

Final Report

A Synthesis and Assessment of Modern and Historic Heavy Metal Contamination in New York/New Jersey Harbor Estuary with Emphasis on Hg and Cd

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Principal Investigators

William F. Fitzgerald and Robert P. Mason

***Department of Marine Sciences,
University of Connecticut, Groton, CT 06340***

Synthesis and Assessment of Heavy Metal Contamination in the Hudson River and New York/New Jersey Harbor Estuary

Prentiss H. Balcom, William F. Fitzgerald, Robert P. Mason
*Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road,
Groton, CT USA*

Abstract

The Hudson River and New York/New Jersey Harbor (NY/NJ Harbor) Estuary like many commercially important rivers and coastal regions have endured centuries of contamination, especially from heavy metal wastes. In general, current and longer-term environmental assessments, predictive modeling, and development of sage management strategies require improved understanding of trace metal biogeochemistry and a historical perspective in coastal and estuarine regions such as the anthropogenically impacted Harbor estuary. Indeed, and over the past 30 to 40 years, there has been considerable research and monitoring on a variety of trace metals in the Harbor. However, there has been limited vetting, interpretation, and synthesis of information in this potentially valuable but diverse and uneven database. Accordingly, we are providing an up-to-date synthesis and assessment of heavy metal contamination for this important urban-industrialized estuarine system.

We examined the distribution and cycling of trace metals (Hg, monomethylmercury [MMHg], Cd, Pb, Cu, Ni, and Zn) in the water column and sediments of the Hudson River and NY/NJ Harbor. This synthesis and assessment involved characterizing distributions of filtered, total, and suspended particle phases of metals, evaluating processes affecting the water column partitioning of metals species, and formulating contemporary mass balances for NY/NJ Harbor. There have been dramatic reductions (typically >80%) in the concentrations of filtered and total metals in the Lower Harbor and NY Bight since the mid-1970s. Our budgets indicate that total inputs of Ni, Cu, and Zn to NY/NJ Harbor have decreased by a factor of 1 to 5.5 as compared to the mid-1970s, while Cd has decreased by a factor of 8 to 24 over the same time period. Assessing long-term trends in Hg inputs/accumulations in the Harbor environs is difficult due to the lack of historic data. Nevertheless, and while there is substantially more contaminant Hg accumulating per unit area of NY/NJ Harbor as compared to the Pettaquamscutt River Estuary, in Rhode Island (whose watershed is rural/residential), a decline in Hg inputs (since the mid-1960s) of a factor of 3-5 is likely.

Keywords: mercury, cadmium, heavy metals, estuaries, rivers, suspended particulate matter

Regional Terms: USA, New York, New York/New Jersey Harbor, Hudson River

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1.0 Introduction

The Hudson River and New York/New Jersey Harbor (NY/NJ Harbor) Estuary represent a large, urbanized river-coastal system that is among the world's most important commercial and recreational coastal resources. Significant shoreline and watershed industrialization has been a long term source of contaminants, both organic (e.g., PCBs) and inorganic (e.g., Hg, Cd, Pb, Ag), which has led to an overall degradation of the ecosystem (Steinberg et al., 2004). This work is focused on heavy metals, their biogeochemical cycling, current and past sources and sinks, and modern day anthropogenic impact and its magnitude relative to the past 30 to 40 years. That is, we have undertaken the substantial scientific challenge of assessing the change in heavy metal inputs, recovery/residence times, and their effects in the dynamic, heavily-used and anthropogenically impacted NY/NJ Harbor Estuary. For example, and more generally, the biogeochemistry of toxic metals is not well studied in estuaries and coastal regions, and despite the order-of-magnitude reductions in point-source inputs since implementation of the Clean Water Act (1972; Sañudo-Wilhelmy et al., 2004), elevated levels of metals persist in some urban estuaries. Sediment and biota in the Hudson River watershed contain elevated levels of metals and other contaminants (Wolfe et al., 1996; Adams et al., 1998; Steinberg et al., 2004), and many locations have sediment metal concentrations that exceed toxicity benchmark values. Although levels of dissolved Cd, Cu, Ni, and Zn have declined in the water column of the Hudson River Estuary since the 1970s, they remain some of the highest ever reported in the United States, and Hg in this estuary continues to exceed current state and federal water quality standards (Sañudo-Wilhelmy et al., 2004).

The impetus for the current study was the need to synthesize published work on the biogeochemical cycling of metals in the Hudson River and NY/NJ Harbor Estuary, and to

critically evaluate the considerable data available in databases that required synthesis and interpretation. For example, several studies have examined the distribution of total and dissolved metals (e.g., Hg, Cd, Pb, Zn, Ni, Cu, Mn, Fe) in the lower Hudson and upper NY/NJ Harbor (e.g., Yang and Sañudo-Wilhelmy, 1998; Sañudo-Wilhelmy and Gill, 1999), or produced mass balance estimates for the lower Hudson River Estuary (Klinkhammer and Bender, 1981; Yang and Sañudo-Wilhelmy, 1998). Feng et al. (2002) and Heyes et al. (2004) studied the transport and sources of metal contaminants in the turbidity maximum of the Hudson River Estuary. Paulson (2005) and Balcom et al. (2008) investigated the sources and distribution of metals in NY/NJ Harbor, and Buck et al. (2005) assessed the distributions and mass balances of dissolved metals in the East River-Long Island Sound system. In addition to the published literature, information on metals and other contaminants in the Hudson River and NY/NJ Harbor is summarized in a variety of reports (e.g., Adams et al., 1998; Fitzgerald and O'Connor, 2001; De Cerreno, 2002; Boehme and Panero, 2003; Steinberg et al., 2004), is available from on-line databases (e.g., USGS, 2008; EMAP, 2008) and CD-ROM (CARP, 2007), or is available upon request from State agencies (e.g., NYSDEC State Waters Monitoring Section [SWMS], 2006).

A primary goal of this effort was to provide a synthesis and assessment of water column and sediment metals data available for NY/NJ Harbor and the Hudson River. As mentioned, given the extensive body of information available from reports, data bases, and published literature, synthesis of existing data is warranted. We have examined the distribution and biogeochemical cycling of trace metals (Hg, monomethylmercury [MMHg], Cd, Pb, Cu, Ni, and Zn) in the water column and sediments of NY/NJ Harbor and the Hudson River, and utilized these results to formulate and constrain contemporary mass balances for the Harbor. Our principal objectives were (1) to characterize the distribution of filtered, particulate, and

suspended particle phases of metals (emphasis on Hg and Cd) in waters throughout the major regions of NY/NJ Harbor and the Hudson River, and to compare contemporary results with those obtained in the 1970s; (2) to provide a first-order evaluation of the major processes affecting water-column distributions and partitioning of metal species (emphasis on Hg and Cd); and (3) to assess the relative strengths of the major sources (rivers, water pollution control facilities [WPCFs], atmospheric deposition, sediment–water exchange) and sinks (burial, exchange with the continental shelf, evasion) of metals in the Harbor.

1.1 Major recent distributional features are as follows:

- 1.1.1* Average total (filtered + particulate) concentrations of Hg (58 to 130 pM), Cd (0.97 to 1.3 nM), other metals, and total suspended solids (TSS) in middle and upper Hudson River (Poughkeepsie to Waterford, NY) surface waters are elevated at Poughkeepsie.
- 1.1.2* Fe-normalized suspended particle concentrations of Pb, Cu, Ni, and Zn were elevated in the upper Hudson at Waterford and Cohoes as compared to Poughkeepsie, indicating watershed sources of trace metals.
- 1.1.3* In the estuarine turbidity maximum (ETM), average total Cd concentrations (0.74 to 1.2 nM, surface waters) are similar to the middle and upper Hudson sites, while average total Hg (54 to 1110 pM, surface and bottom waters) is elevated as compared to the rest of the upper Hudson.
- 1.1.4* The filtered fraction of Cd increases dramatically with salinity (83 to 120% of total Cd) in the lower Hudson River, and higher total Hg and Cd levels are associated with spring high flow periods.
- 1.1.5* Average surface water suspended particle concentrations of Hg (2.20 to 3.54 nmol g⁻¹) and Cd (5.45 to 12.6 nmol g⁻¹) are largely overlapping between the ETM and lower Hudson, but ETM and upper Hudson suspended particle metals concentrations are elevated as compared to the middle Hudson (Poughkeepsie).
- 1.1.6* Average total Hg (145 and 433 pM, surface and bottom waters) and Cd (0.97 and 1.35 nM) concentrations at the mouth of the Passaic River were elevated as compared to the Hudson ETM, while only total Hg (109 pM) was elevated at the mouth of the Hackensack River, and concentrations in the lower East River and the Raritan River were similar to levels in the Hudson ETM.

- 1.1.7* Average suspended particle Hg (9.8 to 20.8 nmol g⁻¹) and Cd (9.6 to 49.2 nmol g⁻¹) concentrations were elevated in both the Hackensack and Passaic as compared to the Hudson, although suspended particle Cd was less near the mouths of rivers.
- 1.1.8* Regional average trace metal concentrations of Hg (3.2 to 166 pM) and Cd (0.19 to 0.90 nM) in NY/NJ Harbor were generally elevated and more variable near the input of major rivers in Newark Bay and the Upper Harbor, roughly corresponding with elevated TSS levels.
- 1.1.9* Harbor Hg and Pb were mainly in the particulate phase, while Cd, Cu, and Ni have more metal in the dissolved fraction at elevated Harbor salinities. There was good agreement between average suspended particle concentrations of Hg (1.1 to 8.7 nmol g⁻¹), Cd (3.1 to 13.2 nmol g⁻¹), and other metals with surface sediment concentrations in the Harbor, while suspended particle concentrations in the ETM were elevated as compared to sediments.
- 1.1.10* Al- and Fe-normalized suspended particle metal concentrations were reduced in the Hudson ETM and elevated in Raritan Bay and at the Rockaway-Sandy Hook transect suggesting metals enrichment due to association with fine particulate material or particulate organic matter.
- 1.1.11* Current annual loadings to NY/NJ Harbor have been estimated for Hg (3100 mol y⁻¹), MMHg (37 mol y⁻¹), Cd (25 Kmol y⁻¹), Pb (850 Kmol y⁻¹), Ni (1700 Kmol y⁻¹), Cu (2800 Kmol y⁻¹), and Zn (7100 Kmol y⁻¹); the majority of inputs are from rivers (38 to 88% of totals). Total inputs are significantly decreased for Cd (8 to 42x), Ni (2 to 5.5x), Cu (1.5 to 3.5x), and Zn (1 to 4x) since the mid 1970s (25 to 30 years) along with the relative contribution of metals from sewage. Hg inputs are likely to have declined by about a factor of 3-5 since the mid-1960s.

