

# Mercury in Long Island Sound Sediments

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## ABSTRACT

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Mercury (Hg) concentrations were measured in 394 surface and core samples from Long Island Sound (LIS). The surface sediment Hg concentration data show a wide spread, ranging from <50 ppb Hg in eastern LIS to >600 ppb Hg in westernmost LIS. Part of the observed range is related to variations in the bottom sedimentary environments, with higher Hg concentrations in the muddy depositional areas of central and western LIS. A strong residual trend of higher Hg values to the west remains when the data are normalized to grain size. Relationships between a tracer for sewage effluents (*C. perfringens*) and Hg concentrations indicate that between 0-50 % of the Hg is derived from sewage sources for most samples from the western and central basins. A higher percentage of sewage-derived Hg is found in samples from the westernmost section of LIS and in some local spots near urban centers. The remainder of the Hg is carried into the Sound with contaminated sediments from the watersheds and a small fraction enters the Sound as *in situ* atmospheric deposition. The Hg-depth profiles of several cores have well-defined contamination profiles that extend to pre-industrial background values. These data indicate that the Hg levels in the Sound have increased by a factor of 5-6 over the last few centuries, but Hg levels in LIS sediments have declined in modern times by up to 30 %. The concentrations of *C. perfringens* increased exponentially in the top core sections which had declining Hg concentrations, suggesting a recent decline in Hg fluxes that are unrelated to sewage effluents. The observed spatial and historical trends show Hg fluxes to LIS from sewage effluents, contaminated sediment input from the Connecticut River, point source inputs of strongly contaminated sediment from the Housatonic River, variations in the abundance of Hg carrier phases such as TOC and Fe, and focusing of sediment-bound Hg in association with westward sediment transport within the Sound.

**ADDITIONAL INDEX WORDS:** Pollution, Hg, contaminants, metals, sewage.

## INTRODUCTION

Long Island Sound (LIS), occasionally referred to as the "urban sea" (KOPPELMAN *et al.* 1976), receives effluents from densely populated regions in both New York State and Connecticut. It is therefore no surprise that the LIS sediments are strongly contaminated with mercury (Hg) and other metals from a variety of sources. Earlier studies of LIS (GREIG *et al.*, 1977; TUREKIAN *et al.*, 1980; GRONLUND *et al.*, 1991; ROBERTSON *et al.*, 1991) and surrounding embayments (SEIDEMANN, 1991; BOPP *et al.*, 1993) documented the level of metal pollution in LIS grab samples and found a trend of increasing metal pollution from east to west. MECRAY and BUCHHOLTZ TEN BRINK (this volume) argue that part of this trend is due to longitudinal change in abundance of fine-grained material in the sediments. The documented Hg concentrations in LIS are comparable to those of other contaminated estuaries and coastal areas (*e.g.*, BOTHNER *et al.*, 1980; THOMPSON *et al.*, 1980; SMITH and LORING, 1981; SANTSCHI *et al.*, 1999). We report here on Hg abundances in LIS surface sediments and in short (<60 cm) sediment cores. This study is part of a larger project that documents the state of metal pollution of LIS and its surrounding salt marshes and estuarine environments (*e.g.*, VAREKAMP, 1991; CROCKETT, 1996;

POPPE and POLLONI, 1998; KREULEN, 1999; MEIGS, 1999; BUCHHOLTZ TEN BRINK *et al.*, this volume; MECRAY and BUCHHOLTZ TEN BRINK, this volume).

Long Island Sound (LIS) has a reduced salinity (20-32 ‰) and a pronounced seasonal stratification in its western part (*e.g.*, KOPPELMAN *et al.*, 1976). The Connecticut River contributes more than 70% of the freshwater influx, with a large load of sediment. The Sound traps sediment efficiently, and areas of deposition and erosion are distributed in patches throughout LIS (GORDON, 1980; BOKUNIEWICZ and GORDON, 1980). Sidescan studies documented an area of sediment erosion and non-deposition near the mouth of the Connecticut River (eastern Sound, east of longitude -72.65), whereas environments of coarse-grained bedload transport (with sand-ribbons and sand waves) are present between the Connecticut River and Hammonasset. Deposition of fine-grained sediment occurs in the central (longitude -72.65 to -73.12) and western basins (longitude -73.12 to -73.5) (KNEBEL *et al.*, 1999; KNEBEL and POPPE, this volume). The westernmost section of LIS (west of longitude -73.5) is the narrowest part of the estuary and has an abundance of fine-grained sediment. Some locations were used for dredge-spoil dumping (*e.g.*, KOPPELMAN *et al.*, 1976; SCHUBEL *et al.*, 1979; TUREKIAN *et al.*, 1980) or outflow from sewage treatment plants

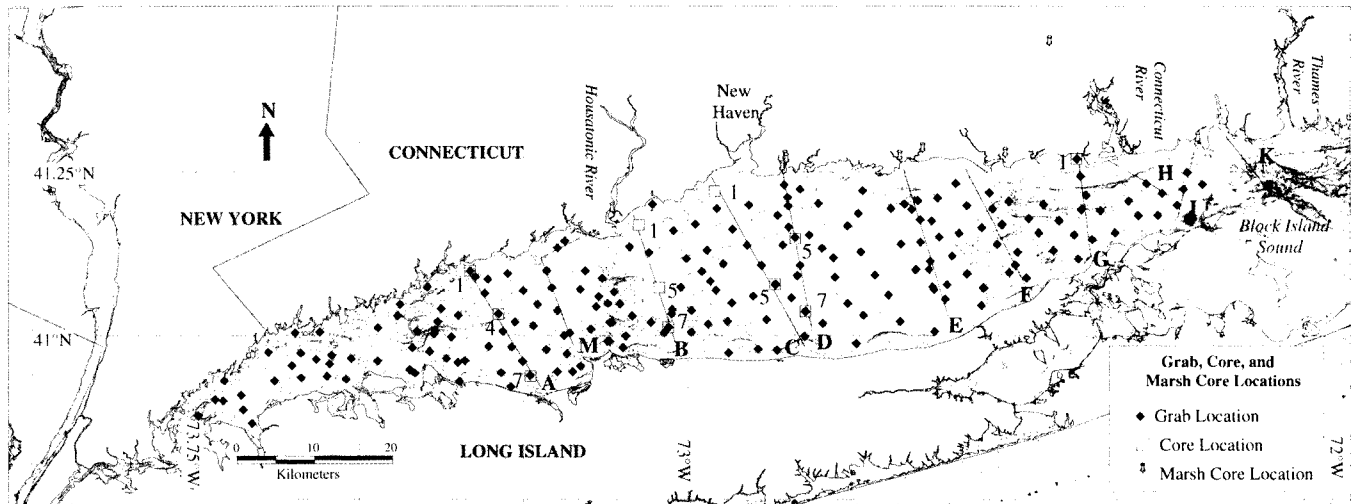


Figure 1. Locations of surface grab samples and core samples measured for mercury concentrations in Long Island Sound. Stations were selected to provide a representative sampling of the Sound for mercury distribution. Bathymetry is in 5 m contours.

(BUCHHOLTZ TEN BRINK *et al.*, this volume). The population density of coastal sites along LIS increases from east to west, and at the same time, the western part is less well ventilated. This combination of enhanced anthropogenic inputs with poor ventilation is commonly seen as the main cause for the occurrence of seasonal anoxia in western LIS (*e.g.*, WOLFE *et al.*, 1991; USEPA, 1994).

Information about the concentrations, accumulation, and transport patterns of Hg in the LIS system has far-reaching applications because Hg pollution in coastal environments has caused restrictions on fisheries, health concerns and ecological risk (*e.g.*, CATO *et al.*, 1980). Industrial release of Hg includes contamination from high-temperature combustion sources, such as coal-fired power plants, municipal and medical waste incinerators, and concrete production. Additional input of Hg comes from wastewater treatment plants (WWTP) and some smaller local industrial sources (GRONLUND *et al.*, 1991; ROBERTSON *et al.*, 1991; TURGEON and O'CONNOR, 1991; USEPA, 1994). About 90% of anthropogenic Hg releases to the atmosphere are emitted in the form of elemental Hg vapor, particulate-bound Hg, and various other forms of oxidized Hg (USEPA, 1997). The approximate residence time of elemental Hg in the atmosphere is about 1 year (FITZGERALD *et al.*, 1998), and atmospheric elemental Hg becomes well mixed throughout the troposphere. Much of the terrestrial Hg contamination results from atmospheric deposition, either from the well-mixed global atmospheric reservoir or from local and regional pollution plumes (MASON *et al.*, 1994). Atmospheric input of Hg to LIS sediments includes both *in situ* deposition directly on the Sound and the influx of particle-bound and dissolved Hg as runoff from the watersheds. The WWTP also provide a source of Hg directly to the Sound and through discharge into the major rivers draining into the Sound.

Some questions addressed in this contribution include:

- What is the spatial distribution of Hg concentrations and burdens in LIS?
- Is the spatial Hg abundance pattern in LIS the result of sedimentary depositional processes within LIS or does it reflect the distribution of Hg sources around LIS?
- What are the relative contributions of Hg for LIS from such sources as WWTP, local point sources, atmospheric deposition, and watershed runoff?

