

Mass balance of heavy metals in New Haven Harbor, Connecticut: Predominance of nonpoint sources

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Abstract

A mass balance was constructed quantifying all known sources and sinks for the metals Ag, Cd, Cu, and Pb in New Haven Harbor, Connecticut, USA. Sources included direct atmospheric deposition, rivers, treated sewage effluent, combined sewer overflows, and permitted industrial discharge. Sinks were burial in sediments, tidal exchange with Long Island Sound, removal in salt marshes, and dredging. All of these fluxes were measured directly, rather than estimated, and uncertainties were quantified. The mass balance closed successfully within the uncertainty of the measurements. Riverine inputs account for most of the total yearly metal flux. Metal concentrations in the river can be approximated as a simple linear function of discharge. Salt marshes remove an amount of metal equivalent to 20%–30% of the flux from the river before it reaches the harbor. Burial in sediments is the major sink for all metals examined, but dredging acts as a substantial short-circuit of this sink. Tidal exchange appears to be a relatively small term; however, it is also the least well quantified. Sewage treatment plant (STP) effluent and combined sewer overflow discharge are minor contributors to the overall metal balance, except in the case of Ag. Metal concentrations in STP effluent are a linear function of discharge. Atmospheric deposition is of minor importance but is comparable to sewage effluent. Lakes can be used as natural collectors and indicators of atmospherically deposited metals.

Although heavy metals are among the most toxic and persistent contaminants of estuaries, we lack a quantitative understanding of their sources, distribution, transport, and fate. For estuarine systems located in industrialized areas, such as urban harbors, this lack of knowledge is complicated by numerous inputs of metal pollution from point and nonpoint sources and by removal and redistribution of contaminated sediments through dredging operations. In order to determine the relative importance of each of these factors to the distribution and fate of heavy metals in an industrialized estuary, a mass balance of Ag, Cd, Cu, and Pb was constructed for the Quinnipiac River/New Haven Harbor system located in south-central Connecticut. The information generated by this study can be used by ecosystem managers to improve water and sediment quality in the most cost-effective way.

Most previous studies of trace metals in estuaries have tended to focus on either the water column (e.g., Boyle et al. 1977; Bowers and Yeats 1978; Mart et al. 1985; Shiller and Boyle 1985; Keeney-Kennicutt and Presley 1986; Valenta et al. 1986; Harper 1988; Balls 1989; Benoit et al. 1994) or sediments (e.g., Greig et al. 1977; Helz and Sinex 1986;

Holmes 1986; Scoulos 1986; Zhang et al. 1988; Windom et al. 1989). Only a few have considered both components in the context of a mass balance (Helz 1976; Klinkhammer and Bender 1981; Santschi et al. 1984; Paulson et al. 1989; Seidemann 1991; Muller et al. 1995; Quemerais et al. 1996; Yang and Sanudo-Wilhelmy 1998). However, when examining a contaminated harbor system, source-specific information is needed to account for the numerous types of point and nonpoint sources of metal pollution, including sewage treatment plants (STP), industrial discharges, atmospheric inputs, polluted rivers, urban runoff, and combined sewer overflows (CSO). For example, depending on the specific system, sewage effluent has been shown to be either a major (Patterson et al. 1976) or minor (Sanudo-Wilhelmy and Fleegal 1991) fraction of total metal loading in estuaries. Furthermore, sampling of sources and sinks should take into account temporal variability to accurately reflect seasonal and storm-based variations in metal loading from the various sources. This applies not only to the source rivers but also to STP effluent and urban runoff.

On the basis of previous surveys of metals in sediments, New Haven Harbor is one of the most badly contaminated sites in Long Island Sound (e.g., Greig et al. 1977), an estuary located in one of the most densely populated areas of the country. However, previous investigations of Long Island Sound estuaries have tended to focus on a larger scale (Turekian et al. 1980), may have been subject to contamination artifacts (Dehlinger et al. 1973, 1974; Turekian et al. 1980), or did not generate a full quantitative mass balance (Applequist et al. 1972). Some individual components that could contribute to a mass balance for New Haven Harbor have been analyzed in the past, such as atmospheric inputs (McCaffrey and Thomson 1980; Varekamp 1991), river impoundment sediments (Bertine and Mendeck 1978), harbor sediments (Applequist et al. 1972; Turekian 1979), and Sound sediments (Thomson et al. 1975; Goldhaber et al.

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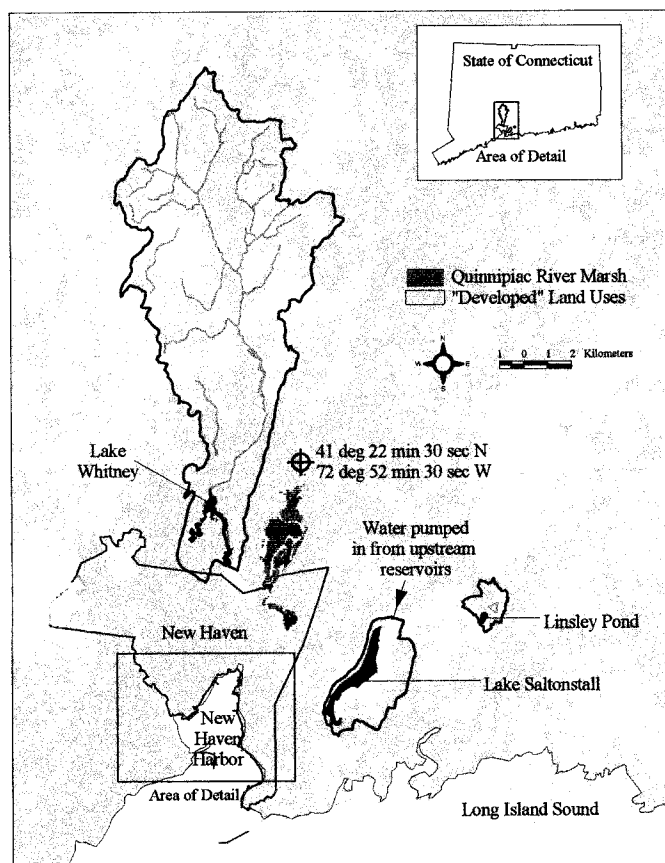


Fig. 1. Location map of Lakes Whitney and Saltonstall and Linsley Pond near New Haven Harbor, including an inset that shows the harbor's location in Connecticut. These three water bodies were selected because of their proximity to the harbor and the expectation that their sediments would mainly reflect atmospheric deposition of metals rather than local surface inputs. Also shown are the lakes' watersheds, built up areas within them that may contribute nonpoint source pollution, and the large salt marsh at the mouth of the Quinnipiac River.

1977; Greig et al. 1977; Lyons and Fitzgerald 1980). But these disparate parts cover unlike metals at widely separated locations, lack information on changes with discharge or time, are outdated or inaccurate because of contamination artifacts, and fall short of establishing a true mass balance.

Mass balances tend to be site-specific, with limited ability to be generalized to other sites. We believe that part of the value of the present study is that it examines an entire system in an integrated way and uses the most rigorous methods available. Importantly, the riverine flux to the harbor—which turns out to dominate—is based on a very large number of high-quality water column measurements taken over a period of 1 yr. Equivalent data have not been used in this way in the past. Each source or sink was studied in detail to avoid the need for approximations. Consequently, two of these (atmospheric deposition and the combination of riverine input and filtration by salt marshes) have already been presented as stand alone publications (Rozan and Benoit 1999; Benoit and Rozan 2001). As such, the methods used here can serve

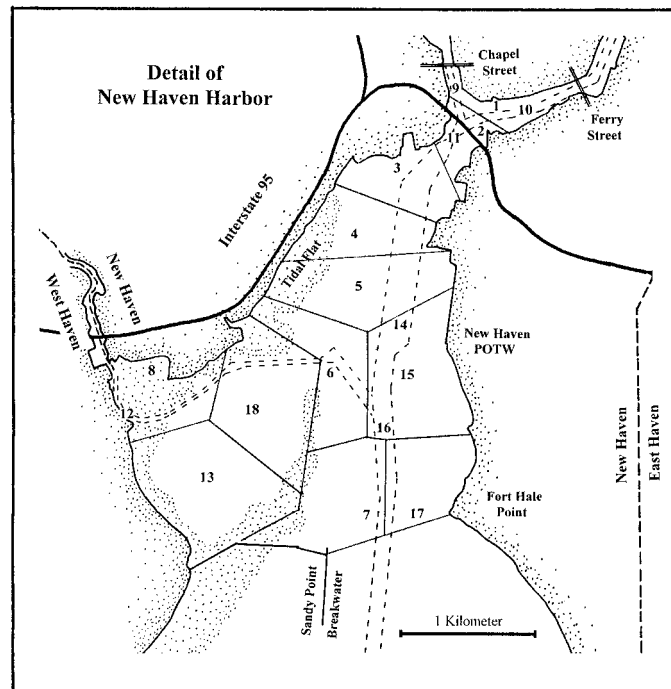


Fig. 2. Map of inner New Haven Harbor showing coring sites. As described in the text, the harbor has been divided into Thiessen polygons. All of the area in a given polygon is closer to its included (nonchannel) core than to any other. For the mass-balance calculation, it was assumed that sediments across each polygon had identical sediment accumulation rate and vertical metal distributions.

as a model for others constructing material mass balances for surface water bodies.

Study site

New Haven Harbor is an embayment in the central part of the north shore of Long Island Sound (Fig. 1) and is the most active port in Connecticut. It is located at the mouth of three rivers: the Quinnipiac, Mill, and West. The City of New Haven, which covers 16.0 km², has a long history of industrial activity, including metal fabrication and finishing, brass manufacturing, and arms production. Its wastewater handling system still employs CSOs in >30% of the city. The largest river, the Quinnipiac (216 cfs average discharge, 1931–1999), also has a watershed characterized by a high level of industrial development and thus is potentially a significant source of metal pollution.