2.0 Methods

As indicated above, the data summarized and evaluated in this manuscript have been derived from a variety of literature sources and databases. Peer-reviewed, published literature was evaluated for appropriateness of the analytical methods and complete presentation of quality assurance/quality control (QA/QC) procedures and results. Metals data obtained from databases (e.g., CARP, 2008; EMAP, 2008), regulatory agencies (e.g., NYSDEC State Waters Monitoring Section [SWMS] and Division of Water), and reports (e.g., Adams et al., 1998) were given

priority in our synthesis if collections and analyses were conducted by contract laboratories that incorporated QA/QC codes and comments.

2.1 Sources of data

2.1.1 Middle and Upper Hudson River

CARP (2007; Hg and Cd, collected 1999-2001) and the NYSDEC SWMS (2007; Pb, Cu, Ni, Zn, collected 1993-2006) have reported surface water concentrations of metals in the middle and upper Hudson and Mohawk Rivers. Upper Hudson (above the dam at Troy, NY) SWMS sampling sites included Waterford (Hudson R.) and Cohoes (Mohawk R. where it enters the Hudson below Waterford) above Albany (NY; Figure 1), and middle Hudson (north of Newburg, NY and south of Albany, NY) SWMS sites included Poughkeepsie (in the tidal portion of the Hudson) and Glenmont (near Albany, NY; station coordinates are given in the caption to Figure 1). CARP sampling sites included Waterford, Cohoes, Poughkeepsie, and a site between Kingston (NY) and Poughkeepsie. Suspended particle metal concentrations were calculated from the difference between total and filtered metals concentrations (total metal only for Zn) and total suspended solids (TSS). The Hg and Cd data reported by the SWMS for the middle and upper Hudson were not used because there were frequent cautionary QA/QC codes such as “below detection limits.”

2.1.2 Lower Hudson River

CARP (2007; Hg and Cd; collected 1999-2001) and several literature studies (Klinkhammer and Bender, 1981 [collected Apr. 1974 and Oct. 1975]; Sañudo-Wilhelmy and Gill, 1999; Yang and Sañudo-Wilhelmy, 1998 [collected Oct. 1995/1996 and Apr. 1996/1997]; Heyes et al., 2004 [collected Oct. 2000 and Feb./June/Nov. 2001]) have reported surface and deep water concentrations of metals (Hg, Cd, Cu, Fe, Ni, Zn, Ag, and Pb) in the lower Hudson

River (south of Newburg, NY; ~25 to 100 km north of the Battery) and the estuarine turbidity maximum (ETM; south of the Harlem River; ~ 4 to 25 km). In this study, the lower Hudson is defined as that portion of the river downstream of Newburgh (NY). The lower Hudson CARP sampling station was between the Harlem River and the Tappan Zee Bridge, the ETM site was south of the Harlem River (station coordinates are given in the caption to Figure 5). In the literature studies, samples were collected at various sites/salinities between the Battery (southern tip of Manhattan; site coordinates are given in the manuscripts) and Newburgh, NY (~100 km upstream). Heyes et al. (2004) examined total and filtered Hg concentrations in the ETM (~4 to ~25 km) only. Suspended particle metal concentrations were calculated as described for the middle and upper Hudson (section 2.1.1). Feng et al. (2002; all metals except Ni and Hg), and Heyes et al. (2004; Hg only) reported suspended particle concentrations of metals in the ETM.

2.1.3 Major rivers

CARP (2007) reported filtered and total Hg and Cd concentrations near the mouths of the Hackensack, Passaic, lower East (collected Feb. 1999 to Oct. 2000) and Raritan Rivers (collected Mar. 2001 to Apr. 2002) where they enter NY/NJ Harbor, and measurements from mid-tidal locations (roughly half the geographic distance of salt water intrusion) were available for some rivers as well. Filtered and total Cd data for several sites in the Raritan River were obtained from Paulson (2005; collected Aug. 1999). Again, suspended particle concentrations were calculated as described in section 2.1.1.

2.1.4 New York/New Jersey Harbor

CARP (2007; Hg and Cd; collected 1999-2001), Balcom et al. (2008; Hg and MMHg; collected 2002-2004), and a study by Paulson (2005; Cd, Pb, Cu, Ni, and Zn [particulate only]; collected Aug. 1999) have reported surface and deep water concentrations of metals in major

regions of NY/NJ Harbor (Newark Bay, Upper Harbor, Raritan Bay, Lower Harbor, and Jamaica Bay). The measurements made by Paulson (2005) were separated into Upper Harbor, Raritan Bay, and Rockaway-Sandy Hook regions for this study. Suspended particle Hg, Cd, and MMHg concentrations were calculated from the difference between total and filtered metals concentrations and total suspended solids (TSS; CARP, 2007). Paulson (2005) measured water column suspended particulate metal concentrations directly. Surface sediment metals concentrations (Hg, Cd, Pb, Cu, Ni, and Zn) from the USEPA Environmental Monitoring and Assessment Program (Adams et al., 1998 [collected Aug. to Oct. 1993 and July to Sept. 1994]; EMAP, 2008 [collected June to Aug. 1998]) were summarized for Jamaica Bay, Raritan Bay, the Lower and Upper Harbors, and Newark Bay. Cu was measured in 1993/1994 only (Adams et al., 1998). Within each region, some of the sediment metals results reported by EMAP were not included in the evaluation since data was selected to correspond to the same geographical regions as the water column data (e.g., East River results were not included with the Upper Harbor).

3.0 Synthesis and Discussion

3.1 *Distribution of metals in the middle and upper Hudson River*

3.1.1 *Filtered metals*

Among middle and upper Hudson sampling stations (Poughkeepsie, Kingston-Poughkeepsie, Glenmont, Waterford, and Cohoes), the average concentrations in filtered waters ranged from 5.6 to 9.5 pM for Hg and 0.08 to 0.14 nM for Cd (CARP, 2007). NYSDEC SWMS (2007) measurements ranged from 3.4 to 3.9 nM for Pb, 12 to 18 nM for Ni, 28 to 150 nM for Cu, and 68 to 89 nM for Zn (Figure 2). Average concentrations of filtered metals were, in general, uniform and not related to upstream distance in the Hudson River, but Cu was clearly

elevated at Poughkeepsie (150 nM; ~125 km upstream from the Battery; Figure S1 [supporting information]). For most of the metals in the middle and upper Hudson, the average percentage in the dissolved phase remained relatively constant among sampling sites, although 65% of total Cd was in the dissolved phase at Kingston-Poughkeepsie, which was high as compared to Cd at the other sampling sites (Figure 2). Filtered metal concentrations did not seem to be related to season (e.g., spring runoff), as concentrations in April and early May (e.g., 125 ± 71 nM Cu at Poughkeepsie; mean \pm SD; 1993-2006) were similar to concentrations measured during the other months of the year (e.g., 152 ± 70 nM Cu at Poughkeepsie). Additionally, filtered metals were not well correlated with parameters such as filtered Al (an indicator of weathering and watershed leaching) or total dissolved solids (TDS) at any of the sampling sites. This suggests that filtered concentrations are controlled more by partitioning than by the strength of inputs, and likely reflect the relative constancy of surface sediment concentrations and TSS over time.

3.1.2 Total metals and suspended particulate matter

Rivers are the largest source of the sediment entering NY/NJ Harbor (~80%), with the majority originating from the Hudson and the Mohawk (Steinberg et al., 2004). Average TSS concentrations were relatively uniform at Glenmont (13.4 mg l^{-1}), Cohoes (12.1 mg l^{-1}), and Waterford (9.6 mg l^{-1}), as were the unfiltered concentrations of most of the metals, but TSS was increased to 49.2 mg l^{-1} at Poughkeepsie (NYSDEC SWMS, 2007; Figure 2). There were corresponding elevations in average total (dissolved + particulate) Hg, Cu, Ni, and Zn at Poughkeepsie (Figures S2 and S3). In a broad sense, this view of suspended particulate matter and total metals concentrations suggests that TSS is a proxy for total metals, which has been noted in a number of studies of rivers (e.g., Balogh et al., 2005; 2006), and that particle loading and/or resuspension associated with enhanced fluvial discharge are important contributors of

metals to the water column of the Hudson River. However, due to the strong association of TSS with total metals concentrations, and depending on factors such as river flow, these concentrations can vary widely on a day to day basis. Therefore, while the distributions of total metals are important in that they represent the actual amount of metal in the water column, and these concentrations are required to calculate mass balances, this parameter has limited usefulness for elucidating mechanisms of transport and sources of metals.