## METHODS AND TECHNIQUES

Sediment samples were collected in LIS (Figure 1) during research cruises in 1996 (SEAX96017 and SEAX96024) and 1997 (JD9701). Cruise tracks are given in MECRAY and BUCHHOLTZ TEN BRINK (this volume). Surface samples were collected with a 30 × 30 cm<sup>2</sup> area grab sampler, which was deployed with subaqueous videocamera control. Surface sediment samples (0–2 cm) were collected from each grab. Short (30–60 cm) cores were recovered from a number of transects across LIS using a hydraulically-dampened piston corer (BOTHNER *et al.*, 1997). The distribution of sampling locations provided a broad spatial coverage of LIS and included sites proximal to coastal marshes that were also studied for Hg contamination (KREULEN, 1999). A selection of 125 surface-sediment samples from SEAX96017 was analyzed for Hg, 57 samples from SEAX96024 and 27 samples from JD9701, for a total of 209 surface samples. Sediment cores were taken along the A, B, C and D transects from the western and central Sound in mud-rich environments, whereas one core was obtained further east along the G transect (Figure 1). A total of 185 core samples (0.5 cm aliquots) were analyzed to provide Hg concentration versus depth profiles for 11 cores.

The grab and core samples were also analyzed for sedimentary parameters, which included grain-size distribution,

water content, total organic carbon (TOC) content (determined by CHN analyzer; see POPPE *et al.*, this volume, for grab sample data from sites on cruise SEAX96017), major element composition, and a suite of metal pollutants (BUCHHOLTZ TEN BRINK and MECRAY, 1998; MECRAY and BUCHHOLTZ TEN BRINK, this volume). In addition, the abundances of the bacterial spore *Clostridium perfringens* (*C. perfringens*) were determined to serve as a tracer for WWTP and other sewage-related effluents (BUCHHOLTZ TEN BRINK *et al.*, this volume).

The Hg concentration was measured by cold-vapor Atomic Absorption Spectroscopy, using a LCD3200 Hg analyzer. This is a double-cell instrument with an absolute detection limit of about one ng Hg. Freeze-dried sediment samples were digested in a mixture of sulfuric and nitric acid, with potassium permanganate and potassium persulfate added. The samples were heated for 30 minutes at 80 °C, shaken for several hours, and then left in the closed extraction vessel for an additional 4–8 hours. The samples were then filtered, and excess oxidant was neutralized immediately prior to analysis with hydroxyl-amine-hydrochloride before the sample was brought up to volume (procedures detailed in KREULEN, 1999). A 10-ml aliquot of this solution was reduced with stannous chloride in an extraction cell with a Hg-free nitrogen stream, and the resulting elemental Hg vapor was quantitatively carried into the analyzer. The instrument was calibrated with Hg vapor standards and Hg<sup>2+</sup> standard solutions. The accuracy and precision were monitored with NIST 2704 (Buffalo River sediment) and in-house standards. The NIST 2704 sample had 82 % recovery with a 12 % standard deviation; this is acceptable given that our method is a leachate procedure and not a complete sediment digestion. A set of modifications to the gas flow path through the extraction cell improved the instrumental precision to about 3 % and lowered the absolute detection limit to 0.3 ng Hg; this improved procedure was applied during analyses of the LIS core samples. The reported Hg concentrations are “acid leachable” Hg levels, which are less than the total Hg concentrations obtained by full sediment digestion. The “acid leachable” Hg concentrations in deep (uncontaminated) sediments are on average 40–50 ppb Hg, which is lower than reported averages for many natural sediments obtained by complete digestion (*e.g.*, 100 ppb Hg). We infer that the measured Hg levels derive largely from adsorbed and loosely bound Hg (probably the contamination fraction) and that the lithic fraction is only partially recovered. The Fe contents of sediments were obtained from complete digests, and precision is discussed in MECRAY and BUCHHOLTZ TEN BRINK (this volume). The error margins and techniques used for the *C. perfringens* data are discussed in BUCHHOLTZ TEN BRINK *et al.* (this volume).

The excess Hg concentrations (Hg\*), or anthropogenic component, were calculated as the total Hg concentration minus the “natural” background, which was taken as 50 ppb Hg (Hg\* = Hg<sub>obs</sub> - 50). The Hg accumulation rates were obtained from sediment mass accumulation rates and Hg concentrations. Core inventories of Hg were calculated using dry sediment densities and the Hg concentrations. Dry sediment densities were approximated from measured water contents and an assumed inorganic grain density of 2.6 g/cm<sup>3</sup>. Cu-

Table 1. Mean Hg concentrations, Hg/Fe, and Hg/MGS values at longitudes -72.65°W and -73.50°W, respectively, the western boundary of the eastern basin and western boundary of the western basin.

Longitude, decimal °W	A -72.65	B -73.5	Ratio B/A
Hg (ppb)	46	214	4.6
Hg/Fe (ppb/%)	21	70	3.3
Hg/MGS (ppb/phi)	13.7	48	3.5

mulative core inventories of Fe and *C. perfringens* were calculated by summing the inventories of each sample slice (the concentration per dry sediment mass × mass dry sediment/slice). All sample slices that contained *C. perfringens* were used, whereas only sample slices that contained excess Hg were used for the Fe inventory calculation; the data were interpolated where necessary. The analytical data were entered into Geographical Information System (GIS) and database software, and are available from the U.S. Geological Survey.

## RESULTS AND DISCUSSION

### Regional Hg Distribution in LIS Surface Samples

The Hg concentrations in LIS surface sediment samples (Figure 2; VAREKAMP *et al.*, in prep.) range from <30 ppb Hg to highly contaminated samples with >600 ppb Hg. The mean concentration level of Hg for all LIS surface sediments is about 140 ppb Hg, but we observe a strong longitudinal concentration gradient. Low Hg values (mean ~20 ppb Hg) are common in the easternmost Sound (east of -72.6° W longitude), whereas higher values are found in the central and western basins (-72.6° W to -73.5° W), with a mean value of 138 ppb Hg. The highest Hg values were found in the westernmost Sound (west of -73.5° W) with a mean value of 367 ppb Hg. The details of the spatial distribution pattern of Hg in LIS are fairly complex, with greater maximum Hg values toward the west, but low Hg concentrations occurring in samples throughout the Sound (Figures 2, 3). Sudden changes in Hg concentration are found at longitudes -72.6° W and -73.6° W. The Hg concentrations in LIS surface sediments in the discharge region of the Housatonic River are slightly higher than in surrounding regions. Modern sediments from coastal marshes (upper 2-cm of salt marsh deposits in Connecticut) have Hg concentrations that range from 97–333 ppb Hg, with an average value of 220 ppb Hg (KREULEN, 1999), higher than the mean value for the adjacent central LIS surface sediment.

The documented east-west Hg concentration gradient may be a result of two distinct factors: (1) sedimentary processes within LIS; and (2) the regional distribution of Hg contamination sources along the Sound. After correction of the Hg concentration data for the influence of depositional environments, we investigate the relationships between Hg concentrations and *C. perfringens*, a sewage tracer.

Sedimentary environments in LIS were described by KNEBEL *et al.* (1999), and were further delineated by KNEBEL and POPPE (this volume). The central and western LIS basin is a depocenter for fine muds, which have much higher Hg con-