At its mouth, the harbor is separated from greater Long Island Sound by a series of three breakwaters, and water exchange occurs through relatively narrow passages. Farther in, the harbor is divided into inner and outer sections by the Sandy Point breakwater on the west and Fort Hale Point on the east (Fig. 2). The upland limit of the inner harbor was taken to be the point where the average low-tide salinity was 20‰. For the Quinnipiac River, this is close to the location of the Ferry Street bridge (41°18'07"N, 72°53'36"W); for the Mill River, it was assumed to be the Chapel Street bridge (41°18'12"N, 72°54'22"W); and for the West River, it was

the Interstate 95 bridge (41°17'0"N, 72°56'25"W, all NAD 1927). The inner harbor as defined here has a total area of 6.63 km² and a watershed area of 630 km². Fine-grained sediments and industrial development are found almost exclusively in and adjacent to the inner harbor. This is also the site of New Haven's three former sewage treatment plants (only one 60 MGD facility remains active), 24 CSOs, and the mouths of the three influent rivers. Each river passes through a marsh system before entering the inner harbor. A large salt marsh sits at the mouth of the Quinnipiac River. The Quinnipiac River marsh is located immediately upstream of the harbor (Fig. 1) and is the largest, with an area near 300 ha. The combination of these features makes inner New Haven Harbor an especially interesting, complex, and useful test case for studying the fate of toxic contaminants in an industrialized estuarine environment and the effectiveness of these estuaries in removing toxins in transit between terrestrial and marine environments.

Water depths in the inner harbor are typically between 1 and 7 m. Dredged areas are maintained to a depth of between 9 and 10 m. A considerable amount of the western shoreline is mud flats that are exposed at low tide. In addition, much of the western lobe of the harbor (areas 8, 13, and 18 on Fig. 2) is very shallow (<1 m) All depths given are mean lower low water. Tidal range in the harbor varies between 2 and 3 m.

Methods

Mass balance calculation—The mass balance calculation was carried out in a manner similar to that described in Benoit and Hemond (1987, 1990), taking into account important dissimilarities between estuarine and lacustrine systems. The goal was to identify and quantify all the major inputs and outputs of metals in the harbor. The difference between the sum of the different fluxes and the measured change in storage, ΔS , indicates any unmeasured production or removal processes, such as groundwater.

$$\Delta S = \text{Atm. Dep.} + \text{Rivers} - \text{Wetlands} + \text{STPs} \\ + \text{CSOs} + \text{Industry} - \text{Burial} \pm \text{Tides} + \text{unknown} \quad (1)$$

where

- ΔS \equiv change in standing stock, including surficial sediments and the water column
- Atm. Dep. \equiv atmospheric deposition
- Rivers \equiv riverine flux
- Wetlands \equiv removal in salt marshes
- STPs \equiv sewage treatment plant effluents
- CSOs \equiv combined sewer overflows
- Industry \equiv permitted industrial discharges
- Burial \equiv burial in sediments below the zone of active exchange with the water column
- Tides \equiv tidal exchange with Long Island Sound; and
- unknown \equiv unknown sources or sinks, calculated by difference

In this formulation, the upper mixed layer of sediments is defined as part of the harbor. This layer is the zone that undergoes rapid mixing, and its depth often can be determined from radionuclide analysis (Benninger et al. 1979;

Peng et al. 1979; Carpenter et al. 1982; DeMaster and Cochran 1982; Robbins 1982; Stordal et al. 1985). This technique identifies the rapidly mixed layer on the basis of the penetration of short-lived radionuclides, like ⁷Be, or an abrupt change in slope of the profile of a long-lived radionuclide, like ²¹⁰Pb. This sediment layer contains nearly all of the standing stock of metals in the harbor (i.e., when compared with the water column) and can continue to exchange metals with overlying water.

Solving for the unknown term requires the integration of each source and sink term over a specific time period, taking note of any temporal variations that occur. For continuous discharges, such as rivers and STP effluent, rating curves needed to be developed to account for the variations in metal concentrations over time and changing flow. For the intermittent discharge of CSOs, the range of metal concentrations and frequency of discharge events needed to be characterized.

One virtue of the mass-balance method is that closure can serve as an internal check when unknown sources and sinks are negligible. For this purpose, it is important to determine the uncertainty of each term of the mass balance so that the statistical significance of the difference term can be evaluated (Benoit and Hemond 1987).

Water samples—Trace metals occur at very different concentrations in freshwaters, saltwaters, waste streams, and sediments, such that each medium requires its own sampling techniques and analytical methods. Although contaminated sediments contain metals in the mg kg⁻¹ range, typical concentrations of metals in water fall in the ng kg⁻¹– μ g kg⁻¹ range. Thus, to avoid contamination artifacts, all water sampling was conducted following strict clean protocols, as described in Ahlers et al. (1990), Benoit (1994), and Benoit et al. (1997). Particulate and dissolved fractions were separated in the field during collection with 0.45- μ m pore size in-line filters (Millipore Durapore HVLP 047 00).

Initial sampling of CSO effluent with clean protocols revealed metal concentrations in the high parts-per-billion range. Because such high levels preclude the possibility that samples would be contaminated, subsequent CSO collections were carried out with an ISCO model 3700 portable auto-sampler to facilitate time-series sampling. Whole-water samples (500 ml) were collected with this device after three line flushes. Filtration (0.45 μ m) was carried out in the laboratory in a class 100 clean room, and all subsequent steps were conducted with clean protocols.

For freshwaters, Pb, Cd, Cu, and Ag were measured after evaporative preconcentration (dissolved phase) or acid leaching (particulate phase) on a Perkin Elmer 3000 graphite furnace atomic absorption spectrometer. For seawater, sewage effluent, or freshwater with a high salt content (due to road salts in the winter), metals were analyzed by use of metal isolation/preconcentration with a chloroform extraction and the complexing agent APDC/DDDC (Bruland et al. 1985). All water sample manipulations were conducted in a class 100 clean room following clean procedures, as outlined in Benoit (1994). Quality Assurance/Quality Control (QA/QC) data are given in Table 1.

Table 1. Summary of trace metal QA/QC Data.

	Cd	Cu	Pb	Ag
Average procedural blank	0.0031	0.038	0.026	0.0018
Precision (1 SD)	0.0020	0.012	0.008	0.0005
Detection limit	0.0059	0.036	0.024	0.0015
SLRS-3 average measurement	0.013	1.35	0.069	—
SLRS-3 1 SD	0.002	0.07	0.010	—
SLRS-3 certified value	0.015	1.35	0.068	—
SLRS-3 certified SD	0.003	0.07	0.007	—

All values are $\mu\text{g L}^{-1}$. SLRS-3 is a certified reference freshwater.

Sediments—Sediment samples were collected by two methods. To avoid disturbing the sediment-water interface, SCUBA divers collected harbor sediment cores with 12.5-cm (inner diameter) PVC tubing (cores 1–8 and 13). The large diameter reduces core compression and provides adequate material for radionuclide analysis by nondestructive gamma counting with a planar Ge detector. Core tubes were presectioned at appropriate intervals (typically 1.5 cm) and taped back together. This design facilitates core sectioning and circumvents the need for extrusion. In areas of high shipping traffic, where diving is hazardous, and for longer cores (≈ 60 cm), 5-cm-diameter gravity cores were taken and sectioned into 5-cm-long segments (cores 9–12, 14–18, and longer duplicates of 1–4). Comparison of 5- and 12.5-cm-diameter cores suggested that compaction was not a problem in the harbor even for the narrower tubing. Marsh cores were hand collected in the 12.5-cm tubes. All cores were stored at 4°C and sectioned in the laboratory within 24 h of collection. Physical characteristics (bulk density and organic matter content) were determined for all sections. For organic matter determination and destruction, sediments were dry ashed in a muffle furnace at 500°C for 12 h prior to digestion. Metals in sediments were extracted by microwave digestion in Teflon bombs (Kingston and Jassie 1988) with concentrated HNO_3 and HF, followed by measurement with a Perkin Elmer 3300 simultaneous inductively coupled plasma atomic emission spectrometer.

Radionuclides were measured by nondestructive gamma spectrometry. Approximately 100 g (dry weight) samples were sealed in gas-tight, aluminum cans and counted by use of a low-background planar Ge detector. ^7Be was measured immediately after can sealing to confirm integrity of core tops and to assess short-timescale mixing. Total and excess ^{210}Pb were measured by the method of Cutshall et al. (1983) following a ≥ 21 -d equilibration period to allow ingrowth of ^{222}Rn daughters, which are measured in secular equilibrium with parent ^{226}Ra . In unmixed cores, ^{137}Cs provides a marker for the 1963 horizon of maximum atmospheric weapons testing and thus an average sedimentation rate since that time (Robbins and Edgington 1975). All core samples were measured for at least 11 h, to maximize counts and minimize uncertainty introduced by the random nature of the decay process.

Atmospheric input—Atmospheric deposition of metals has not been monitored in the New Haven area. Instead, we sought to evaluate the historical flux by measuring accu-

mulation in an existing natural collector. Required is a clean system where *local* pollution input was minimal and regional atmospheric deposition would be the dominant source of metals. High salt marsh cores have been used for this purpose, but evidence of tidal inputs to such sites (Varekamp et al. 2000) suggests that lakes are preferable as collectors of regional atmospheric inputs. Three local lakes were selected on the basis of their close proximity to the harbor and their relatively undeveloped watersheds (Fig. 1). Two sediment cores were collected from each lake by SCUBA divers, using the same methods as for the harbor sediment cores. The sediments were analyzed for Ag, Cd, Cu, Pb, ^{210}Pb , ^7Be , and ^{137}Cs . The radionuclides were used to calculate sedimentation rates, assess potential mixing, and evaluate sediment focusing (Benoit and Rozan 2001). The sedimentation rate was then multiplied by the metal inventory in the surficial layer of sediments to yield a current net flux. The resulting value was then corrected for any metal added by contribution from the watershed or by sediment focusing by normalizing to the ratio (Kada and Heit 1992)

$$R = \frac{\text{(measured } ^{210}\text{Pb}_{\text{xs}} \text{ inventory in sediments)}}{\text{(} ^{210}\text{Pb}_{\text{xs}} \text{ inventory expected from direct atmospheric deposition)}}$$

The assumption is that metals added to the watershed or lake behave in a manner similar to ^{210}Pb , which has only regional atmospheric sources and no local ones. If local sources of metals are absent, metal: ^{210}Pb ratios should be consistent across sites. (This is a necessary, not sufficient, condition for a lack of local sources. Details are given in Benoit and Rozan 2001.)

Others—For the mass balance, direct industrial discharge contributions and losses from dredging operations in the harbor were calculated from monitoring records filed with the Connecticut Department of Environmental Protection and Army Corps of Engineers (ACOE).

Results

Figure 3 summarizes the final mass balance. In this figure, sinks are grouped on the left, sources are in the middle, and their sum to the right. Each term and its uncertainty are described in the following sections.