Similar to the filtered phase, the concentrations of total Cd (0.97 to 1.32 nM; excluding Kingston-Poughkeepsie; CARP, 2007) and Pb (20 to 31 nM; NYSDEC SWMS, 2007) varied little among sampling sites (Figure 2) in the middle and upper Hudson. Particle phase Cd and Pb (64 to 83% of total metal) were high at each sampling site (see Table S1 for K_D values). Total Cd was reduced to 0.19 nM at the Kingston-Poughkeepsie site, however, with only 34% (as noted) in the particulate fraction. In contrast, the concentrations of total Hg (58 to 130 pM; CARP, 2007), Cu (51 to 230 nM), Ni (16 to 44 nM), and Zn (106 to 210 nM; NYSDEC SWMS, 2007) were elevated at Poughkeepsie as compared to relatively uniform concentrations at Glenmont, Waterford, and Cohoes (Figure 2; Figures S2 and S3). In general, total metals concentrations showed little variability among seasons at Waterford and Poughkeepsie (Figures S6 and S7), although stream flow was significantly higher during the spring. While particle phase Hg was dominant at each site (71 to 91% of total metal), the particulate fraction ranged from only 29 to 40% among sites for Cu and Ni (50% of Ni at Poughkeepsie). The percent of total Zn as particulate was not calculated due to the limited measurements of filtered Zn [1993-1996] at each site (NYSDEC SWMS, 2007). Overall, such differences are consistent with the known propensity for the different metals to bind to suspended material, with Hg being the most strongly bound. Other studies in similar ecosystems (e.g. Lawson et al., 2001) have found

similar differences in the fraction of the metal as particulate. Given the importance of the particulate phase in driving total metal concentration, the elevation in total Hg, Cu, and Ni at Poughkeepsie is consistent with an increase in the particulate fraction. For Cu, both filtered and particulate concentrations increased proportionally at Poughkeepsie, suggesting differences in the degree of partitioning between sites.

3.1.3 Suspended particle concentrations

Although concentrations of water column metals generally increased near Poughkeepsie in the middle Hudson, on a mass basis, suspended particle and Fe-normalized suspended particle concentrations of Pb, Cu, Ni, and Zn were highest at Cohoes and Waterford and reduced at Poughkeepsie (Figure 3). Fe is often used to normalize the concentrations of trace metals to reduce the influence of factors such as particle grain size. For each sampling site, average suspended particle concentrations of Zn (6.2 to 22.8 $\mu\text{mol g}^{-1}$; calculated from particulate Zn concentrations only), Pb (0.63 to 7.4 $\mu\text{mol g}^{-1}$), Cu (2.0 to 4.7 $\mu\text{mol g}^{-1}$), and Ni (0.64 to 1.6 $\mu\text{mol g}^{-1}$) all showed a decreasing trend downstream (NYSDEC SWMS, 2007; Figures S1 and S5). Suspended particle molar metal to Fe ratios (mol/mol; assumes that all Fe is in the particulate phase) ranged (averages at each site) from 25 to 40 $\times 10^{-4}$ for Cu, 7 to 20 $\times 10^{-4}$ for Pb, 8 to 16 $\times 10^{-4}$ for Ni, and 71 to 202 $\times 10^{-4}$ for Zn, and showed a decreasing trend from Cohoes to Poughkeepsie (Figure 3; Figure S4). In general, suspended particle metals concentrations showed little variability among seasons at Waterford and Poughkeepsie (Figures S6 and S7). These trends in suspended particle metal concentrations and suspended particle metal to Fe ratios suggest that there are upstream sources of particulate metals to the Hudson River. Sañudo-Wilhelmy and Gill (1999) stated that high levels of dissolved Pb and Hg observed upriver (during the spring flood period) suggested that these metals may be mostly

derived through runoff from the surrounding catchments, and that this was consistent with atmospheric deposition as a principal transport vector. The high upriver concentrations may also suggest historic contamination and long-term inputs from watershed erosion. In many river-estuarine systems (e.g., Sañudo-Wilhelmy and Gill, 1999; Sakata et al., 2006), a continental runoff source for trace elements is supported by concentration covariances with major soil constituents such as Fe and Al.

As discussed above, concentrations of Hg (CARP, 2007) and TSS (NYSDEC SWMS, 2007) are elevated at Poughkeepsie as compared to sites upstream (Figure 2). However, when data for the same time period (1999-2001) from CARP and NYDDEC SWMS are compared (Figure 4), average suspended particle Hg (6.8 to 10.2 nmol g⁻¹) at Waterford and Cohoes was enhanced 3 to 5 times as compared to Poughkeepsie (2.1 nmol g⁻¹). Similarly, upstream suspended particle Cd (10.0 to 14.2 x 10⁻² μmol g⁻¹) were enhanced 4 to 6 times compared to Poughkeepsie (2.2 x 10⁻² μmol g⁻¹), indicating that the upstream sites are likely sources of Hg and Cd to the Hudson. Combining metals data from CARP (2007) with Fe from NYSDEC SWMS (2007; *n* = 17-18; collected 1999 to 2001), average suspended particle molar metal to Fe ratios (mol/mol; assumes that all Fe is in the particulate phase) ranged from 0.3 to 1.2 x 10⁻⁵ for Hg, and 0.31 to 1.61 x 10⁻⁴ for Cd among sites. As for the other metals discussed above, normalized suspended particle metals decreased downstream from Waterford and Cohoes to Poughkeepsie. Upper Hudson total (dissolved + particulate) Hg:Fe ratios (9.2 to 11.6 x 10⁻⁶ mol/mol) are 7 to 8 times higher than a dissolved Hg:Fe ratio (1.4 x 10⁻⁶ mol/mol; Sañudo-Wilhelmy and Gill, 1999) reported for the lower Hudson River and Hudson estuarine turbidity maximum (~4 to 100 km above the Battery), and 18 to 23 times higher than that reported for the upper continental crust (0.51 x 10⁻⁶ mol/mol). Sañudo-Wilhelmy and Gill (1999) indicated that

rather than just weathering processes alone, the elevated total Hg concentrations in the upper Hudson appeared to be related to recent anthropogenic Hg emissions deposited in catchment areas, and the continual additions of these historic inputs to the watershed due to erosion, groundwater inputs, and other on-going sources.

3.2 Distribution of metals in the lower Hudson River

The majority of the published literature on trace metals in the Hudson River estuary (e.g., Yang and Sañudo-Wilhelmy, 1998; Sañudo-Wilhelmy and Gill, 1999; Heyes et al., 2004) deals with the lower Hudson (0 to ~100 km north of the Battery). Analysis of this information required considerable synthesis as the data is for filtered, total, and particulate metal fractions from a variety of locations and water depths.

3.2.1 Filtered metals

Filtered metal concentrations from CARP (2007) and various literature studies have been summarized for the estuary turbidity maximum (ETM; ~4 to ~25 km above the Battery) and the lower Hudson River (~25 to ~100 km; Table 1). The ETM is the region near the mouth of rivers where there is enhanced sediment resuspension due to tidal and river action. Average surface water filtered concentrations for some metals (e.g., Cu, Ni, Hg) at sites in the lower Hudson (Table 1, Figure 5) were similar to the middle and upper Hudson (Poughkeepsie and upstream). However, average filtered Cd (0.43 and 0.67 nM) was elevated, while filtered Zn (18 nM) and Pb (0.95 nM) were reduced (Table 1), in the lower as compared to the upper Hudson. Surface water filtered metals concentrations in the ETM were generally higher than those in the lower Hudson (Table 1; with the exception of Fe and Pb), but there was considerable variability associated with these concentrations (coefficient of variation [CV; SD/mean x 100] ranges from 16 to 174%) for both regions, and the error associated with the means overlap. Although measurements in

bottom waters were generally limited, Heyes et al. (2004) measured bottom water filtered Hg in the ETM and found average concentrations (49.4 and 37.9 pM) that were nearly twice as high as those in surface waters (24.8 pM; Table 1).

As noted by Sañudo-Wilhelmy and Gill (1999), filtered metal concentrations measured by Klinkhammer and Bender (1981) in the surface and bottom waters of the ETM and lower Hudson during the 1970s (Table 1) were elevated as compared to more recent measurements in the same regions. This decline is thought to reflect improvements in sewage treatment and the elimination of industrial sources of metals to the Hudson River (Yang and Sañudo-Wilhelmy, 1998). Filtered metals concentrations are particularly useful for this type of comparison, assuming that the dissolved-particulate partitioning has remained constant, since varying levels of suspended particulate material are not a confounding factor. Sañudo-Wilhelmy and Gill (1999) state that median dissolved concentrations in surface waters of the Hudson have declined 36 to 56% for Cu, 55 to 89% for Cd, 53 to 85% for Ni, and 53 to 90% for Zn, although it was noted that there were some overlapping data points. For example, filtered Cd measured in April 1974 by Klinkhammer and Bender (1981; 2.58 ± 0.73 ; mean \pm SD) are clearly higher than the filtered levels measured by Sañudo-Wilhelmy and Gill (1999; 0.55 ± 0.32), but the error associated with the Klinkhammer and Bender October 1975 mean filtered Cd (2.05 ± 1.41) overlaps the more recent measurements (0.71 ± 0.35). Although there is evidence of reduced filtered metals concentrations since the mid-1970s, it should be noted that Klinkhammer and Bender (1981) collected deep water samples that may have had elevated metals concentrations as compared to surface waters (e.g., Balcom et al., 2008), and that the errors associated with the means of the earlier measurements generally overlap with more recent measurements.

A seasonal comparison has been made using filtered Hg and Cd measurements (CARP, 2007; Figure 5). The comparison extends about 250 km upstream from the ETM (Manhattan) to Waterford (above the dam at Troy). Overlapping error bars (SE; plotted when there were data from multiple samples at a site) indicate that filtered Hg concentrations are generally similar from the ETM to the upper Hudson (Figure 5c). In the spring of 1999, filtered Hg was elevated in the lower Hudson and ETM as compared to concentrations measured in the spring and summer of 2000. Although filtered Cd concentrations are similar among seasons in the upper Hudson (Figure 5d), there was a dramatic increase in the spring of both 1999 and 2000 (0.49-0.73 nM) for the ETM and lower Hudson. Yang and Sañudo-Wilhelmy (1998) also reported that dissolved Cd showed non-conservative excesses (~1.0-1.2 nM maxima) across the whole lower Hudson/ETM salinity gradient during both low (October) and high (April) river flow conditions. Indeed, average (\pm SD) surface filtered Cd concentrations in both the ETM (0.90 ± 0.28 nM; includes a value of 1.42 nM measured in Oct. 2001 that is not included in Fig. 5d) and lower Hudson (0.67 ± 0.24 nM) are similar to total Cd concentrations in the same regions (0.74 ± 0.28 nM and 0.81 ± 0.03 nM, respectively; Table 1, Figure 5b). CARP measurements made in February (1999 and 2000) have been included with spring values (March through May) since the values fall within the range of the spring measurements, and only a few winter measurements were made in the CARP program.