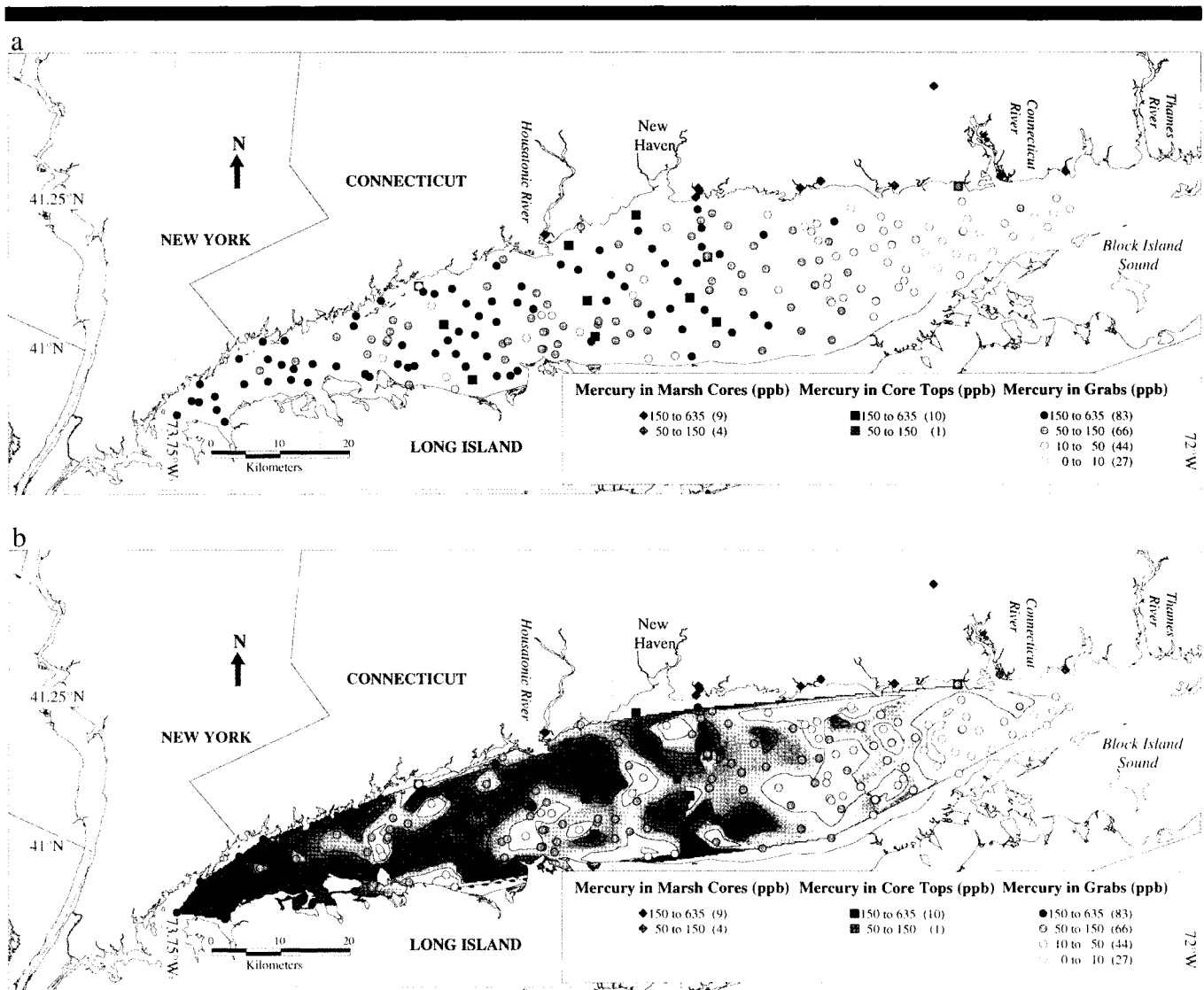


Figure 2a. Mercury concentrations (ppb) in the surface samples (0–2 cm) of LIS. Symbols depict the collection method and grayscale identifies the concentration range. Ranges shown indicate where samples are elevated above naturally-occurring background values and where a potential for toxicity may exist. Ranges are defined by the pre-anthropogenic background level (50 ppb) determined in the LIS cores, and the Effects Range-Low (ER-L of 150 ppb) sediment quality criteria of LONG *et al.* (1996, 1998). Figure 2b. Mercury concentrations (ppb) represented by triangulation gridding to illustrate the spatial extent of high and low values.

centrations than the sediments from the sandy, erosional or transportational environments of eastern LIS (Figure 2). Indeed, the strong jump in Hg concentrations at longitude  $-72.6$  coincides with the boundary between the transportational and depositional sedimentary environments (KNEBEL and POPPE, this volume). Much of the variation in the LIS Hg data may thus be caused by differences in sediment composition. The Hg in marine sediment is predominantly associated with fine-grained Fe-oxides and with organic matter (RAI and ASTON, 1982; BUCHHOLTZ TEN BRINK, 1987; JENNE, 1998) that can be coating the clay-size clastic fraction (MAYER, 1994). Thus, we must consider the influence of variations in abundance of these specific carrier materials on the bulk Hg concentrations. To correct for the influence of sedi-

ment composition, we investigated relationships between the mean grain size (MGS), percentage of sediment  $<63$  micrometer (% fines), contents of TOC, and the Al and Fe concentrations. The latter is commonly used as an empirical proxy for the abundance of fine-grained matter and Fe-Mn oxides in sediments (e.g., BENOIT *et al.*, 1999). The relationships between Hg and TOC as a carrier phase are complicated by the existence of a multitude of sources for organic carbon in LIS.

Plots of Fe versus MGS or % fines of LIS surface sediments show strong linear correlations, except for some unusual Fe-rich samples from the eastern Sound (MECRAY and BUCHHOLTZ TEN BRINK, this volume). Graphs of Fe/MGS and Al/MGS versus longitude show no significant east-west trend, indicating that normalization of contaminant data on one of

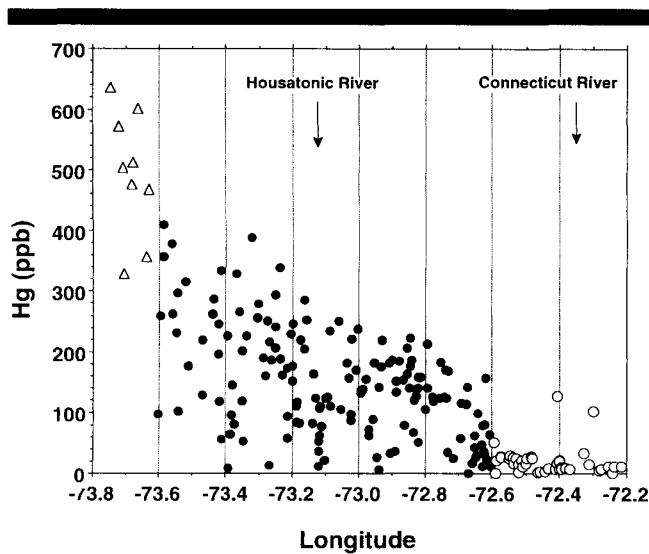


Figure 3. Hg distribution in LIS surface sediments, showing a trend of increasing Hg concentrations towards the west. Sudden changes occur near  $-72.6^{\circ}$  W and near  $-73.6^{\circ}$  W longitude. Open circles represent samples from the eastern Sound (east of longitude  $-72.6^{\circ}$  W); filled dots represent samples from the central Sound (between longitude  $-72.6^{\circ}$  W and  $-73.6^{\circ}$  W); open triangles represent samples from the westernmost Sound (west of longitude  $-73.6^{\circ}$  W).

these elements substantially reduces the influence of substrate characteristics on analytical results. The Hg/Fe and Hg/MGS parameters provide a first approximation of 'grain-size-normalized' Hg abundances, or the amount of Hg carried per unit weight of fine-grained sediment. The MGS values show a positive correlation with Hg concentrations, although abundant scatter is observed. Samples from the westernmost end of LIS, which have very high Hg concentrations, plot off that trend (Figure 4). Correlations between Fe and Hg concentrations are more complex (Figure 5); samples with Fe contents up to about 1.5% tend to have very low Hg abundances, but a broad positive correlation is observed for sediments with higher Fe contents. These binary graphs indicate that different sediment characteristics alone do not explain all the variation in Hg concentrations.

The graphs of Hg/Fe and Hg/MGS versus longitude show an increase towards the western part of LIS (Figure 6), with a reduced scatter in data points for the central and western basin for Hg/MGS (Figure 6B). The high Hg/MGS values in the eastern Sound are not considered to be significant, because the Hg analyses of these very coarse sediments were all near the detection limits. We calculated mean Hg concentrations, Hg/Fe and Hg/MGS values at  $-72.65^{\circ}$  W and  $-73.50^{\circ}$  W longitude (respectively the boundaries of the central and west basins) to establish how much of the east-west trend in Hg can be attributed to longitudinal variations in sediment composition (Table 1). The normalization to Fe contents and to MGS gave about similar results, and the normalization procedures remove about 25 % of the east-west trend in Hg concentrations.

We conclude that the regional Hg distribution in LIS surface sediments is significantly influenced by LIS sedimenta-

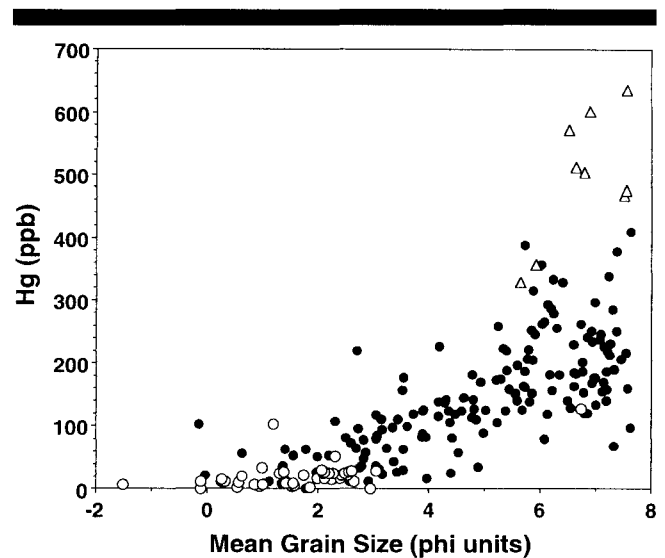


Figure 4. Mean grain size and Hg values of LIS surface sediments, showing a positive correlation for the east and central LIS data set. Samples from the westernmost Sound have Hg concentrations  $>300$  ppb and fall outside this array. Symbols are the same as in Figure 3.

tion processes, with increased Hg levels in the fine-grained depocenters of the central and western Sound. In addition, we find significant increases in Hg concentrations per "unit of fine-grained sediment" towards the west, suggesting that there are more or greater Hg sources located around the western Sound. In addition, the sediments at the extreme westernmost end of LIS stand out in these "normalized longitudinal plots" as more contaminated with Hg than predicted by the simple east-west trend.

