.G. Rada. 1990. Partitioning and bioavailability of mercury in an experimentally acidified Wisconsin lake. *Environmental Toxicology and Chemistry* 9: 909.