Yang and Sañudo-Wilhelmy (1998) reported that although concentrations of dissolved metals appeared to strongly depend on the season and/or river discharge, as seen with CARP data in the present study (Figure 5), the highest dissolved concentrations were generally detected under conditions of low freshwater discharge and limited hydraulic flushing. Sañudo-Wilhelmy and Gill (1999) noted that a gradual increase in dissolved Ni and Cu levels towards the New

York City region suggested that concentrations of these metals are influenced by sources such as benthic remobilization from contaminated sediments. Yang and Sañudo-Wilhelmy (1998) reported that filtered Cd accounted for 70-80% of the total Cd at most sampling locations, and CARP Cd results indicate similar partitioning. The relatively low contribution of particulate Cd to the total Cd pool has been reported previously for other estuaries, and this partitioning is consistent with the relatively low particle reactivity of the element (Lee et al., 1984; Comans and Dijk, 1988).

.3.2.2 Total metals and suspended particulate matter

The average (\pm SD) surface concentration of total Hg in the lower Hudson (144 ± 75 pM; Table 1) was similar to the concentration at Poughkeepsie in the upper Hudson (Figure 5a), but as expected based on TSS levels (Table 2 and Figure 2), greater than total Hg at sites upstream of Poughkeepsie (e.g., Waterford). Conversely, average total surface Cd concentrations in the lower Hudson (0.81 ± 0.03 nM and 0.55 ± 0.30 nM; Table 1) were somewhat less than those at Poughkeepsie and Waterford (Figure 5b; see Table S1 [supporting information] for K_D values). Surface total Cd concentrations for the ETM site (0.74 ± 0.28 nM and 1.15 ± 0.86 nM; Table 1) were roughly the same as those at the lower Hudson site. Although surface total Hg measured by CARP (2007) was somewhat less in the ETM than the lower Hudson (Table 1), Heyes et al. (2004) reported a high average concentration (264 ± 194 pM) in the surface waters of the ETM. Generally, the errors associated with mean total metal concentrations for the ETM and lower Hudson overlap, but there is considerable variability associated with surface concentrations (CV ranges from 4 to 82%) for both regions. It is notable that average total Hg in bottom waters of the ETM (1112 and 613 pM) reported by Heyes et al. (2004) were 2 to 4 times higher than those in surface waters (264 pM; Table 1).

As for filtered metals, total Hg and Cd (CARP, 2007) were compared seasonally along the Hudson River (Figure 5). During the spring of 1999 and 2000, average total Hg and Cd were higher in the ETM and lower Hudson than in the upper Hudson (Figures 5e and 5f). In the spring of 2000, total Hg was elevated at all sampling sites, and Cd was elevated at Poughkeepsie, as compared to concentrations measured in the fall of 1999 and summer of 2000. Elevated total Hg and Cd concentrations may be associated with resuspension and transport of elevated levels of particulate material during spring high-flow periods. CARP measurements made in February of 1999 and 2000 have been included with spring values (March through May) since these values fall within the range of the spring measurements, and, as noted, few winter measurements were made during the program.

3.2.3 Suspended particle concentrations in the lower Hudson

During a tidal cycle study in the Hudson ETM, average surface and bottom water suspended particle concentrations of Cu, Fe, Zn, Ag, and Pb were similar and had overlapping errors (Table 2; Feng et al., 2002). However, bottom water average suspended particle concentrations of Cd ($15.95 \text{ nmol g}^{-1}$) in the ETM were elevated as compared to average surface values of 8.27 nmol g^{-1} (Feng et al., 2002) and 6.55 nmol g^{-1} (CARP, 2007), and as compared to the lower Hudson (5.45 nmol g^{-1} ; CARP, 2007; Table 2). Yang and Sañudo-Wilhelmy (1998) reported elevated surface water suspended particle Cd concentrations in the ETM ($12.59 \text{ nmol g}^{-1}$) and lower Hudson ($10.16 \text{ nmol g}^{-1}$), although uncertainties overlap with those reported by Feng et al. and CARP. Bottom water average suspended particle levels of Hg in the ETM (4.62 and 3.17 nmol g^{-1} ; Heyes et al, 2004) were slightly elevated as compared to surface waters (2.2 nmol g^{-1}), but similar to CARP measurements made in the lower Hudson (3.54 nmol g^{-1} ; Table 2). The average suspended particle concentration of Hg ($0.64 \pm 0.15 \text{ nmol g}^{-1}$, $n = 3$; CARP,

2007) at the Kingston-Poughkeepsie site, the only site in the middle or upper Hudson where the calculation could be made, was low as compared to the lower Hudson, while Cd (5.03 nmol g^{-1} , $n = 2$) at Kingston-Poughkeepsie was comparable to the lower Hudson.

Average surface water suspended particle concentrations of Pb ($1.74 \text{ } \mu\text{mol g}^{-1}$) and Zn ($11.9 \text{ } \mu\text{mol g}^{-1}$; Table 2; Feng et al., 2002) in the ETM are elevated as compared to Poughkeepsie (Figure 3), and low as compared to the Glenmont, Cohoes, and Waterford sites (4.3 to $7.4 \text{ } \mu\text{mol g}^{-1}$ for Pb and 21.9 to $22.8 \text{ } \mu\text{mol g}^{-1}$ for Zn; NYSDEC SWMS, 2007) in the upper Hudson. Similarly, average surface suspended particle concentrations of Cu in the ETM ($2.72 \text{ } \mu\text{mol g}^{-1}$) are slightly elevated relative to Poughkeepsie and Glenmont, but less than upper Hudson sites at Waterford and Cohoes (3.3 to $4.5 \text{ } \mu\text{mol g}^{-1}$; Figure 3). In contrast, Fe-normalized suspended particle concentrations indicate that Cu:Fe, Pb:Fe, and Zn:Fe ratios are elevated in both the ETM and upper Hudson as compared to Poughkeepsie (Figure 6). Of particular note are the elevated Fe-normalized suspended particle concentrations (mol/mol) of Cu at Cohoes (52.9×10^{-4}), Pb in the ETM (20.8×10^{-4}), and Zn at the ETM, Cohoes, and Waterford (189 to 233×10^{-4} ; Figure 6). Point source contamination (e.g., benthic resuspension, WPCFs) to the ETM is the likely source of the elevated suspended particle metals concentrations (Yang and Sañudo-Wilhelmy, 1998).

Suspended particle metals concentrations in the ETM were generally higher than those in surface sediments; Cd and Zn are increased by a factor of 3 to 5 in the water column (Feng et al., 2002; Table 2), while Hg shows no difference between sediments and bottom water (Heyes et al., 2004). Enhancements are likely due to differences in grain size (i.e., clay minerals) between the suspended particles and surface sediments (Feng et al., 2002). Fine-grained bottom sediments are resuspended by tides and currents, and these particles and associated contaminants may be transported over a wide distance up- and down-estuary (10-20 km along the axis of the river)

during the course of a tidal cycle (Heyes et al., 2004). Metal:Fe ratios oscillate with time (e.g., adsorption and desorption as particles are transported through water of different salinities) and there is a general increase with salinity over the course of a tidal cycle (Feng et al., 2002).

3.3 Distribution of metals among major rivers entering NY/NJ Harbor

Total Hg at the mouths of the Hackensack River (109 ± 44 pM; mean \pm SE), and particularly the Passaic River (154 ± 8 pM surface, 433 ± 144 pM bottom; CARP, 2007; Figure 7), are elevated as compared to the mouth of the Hudson (ETM; 53.9 ± 10.6 pM; Figure 5). Mid-tidal stations on both the Hackensack (787 ± 233 pM) and the Passaic (408 ± 182 pM) are clearly elevated as compared to surface total Hg concentrations at the mouths of these rivers, and as compared to Poughkeepsie (130 ± 44 pM; mid-tidal) on the Hudson. These Hg levels in the Hackensack are not surprising. Within the Hackensack Meadowlands, Eight-Day Swamp (Weis et al., 2005) and Berry's Creek (Cardona-Marek et al., 2007) are downstream from several contaminated Superfund sites, and these areas are known to be contaminated with heavy metals (especially Hg and MMHg). Conversely, surface total Hg concentrations for the lower East River (57 ± 14.5 pM; the lower east River is the region between the Brooklyn Bridge and Hell Gate) and the Raritan River (57.5 ± 6.5 pM; upstream of the mouth in the lower reaches of the river; CARP, 2007; Figure 7) are similar to concentrations in the mouth (ETM) of the Hudson. Bottom water total Hg in the Raritan (91.6 ± 11.2 pM) was elevated compared to surface waters, but still much less than levels measured in Passaic bottom waters. Filtered Hg concentrations are low at the mouth and mid-tidal stations on each river (4.1-13.0 pM; mean \pm SE; Figure 7) as compared to total Hg, with an average of 83 to 98% of the Hg in the particulate phase (see Table S1 for K_D values [supporting information]).