Atmospheric deposition—In each instance, the distribution of radionuclides in the sediments of these three lakes suggested that sediment accumulation rates had increased at some point in the past (Bertine and Mendeck 1978; Brugam 1978; Benoit and Rozan 2001). In contrast, recent data (past 25 yr or longer) indicated that conditions have been constant for several decades. These recent measurements were therefore used in analysis of atmospheric metal deposition. On the basis of these data and their extrapolation, inventories of excess ^{210}Pb were found to be greater than measured direct atmospheric input in New Haven (≈ 12.7 pCi cm^{-2} , Graustein and Turekian 1990). Specifically, Linsley Pond and Lakes Saltonstall and Whitney had 19 ± 2.3 , 43 ± 4.3 , and 116 ± 10 pCi cm^{-2} , respectively. These amounts correspond

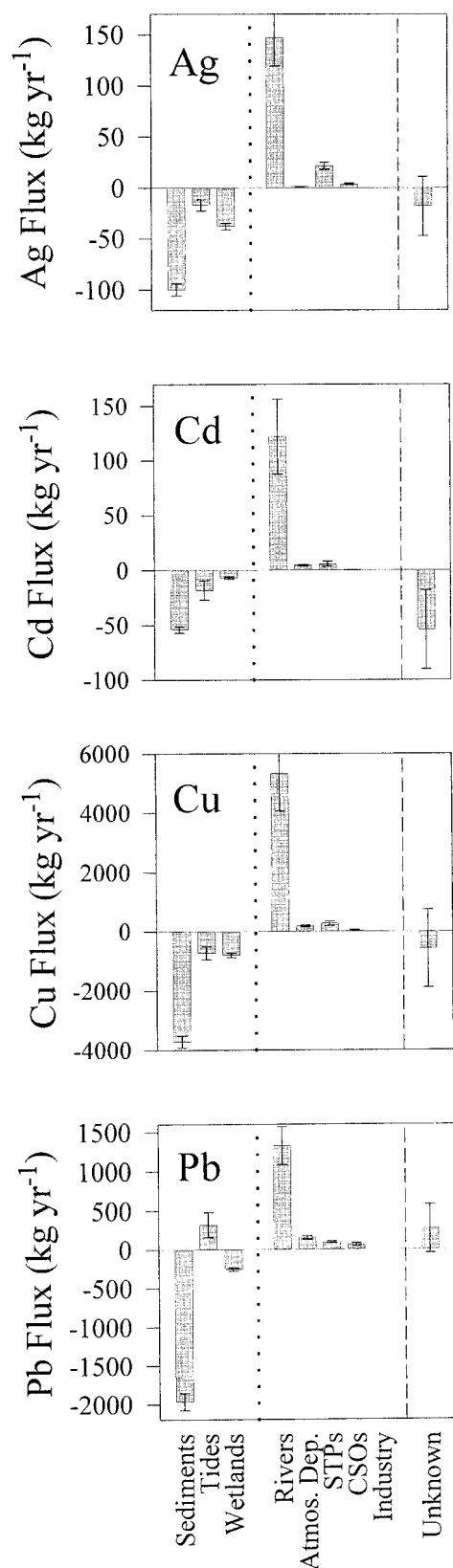


Fig. 3. Mass balance of Ag, Cd, Cu, and Pb for New Haven Harbor, Connecticut, prepared for the years 1995–1996. Sinks are grouped on the left of the dotted line and sources to the right, whereas their sum is shown on the extreme right. (One exception

to focusing factors of 1.48 ± 0.18 , 3.4 ± 0.34 , and 9.2 ± 0.81 , consistent with known characteristics of the lakes and their watersheds (Fig. 1). These values imply that Linsley acted as the simplest collector, whereas Saltonstall was intermediate and Whitney displayed the greatest redistribution of metals from the watershed or lake basin to the sampling sites.

Metal inventories corrected (divided) by these factors were not always in complete agreement (Table 2). We assumed that consistent and low inventories were most likely to be indicative of atmospheric-only inputs (the information sought here) and that higher amounts reflected various forms of local contributions unrelated to regional aerial supply. Within statistical uncertainties, Linsley had the lowest inventories for all four metals. It was identical to Saltonstall for Pb and equivalent to both other lakes for Cd. On this basis, Linsley data were used uniquely for Ag and Cu, whereas averages with other lakes were used for Pb and Cd.

Rivers—Rivers were an important subject of this study, not only because of their potential as a contaminant source but also because of the scarcity of existing reliable information on riverine trace metals. Depending on the extent of watershed development, rivers have been suggested to contribute either a large or small fraction of the total anthropogenic input to an estuary (e.g., Paulson et al. 1989). Three rivers drain into New Haven Harbor. The largest, the heavily industrialized Quinnipiac River, had a mean discharge (1995) of 205 cfs and an annual peak flow of 2300 cfs. Five STPs (secondary treatment) are located in the watershed and discharge directly to the river. The smaller Mill and West Rivers both had mean discharges of ~ 50 cfs and peak flows of 420 cfs. Both of the smaller rivers have comparatively undeveloped watersheds that are partly managed for drinking water supplies. Measurements on all three rivers revealed the Quinnipiac to be the most severely contaminated by a $>5:1$ margin (in terms of concentration). (One exception to this generalization was that Pb concentrations in the West River were on average only 25% lower than those in the Quinnipiac.) The higher metal concentrations and much greater flow of the Quinnipiac cause the metal flux in this river to exceed that of the Mill and West Rivers by over an order of magnitude for all four metals. Because the Quinnipiac River accounts for the majority of river-borne metal pollution entering the harbor, it was studied in the greatest detail.

Results showed that metal fluxes change dramatically with discharge, and this was factored into calculation of the annual flux of metals from the Quinnipiac River to New Haven Harbor. A total of 39 biweekly samples were collected and correlated with discharge. The resulting linear regressions (Fig. 4), relating metal loading to discharge, were all highly significant ($P \leq 0.001$). These curves were then used to

← is tidal exchange of Pb, which was measured to be a source to the harbor but is grouped in its conventional position with sinks.) Error bars are 1 SD or equivalent and were calculated as described in the text. The balance closes within 1 SD uncertainty for Ag, Cu, and Pb, and within 2 SD for Cd.

Table 2. Summary of calculated metal accumulation rates in sediments of three New Haven area lakes. Values listed have already been corrected (divided) by the listed focusing factor. This number is the ratio of ^{210}Pb inventory at the coring site to that of direct atmospheric deposition alone and reflects delivery from the watershed and redistribution within the lake for regionally delivered substances. The lowest value(s) (in boldface type) were used for each metal, because higher levels are believed to reflect contributions from local sources.

	Ag		Pb		Cd		Cu		Focusing factor
	($\text{mg cm}^{-2} \text{ yr}^{-1}$)	(+/-)	($\text{mg cm}^{-2} \text{ yr}^{-1}$)	(+/-)	($\text{mg cm}^{-2} \text{ yr}^{-1}$)	(+/-)	($\text{mg cm}^{-2} \text{ yr}^{-1}$)	(+/-)	
Whitney	0.0324	0.0032	8.39	0.83	0.076	0.007	12.8	1.26	9.2×
Linsley	0.0170	0.0026	2.33	0.350	0.073	0.011	2.7	0.40	1.48×
Saltonstall	0.0510	0.0064	2.30	0.291	0.059	0.008	44.6	5.6	3.4×
best	0.0170	0.0026	2.31	0.320	0.069	0.009	2.7	0.40	

derive daily average metal concentrations, which were combined with measured discharge, and a total year's flux of river-borne metals was calculated.

For comparison, several individual rain storms were measured over the course of their entire hydrographs, and the resulting metal fluxes were compared with the calculated values. The regressions tended to underestimate these individual storms. This is probably due to the way in which the regressions were developed. Sampling occurred at fixed intervals and intentionally captured variations due to both storms and seasonal changes in base flow. In the Quinnipiac River, storm discharges took longer to recede than the corresponding suspended particulate loads. Therefore, the bi-weekly sampling tended to act like a low-pass filter and smooth the sediment loading. Because particulate metal made up the majority of the total metal loading, the short-term variations from storms were not effectively captured in the regressions. A more detailed description of the metal behavior in the Quinnipiac River is given in Benoit et al. (unpubl. data). The key outcome is that the calculated input from rivers is slightly underestimated because storms are underrepresented.

Metal removal in salt marshes—As was stated earlier, salt marshes do not act as simple atmospheric collectors. Instead, they contain substantial quantities of metals scavenged from daily tidal flushing. Because the riverine input was based on measurements taken upstream of the estuary, removal of metals by salt marshes should be considered as a loss term in the harbor mass balance (Fig. 3). The efficiency of the Quinnipiac River marsh at removing heavy metals was established via two independent kinds of measurements: (1) metal inventories in marsh sediments and (2) nonconservative behavior of heavy metals in the water column along the salinity gradient.

A total of 34 cores were taken from the Quinnipiac River's tidal marsh, extending from the freshwater end member ($41^{\circ}22'02''\text{N}$, $72^{\circ}52'30''\text{W}$) to the harbor entrance ($41^{\circ}19'14''\text{N}$, $72^{\circ}53'25''\text{W}$) and laterally into the marsh on each side of the river channel. The resulting metal concentrations in marsh sediments show a clearly defined gradient decreasing with downstream distance but independent of lateral distance from the channel (Fig. 5 and Rozan and Benoit 1999). Additional measurements revealed that the river channel sediments themselves were composed mostly of sand and consequently contained low metal concentrations. To test whether the heterogeneity of sediments controlled the metal

distribution, heavy metals were normalized to Fe and organic matter. The resulting ratios exhibit distributions similar to those of the unnormalized heavy metals.

Metal concentrations measured in the marsh core tops and an average sediment accumulation rate were combined to calculate annual metal removal rates. A sediment accumulation rate of 0.33 cm yr^{-1} was used on the basis of the relative sea-level rise in this region as documented in the marsh accumulation rates in several Long Island estuary marshes (Varekamp 1991; Anisfeld et al. 1999). This number was confirmed by dating three cores from the northern section of the marsh; sediment accumulation rates in these cores ranged from 0.28 to 0.35 cm yr^{-1} .

In the mass balance calculation, the values used for metal concentrations in the sediments were based on a linear regression of metal concentration on distance downstream (sample data Fig. 5 and Rozan and Benoit 1999). To determine a flux per area, the marsh was divided into 12 500-m-long sections according to distance downstream. In each section, the regression-derived metal concentration was multiplied by the yearly sediment accumulation rate and sediment bulk density. This areal flux was then multiplied by the specific sectional area to obtain the amount of metal being removed. Finally, these sectional values were summed to give the overall metal accumulation rate for the entire marsh, the number used in the mass balance. Comparing this number with the metal flux in the river, heavy metal removal from the freshwater end member was 26% for Ag, 7% for Cd, 15% for Cu, and 19% for Pb. These represent upper limits on removal of *riverine* metals per se, because some of the metal delivered to the marsh by tidal flushing is from marine sources.