We investigated the relationship between Hg and TOC in

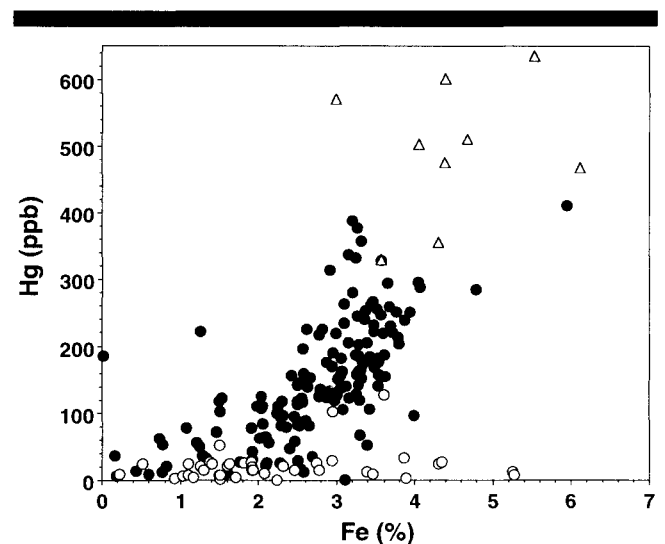
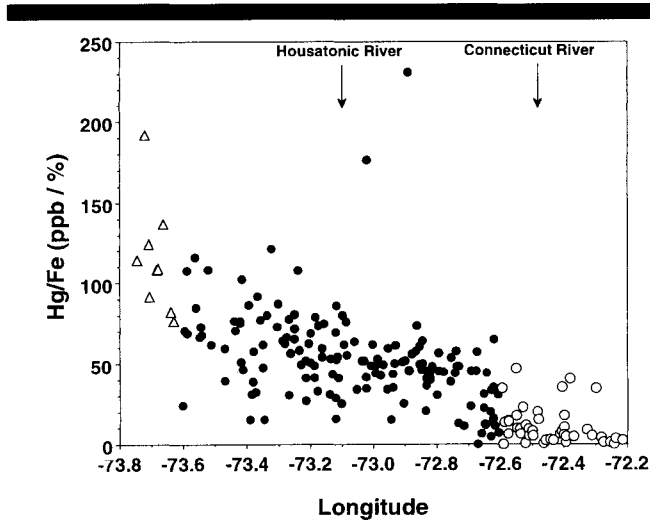
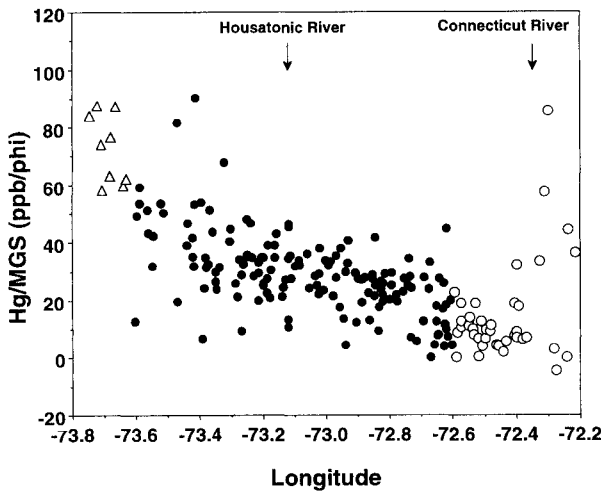


Figure 5. Relation between Hg and Fe contents. Samples with Fe contents  $>6.5\%$  (from eastern LIS) have been omitted. Symbols are the same as in Figure 3.



(a)



(b)

Figure 6. (a) Hg/Fe versus longitude, and (b) Hg/MGS versus longitude ( $^{\circ}$ W). Both graphs show an increase towards the west, with high values in the westernmost end of LIS. Symbols are the same as in Figure 3.

sediments for the SEAX96017 data set. The plot of Hg versus TOC (Figure 7) indicates that Hg concentrations show quite a range for a given TOC value, indicating that TOC is not the only parameter that controls the Hg concentrations in the sediment. The abundances of other host phases (e.g., Fe-oxides) affect the Hg concentrations as well. The Hg/TOC values vary between  $<20$  and  $>300$  (ppb/%) with increasing values westward (Figure 8). Samples from the transition zone near longitude  $-72.6^{\circ}$  W have low Hg concentrations but very low TOC ( $<0.2\%$ ), creating high Hg/TOC values. A few samples from the Housatonic River outflow area have relatively high Hg/TOC values, suggesting the presence of Hg that is not associated with organic carbon. When we first normalize the Hg values on a sediment parameter like Fe contents (e.g., plotting (Hg/Fe)/TOC versus longitude), the westward trend of increasing Hg/TOC values still persists in the central part

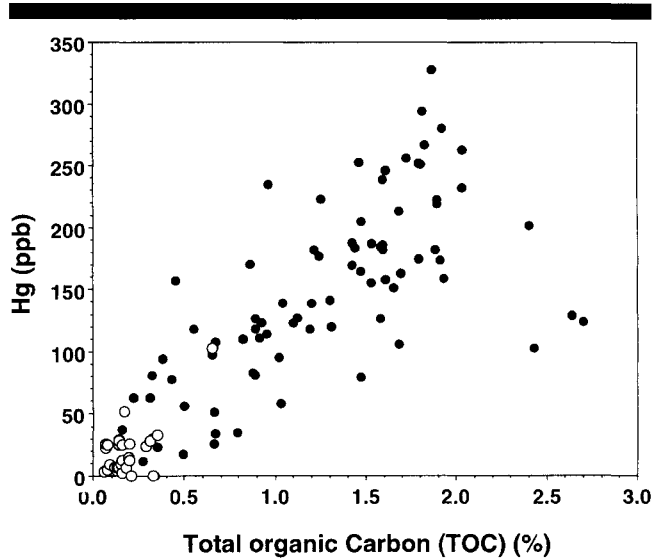


Figure 7. TOC (Total Organic Carbon) versus Hg concentrations in the SEAX96017 data set, showing a positive correlation. Symbols are the same as in Figure 3.

of the Sound, indicating additional sources of Hg in the western LIS.

The origins of organic matter in LIS include debris of terrestrial organic material, marine organic matter that is produced *in situ*, and organic contaminants from WWTP effluents (e.g., KROM and BENNETT, 1985). The carbon/nitrogen (C/N) values of the organic matter reflect its origin, such that C/N values of terrestrial matter are high (15–150) compared to those of open marine organic matter (C/N $\sim$ 6); coastal pro-

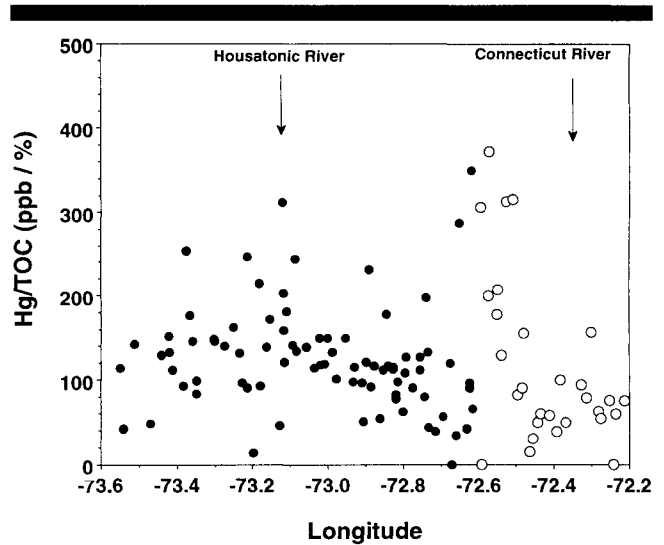


Figure 8. Hg/TOC (Total Organic Carbon) values for SEAX96017 samples versus longitude ( $^{\circ}$ W), with a steady increase towards the west. Samples between longitudes  $-72.5^{\circ}$  W and  $-72.6^{\circ}$  W have very low TOC ( $<0.2\%$ ) and therefore high Hg/TOC values. Symbols are the same as in Figure 3.

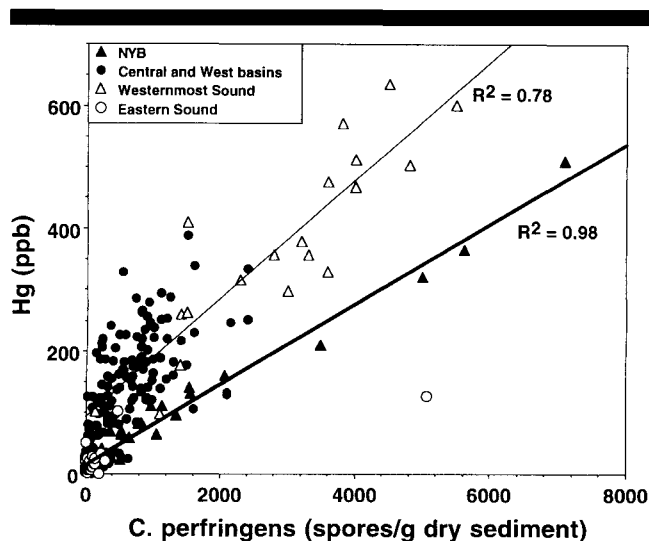


Figure 9. *C. perfringens* abundances versus Hg concentrations in LIS and New York Bight (NYB) surface sediment samples. The correlation lines for the NYB samples (heavy line) and for LIS samples west of longitude  $-73.5^\circ$  W (thin line) are indicated with their respective  $R^2$  values.

ductivity may create organic matter with C/N values of 6–9 and sewage commonly has C/N values of 11–13 (e.g., THORNTON and MCMANUS, 1994; ANDREWS *et al.*, 1998). Most LIS surface-sediment samples have C/N values around 10 (POPPE *et al.*, this volume), suggesting that carbon is derived from a mixture of local primary production, sewage waste and terrestrial organic carbon. High C/N values in excess of 50 occur in the eastern Sound, indicating the prevalence of mainly terrestrial organic matter in that region. The highest Hg concentrations are found in sediments with the lowest C/N values, suggesting that terrestrial organic matter is not the dominant carrier or substrate of Hg to LIS. Other studies also have found that terrestrial organic matter is not an important carrier of Hg (e.g., DAMIANI and THOMAS, 1974), except where paper industries release wood pulps contaminated with Hg (THOMPSON *et al.*, 1980).