Total Cd in surface water at the mouth of the Hackensack River (0.63 ± 0.11 nM; mean \pm SE; CARP, 2007; Figure 7) is similar to the Hudson ETM (0.74 ± 0.14 nM; Figure 5), while surface levels are somewhat elevated at the mouth of the Passaic River (0.97 ± 0.32 nM surface, 1.32 ± 0.29 nM bottom). The mid-tidal station on the Hackensack (0.79 ± 0.30 nM) was similar to the mouth of the river, but Passaic mid-tidal Cd concentrations (1.44 ± 0.44 nM; Figure 7) were the highest measured among the river stations, and similar to surface total Cd at Poughkeepsie (1.32 ± 0.67 nM; mid-tidal; Figure 5) on the Hudson. As was the case with Hg, total Cd concentrations at the surface in the lower East River (0.58 ± 0.03 nM; Figure 7) were similar to the Hudson ETM, but surface (0.41 ± 0.08 nM) and bottom (0.45 ± 0.15 nM) concentrations in the Raritan River were reduced. Paulson (2005) reported higher total Cd (1.0 ± 0.02 nM; $n = 9$) for surface and bottom waters of the Raritan River (collected August 1999; several sites including the mouth in the lower reaches of the river). As was the case for the Hudson ETM, greater than 95% of Cd in the Raritan was in the dissolved phase. As discussed previously, Cd associates strongly with Cl^- ions in saline waters, and given its relatively low affinity for particles, tends to be dominated by the dissolved phase. Surface filtered Cd concentrations near the river mouths ranged from 0.40 to 0.84 nM (87-99% in dissolved phase), but were reduced (0.30 to 0.31 nM, 22-39% in dissolved phase) at lower salinities in surface waters of the mid-tidal regions.

Suspended particle Hg concentrations are clearly elevated at all sampling sites on the Hackensack and Passaic Rivers (9.8 to 20.8 nmol g^{-1} ; CARP, 2007; Figure 7) as compared to the Hudson ETM and lower Hudson (2.2 to 4.63 nmol g^{-1} ; Table 2). Concentrations for the lower East River and Raritan Rivers (2.3 to 4.7 nmol Hg g^{-1}), however, are quite similar to the Hudson River. Interestingly, surface water suspended particle Cd concentrations at the mouth of the

Hackensack and Passaic (9.6 to 14.3 nmol g⁻¹; Figure 7) are similar to surface water sampled at sites on the Hudson (5.4 to 12.6 nmol g⁻¹; Table 2), which may be attributed to the dominance of dissolved phase Cd at elevated salinities. Paulson (2005) reported suspended particle Cd concentrations of 6.82 ± 3.16 nmol g⁻¹ (mean ± SE; August 1999) for the Raritan River, which is within the range of values reported near the mouth of the other rivers, and is well below concentrations reported by CARP for the Raritan (20.2 nmol Cd g⁻¹). Suspended particle Cd concentrations are low (2.3 nmol g⁻¹) in the lower East River.

3.4 Distribution of metals in New York/New Jersey Harbor Estuary

3.4.1 Filtered metals

Among regions of NY/NJ Harbor, the average metals concentrations in filtered waters ranged from 2.0 to 8.2 pM for Hg and 0.21 to 0.61 nM for Cd (CARP, 2007), 0.08 to 0.11 pM for MMHg and 2.8 to 4.8 for Hg (Balcom et al., 2008), 0.26 to 0.62 nM for Cd (Table 3), 0.16 to 0.40 nM for Pb, 10.3 to 20.5 nM for Ni, and 6.3 to 11.4 nM for Cu (Paulson, 2005; Figure 8). Filtered concentrations of each metal were relatively uniform across the Harbor environs, with the exception of elevated levels of Ni in Raritan Bay, reduced concentrations of Cd in NY Bight, and reduced levels of Pb and Cu at the Rockaway-Sandy Hook transect (Figure 8).

Filtered metals concentrations remained relatively constant in the Harbor over a 5 to 8 year period (1995-2003). Upper and Lower Harbor filtered Hg reported by Balcom et al. (2008; 3.3 ± 1.5 and 4.4 ± 3.4 pM, respectively; mean ± SD) and CARP (2007; 4.9 ± 1.6 and 3.6 pM, respectively; Figure 8) overlap measurements made by Sañudo-Wilhelmy and Gill (1999; Table 3) in the mid-1990s. Similarly, CARP filtered Cd in the Upper and Lower Harbors (0.38 ± 0.12 and 0.48 ± 0.1 nM, respectively) are within the error of measurements made by Sañudo-Wilhelmy and Gill (1999) and Paulson (2005; Table 3). Upper Harbor filtered Pb (0.4 ± 0.16

nM) and Ni (12.1 ± 2.95 nM; Figure 8; Paulson, 2005) are in agreement with earlier values reported by Sañudo-Wilhelmy and Gill (1999; Table 3), but the filtered Cu measurements made by Paulson (9.04 ± 2.12 nM) are significantly lower than the earlier measurements.

There have been dramatic reductions in filtered and total metals concentrations in NY Bight and the Lower Harbor since the mid-1970s, with most of the decrease is attributable to dissolved metals (Figure 9). As discussed previously, total metals concentrations are largely determined by TSS levels at the time the measurements were made, while the decline in filtered metals concentrations represents an actual trend over 25-years. Compared to earlier filtered metals measurements in NY Bight (surface and deep; Klinkhammer and Bender, 1981), average levels of surface filtered metals in the Lower Harbor (Table 3) were reduced by 76% for Cd, 61% for Cu, 83% for Ni, and 84% for Zn over a period of 23 years (Sañudo-Wilhelmy and Gill, 1999). Additionally, over about 25 years, average filtered metal (surface and deep) measurements made by Paulson (2005) at the Rockaway-Sandy Hook transect were reduced by 88% for Cd, 87% for Cu, and 89% for Ni as compared to the Klinkhammer and Bender (1981) mid-70s measurements (Figure 9). These are conservative estimates because NY Bight levels are expected to be less than those at sites within the Rockaway-Sandy Hook transect.

3.4.2 Total metals and suspended particulate matter

As discussed and shown previously for Hg (Balcom et al., 2008), distributions of most total metal concentrations in NY/NJ Harbor are related to TSS. Average TSS concentrations (CARP, 2007) were relatively uniform in the Upper Harbor, Raritan Bay, and Lower Harbors (10.3 to 12.1 mg l⁻¹), elevated in Newark and Jamaica Bays (19.5 to 19.6 mg l⁻¹), and significantly reduced in the NY Bight (1.8 mg l⁻¹; Figure 8). A single TSS measurement (33.5 mg l⁻¹) from July 1999 accounts for the elevated average TSS in Jamaica Bay. Paulson (2005)

reported a decreasing trend in average TSS values from the Upper Harbor (6.8 mg l⁻¹) to Raritan Bay (4.8 mg l⁻¹) to the Lower Harbor (3.9 mg l⁻¹) in August 1999, and although the concentrations are lower than the average TSS reported by CARP, the errors (SD) are widely overlapping. Balcom et al. (2008) found relatively uniform regional average TSS (21.1 to 23.4 mg l⁻¹) levels that were strongly influenced by concentrations in May (170 mg l⁻¹ value not included in Newark bay average). As discussed below, distributions of total metals in NY/NJ Harbor suggest that particle loading and/or resuspension associated with fluvial discharge are important contributors of metals to the water column of the Harbor.

In contrast to the filtered phase, there was considerable variability in the average concentration of total (unfiltered) trace metals among regions of NY/NJ Harbor. The amounts of metals were higher near major river inputs (Newark Bay, Upper Harbor, and Raritan Bay) to the Harbor, although there is considerable variance associated with the means, and lower nearer to the ocean end member (NY Bight; Figure 8). Much of this variability is attributable to higher TSS levels associated with fluvial inputs to NY/NJ Harbor. The average concentrations of total Hg (3.2 to 166 pM; CARP, 2007) were highest in Newark Bay and showed a marked decrease in the higher salinity waters of the Lower Harbor, Jamaica Bay, and the NY Bight (Figure 8). Particulate phase Hg was high in each region of the Harbor (63 to 98% of total metal; see Table S1 for K_D values [supporting information]). Average regional concentrations of total Hg reported by Balcom et al. (2008; 53.9 to 355 pM; >90% particulate Hg; Figure 8) were generally elevated as compared to the CARP values. In particular, the average Hg concentration for Newark Bay was affected by elevated bottom water concentrations (CARP values are for surface water only), and Jamaica Bay was influenced by increased concentrations during the spring (May 2003). Average total MMHg concentrations (0.29 to 1.12 pM; Balcom et al., 2008) were highest

in Newark Bay and relatively uniform in other areas of the Harbor; the particulate fraction ranged from 68 to 83% of total metal (Figure 8). Both CARP (2007; 0.19 to 0.90 nM; Figure 8) and Paulson (2005; 0.30 to 0.62 nM; Table 3) showed that average regional total Cd levels decreased with increasing distance from the mouth of the Hudson River. Total Cd reported by Paulson (2005) were similar to CARP values in the Upper Harbor, Raritan Bay, and Rockaway-Sandy Hook transect, and the Yang and Sañudo-Wilhelmy (1998) Upper and Lower Harbor total Cd levels (Table 3) were also comparable CARP. As expected, the proportion of Cd on particles was only 11 to 26% in the saline waters of NY/NJ Harbor.

Paulson (2005) reported higher Pb, Cu, and Zn levels at elevated TSS levels in the Upper Harbor (Figure 8). Average total concentrations of Pb (4.35 to 18.4 nM), Cu (9.81 to 24.4 nM), Ni (10.5 to 22.0 nM), and Zn (9.36 to 25.3 nM) generally decreased between the Upper Harbor and the Rockaway-Sandy Hook transect (Paulson, 2005; Figure 8). Ni was an exception, and was slightly elevated in Raritan Bay as compared to the Upper Harbor and Rockaway-Sandy Hook. The particulate fraction was dominant for Pb (92 to 98% particulate), while Cu (30 to 58%), and particularly Ni (7 to 30%), have much more metal in the dissolved fraction in NY/NJ Harbor.