For comparison, a second method was used to estimate metal removal efficiency by the marsh, viz. direct water column measurements. Water samples were collected synoptically across the salinity gradient of the river within the marsh at different seasons. Metals were plotted as a function of the conservative tracer salinity in order to evaluate removal efficiency (Boyle et al. 1977). With this approach, heavy metal removal was estimated to be 33% for Ag, 21% for Cu, and 43% for Pb. Cd exhibited substantial seasonal variability. During the late spring through early fall, water column measurements documented a decrease in particulate Cd but an increase in dissolved Cd along the salinity gradient. Total metal concentrations decreased by $<10\%$ as the salinity increased to 20 psu. During the colder months, both the particulate and dissolved fractions decreased nonconservatively

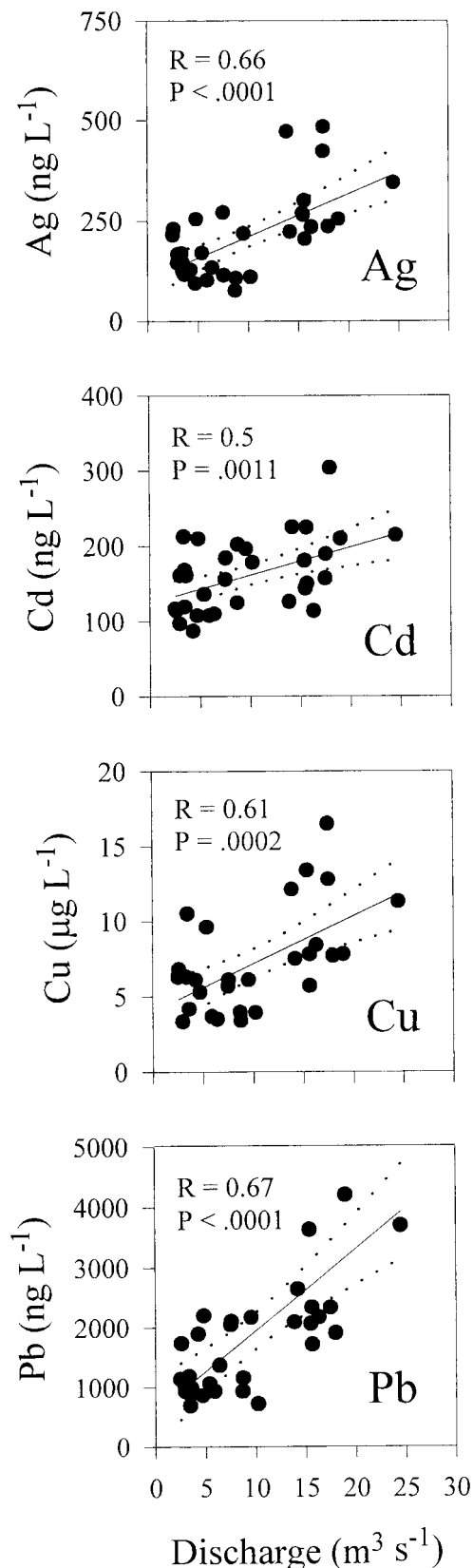


Fig. 4. Total (particulate plus dissolved) Ag, Cd, Cu, and Pb concentrations as a function of discharge in the Quinnipiac River for 39 samples collected at fixed intervals over a period of 1 yr.

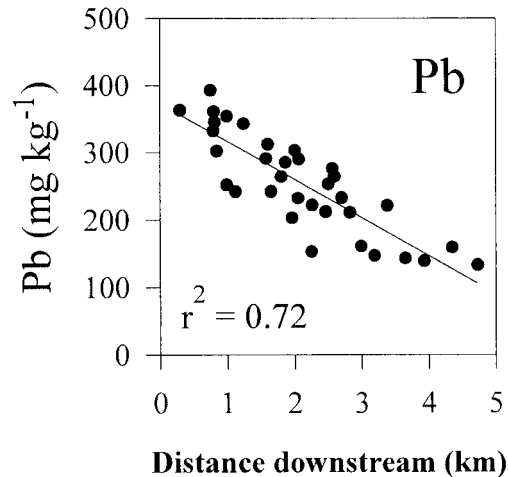


Fig. 5. Regression of Pb levels in surficial salt marsh deposits on distance downstream. Sorting data according to lateral distance into the marsh caused no improvement in the regression.

along the salinity gradient. In these cases, Cd removal was $\leq 15\%$. For a yearly efficiency, a weighted average indicated 10% removal.

Overall, the two methods for estimating metal removal by the salt marshes are in agreement. However, water column measurements exhibit much greater variability, have a strong seasonal component, and require much greater measurement effort to achieve a comparable level of reliability. Because of their greater uncertainty, the synoptic water column data were not used in the mass balance calculation, except insofar as they provide independent confirmation of results on the basis of sediment measurements. A more detailed examination of the methodology used to estimate marsh removal efficiencies is described in Rozan and Benoit (1999).

Sewage treatment plants—The New Haven wastewater treatment system was upgraded in 1980 from three primary plants to a single secondary treatment facility (60 MGD capacity). The question of how much this upgrade reduced heavy metal loading to the harbor is complicated by the existence of CSOs and an internal bypass within the STP itself. In New Haven (like most older US cities), sanitary sewers are combined with storm sewers that carry street runoff. The combined sewage passes through the treatment process when total flows are low. When combined flows exceed pipe capacities during storm events, CSOs located through the city discharge excess untreated storm and sanitary sewage directly into the harbor and surrounding rivers. Furthermore, when the flow to the STP reaches $2.6 \text{ m}^3 \text{ s}^{-1}$ (60 MGD), secondary treatment within the plant is bypassed, and some of the waste is treated only to the primary level before being discharged into the harbor.

As with the rivers, correlations relating metal concentra-

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Discharge data were taken from US Geological Service gauging station 01196500—Quinnipiac River at Wallingford, Connecticut. Dotted lines are the 95% confidence intervals of the regression.

tions to discharge were generated for the STP (Fig. 6). Periodic sampling revealed that, unlike the continuously variable loadings from the Quinnipiac River, the total metal concentrations in the STP effluent tended to be bimodally distributed, with one level for normal operating conditions (30–40 MGD) and one for bypass conditions (>60 MGD). Short residence times within the sewer system tended to minimize the time at any intermediate flow condition. Nevertheless, these two end members fell along a continuous trend, and the data could be treated as if they were continuous. The positive correlation between metal concentrations and discharge is expected, because water residence time in the plants is lower at higher flows, and this reduces treatment efficiency.

Combined sewer overflows—There are a total of 24 CSOs in the New Haven sewer system. These serve ~1600 ha of the city, including most of the downtown area. The city's sewers are grouped into three parallel networks. Each network is served by an independent pumping station (30 MGD capacity). At each pumping station, there is a CSO outfall that discharges directly to New Haven Harbor during high flows. Unfortunately, there are no flow measurement systems associated with any of the CSOs, and only on/off times are recorded for two of the major CSOs. Therefore, to estimate the potential discharge volume, a first-order estimate of the drainage volume for the storm sewer system in the City of New Haven needed to be calculated. With use of storm sewer pipe diameters, CSO capacities, and pump station pumping rates, discharge estimates were calculated for a variety of storm sizes. Estimates were based on the amount of water a storm would produce in the given collection area of each CSO. If the volume was not sufficient to cause an overflow, it was added to the volume collected in the area of the next downstream CSO. Once an overflow threshold was reached, the additive volume was held constant. For most storms, the overflows at the pumping stations tended to be limited by the pumping capacities and generally overflowed first. For this reason, the CSOs at the pumping station were monitored for this work.

The metal concentration in CSO discharges appeared to be controlled by the ratio of untreated sewage to storm runoff. (In addition, Cu and Pb exhibit a small first-flush effect.) Therefore, to determine the total metal flux to the harbor on an annual basis, concentrations of the metals were measured in storms of various sizes. Separate winter nonstorm sampling was also used to determine the effect of snowmelt, which caused two large overflows. To account for the possible effect of daily and weekly variations in sewage volume that might be caused by changing patterns of water use in the city, separate measurements were made of day, night, weekday, and weekend storms. On the basis of these results, CSO discharges were grouped into three general categories: (1) daytime storms, (2) nighttime storms, and (3) snowmelt. For each category, metal fluxes were tabulated based on storm size or snowmelt. (In the case of a snowmelt that occurred because of a rain storm, the rain categories were used with an adjustment made to their discharge volumes based on the amount of the snow loss.) These tables were then used to estimate the metal fluxes from all unmeasured

storms with >2 cm rainfall (the limiting case for CSO discharge) and summed with individual snowmelts for a yearly input.

Industrial discharges—Today, direct permitted industrial input is a minor contributor to heavy metal loading in most estuaries because of reductions achieved under clean water regulations. Although the majority of industrial outfalls in New Haven are a combination of storm drains and cooling water discharges, there are also two metal finishing plants that discharge heavy metals directly into New Haven Harbor. H.B. Ives, which is permitted to discharge five heavy metals, including Cu, has an average waste stream of $0.0015 \text{ m}^3 \text{ s}^{-1}$ and an average monthly limit of 1 mg L^{-1} for Cu. Sargent and Company, which discharges six heavy metals, including Cu, has an average daily flow of $0.0047 \text{ m}^3 \text{ s}^{-1}$ with a maximum daily Cu concentration of 2.0 mg L^{-1} . Taking the most extreme case, full permitted concentration combined with maximum discharge, industrial inputs for both companies are $<1 \text{ g of Cu d}^{-1}$ or $<0.37 \text{ kg yr}^{-1}$.

Tidal exchange with Long Island Sound—The delivery of heavy metals to Long Island Sound by suspended sediments from polluted, industrialized harbors is of great concern, so a key part of the study was to evaluate this flux. The water balance in the harbor is dominated by tidal exchange with Long Island Sound, and there is a need to carefully delimit this flux for purposes of calculating the overall harbor mass balance. Ideally, this requires an understanding of how metal concentrations vary over (1) the semidiurnal tidal cycle, (2) the lunar tidal cycle, and (3) seasonal changes. In an effort to achieve this goal, samples were collected repeatedly at a station at the inner harbor's mouth over full 12-h tidal cycles for spring and neap tides in each season.