The concentration of *C. perfringens* in sediment samples can be used as a tracer for sewage-derived material in LIS (BUCHHOLTZ TEN BRINK *et al.*, this volume). The *C. perfringens* abundances in all LIS surface samples show a positive correlation with Hg values ( $R^2 = 0.66$ , *C. perfringens* values  $>8000$  removed). Sediment samples from near New York City (west of  $-73.5^\circ$  W longitude) show a stronger positive correlation with *C. perfringens* abundances ( $R^2 = 0.78$ ), but the trend line has a positive intercept on the Hg axis (Figure 9). The correlation for samples from only the central Sound is weaker, with  $R^2 = 0.46$ . The overall scatter and the position of this “western LIS trend line” suggest that factors other than WWTP effluents also contribute to the Hg burden of the LIS sediments. By comparison, surface sediment samples from the New York Bight (NYB) area (BUCHHOLTZ TEN BRINK *et al.*, 1996) are heavily contaminated with sewage as a result of offshore sewage dumping at the 12 mile dump site (STUDHOLM *et al.*, 1995). Samples from the NYB that have

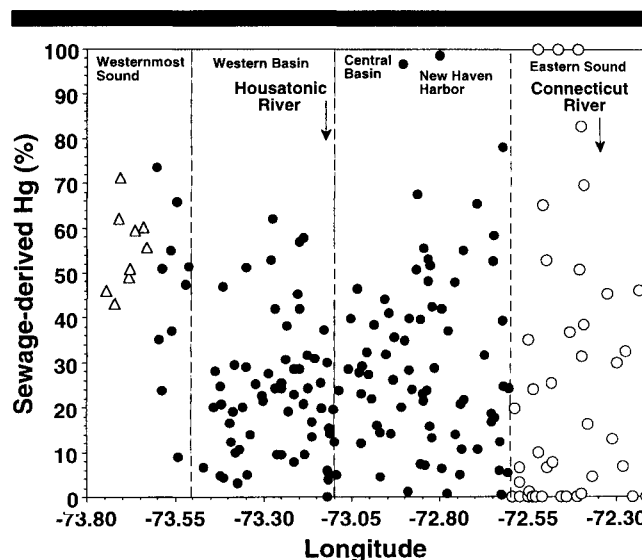


Figure 10. The sewage-derived fraction of Hg in LIS surface sediments as a function of longitude. The highest levels of sewage-derived Hg are found in the westernmost end of LIS, New Haven Harbor and near Old Saybrook. The fraction of Hg that is derived from WWTP/sewage sources is based on Hg/*C. perfringens* data from the New York Bight (NYB) 12-mile dump site. Symbols are the same as in Figure 3.

Hg concentrations in the same range as the LIS samples show a very strong correlation ( $R^2 = 0.98$ ) between Hg and *C. perfringens* abundances (Figure 9). Moreover, the NYB trend line passes close to the origin of the axes, indicating that sewage waste is the main source of Hg in those sediments. We estimate the Hg contributions from WWTP and other sewage-related effluents to LIS surface sediments by using the ratio between Hg and *C. perfringens* burdens in the NYB sediments as a proxy for an exclusively sewage-derived component. Using this approach, the calculated contributions show a wide range ( $<5$  to  $>90$  %) of sewage-derived Hg (Figure 10). Most sediment samples from the westernmost end of LIS have sewage-derived Hg contributions between 45 and 75 % in combination with very high Hg concentrations. Two samples from near New Haven Harbor seem to have almost pure sewage-derived Hg as does a sample taken in a bay near Old Saybrook (longitude  $-72.4^\circ$  W). Several samples from the eastern Sound have high sewage-derived Hg contributions, up to 100%, but most samples have low Hg concentrations. Many of the samples in the central and western basins have sewage-derived Hg contributions of 5–50 %. Thus, we infer that WWTP and other sewage-related effluents have contributed a significant fraction of the Hg load to most of the LIS surface sediments. Sewage contributed a large quantity of Hg to the westernmost Sound, whereas in several samples in the eastern Sound, the small amount of Hg that is present is largely sewage-derived.

In summary, Hg concentrations show an east-west gradient both in the Hg concentrations and in the various normalized graphs. About 25 % of the variation in Hg concentrations is related to depositional processes, with higher levels of Hg in the mud-rich western sections of LIS. Despite

vigorous tidal stirring of water and sediment in the Sound, some spatial structure remains in the Hg concentration map. The patchiness in Hg concentrations in LIS (Figure 3) derives both from the distribution of depositional environments and from the presence of local Hg sources. Sewage-derived Hg inputs dominate near New York City, New Haven, and several spots in the eastern Sound; a Hg-rich sediment component exists near the mouth of the Housatonic River.

### Historical Record in Sediment Cores

The sediment cores have Hg concentrations of 30–1270 ppb Hg and the profiles of Hg concentration versus depth-in-core (Figure 11) show large differences between cores. Classic contamination features are observed in Hg-depth profiles from cores along the A transect and some cores along the northern side of LIS (core G1C1 and C1C2, Figure 11). Cores taken more towards the center of the basin, *i.e.*, cores B5C5, B7C1, D5C3 and D7C4, have relatively constant Hg concentrations throughout the cores. Low, presumably natural, background values of about 30–50 ppb occur in the deep core sections of the A transect cores and cores B7C1 and G1C1. In the A transect cores, the Hg concentrations increase upcore from these values to peak at 300–500 ppb Hg, and then decline to 200–300 ppb Hg in the sediments that were deposited most recently. These profiles are similar to salt marsh Hg records from Connecticut (KREULEN, 1999), both in shape and in magnitude of Hg concentration. The other cores from the northern Sound (B1C2, C1C2, G1C1) also have declining Hg concentrations in the upper core sections, but have significantly different Hg concentrations and sedimentation rates. The peak to background ratios of Hg (*i.e.*, enrichment factor) in the A and G cores vary from 6 to 9; the reduction in Hg concentration since the time of maximum Hg contamination levels is about 30%. Core G1C1 shows a record for Hg contamination that has peak Hg levels around 200 ppb Hg and a decrease to about 120 ppb Hg in the uppermost sediments. This core is located west of the mouth of the Connecticut River in an embayment near the town of Old Saybrook. The G1C1 core Hg profile shows similarities to a profile from Great Island marsh in the Connecticut River estuary (KREULEN, 1999), but the marsh core has higher absolute values (up to 350 ppb Hg). Core B7C1 has a smooth contamination profile and reaches background values at about 50 cm depth.

Mercury profiles in the cores can provide a record of Hg accumulation that may reflect LIS-wide temporal trends in Hg fluxes, but they can also be influenced by sediment reworking processes. Major element analysis and x-radiographs of the cores (BUCHHOLTZ TEN BRINK, unpublished data) quantify lithological variations within a core. Normalization to iron content was used to correct for variable lithology within a core, but most cores (with the exception of G1C1) were quite uniform so the corrections are inconsequential. Core B1C2, taken near the mouth of the Housatonic River, has high Hg levels throughout, with one sample as high as 1270 ppb Hg. Similarly high Hg levels (1200 ppb) were found in sediments deposited during the 1960's in the Knell's Island marsh of the Housatonic River estuary (BREault and HARRIS, 1996; KREULEN, 1999). These marsh sediments are also