3.4.3 Suspended particle and surface sediment metals

The concentrations of metals on suspended particles can be used as a tracer for suspended particulate matter in the water column, and are useful for identifying mechanisms controlling distributions of metals in the water column (Paulson, 2005; Balcom et al., 2008). Sediment resuspension is an important process influencing the distribution of particles (i.e., TSS) in the water column, and, therefore, suspended particle metals concentrations were compared to surface sediment metals concentrations in the major regions of NY/NJ Harbor. Regional average

suspended particle concentrations ranged from 3.2 to 7.8 nmol g⁻¹ for Hg and 12.3 to 24.7 pmol g⁻¹ for MMHg (Balcom et al., 2008), 1.1 to 8.7 nmol g⁻¹ for Hg and 3.1 to 13.2 nmol g⁻¹ for Cd (CARP, 2007), 0.8 to 2.9 μmol g⁻¹ for Pb, 0.9 to 2.1 μmol g⁻¹ for Cu, 0.3 to 0.7 μmol g⁻¹ for Ni, and 2.0 to 3.8 μmol g⁻¹ for Zn (Paulson, 2005; Figure 10). Regional average surface sediment concentrations ranged from 2.4 to 7.4 nmol g⁻¹ for Hg and 11.3 to 32.9 pmol g⁻¹ for MMHg (Balcom et al., 2008; Hammerschmidt et al., 2008), 1.0 to 12.3 nmol g⁻¹ for Hg, 0.8 to 12.8 nmol g⁻¹ for Cd, 0.3 to 1.3 μmol g⁻¹ for Pb, 0.1 to 1.9 μmol g⁻¹ for Cu, 0.1 to 0.7 μmol g⁻¹ for Ni, and 0.6 to 4.4 μmol g⁻¹ for Zn (EMAP, 2008; Adams et al., 1998; Figure 10; Figures S8, S9, S10, S11; Tables S2, S3, S4, S5). Overall, there was good agreement between suspended particle and surface sediment metals concentrations. The only notable exception was Pb in the Upper Harbor, where suspended particle concentrations were significantly elevated above those in sediments.

Average suspended particle Hg concentrations reported by CARP (2007) and Balcom et al. (2008; Figure 10) are similar for Newark Bay and the Upper Harbor, but Balcom and co-workers found elevated suspended particle concentrations in Jamaica Bay that were thought to be attributable to WPCF inputs. Balcom et al. (2008) found dilution of Lower Harbor suspended particle Hg levels as compared to surface sediment Hg concentrations during three seasons, which is likely the result of water exchange with New York Bight through the Ambrose Channel conduit (Paulson, 2005). There is no Lower Harbor suspended particle Hg data available from CARP, and no Lower Harbor data available for the other metals, but average suspended particle Cu, Ni, and Zn are slightly less than average surface sediment concentrations in Raritan Bay (Paulson, 2005). Although not plotted in Figure 10, regional average suspended particle Cd concentrations (4.78 to 13.29 nmol g⁻¹) reported by Paulson (2005) agree well with CARP (2007)

concentrations. Average surface sediment Hg concentrations reported by Balcom et al. (calculated from data presented in Hammerschmidt et al., 2008) were similar to those reported by EMAP (2008) in the Upper Harbor and Jamaica Bay, but sediment Hg was reduced in Newark Bay and elevated in the Lower Harbor as compared to EMAP.

As was the case for total metals, the highest levels of suspended particle and surface sediment metals were generally observed near fluvial sources in Newark Bay, the Upper Harbor, and Raritan Bay, and concentrations were generally lower in the Lower Harbor and Jamaica Bay (Figure 10). Surface water suspended particle Hg ($4.3 \pm 2.4 \text{ nmol g}^{-1}$; mean \pm SD) and Cd ($11.0 \pm 9.1 \text{ nmol g}^{-1}$; CARP, 2007) concentrations in the Upper Harbor are similar to the surface and bottom concentrations reported for the ETM (Table 2), but this was not the case for all metals. Surface and deep Pb concentrations ($2.9 \pm 0.8 \text{ } \mu\text{mol g}^{-1}$; Paulson, 2005) in the Upper Harbor are elevated as compared to the ETM, while Cu ($2.1 \pm 0.6 \text{ } \mu\text{mol g}^{-1}$) and Zn ($3.8 \pm 1.5 \text{ } \mu\text{mol g}^{-1}$) levels were reduced.

3.4.4 Comparison of normalized suspended particle and sediment metals

In contrast to suspended particle concentrations, Fe- and Al-normalized suspended particle concentrations of Cd, Pb, Cu, and Zn (mol/mol) are generally lower in the Hudson ETM and higher in the Raritan Bay and Rockaway-Sandy Hook transect regions of NY/NJ Harbor (Figure 11). The influences of TSS distributions are largely accounted for by normalizing, so these trends may be indicative of sources or reservoirs of the metals in the Harbor. Although error bars (SE) for normalized suspended particle metals sometimes overlap among the Upper Harbor, Raritan Bay, and Rockaway-Sandy Hook, normalized metals ratios are clearly reduced for Cd, Pb, and Cu in the ETM (Figure 11). Fe-normalized suspended particle Zn was elevated at the 10 km ETM sampling site as compared to the 4 km site due to differences in particulate Zn

concentrations (Feng et al., 2002), while Al-normalized Zn showed little change through the ETM and Harbor. Fe-normalized Ni was elevated at Rockaway-Sandy Hook as compared to the Upper Harbor, but Al-normalized Ni was uniform and there were no measurements available from the ETM.

Paulson (2005) looked at regressions of particulate metals against particulate Fe for each region of NY/NJ Harbor and found high correlation for the major elements Zn, Ni, Cu, and Pb, indicating that element:Fe ratios were relatively constant throughout the regions of the Harbor, although the ETM was not included in the study. Particulate Cd, however, as indicated in Figure 11, exhibited significant differences in element:Fe ratios among regions of the Harbor (analysis of covariance; Paulson, 2005). Additionally, Paulson found that the Pb:Fe ratios of suspended particulate matter from the Upper and Lower Harbors were higher than the ratio for Hudson River surface waters, and theorized that the particle size of suspended matter in Lower NY/NJ Harbor was probably smaller than that in the Hudson. It is likely that, larger, less metal-enriched suspended matter from the Hudson settles from the water column, leaving the remaining smaller, metal-enriched suspended matter to enter the lower reaches of the Harbor. In addition to the influence of particle sorting, biological uptake of metals may be significant. Despite a decrease in sediment grain size and total organic carbon (TOC), CARP (2007) data indicated a sharp increase in water column particulate organic carbon (POC) in Raritan Bay and the Lower Harbor (Figure 11). There may be enrichment in metals associated with increased carbon production in the lower reaches of NY/NJ Harbor.

In contrast to water column normalized suspended particle ratios, surface sediment metal:Al and metal:Fe ratios generally decreased between the Upper and Lower Harbor (Figure 11). The sediments of NY/NJ Harbor are largely supplied from the major rivers entering the

Harbor (Steinberg et al., 2004; Abood, 1999). Since metals are associated with suspended particulate matter, it's not surprising that sediment metal concentrations decrease with increasing distance from fluvial sources (ETM to the Lower Harbor; Figure 11). Additionally, sediment silt/clay and TOC levels (Adams et al., 1998) are elevated in the Upper Harbor as compared to NY Bight (Figure 11), and many metals tend to associate with fine particulate material and with organic matter. In the lower reaches of NY/NJ Harbor, normalized suspended particle metals are clearly elevated as compared to normalized sediment metals (Figure 11). Mean Fe- and Al-normalized suspended particle to sediment metal ratios (Cd, Pb, Cu, Ni, and Zn) in the ETM (10 km) ranged from 1.1 to 1.5 (4.4 to 4.6 for Zn), while ratios for the Rockaway-Sandy Hook transect (compared to Lower Harbor sediments) ranged from 1.9 to 15.6.

3.5 Fluxes of metals to NY/NJ Harbor

A primary goal of this study was to formulate biogeochemical mass balances for Hg, MMHg, Cd, Pb, Ni, Cu, and Zn in the waters of NY/NJ Harbor. Major sources of metals to the Harbor include rivers, water pollution control facilities (WPCFs), atmospheric deposition, and benthic flux. Export terms considered include estuarine exchange, sediment burial, bioaccumulation and (photo)demethylation (MMHg only), and gas exchange at the air-water interface (elemental Hg only). The design of our budgets is similar to those of Klinkhammer and Bender (1981), who employed a three-box model that included the freshwater Hudson River, the Hudson estuary and NY/NJ Harbor, and NY Bight. They posited that given that there is little natural freshwater input from tributaries or groundwater to NY/NJ Harbor and the lower Hudson River, the combined estuarine system is essentially a mixture of three end-members: Hudson River water, New York Bight water, and Manhattan/New Jersey sewage. The mass balances produced in this study are derived from databases and the literature, which contain observations

from collection made at various times of the year (including both high-flow and low-flow conditions), and, therefore, represent a seasonally-averaged estimate of total metal cycling in NY/NJ Harbor. The impact of storm events on metals fluxes is included, although not considered separately within the annual budgets.

3.5.1 River fluxes

A net southerly flow exists in the Hudson River below the Green Island Dam at Troy (NY), and this provides the freshwater input that creates the Hudson River Estuary (Geyer and Chant, 2006). The flow and mixing is affected by a variety of physical forces. In particular, the tide extends 250 km up river to the dam at Troy, and tidal currents move both north and south through the Hudson. Mean monthly volume fluxes for the Hudson River at the Green Island station (below dam at Troy; USGS 2002-2004) were used to calculate the river fluxes of metals in this study. The average (\pm SE) Hudson volume flux for this period was $1.4 \pm 0.1 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$ (USGS, 2008), which equates to a flux of $2.3 \pm 0.2 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$ at the mouth of the Hudson after applying a watershed correction factor of 1.58 (Balcom et al., 2008; Fitzgerald and O'Connor, 2001). This volume flux is comparable to the estimate of Simpson et al. (2006; $2.0 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$) for the mean annual “natural” discharge from the Hudson at the Battery, which includes the contribution of the New York City water supply from the Catskill and Croton drainage areas.