Sampling in this way (and as a function of water depth) provided information on changes in metal concentration over the tidal cycle. Specifically, average concentrations for flooding and ebbing waters were calculated and their difference multiplied by the tidal prism volume (Duxbury 1964; Anonymous 1971; McCusker and Bosworth 1979) to derive the tidal exchange flux. It is well known that using average concentrations in this way can lead to biased results for salt marshes (Boon 1980; Nixon 1980) and estuaries (Kjerfve et al. 1981), but we lacked more detailed flow information that might have eliminated this problem. No detailed hydrographic model exists for the harbor, but analysis of surface drogues has shown that currents vary only within a limited velocity range between Sandy Point and Fort Hale Point (Duxbury 1964). For this reason, we believe that a depth profile at a single station was representative of the water and metal flux through this cross-section.

Recent studies have suggested that transport processes can be very different in dredged channels compared to tidal flats, with residual currents even having different signs in the two zones (Valle-Levinson and Lwiza 1995). In New Haven Harbor, the dredged channel represents only a small fraction of the mouth's cross section (<10%), and this effect is believed to be only second order. To elucidate vertical spatial variability, three depths were measured for the initial tidal cycle samples: 1 m off the bottom, 1 m below the surface, and a

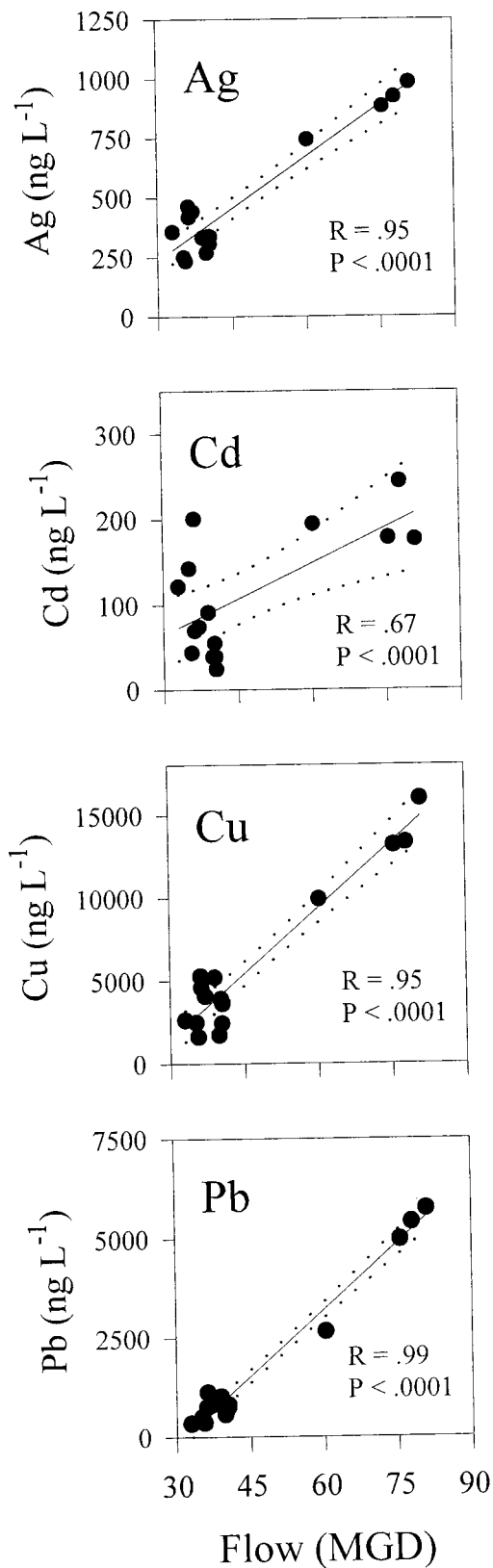


Fig. 6. Regressions relating total metal levels in sewage treatment plant effluent to discharge. The data fall on a continuous trend but tend to segregate into one of two narrow ranges, depending on whether measurements were made in dry or wet weather (high or

middepth sample halfway between the other two samples. The first two tidal cycles showed similar values for the mid-depth and bottom sample, and, on all subsequent dates, only bottom and surface samples were collected. For metals other than Ag, even these two samples matched closely on all dates.

The tidal cycle sampling revealed different patterns for each metal (typical data, Fig. 7). Cu consistently was exported from the harbor at all depths on a year-round basis. The surface waters often contain slightly lower amounts of Cu than the bottom waters, possibly because of dilution by the West River. Ag also is consistently exported from the harbor; however, a larger difference was observed between surface and bottom waters. Bottom waters actually carry a net input, although rather minor, whereas surface waters exported Ag. This difference is almost certainly due to the large amount of Ag discharged in treated STP effluent (Sanudo-Wilhelmy and Flegal 1991; Sanudo-Wilhelmy and Flegal 1992; Ravizza and Bothner 1996). Cd and Pb showed greater temporal variability than Ag and Cu. Cd tended to be exported to Long Island Sound in the fall, winter, and spring and to be imported during the summer. This change may be explained in part by remobilization of Cd from sediments during summer periods of suboxia. This hypothesis is supported by the large proportion of dissolved Cd compared with particulate metal in the water column, and the large increase in dissolved Cd during the summer relative to other times of the year. Pb also showed a seasonal dependence, being exported in the summer and imported the rest of the year. Because the occurrence of this seasonality is inferred from relatively few measurements, it has not been documented with certainty. If it is real, the cause is unknown.

Sediment burial and ΔS —A total of 22 sediment cores (Fig. 2) were collected from the inner harbor and analyzed for trace metals (Ag, Cd, Cu, and Pb), transition metals (Al and Fe), bulk density, and organic matter abundance as a function of depth. Thirteen of these cores (1–8, 13, and longer duplicates of 1–4) were analyzed for the radionuclides ^7Be , ^{210}Pb , ^{226}Ra , and ^{137}Cs . These measurements allowed for determination of losses to burial and ΔS , as well as for normalization of the trace metals to Fe, Al, and organic matter.

Sediment data revealed that the harbor is a complex, dynamic environment. In most locations, especially near the harbor's mouth and in the western lobe, depth profiles of radionuclides exhibited simple distributions that were easy to interpret (Fig. 8). In other instances, especially near the harbor's head, profiles were more complex, with evidence either of mixing to variable depth or discontinuous deposition (Fig. 9).

Channel cores consistently exhibited deep maxima in the trace metals we measured (Fig. 10). Cores from undredged areas either had maxima near the surface or more irregular patterns of trace metal distribution (Fig. 11) but did not have

←

low flow). Dotted lines are the 95% confidence interval of the regression.

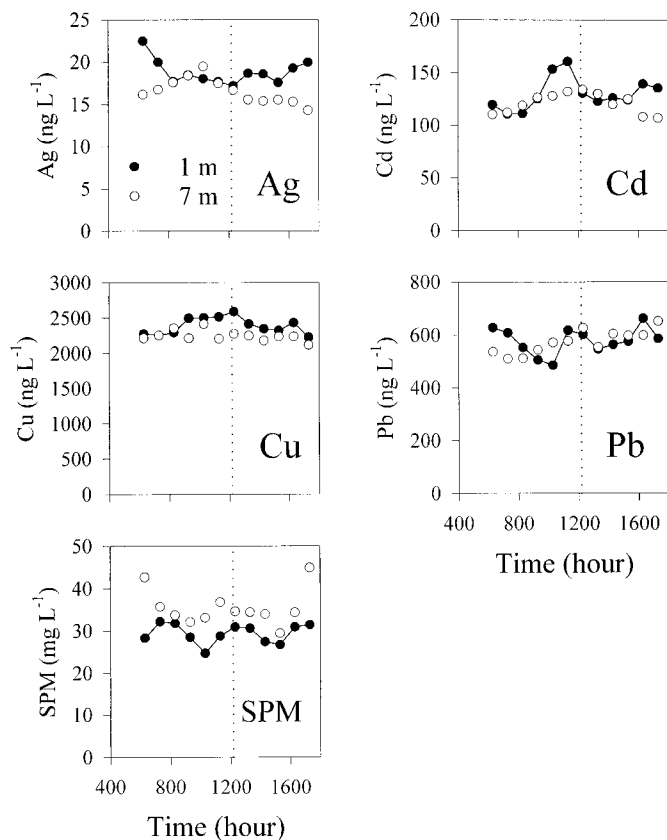


Fig. 7. Typical total metal concentrations and SPM over a tidal cycle (11 August 1995) for a station at the mouth of New Haven Harbor. High water occurred at 12:17 (dotted lines). Small differences are observed between surface and bottom waters on any given date. Results differ significantly among metals and also from one sampling date to the next.

deep maxima. On the basis of this dissimilarity and differences in sediment accumulation rates (described below), we believe that different sedimentary regimes exist in dredged and undredged areas; consequently, they were treated independently in the mass-balance calculations. First, Thiessen polygons were drawn to divide the undredged harbor bottom into 12 sections that represented the areas nearest to shallow water cores 1–8, 13, 15, 17, and 18. For the mass balance, the entire area within a polygon was assumed to have conditions identical to those of its corresponding core. The undredged area was further subdivided between the western lobe (polygons 8, 13, and 18), which had much lower sediment accumulation rates, and the remainder of the harbor. Because cores for polygons 15, 17, and 18 were not dated, the average sediment accumulation rate for western lobe polygons was applied to 18, and that of the remaining undredged polygons was applied to 15 and 17 (Table 3).