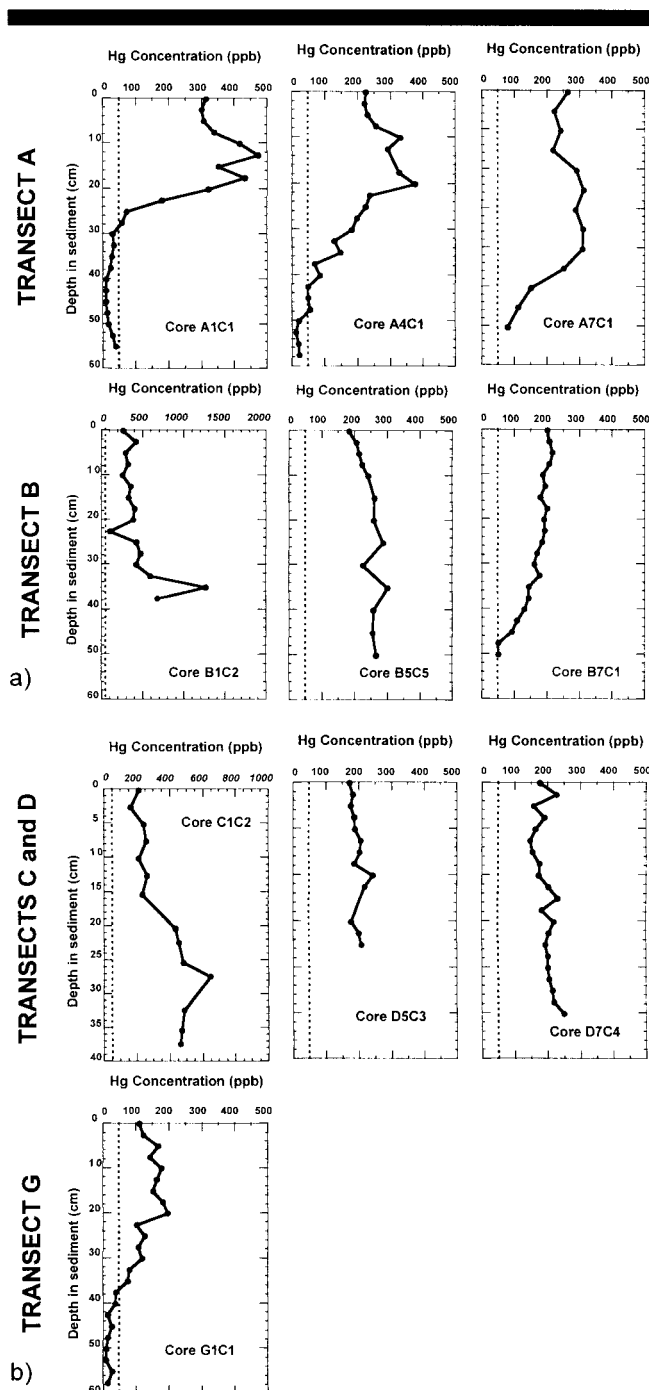


Figure 11. (a) Mercury-depth profiles for cores from transects A and B; (b) Mercury-depth profiles for cores from transects C, D and G. See Figure 1 for locations of core transects.

strongly enriched in Cu and Zn (MEIGS, 1999), and core B1C2 shows high levels of these elements as well (BUCHHOLTZ TEN BRINK *et al.*, 1999). The high Hg concentration in core B1C2 is probably a result of contaminated sediment influx from the Housatonic River. The Hg pattern, *C. perfringens* profile (BUCHHOLTZ TEN BRINK *et al.*, this volume) and  $^{210}\text{Pb}$ – $^{137}\text{Cs}$



Table 2. Cumulative core inventories of  $Hg^*$ , Fe and *C. perfringens*. See Figure 1 for core locations, cores number sequentially from north to south.

Core	$Hg^*$ ng/cm <sup>2</sup>	Fe 10 <sup>-2</sup> g/cm <sup>2</sup>	<i>C. perfringens</i> spores/cm <sup>2</sup>
A1C1	8685	117	14989
A4C1	7725	195	13150
A7C1	6967	133	11517
B1C2	17326	156	78300
B5C5	11829	207	43529
B7C1	6452	226	15748
C1C2	14135	169	30937
C5C1	4394	96	21059
D5C3	6903	152	49114
D7C4	8726	230	11011
G1C1	3828	148	95866

data (BUCHHOLTZ TEN BRINK, unpub. data) indicate sediment reworking and a very high sediment accumulation rate. Evidence for sediment reworking was also found for cores B5C5, B7C1, D5C3 and D7C4.

These core records indicate that LIS sediments are heavily contaminated with Hg, and that Hg levels have increased by approximately a factor of 6 since the start of the industrial revolution. They also show decreases in Hg concentration over the upper 10–20 cm, suggesting that Hg fluxes have declined over the last few decades, as has been observed for Hg data from salt marsh peat cores along LIS (KREULEN, 1999).

The decrease in Hg concentration that is observed in the sediment cores may reflect the effort that has been made in recent decades to reduce Hg contamination (USEPA, 1997). The detrimental health effects that result from Hg exposure are well-known, but analyses of total mercury in sediments are not an absolute measure for the actual Hg toxicity to marine organisms. Only the fraction that is bio-available can be metabolized by organisms. The sediment concentrations do provide one criteria for estimating the potential for toxic effects (USEPA, 1998). The environmental effects-low (ER-L) criteria (LONG *et al.*, 1996, 1998) of 150 ppb Hg is exceeded in most of the 1996/1997 surface samples collected from depositional regions west of transect D, near New Haven (Figure 2). This criteria separates sediments into those where detrimental biological effects that can be attributed to Hg “rarely” occur from those where they “occasionally” occur. No surface sediment values exceeded the ER-M of 710 ppb, the range in which toxic effects “frequently” occur.

### Hg Inventories and Accumulation Rates in Cores

An estimate of the total amount of Hg that has accumulated over time at a given location is provided by the calculated cumulative core inventories. We calculated  $Hg^*$  (the anthropogenic component) cumulative inventories for all studied cores. The cumulative inventories are a direct function of the rate of sediment accumulation and the concentration of Hg in the accumulating sediment, which is strongly affected by the amount of fine-grained sediment. The core sample slices have calculated bulk dry densities of about 1 g/cm<sup>3</sup>, with a range from 0.65 to 1.8 g/cm<sup>3</sup>. To account for differences in the amount of fine-grained sediment between cores and dif-

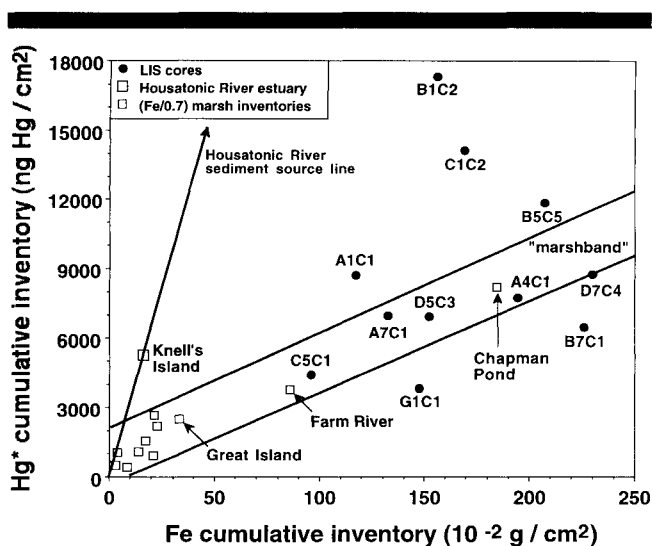


Figure 12. Cumulative core inventories from Connecticut marshes (open symbols) and LIS cores (closed symbols). Data from Connecticut coastal salt marshes include the Farm River marshes near East Haven, Great Island marsh from the Connecticut River estuary and marshes from small watersheds near Clinton, Guilford, and Niantic (KREULEN, 1999). Data from Chapman Pond, a freshwater marsh along the Connecticut River, probably best represent the composition of fine-grained Connecticut River sediment. These data plot together in the “marshband” which is representative of average, contaminated sediment carried into LIS by the major rivers. The data from Knells Island, located in the estuary of the Housatonic River, plot outside the marsh band. These sediments are very rich in Hg, reflecting a local Hg point source. The line through the origin and the Knells Island data point defines the characteristics of sediment from the Housatonic River.

ferences in sediment accumulation rate, we also calculated cumulative Fe inventories. These provide a means to assess the time-integrated  $Hg^*$  contamination signal versus core-averaged sediment parameters. The  $Hg^*$  inventories are minimum values for those cores that do not reach background values in the deeper core sections. The obtained  $Hg^*$  cumulative inventories range from 3828 ng/cm<sup>2</sup> for the most eastern core location (G1C1) to very high values near the mouth of the Housatonic River (17,326 ng  $Hg^*$ /cm<sup>2</sup> for core B1C2), with the other cores having intermediate values. The cumulative  $Hg^*$  inventories decrease from north to south along the A, B and C transects (Table 2).