The flux of metals from the Hudson River to NY/NJ Harbor was estimated based on the water volume flux at the mouth of the Hudson and the combined average unfiltered (total) concentration of each metal from Waterford (Hudson River) and Cohoes (Mohawk River) sampling stations (Table 4). Hg, Cd, and Pb data were from CARP (2007), and the very high total Cd measurements at Waterford (5.43 nM) and Cohoes (6.49 nM) from 6/7/2000 were not included in the average total Cd concentrations used to calculate the river flux. Total MMHg

levels were estimated using CARP average (\pm SE) dissolved MMHg (0.29 ± 0.11 pM) and the average dissolved:total MMHg ratio (0.32 ± 0.04 ; $n = 8$) from Balcom et al. (2008). The dissolved:total MMHg ratio approach is based on measured 0.2- μ m filtered and particulate MMHg concentrations from NY/NJ Harbor, and the estimated total MMHg concentrations (dissolved+particulate; 0.89 ± 0.35 pM; Table 4) were used to calculate fluxes. Approximately bimonthly measurements of Ni, Cu, and Zn for the Waterford and Cohoes sites were obtained from the NYS DEC State Waters Monitoring System (SWMS, 2007; Table 4). Although WPCF effluent metals concentrations are typically elevated as compared to rivers, Balcom et al. (2008) calculated that municipal WPCFs discharging directly to the Mohawk and Hudson Rivers north of Waterford, NY (2.0×10^8 m³ y⁻¹; nominal flow) contribute only about 1% to the total volume flux of the Hudson River (NYS DEC, unpublished data), and, therefore, have little impact on the total metals flux from the Hudson. Annual Hudson River fluxes to NY/NJ Harbor were calculated for MMHg (20 ± 8 mol), Hg (1900 ± 750 mol), Cd (13 ± 6 Kmole), Pb (680 ± 63 Kmole), Ni (575 ± 312 Kmole), Cu (1542 ± 603 Kmole), and Zn (2569 ± 552 Kmole).

The Hudson contributes about 90% of fluvial flow to NY/NJ Harbor, while the Raritan, Passaic, and Hackensack Rivers provide much of the remaining 10% (Fitzgerald and O'Connor, 2001; USGS, 2008). Therefore, the flux of metals from rivers is largely attributable to the Hudson, and inputs of metals to NY/NJ Harbor from all fluvial sources were estimated by scaling the Hudson River flux by a factor of 1.1 rather than treating each river individually. The estimated annual input (\pm SE) of metals from all rivers to NY/NJ Harbor ranged from 23 ± 9 moles for MMHg to 2800 ± 610 Kmole for Zn (Table 5). The river Pb flux (750 ± 70 Kmole; Table 5) calculated from CARP data is significantly higher than an estimate (190 ± 70 Kmole) based on NYSDEC SWMS (2007) average (\pm SE) water Pb data (7.57 ± 2.56 nM), and the

SWMS data were not used in our budget. Although SWMS water Cd concentrations in the upper Hudson were generally below detection limits, and were not included earlier in this manuscript, it is worth noting that the estimated annual flux of Cd from rivers (12.7 ± 2.6 Kmol) based on those measurements (0.5 ± 0.1 nM) is statistically the same as the flux calculated using CARP Cd data (Table 5). The variance terms for the metals fluxes were determined by propagation of errors based on the variability (SE) associated with the average Hudson monthly flow rates and metals concentrations.

3.5.2 East River flux

The East River is a narrow, tidally dominated channel that connects LIS and Upper NY/NJ Harbor, and tidal mixing is an important mechanism for transport of pollutants between these water bodies (Blumberg and Pritchard, 1997). With no significant natural sources of fresh water, sewage outflows are the largest direct source of “fresh water” to the East River (Geyer and Chant, 2006). Results of a model simulation indicate that the net long-term volume flux of water in the East River is directed out of LIS and into NY/NJ Harbor at a rate of about $355 \text{ m}^3 \text{ s}^{-1}$ (Blumberg and Pritchard, 1997).

Average total Hg and Cd measurements from the lower East River (CARP, 2007; Table 4) were used to estimate fluxes to NY/NJ Harbor. Total MMHg levels were estimated using CARP average (\pm SE) filtered MMHg measurements (0.08 ± 0.01 pM) and the average dissolved:total MMHg ratio (0.32 ± 0.04 ; $n = 8$) from Balcom et al. (2008). Average (\pm SE) filtered concentrations of Cd (0.23 ± 0.03 nM), Pb (0.28 ± 0.13 nM), Cu (25.1 ± 2.8 nM), Ni (31.9 ± 4.4 nM), and Zn (42.6 ± 2.2 nM) for the lower East River were available from Buck et al. (2005), but total concentrations were needed to estimate fluxes. Estimates of total metals concentrations were obtained from average (\pm SE) dissolved:total ratios for Cd (0.32 ± 0.04), Pb

(0.33 ± 0.08), Cu (0.86 ± 0.02), Ni (0.83 ± 0.02), and Zn (0.36 ± 0.05), based on measurements of estuarine filtered and total metals concentrations by Wen et al. (1999). Fluxes from the East River to NY/NJ Harbor (Table 5) were estimated using mean total lower East River concentrations of each metal (south of Hell Gate; Table 4) and a river volume flux of $1.1 \pm 0.1 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$ (Blumberg and Pritchard, 1997). As a constraint over on East River flux estimates, the Cd flux was also estimated using water concentration data from CARP. The calculated fluxes of $6.5 \pm 0.6 \text{ Kmol}$ (CARP) and $3.3 \pm 0.5 \text{ Kmol}$ (Buck et al.) agree within a factor of 2. As expected, the estimate based on the dissolved:total ratio (Buck et al., 2005) is lower than the CARP estimate since the former does not include the contribution of total Cd from unfiltered WPCF effluent. The variance term was calculated by propagation of errors based on the variance associated with the river volume flux estimate and variability (SE) in measured metals concentrations for the East River.

3.5.3 *Water pollution control facility flux*

The fluxes of Hg, Cd, and Pb from water pollution control facilities (WPCFs; Table 5) were calculated from volume-weighted average concentrations (CARP, 2007; Table 4) for the six East River WPCFs (New York City Department of Environmental Protection [NYCDEP]), and the total discharge of effluent ($1.4 \times 10^9 \text{ m}^3 \text{ y}^{-1}$; NYC DEP, 2003) from non-East River WPCF sources that discharge into NY/NJ Harbor. An unknown portion of the metals associated with effluent from the East River WPCFs reaches NY/NJ Harbor (Balcom et al., 2004), and it is assumed that the input of these metals is included in the East River flux estimated in section 3.5.2. Metals levels in the East River WPCFs are taken to be representative of the metal concentrations in all WPCF effluents entering NY/NJ Harbor. The uncertainty associated with the effluent volume flux (SE) was estimated to be $5.0 \times 10^6 \text{ m}^3 \text{ y}^{-1}$, based on the combined

variance of monthly mean discharge rates (1995-1997) for the East River WPCFs (Balcom et al., 2004). The variance term for WPCF fluxes was calculated by propagation of errors based on the variability (SE) associated with the monthly mean WPCF discharge rates and the variability associated with the volume-weighted metals concentrations.

Filtered MMHg concentrations were available for the six East River WPCFs (CARP, 2007), but as discussed previously, total MMHg (dissolved + particulate) concentrations are needed to estimate fluxes. Filtered and particulate MMHg were determined for two large WPCFs discharging to the Connecticut River ($n = 13$; Balcom et al., 2004), and we estimated a dissolved:total MMHg ratio of 0.45 ± 0.06 (Balcom et al., 2008). This ratio was applied to the average (\pm SE) filtered MMHg concentrations (1.1 ± 0.4 pM, $n = 12$) in effluent from the East River WPCFs to calculate total MMHg levels. The volume-weighted total MMHg concentration was estimated to be 2.56 ± 0.24 pM (Table 4), and the WPCF MMHg flux to NY/NJ Harbor (3.7 ± 0.4 mol y^{-1} ; Table 5) was calculated in the same manner as described above. This estimated MMHg flux from WPCFs is about 3% of the total Hg flux.

Estimates of the fluxes of Pb, Ni, Cu, and Zn from WPCFs to NY/NJ Harbor were made using data provided by the NYSDEC Division of Water. Average monthly inputs were calculated from average daily maximum fluxes (2001-2007) for each of 11 WPCFs (Port Richmond, Wards Island, Bowery Bay, Owls Head, Oakwood Beach, Hunts Point, Newtown Creek, 26th Ward, North River, Yonkers Joint, and Red Hook) discharging to NY/NJ Harbor. Annual fluxes were calculated for Pb (34.6 Kmol y^{-1}), Cu (384 Kmol y^{-1}), Ni (169 Kmol y^{-1}), and Zn (1031 Kmol y^{-1}). These 11 WPCFs account for about 65% (1.57×10^9 m³ y^{-1}) of the effluent discharged to the Harbor, so the fluxes were scaled to represent the flux from all WPCFs (including East River) discharging to NY/NJ Harbor (2.41×10^9 m³ y^{-1} ; NYC DEP, 2003; Table

5). The WPCF flux estimates for Pb, Cu, Ni, and Zn include the discharge from the East River WPCFs, since the reported East River flux of these metals (Table 5) does not include the East River WPCF flux. WPCF Pb flux estimates calculated from independent sources (CARP and NYSDEC; Table 5) agree within a factor of 2, although, as expected, the estimate based on CARP data is less ($24 \pm 3.8 \text{ Kmol y}^{-1}$) since it does not include the contribution of the East River WPCFs.