The dredged areas were treated in a parallel manner, with channels divided into six sections on the basis of proximity to cores collected in these deeper regions (9–12, 14, and 16). Dredged areas did not have any reliably datable cores. An analysis of dredging records (volume of dredged material, dredged area, and time between dredging campaigns) indicated that average sediment accumulation rate in these areas

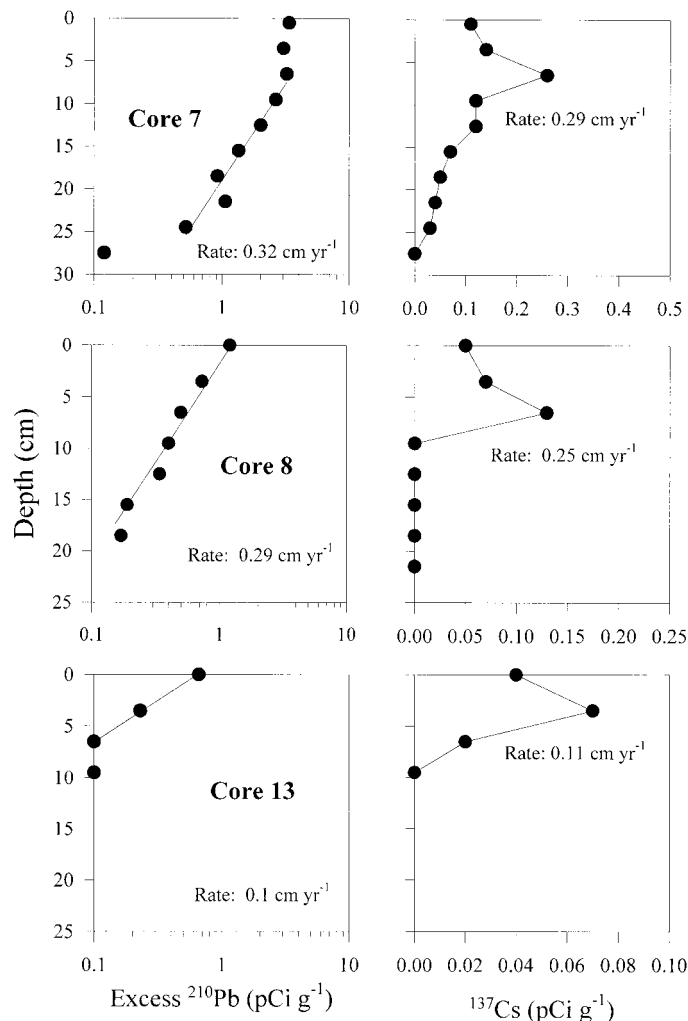


Fig. 8. Radionuclide distributions in some cores from the western lobe (8 and 13) and near the mouth (7) of New Haven Harbor. ^{137}Cs exhibits sharp peaks, and excess ^{210}Pb follows simple exponential decline with depth. Both dating methods are in agreement and sediments appear to have been deposited at steady rates with little postdepositional mixing.

was 3 cm yr^{-1} , roughly three times greater than that in the shallower areas. (Unusually high sediment accumulation rates in these zones is probably related to the overdeepening caused by dredging.) The total of the dredged region was only 13% of the total harbor area, so relatively large variations in the assumed sediment accumulation rate have little effect on the overall mass balance. Table 2 summarizes polygon areas, fraction of harbor bottom, and sediment accumulation rates either measured directly from ^{210}Pb and ^{137}Cs , inferred from nearby cores, or derived from dredging records.

Separating the mass balance term for long-term burial (Burial) from that for change in storage in the active surface zone (ΔS) requires a clear distinction between mixed surface sediments and deeper ones. The radionuclide and trace-metal data allowed unambiguous separation in only some cases. Consequently, we decided to combine these two terms, be-

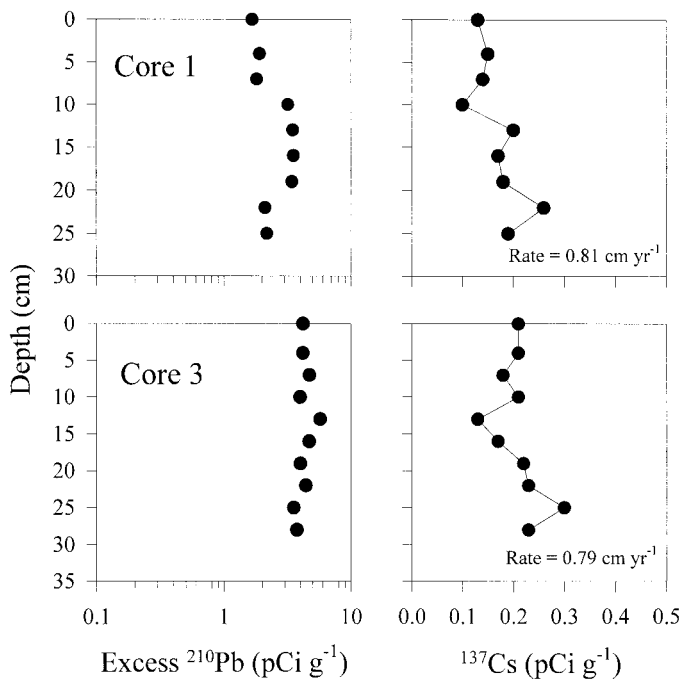


Fig. 9. Radionuclide distributions in two cores from near the harbor's head. ^{137}Cs peaks are broader and lower, and ^{210}Pb exhibits irregular patterns. Sediments may have been partially mixed at these sites.

cause their sum could be determined from the existing data with low uncertainty:

$$\Delta S = \text{Input (metals added to sediments each year)} \\ - \text{Burial}$$

$$\Delta S + \text{Burial} = \text{Input}$$

Calculation of this combined sediment term of the mass balance required two pieces of information: (1) sediment accumulation rate (derived from radionuclide profiles or dredging records) and (2) trace metal concentration in newly added sediments (determined from metal profiles in cores). The latter data were taken to be equal to metal levels in surficial sediments. In most instances there was little, or only irregular, variation with depth, which suggests that metal inputs to sediments have not changed substantially in recent years (Fig. 11). This inference supports use of surface concentrations to represent recently added metal values. The one exception to near constant levels in shallow (upper 20 cm) sediments occurs in the western lobe (Fig. 12). There, very slow sediment accumulation rates record a gradual decrease in metals over time. In this region, sharp ^{137}Cs peaks, lack of ^7Be penetration, and concordance of ^{210}Pb and ^{137}Cs ages all provide evidence that surficial sediments are unmixed (Fig. 8) and again support use of surficial metal measurements to represent recently deposited values.

Dredging—In addition to burial losses, metals are removed periodically from the harbor bottom by dredging. Dredging of channel areas in New Haven Harbor takes place every ~ 15 yr, with the most recent having occurred in 1993.

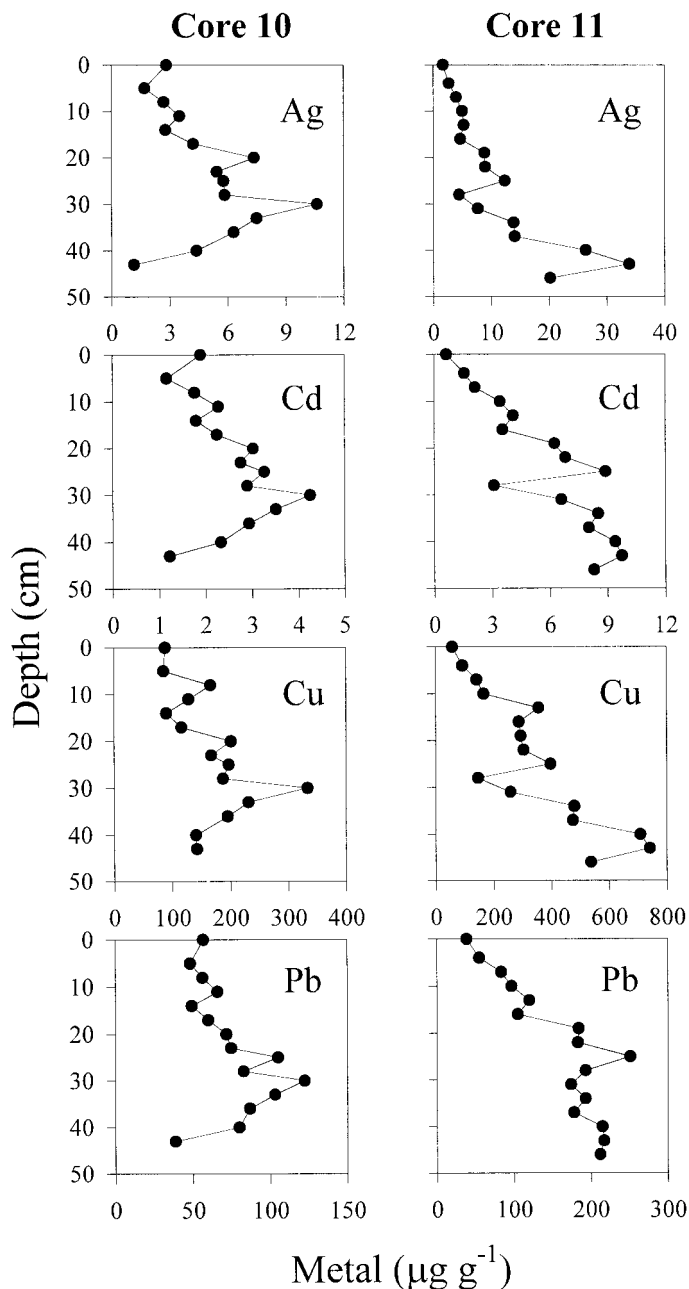


Fig. 10. Example trace metal distributions in channel cores. Depth profiles are characterized by deep maxima, with gradual declines toward the surface.

Approximately 13% of New Haven Harbor is allocated to shipping channels, turning basins, and berthing areas. Although all other terms of the mass balance were based on data for a specific year (1995–1996), the dredging term reflects an average based on data for the previous 15 yr. Over this same time period, other terms may have changed substantially. Still, because of its episodic nature, this approach gives a more representative sense of the importance of dredging over the long term. It is important to bear in mind that dredging data are not completely comparable to other terms in the mass balance. Dredging did not occur during

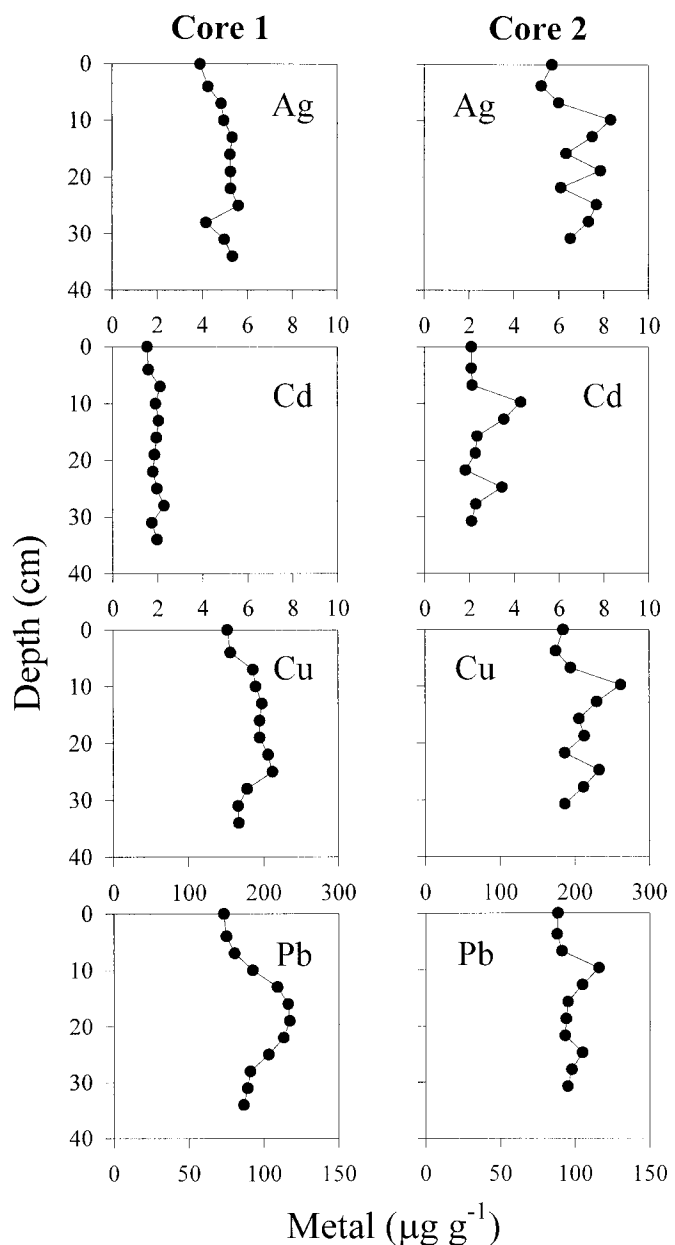


Fig. 11. Example trace metal data from undredged areas outside of the harbor's western lobe. Depth profiles tend to be nearly constant or irregular with depth.

the year covered by this mass balance and is included only for comparison purposes.