We made a comparison between the Connecticut marsh core data and the LIS core data to investigate the contribution of riverine sediment-bound Hg sources (Figure 12). The Fe concentrations in the marsh core samples were obtained with a different leaching procedure than that employed for the LIS samples. The sample procedure for marsh sediments recovers about 70 % of the total Fe (MEIGS, 1999), so we estimated the marsh inventories for total Fe by multiplying the calculated Fe inventories by a factor of 1.43. The Connecticut marsh core data plot in a broad band whose position is strongly influenced by the data from Chapman Pond, a freshwater cove along the Connecticut River. The coastal marshes may receive sediment inputs from both rivers and LIS, but Chapman Pond contains strictly riverine sediments. This

“marshband” thus defines contaminated sediment sources to LIS with a time-averaged  $\text{Hg}^*/\text{Fe}$  value. The Connecticut River is the main supplier of sediment to LIS (LEWIS and DIGIACOMO-COHEN, this volume), and the marshband in Figure 12 is dominated by the Connecticut River sediment signature. The rather constant  $\text{Hg}^*/\text{Fe}$  inventory ratios for Connecticut marsh sediments have been explained as contamination resulting from largely atmospheric Hg deposition in the watersheds (KREULEN, 1999). Knell's Island marsh in the Housatonic River estuary has a very large  $\text{Hg}^*$  inventory, which is probably the result of local Hg point sources upstream (KREULEN, 1999). This data point is therefore displaced above the general “marsh band” (Figure 12), and is used to define the signature of sediments from the Housatonic River. The fine-grained sediments in LIS are largely a mixture of sediments brought in by the Connecticut and Housatonic Rivers (BREault and HARRIS, 1996; LEWIS and DIGIACOMO-COHEN, this volume). We would therefore expect that LIS core inventories plot between the “marsh band” and the Housatonic River sediment source line. The Hg contributions from sewage may further enhance the  $\text{Hg}^*$  core inventories. The  $\text{Hg}^*/\text{Fe}$  ratios for surface sediments with a high percentage Hg from WWTP varies from 20–180, although the sediments from the westernmost Sound with a strong sewage component (60–70%) have  $\text{Hg}/\text{Fe}$  values that cluster around 100. Sewage contributions thus create data points higher up in the diagram. Cores A1C1, B1C2 and C1C2 from the northern (Connecticut) side of LIS all plot well above the “marsh band”, whereas core B5C5 plots just above the band. The core sediments from A1C1 and B1C2 are presumably made up of a mixture of Housatonic River and Connecticut River sediment with additional sewage contributions. Core C1C2 is rather remote from the entrance of the Housatonic River and may have received Hg-rich sediment from the Quinnipiac River and/or sewage (ESSER and TUREKIAN, 1993). Other LIS cores, mainly from central and southern LIS sites, have inventories that plot near or in the “marshband”. These core sites (A7C1, A4C1, B5C5, D5C3, C5C1, D7C4) probably have sediment inputs that is predominantly from the Connecticut River, with lesser amounts from the Hg-rich sediment source of the Housatonic river. Cores G1C1 and B7C1 plot below the “marshband”, and it is possible that we have to invoke an additional, Hg-poor sediment component for these locations. Old, uncontaminated sediments that are eroded from eastern LIS (KNEBEL and POPPE, this volume; LEWIS and DIGIACOMO-COHEN, this volume) may provide such a Hg-poor sediment source.

The core Hg data can be converted to Hg fluxes when time markers are available. We currently have only preliminary data available for sediment ages derived from the analyses of the isotopes  $^{210}\text{Pb}$  and  $^{137}\text{Cs}$ . Mass accumulation rates, determined from model fits to the core isotope data (BUCHHOLTZ TEN BRINK, unpublished data) vary between 0.01 and 0.6  $\text{g}/\text{cm}^2/\text{y}$ , with the highest value in core B1C2. KNEBEL and POPPE (this volume) calculated an average accumulation rate for the whole Sound of 0.08  $\text{g}/\text{cm}^2/\text{y}$ . Mercury accumulation rates for the studied cores, based on these sediment accumulation rates and measured Hg concentrations, range from 1 (background) to 250  $\text{ng Hg}/\text{cm}^2 \text{ y}$  (peak). Alternatively, we

can obtain time-averaged  $\text{Hg}^*$  accumulation rates by dividing the  $\text{Hg}^*$  core inventories by the average time period of pollution (~140 years, KREULEN, 1999). These time-averaged values range from 27–84  $\text{ng Hg}^*/\text{cm}^2 \text{ y}$ , with higher values (100–123  $\text{ng Hg}^*/\text{cm}^2 \text{ y}$ ) near the outlet of the Housatonic River (core B1C2) and for core C1C2 further east near the urban outfall area of New Haven. These time-averaged  $\text{Hg}^*$  accumulation rates are higher than those calculated from the Connecticut marsh cores, which range from 3 to 37  $\text{ng Hg}^*/\text{cm}^2 \text{ y}$  (KREULEN, 1999). These differences in Hg accumulation rates are attributed to the accumulation in the Sound of predominantly muddy sediments while the marshes primarily accumulate plant debris. Chapman Pond, a mud-rich freshwater marsh along the Connecticut River does have a high average  $\text{Hg}^*$  accumulation rate (about 74  $\text{ng Hg}/\text{cm}^2/\text{y}$ , KREULEN, 1999) that is comparable to values in the Sound.

Measured and calculated modern atmospheric Hg deposition rates in the LIS region are between 1–3  $\text{ng Hg}/\text{cm}^2 \text{ y}$  (JENSEN and JENSEN, 1991; RIUND and TATSUTANI, 1998; FITZGERALD, personal communication, 1999), which is much smaller than the  $\text{Hg}^*$  accumulation rates that are estimated here for LIS sediments. We therefore conclude that LIS received much of its Hg through particle-bound and/or dissolved Hg import from the major rivers and sewage treatment facilities. The *in situ* atmospheric deposition of Hg is only a very small part of the total Hg LIS sediment budget.

### Spatial and Temporal Trends for Hg in Long Island Sound Sediments

In this section we combine the core data with those from the surface sediments to establish variations in Hg source strength over time and by location in the Sound. The Hg and *C. perfringens* abundances in those LIS cores with well-defined contamination profiles (A1C1, A4C1, A7C1, B7C1, G1C1) show changing ratios of Hg to *C. perfringens* over time. The Hg concentrations decline in the upper 10–15 cm of most cores (Figure 13), whereas the *C. perfringens* abundances increase exponentially to the core top (BUCHHOLTZ TEN BRINK *et al.*, this volume). The concentrations of both *C. perfringens* and Hg are controlled by the abundance of fine-grained sediment, creating a general coherence between Hg and *C. perfringens* concentrations. That coherence is lost in the uppermost core section, where *C. perfringens* commonly have their highest values and Hg levels have decreased. We interpret the decreased Hg concentrations to be a result of reductions in Hg sources in recent decades (*e.g.*, ENGSTROM and SWAIN, 1997; KREULEN, 1999). The increasing *C. perfringens* concentrations result from increased population densities around LIS and enhanced focusing of sewage effluents into the Sound as a result of the construction of WWTP.

In the lower sections of these cores, the Hg concentrations rise relatively fast compared to the increase in *C. perfringens* concentrations (Figure 13). The increase in *C. perfringens* concentrations is an exponential function that probably parallels the population increase (BUCHHOLTZ TEN BRINK *et al.*, this volume). The amount of Hg introduced into the environment during the early period of industrialization was larger relative to the population total than it was in the 20<sup>th</sup> cen-

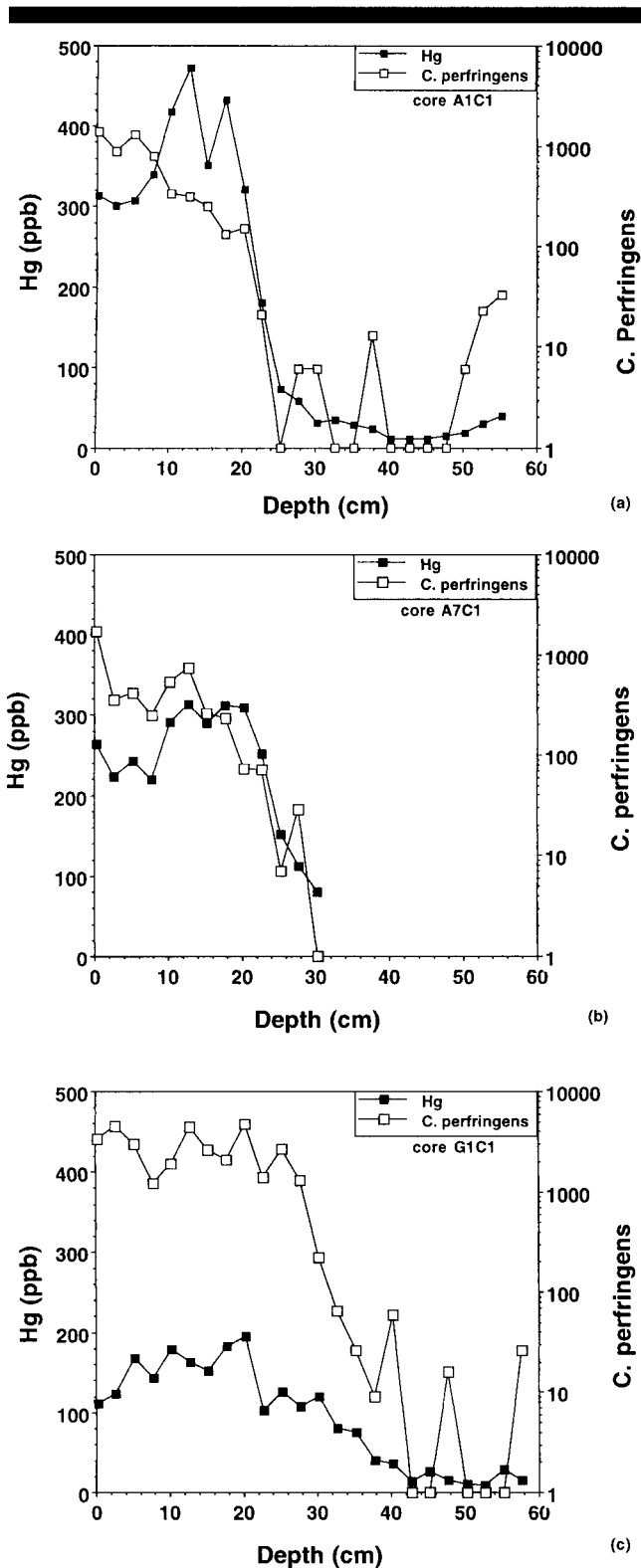


Figure 13. Hg and *C. perfringens* abundances in LIS cores with well-defined Hg contamination profiles. a) Core A1C1; b) Core A7C1; and c) core G1C1 (from near Old Saybrook). Note the logarithmic scale for the *C. perfringens* concentrations in spores/g dry sediment. The correlated variations in Hg and *C. perfringens* in core G1C1 are caused by sandy intercalations poor in both constituents (see X-radiograph in BUCHHOLTZ TEN BRINK *et al.*, this volume).

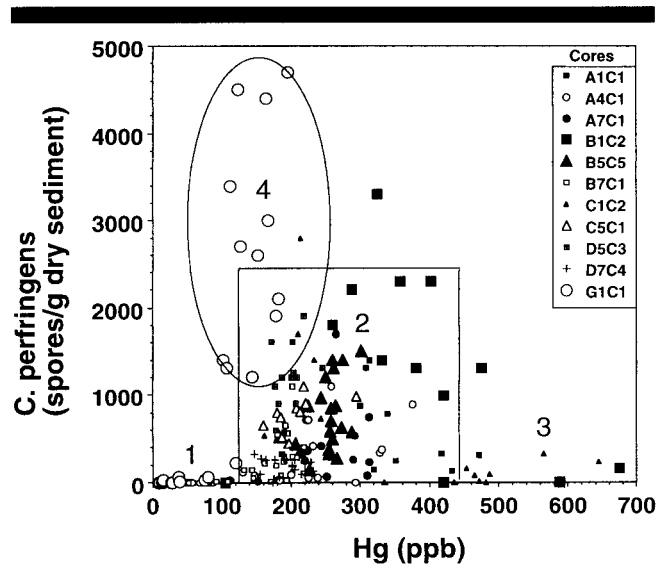


Figure 14. Individual Hg-*C. perfringens* data points from all LIS cores, showing the field of early Hg contamination (1), the period of Hg contamination with abundant WWTP effluents (2), and data points from sediments that are largely influenced by Hg point source pollution (3) such as the Housatonic river. The core G1C1 samples stand out because of their high abundances of *C. perfringens* with modest Hg concentrations (4).

ture. It is significant that the onset of Hg contamination occurs in exactly the same sample slice as the initial increase in *C. perfringens*, confirming that the Hg contamination is anthropogenic. The *C. perfringens* depth distribution is used here as an anthropogenic indicator, because early Hg contamination was most likely not sewage derived.

The entire set of core data is used to portray the impact of population density, with its associated sewage-derived Hg contamination, and point sources of Hg on the Hg accumulation in LIS (Figure 14). Field one depicts those data points that are from the period of early Hg contamination, when *C. perfringens* concentrations were low. Field two encompasses data points from the period of greater Hg contamination, when increased population densities and greater impact of sewage-derived Hg contamination is observed. Those samples having large Hg point source contributions and relatively low *C. perfringens*, *e.g.*, sediment from the Housatonic River, fall within field three; these are primarily from cores B1C2 and C1C2. Field four contains data from core G1C1 (located near Old Saybrook), in which the very high *C. perfringens* concentrations (BUCHHOLTZ TEN BRINK *et al.*, this volume) and more modest Hg concentrations reflect a local source.

Core inventories provide yet another way of distinguishing Hg sources, using the relationships between *C. perfringens* abundances and Hg concentrations. Core inventories are graphed, together with the trend line of the NYB surface sediment samples that shows pure sewage-derived Hg contributions (Figure 15). All of the LIS cores except G1C1 plot above the NYB trend line. This displacement away from the NYB trend line may point to Hg sources other than sewage, but may also derive from the fact that Hg/*C. perfringens* values for pure sewage may have changed over time. The NYB

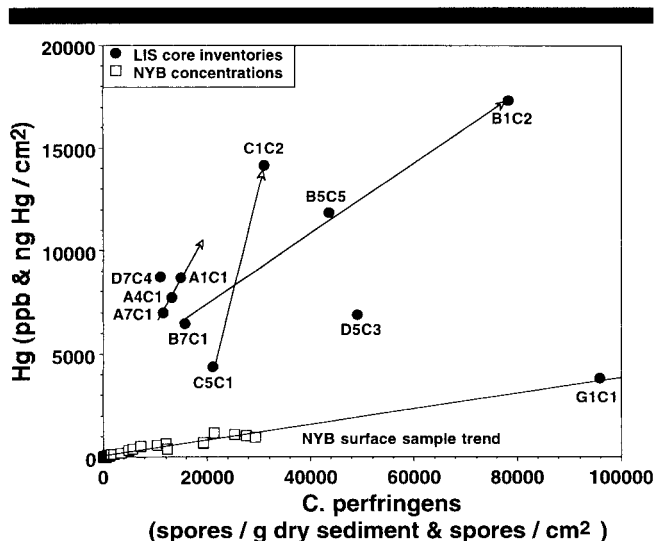


Figure 15. LIS core inventories for Hg and *C. perfringens*. The concentration values of Hg and *C. perfringens* from New York Bight (NYB) surface sediment samples are also shown to indicate the trend for Hg that is known to be strictly derived from a sewage source. All core inventories except for G1C1 are displaced above the NYB correlation line, suggesting additional Hg sources besides sewage discharge. The arrows indicate trends of increasing Hg inventories along the A, B and C transects from Long Island toward the Connecticut coastline, suggesting local Hg-rich sediment sources such as the Housatonic River.

correlation line is largely based on sewage discharges in the 1980s, with Hg/*C. perfringens* values that may be lower than those from the preceding period. Mercury core inventories from transects A, B and C increase from south to north (arrows), and move away from the "sewage" line. The sewage contribution is greater in the west and north of LIS (BUCHHOLTZ TEN BRINK *et al.*, this volume), so this N-S trend likely indicates also increasing contributions from non-sewage Hg sources to the north. Core B1C2 plots farthest away from the NYB trend line, which is probably attributable to the strongly Hg-contaminated sediments that originate from the Housatonic River. The G1C1 core, with its very high *C. perfringens* abundances, plots on the NYB "pure sewage" line, suggesting that WWTP effluents probably are the dominant contributor of Hg to these sediments. Surface sediment near this core location also had an Hg concentration that was close to 100 % derived from sewage. These relationships in cores support the findings from surface sediment samples and indicate that Hg contributions from WWTPs are dominant in several samples from the western Sound and in some samples from the eastern Sound.

### CONCLUSIONS

Mercury concentration data from surface sediment and core samples have more than an order of magnitude variation as a result of fine-grained, contaminated sediment focusing and the presence of local Hg sources. The geographic distribution of Hg in LIS surface sediments shows low Hg concentrations in the east, with a jump in concentrations near longitude  $-72.6^{\circ}$  W, followed by a gradual increase westward,

and highest values close to New York City. Part of the spatial variation is a result of regional changes in bottom sedimentary environments and sediment composition. The fine-grained sediments that are abundant in western LIS contain much more Hg than the fines-depleted sediments in the eastern Sound. Normalization of the Hg data to grain-size removes about 25 % of this east-west gradient, but a residual trend remains that is related to Hg sources in western LIS.

The relations between TOC and Hg concentrations are complex, because of the different sources of TOC, but the Hg/TOC values in LIS also show a crude increase from east to west. The samples in central and western LIS that have high Hg concentrations also have abundant sewage-derived Hg. Further studies are needed to determine if the sedimentary organic matter in western LIS is also an important Hg carrier, if TOC and Hg have a shared origin, or if a more complex linkage through local productivity should be invoked.

The main Hg sources for LIS consist of (1) Hg-contaminated sediments from the Connecticut River (end-member found in Chapman Pond sediments), (2) the much more severely Hg-contaminated sediments from the Housatonic River (end-member found in Knell's Island sediments), and (3) sewage and WWTP sources (abundant in westernmost LIS). *In situ* atmospheric deposition probably contributes a small component of Hg contamination as well. The sewage and WWTP effluent-derived Hg account for 0–50 % of the Hg burden in most LIS sediments, with higher contributions near New York City (45–75 %), New Haven (close to 100 %) and in the eastern basin (up to 80 %). The core studies show a synchronous increase in *C. perfringens* and elevated Hg concentrations, strongly suggesting that the Hg contamination is anthropogenic in character. The Hg concentrations decrease in the upper sediment layers, whereas the *C. perfringens* concentrations increase. Either the Hg burdens in sewage have decreased over the recent decades or the strength of other Hg sources to LIS has diminished; most likely both factors played a role in the changing pattern of Hg/*C. perfringens* values toward the core tops. Investment should continue in programs aimed to reduce Hg pollution since the Hg concentrations in many sediment samples from the Sound remain above the sediment quality criteria that trigger environmental concern.

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