Error analysis—In the following, standard propagation-of-error methods (Taylor 1982) were used to combine uncertainties of the various measurements that were brought together in calculation of final sources and sinks.

Atmospheric deposition: Terms in the mass balance other than riverine input and losses to burial were relatively low, so higher relative uncertainty has a smaller influence on the overall balance. Uncertainties for atmospheric deposition were calculated on the basis of the regressions used to derive

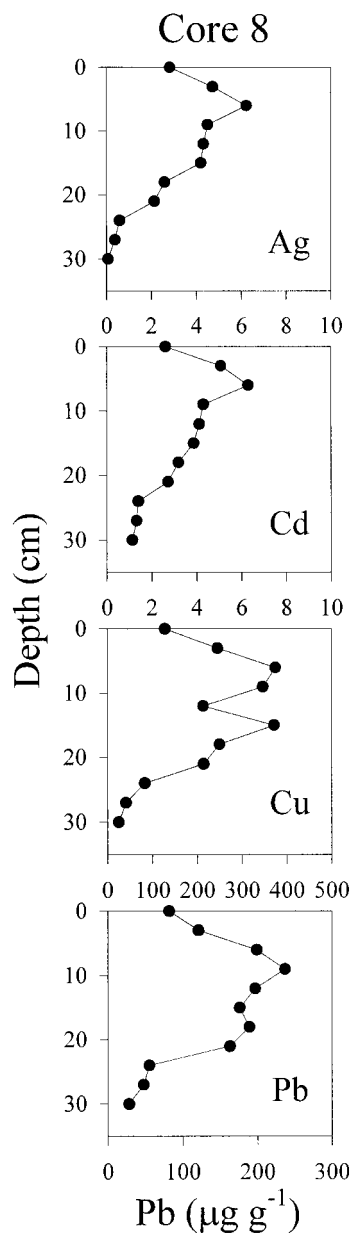


Fig. 12. Example trace metal data in a core from the western lobe. Metals have a near-surface maximum and decline toward the surface. Radionuclide data show that the core is not mixed, so surficial sediments should reflect recent inputs.

sediment accumulation rates and focussing factors, whereas uncertainty in measurement of metal concentrations was judged to contribute a negligible part of the overall uncertainty. The uncertainty of the ^{210}Pb data was based on statistical analysis of a regression over several data points in each core, so it was well characterized. Metal concentrations showed a smooth distribution in near-surface sediments, and uncertainty in this term was assumed to be negligibly small. In any event, atmospheric deposition ended up to be one of the smallest terms of the mass balance, so its uncertainty was not critical.

Rivers: Rivers were an important source in the mass bal-

Table 3. Summary of sedimentary data. Uncertainties on sediment accumulation rates are based on standard errors of regressions for ^{210}Pb (c.i.c. model) and the finite thickness of the depth increment containing the ^{137}Cs peak, known to occur in 1963. When both methods yielded rates, their uncertainties were combined by standard propagation of error methods.

Core	Type	Area		Sediment accumulation		Source
		(ha)	(%)	Rate (cm yr^{-1})	Uncer	
1	Undredged	16.7	2.5	0.89	0.12	Core 1 and duplicate
2	Undredged	11.7	1.8	1.41	0.25	Core 2 and duplicate
3	Undredged	25.5	3.8	0.78	0.05	Core 3 and duplicate
4	Undredged	42.8	6.5	1.31	0.05	Core 4 and duplicate
5	Undredged	65.4	9.9	0.91	0.27	Core 5
6	Undredged	52.1	7.9	1.98	0.20	Core 6
7	Undredged	56.7	8.6	0.31	0.03	Core 7
8	Lobe	30.8	4.6	0.27	0.02	Core 8
9	Channel	2.4	0.4	3	0.6	Dredging records
10	Channel	5.3	0.8	3	0.6	Dredging records
11	Channel	19.6	3.0	3	0.6	Dredging records
12	Channel	9.0	1.4	3	0.6	Dredging records
13	Lobe	101.2	15.3	0.11	0.002	Core 13
14	Channel	24.8	3.7	3	0.6	Dredging records
15	Undredged	58.1	8.8	1.08	0.20	Average of cores 1–7
16	Channel	25.9	3.9	3	0.6	Dredging records
17	Undredged	36.0	5.4	1.08	0.20	Average of cores 1–7
18	Lobe	79.3	12.0	0.19	0.08	Average of cores 8 and 13
	Total	663	100			

ance and were studied in detail. Consequently, the uncertainty of this term was well characterized. Uncertainty was based on the standard error of the regression of metal concentration on discharge. Uncertainty in the daily discharge values, gauged directly by the US Geological Service, was judged to be small compared with the ~20% uncertainty of the concentration regressions.

Removal by salt marshes: Metal removal in the marsh

Table 4. Metal mass balance for New Haven Harbor, Connecticut. Negative values mean that metals were lost from the harbor. Uncertainties were calculated as described in the text.

	Ag (kg yr^{-1})	Cd (kg yr^{-1})	Cu (kg yr^{-1})	Pb (kg yr^{-1})
$\Delta\text{S} + \text{Burial}$	-100	-54	-3700	-1970
\pm	5.9	3.0	210	107
Tides	-17.1	-18.2	-790	320
\pm	5.5	8.9	230	160
Wetlands	-38	-7	-810	-250
\pm	3.2	1	82	23
Rivers	147	122	5300	1330
\pm	28	35	1280	240
Atm Dep	1.1	4.6	179	153
\pm	0.17	0.57	27	21
STPs	21.5	5.7	270	94
\pm	3.5	2.3	70	12
CSOs	3.7	0.26	51	61
\pm	0.7	0.06	18.5	20
Industry	0	0	0.37	0
\pm				
Unknown	-18	-54	-580	267
\pm	29	36	1320	310

varies both in time (e.g., varying freshwater inputs) and space (e.g., lateral distance along the main river channel). Short-term temporal variability was eliminated by measuring the metal inventories in the surficial layers of the marsh, which integrate varying conditions over several years. Spatial variability was quantified by measuring a large number of cores and then calculating the regression of metal inventory on downstream distance. Differences between measured inventories and those predicted by this regression provide an indication of the uncertainty of the removal term (i.e., the difference between the real system and the model used). The linear regression produced was very significant ($n = 34$, $P < 0.001$) for all metals, and the standard error of the regression was of the order of 10%. The regression-based error estimate for the metal flux in Table 4 reflects the uncertainty for the metal concentration in the sediment. All other factors were assumed to contribute negligible error.

STPs: The contribution of metals by STP effluent was easily quantified. The strong correlation of metal concentration with discharge and the availability of continuous flow data provided an accurate flux measurement. The uncertainty of the value for STP loading was based on the standard error of the regression of metal concentration on discharge. The discharge values themselves, which are measured by the STP operators, were assumed to contribute negligible error to the result.

CSOs: Unlike STP effluent, CSO input was difficult to estimate because of the lack of continuous discharge data and inherent variability in the metal concentrations caused by changing proportions of sewage and urban runoff. In addition, because of reliance on the simple, categorical method described earlier, metal concentration estimates were subject

to significant error. In each case, individual storm overflows were correlated with the closest measured category. However, with use of this simplified categorical system, the uncertainty associated with CSO discharge in a particular category could still be quite high. This large uncertainty is a result of both the small number of categories and also the limited number of storms ($n = 9$) used to generate the categorical predictions. In the end, CSOs proved to be among the most difficult terms to predict reliably in relation to the amount of analytical effort expended. Fortunately, this term was also one of the smallest in the mass balance.

Tidal exchange: Tidal exchange with Long Island Sound was among the largest terms with substantial uncertainty. Concordance of metal concentrations at different water depths and smooth variations over the tidal cycle (Fig. 7) attest to the good quality of measurements. The uncertainty is due to (1) the real variability of the flux, which our monitoring shows to be substantial from one tidal cycle to the next; (2) the small difference between metal concentrations in flood and ebb tides; and (3) lack of detailed information on variations in flow over time. The listed uncertainty (Table 2) for this term is simply the variance for the four measured tidal cycles. With such a small sample, it is quite possible that the uncertainty is under- or overestimated substantially. Because most of this variability is real, increased monitoring would almost certainly reduce uncertainty. It would be especially desirable to have additional measurements during storm events, when conditions may be very different, but these are difficult to achieve logistically. An alternative being considered is to continuously monitor turbidity (as a surrogate for particulate matter) with an automated water quality system and to rely on a correlation between suspended matter and metals to improve reliability of this term. Finally, direct flow measurements combined with the temporally varying concentration data would be preferable to calculations based on total tidal volume.

Burial: This was one of the largest terms of the mass balance. The spatial variability of metals in the sediments of New Haven Harbor (Figs. 10–12) was more complex than that for the marsh (Fig. 5), perhaps because of the multitude of localized inputs (three rivers, an STP outfall, several CSOs, and tidal exchange with Long Island Sound), sediment removal by dredging, and natural variability of harbor sediments. In an effort to accurately characterize the heterogeneity of the harbor sediments, a total of 22 cores were collected, of which 13 were dated. No simple pattern was evident in the data, except that locations in the western lobe or near the mouth of the harbor had low sediment accumulation rates ($\approx 0.3 \text{ cm yr}^{-1}$) and those in the rest of the harbor were higher ($\approx 1 \text{ cm yr}^{-1}$). For this reason, each polygonal region was treated separately. Uncertainties were determined for each area, and they were then combined (in quadrature; Taylor 1982) to yield a total value.

The calculated uncertainty was based on propagation of the error associated with calculating sediment accumulation rates. This is a combination of the standard error of the regression used in the ^{210}Pb analysis (constant initial concentration model; Krishnaswami et al. 1971) and the uncertainty of the ^{137}Cs -derived rate (a function of the sampling interval

size). The error associated with other factors, including measurement of metal concentrations, bulk densities, and sediment areas were all assumed to provide negligible error compared with sediment accumulation rate.

Discussion

In examining the final mass balance (Fig. 3 and Table 4), important similarities and some differences are evident when comparing the four metals. Foremost, the balance can be approximated as an equilibrium between metals delivered by rivers and those deposited in sediments, either in the harbor or its salt marshes. Other sources and sinks tend to be minor, including loss to Long Island Sound in tidal waters. This means that the harbor acts as an efficient trap of metals and acts to protect the Sound from contamination. Indeed, for Pb, the harbor seems to act as a net sink for metal in the Sound, because the data indicate a positive flux (i.e., from the Sound to the harbor).

Relative size of sources and sinks—For most metals, the sources in order of magnitude are Rivers \gg Atm. Dep. \approx STPs $>$ CSOs \gg Industry. Sinks typically occur in the order Sediments \gg Tides \approx Wetlands. Perhaps most surprising in this sequence is that sewage effluent is so low in relation to rivers and even atmospheric deposition in some cases. The rivers in this instance do *not* represent mainly indirect contributions from sewage treatment plants. Although there are five STPs that discharge to the Quinnipiac River, they serve a combined population that is smaller than that which contributes to the New Haven regional plant that we measured. Instead, metals in the Quinnipiac River are from nonpoint sources: contaminated bank and floodplain deposits (Benoit 1994). These metals originated from metal plating and fabricating industries that thrived in the Quinnipiac valley from the middle of the last century until World War II. They have left a legacy of pollution whose effects are still clearly measurable. Nevertheless, the Quinnipiac River is not unique, at least regionally. Metal levels in the nearby Naugatuck River are at least as high as those in the Quinnipiac (Rozaan 1998).

The delivery of metals by the river represents a rather small fraction ($\sim 10\%$) of atmospheric deposition to the Quinnipiac's watershed. Still, we are confident that this is not the ultimate source for most riverine metal, for three reasons. First, Benninger (1978) has shown, using ^{210}Pb , that much less than 1% of atmospherically delivered metals are exported annually by Connecticut rivers. Second, we have measured greatly elevated metals in the floodplains of the Quinnipiac River below the city of Meriden, and this matches where metals in the river increase (Benoit 1994). Third, one would expect most rivers in Connecticut to carry comparably high amounts of metals if regional atmospheric deposition were the source, and this is not the case.

Perhaps more surprising than the relative size of riverine and sewage inputs is that atmospheric deposition rivals (in the case of Cd and Cu), and sometimes exceeds (Pb), treated sewage as a source. This is in clear contrast to earlier times, when New Haven had only primary treatment and STPs were clearly the major source to the harbor (Applequist et al. 1972). The current condition seems to be a consequence

of the very effective removal of metals in modern secondary treatment plants (Shafer et al. 1999). It is striking how low total concentrations of metals are from this source. As an example, all of the sewage samples we collected were well below the *drinking* water standard for Pb.

Source of Long Island Sound metals—The apparently low natural (nondredging) export of metals in tidal waters raises the question of the source of elevated metals in the sediments of Long Island Sound. Surveys show that these metals occur at higher levels than can be accounted for by atmospheric deposition alone (Mecray and Brink 2000), and there is a suggestion that concentrations are higher near contaminated harbors than surrounding locations. Several possible mechanisms might explain this observation.

The simplest possibility is that our measurements of tidal losses are biased low. The unaccounted-for loss terms for Ag, Cd, and Cu may, in fact, be tidal. This additional export could then contribute to Long Island Sound sediments.

Another potentiality is that metals are added mainly directly from sewage treatment plants in the New York City region. It is known that this is the primary source of contaminant N to the Sound, for example. Metals could then be redistributed in fine sediments throughout the basin. Such internal cycling has been hypothesized elsewhere (Mecray and Brink 2000) without specifically identifying sources.

A third prospect is that metals were mainly added in the past, when effluent treated only to primary standards were added to the harbor and when industrial inputs were much greater than today. The much greater flux, different form, and probably lower proportional level of removal in marshes (they are upstream from the harbor) may have allowed a much greater fraction to be exported with tides in the past.

Uncertainties of individual terms—Considering mass-balance terms individually, two stand out as having large uncertainties, either absolutely or in comparison to their size: Tides and Rivers. The tidal error is roughly half of the tidal source/sink's calculated size, rendering the magnitude and even sign of this term suspect. Reducing the uncertainty of Tides would require measurement of additional tidal cycles (especially those that occur in conjunction with storm events).

The absolute magnitude of the riverine uncertainty is large compared with other mass balance terms, although not relative to riverine inputs themselves. This means that, whereas the riverine input is adequately characterized, it contributes in a major way to the uncertainty associated with closure of the mass balance. The scatter of metal concentrations around the regression on discharge (Fig. 4) is in large part a consequence of the asymmetrical link between discharge and suspended particulate matter; the ascending limb of storm hydrographs carries more suspended particulate matter (SPM) and associated metals than does the descending limb. Indeed, the correlation between metal concentrations and SPM is stronger than that with discharge, but only the latter is monitored continuously, as is required for the mass-balance calculation. As with Tides, improvement might be obtained by continuously monitoring turbidity with an automated water quality meter. Turbidity could then be used to

estimate particulate matter (Suk et al. 1999) and metals with lower uncertainty.

Mass-balance closure—The unknown term (or closure of the mass balance) is shown on the far right of the four plots of Fig. 3. For three of the metals (Ag, Cd, and Cu) it is negative (a sink is missing or underestimated or a source is overestimated), whereas for Pb it is positive. For Ag, Cu, and Pb, this term is <1 SD different from 0, and for Cd it is much less than 2 SD different from 0. Thus, the mass balance closes within the uncertainty of the measurements given the conventional probability threshold of 0.05.

Despite successful closure of the mass balance, the Unknown term is undesirably large compared with several of the other values in the mass balance, especially for Cd. It seems unlikely that there is actually an unknown source or sink of this magnitude. Instead, the unknown term probably reflects errors in estimation of the known sources and sinks. Improvement would most likely be achieved by decreasing the uncertainty of either the tidal or riverine fluxes. If the tidal term is the main problem, tides must currently be underestimated. Interestingly, this is true across metals, even though the tidal flux changes sign among metals (Ag, Cd, and Cu vs. Pb), because this is in the same sense as the resultant mass balance closure error in every case. Such an underestimation seems plausible, because storm events were not sampled, and these are likely to result in greater transport of sediments and metals. As was described earlier, the riverine input is believed to be somewhat of an underestimate because of storm-related biases. If this is in fact the case, it actually exacerbates the mass balance closure problem for Ag, Cd, and Cu, although it helps for Pb. On this basis, we believe that tides, rather than rivers, constitute the main existing question.

Minimizing closure error is best achieved by devoting greatest measurement resources to the largest terms of a mass balance. Unfortunately, these are not always known a priori. For example, conventional wisdom would have favored placing great emphasis on STPs and little on rivers, but that strategy would have been a mistake in this instance.

We found that uncertainty was lowest for components where natural collectors were available that integrated the short term variability of fluxes (e.g., wetlands, sediments, and lakes). Next best were terms where simple relationships could be established between the magnitude of fluxes and some easily measurable parameter, like discharge (e.g., rivers and STPs). Most problematic were terms that lacked integrating collectors and were variable in apparently nonsystematic ways (e.g., tides and CSOs).

Management implications—The Unknown terms fall within the combined uncertainty of the mass balance and attest to the fact that the tidal exchange term, although uncertain, at least has the correct order of magnitude. Lacking further data, it is still impossible to say with certainty whether the harbor supplies metals to Long Island Sound or vice versa. It is clear that the quantity of metals that reach the Sound from the harbor is much smaller than the sum of inputs to the harbor. In other words, under present condi-

tions, New Haven Harbor does act to prevent substantial metal loading to Long Island Sound.

People bypass this protective capability when they dredge the harbor and deposit the spoils in Long Island Sound, as occurs every ~15 yr. Our calculations suggest that this periodic dredging flux, averaged on an annual basis and across the four metals measured, is on the order of 30% of total sources to the harbor. This number is similar in magnitude (although larger by about a factor of two) to current natural tidal exchange fluxes. Comparing it with some of the sources, dredging is comparable to 35% of the riverine inputs to the harbor or 520% of the STP inputs. Dredging and disposal of dredged material are thus significant components of metal fluxes within this harbor. Perhaps the main reason that dredging is not of even greater import, when expressed on an average annualized basis, is that the portion of the harbor that is dredged is a minor fraction of the total area (~13%).

Sewage treatment plants have often been implicated as key contributors of metals and other contaminants to aquatic environment (Hubbard and Hashim 1987; Seidemann 1991; Buckley and Winters 1992; Bricker 1993; Voutsinou-Taliadouri and Varnavas 1995; Bricker 1996). In this study, STP effluent was dwarfed by riverine inputs. Although there are five additional STPs in its watershed, our measurements (Benoit et al. unpubl. data) reveal that nonpoint sources rather than STPs are currently responsible for most of the Quinnipiac River's metal burden. The relatively small contribution from STPs compared with past times may reflect the higher level of treatment (secondary vs. primary) mandated by existing regulations. Whatever the cause, we can state unquestionably that further improvement of sewage treatment to remove greater quantities of metals would have a trivial effect on total metal loading in New Haven Harbor.

Being able to establish the relative quantitative significance of each source and sink is an important step in the establishment of management strategies for estuarine systems. Decision makers need to be able to know how various options will affect the overall contaminant balance. Clearly, on the basis of the results of this study, there is little point in targeting reduction of metal releases from the STP, except perhaps for effects in the immediate vicinity of the effluent outfall. Past contamination of the watershed of the Quinnipiac River (Benoit 1994; Rozan et al. 1994) has left a legacy of metal pollution that continues to be released as a major, and largely uncontrollable, nonpoint source.

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