3.5.4 *Benthic flux*

With the exception of MMHg (Hammerschmidt and Fitzgerald, 2008), there are no direct measurements of benthic flux (sediment-water) available for the trace metals of interest in NY/NJ Harbor. Therefore, measured estuarine fluxes in the literature were used to estimate benthic fluxes in NY/NJ Harbor. Mason et al. (2006) used sediment core flux chambers collected in the Baltimore Harbor (MD) region of Chesapeake Bay to measure fluxes of Hg ($119 \pm 261 \text{ nmol m}^{-2} \text{ y}^{-1}$), MMHg ($3.8 \pm 6.3 \text{ nmol m}^{-2} \text{ y}^{-1}$), Cd ($2205 \pm 7319 \text{ nmol m}^{-2} \text{ y}^{-1}$), Pb ($234 \pm 1123 \text{ nmol m}^{-2} \text{ y}^{-1}$), and Zn ($1611 \pm 4041 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$). Warnken et al. (2001) measured the flux of Ni ($612 \pm 89 \text{ nmol m}^{-2} \text{ y}^{-1}$) using benthic chambers in Galveston Bay (TX), and Riedel et al. (1997, 1999) measured Cu ($330 \pm 108 \text{ nmol m}^{-2} \text{ y}^{-1}$) fluxes using microcosms and intact sediment cores (high and low dissolved oxygen) from Baltimore Harbor. The estimated fluxes of trace metals from NY/NJ Harbor sediment (Table 5) were calculated using the literature flux measurements and the estimated surface area of Harbor sediment ($5.0 \times 10^8 \text{ m}^2$). Hammerschmidt et al. (2008) estimated the diffusional flux of MMHg from the sediments of NY/NJ Harbor ($8 \pm 4 \text{ mol y}^{-1}$), and the error (SE) associated with this estimate overlaps the estimate of MMHg flux based on Mason et al. (2006) measurements ($2 \pm 3 \text{ mol y}^{-1}$; Table 5). Estimates of NY/NJ Harbor Zn flux based on Mason et al. (2006; $810 \pm 2000 \text{ Kmol y}^{-1}$) and

Warnken et al. (2001; $430 \pm 40 \text{ Kmol y}^{-1}$) agree within a factor of 2, although the error associated with the Mason et al. estimate is large. Finally, although not included in the budget, the estimated Harbor Fe flux based on Mason et al. ($1.43 \pm 0.9 \times 10^5 \text{ Kmol}$) agrees well with measured benthic Fe flux ($1.4 \pm 0.5 \times 10^5 \text{ Kmol}$) in the Harbor (The Academy of natural Sciences of Philadelphia, 1995).

3.5.5 *Direct atmospheric deposition*

There is limited information available on the atmospheric deposition of metals to the NY/NJ Harbor region. Therefore, direct atmospheric deposition of metals to NY/NJ Harbor was estimated from wet and dry deposition rates available for the Tokyo (Japan) urban estuarine environment (Sakata et al., 2006b; Sakata and Marumoto, 2004). Average atmospheric deposition of Hg ($121 \pm 10 \text{ nmol m}^{-2} \text{ y}^{-1}$; 56% wet deposition), Cd ($2.2 \pm 0.3 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; 57% wet), Cu ($90.8 \pm 14.9 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; 35% wet), Pb ($76.2 \pm 12.4 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; 60% wet), and Ni ($75.2 \pm 8.0 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; 16% wet) were obtained from Sakata et al. (2006b; average fluxes from biweekly collections at 10 sites), while Zn ($1110 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; 25% wet) deposition (no indication of variance) was reported by Sakata and Marumoto (2004; average flux from biweekly collections at one site). These bulk (wet + dry) deposition fluxes were scaled to the surface area of NY/NJ Harbor ($5.0 \times 10^8 \text{ m}^2$) to estimate direct atmospheric deposition of each metal to the Harbor (Table 5). The variance term was calculated by propagation of errors for the combined variability (SE) associated with wet and dry deposition of each metal. Atmospheric deposition of MMHg was calculated to be $0.9 \pm 0.1 \text{ mol y}^{-1}$ based on the assumption that it is 3% of the NY/NJ Harbor Hg flux (Balcom et al., 2008; Table 5), which is the average MMHg:HgT ratio for coastal precipitation (Hammerschmidt et al., 2007). The error for the MMHg flux is assumed to be the same proportion as the error for the Hg flux, but is only approximate.

The use of Tokyo bulk deposition flux measurements to estimate atmospheric trace metal fluxes to NY/NJ Harbor is supported by comparison with atmospheric deposition reported in the literature. Balcom et al. (2008) estimated Hg wet deposition ($54 \pm 8 \text{ nmol m}^{-2} \text{ y}^{-1}$) using results from the Mercury Deposition Network (MDN; 2006), and calculated direct Hg deposition to NY/NJ Harbor of $30 \pm 4 \text{ mol y}^{-1}$ (Table 5). This estimate is within a factor of 2 of estimated bulk Hg deposition to NY/NJ Harbor ($60 \pm 5 \text{ mol y}^{-1}$), and agrees well with the Tokyo wet only Hg deposition estimate ($34 \pm 4 \text{ mol y}^{-1}$; Sakata et al., 2006b). Yi et al. (2006) have measured atmospheric dry deposition of Pb ($88 \pm 41 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$), Ni ($47 \pm 9 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$), Cu ($115 \pm 45 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$), and Zn ($530 \pm 162 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$) near NY/NJ Harbor (New Brunswick and Jersey City, NJ; combined average deposition rates from intensive surveys lasting from hours to several days and 12-day integrated collections; used modified MIC-B collectors and greased strips). These dry deposition fluxes are similar to those for Pb ($76 \pm 6 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$) and Cu ($91 \pm 13 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$) reported by Sakata et al. (2006b), and the Zn dry deposition flux ($832 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$) reported by Sakata and Marumoto (2004), but Ni fluxes seem to be somewhat elevated ($75 \pm 8 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; Sakata et al, 2006b) in the Tokyo Bay region as compared to the Harbor. Sakata and Marumoto (2004) compared their dry deposition fluxes to measurements in other urban areas and found that Tokyo (Komae) deposition fluxes of Cu, Pb, and Zn were a factor of 1 to 4 smaller than those from Chicago (IL), and a factor of 6 to 20 smaller (factor of 150 for Cd) than Izmir, Turkey. Therefore, our atmospheric metals flux estimates for NY/NJ Harbor are likely conservative as compared to other urban areas.

3.5.6 Metals fluxes out of NY/NJ Harbor

The major processes removing trace metals from NY/NJ Harbor include estuarine exchange with the continental shelf and burial in sediment. Additional sinks include evasion of

elemental Hg (Hg^0), and bioaccumulation and (photo)demethylation of MMHg. Exchange between the Harbor estuary and the adjacent continental shelf was estimated using the total net volume flux of freshwater to the Harbor ($3.64 \pm 0.21 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$), which includes inputs from all major rivers, the East River, and WPCF effluent. This flux is comparable to that estimated for net exchange of water through the Rockaway-Sandy Hook transect at the mouth of the Harbor ($3.2 \times 10^{10} \text{ m}^3 \text{ y}^{-1}$; Geyer and Chant, 2006). Mixing of the water column is vigorous in the Lower Harbor and Raritan Bay, and total Hg and MMHg distributions were found to be relatively homogeneous (Balcom et al., 2008). The net flux of water out of the Harbor was multiplied by the combined mean total metal concentrations in the Lower Harbor (Rockaway-Sandy Hook data for Cd, Pb, Ni, Cu, and Zn) and Raritan Bay (Table 4; surface and bottom waters) to yield estuarine exchange fluxes (Table 5). Variance terms were calculated by propagation of errors based on the variance (SE) associated with the volume flux of water leaving the Harbor and the combined metals concentrations.

Mercury and MMHg have unique characteristics that lead to additional sink terms in their budgets. Evasion of Hg^0 from surface waters of NY/NJ Harbor was estimated by scaling the mean flux ($125 \pm 40 \text{ nmol m}^{-2} \text{ y}^{-1}$; Rolffhus and Fitzgerald, 2001) from nearby Long Island Sound (LIS). When scaled to the surface area of the Harbor ($5.0 \times 10^8 \text{ m}^2$), the estimated Hg^0 flux is $60 \pm 20 \text{ mol y}^{-1}$ (Balcom et al., 2008; Table 5). MMHg is decomposed photochemically in surface waters (Sellers et al., 1996; Hammerschmidt and Fitzgerald, 2006), and MMHg photodecomposition in NY/NJ Harbor was estimated from the relationship between the rate of demethylation, intensity of photosynthetically active radiation (PAR), and dissolved MMHg concentration determined for arctic lakes (Hammerschmidt and Fitzgerald, 2006). The estimated loss of MMHg by photodecomposition is $2 \pm 1 \text{ mol y}^{-1}$ in the Harbor, assuming a mean annual

PAR flux of about $25 \text{ E m}^{-2} \text{ d}^{-1}$, a PAR attenuation coefficient of about -0.7 m^{-1} in the turbid waters of the Harbor (NYC DEP, 2003), and an average dissolved MMHg level of $0.10 \pm 0.01 \text{ pM}$ (Balcom et al., 2008).

3.6 *Mass balances for total metals in NY/NJ Harbor*

3.6.1 *Sources and sinks of total metals*

We have estimated current annual loadings of Hg (3100 mol y^{-1}), MMHg (37 mol y^{-1}), Cd (25 Kmol y^{-1}), Pb (850 Kmol y^{-1}), Ni (1700 Kmol y^{-1}), Cu (2800 Kmol y^{-1}), and Zn (7100 Kmol y^{-1}) to NY/NJ Harbor (Table 5). The uncertainty associated with the total inputs was calculated as the geometric mean of the errors associated with the other sources for each metal. River inputs are the largest source of each metal (38 to 88% of total inputs) to the Harbor (Figure 12). The East River is the next largest source for the majority of the metals, accounting for 11 to 26% of total inputs for Hg, Cd, Ni, Cu, and Zn, but only 8% for MMHg and 1% for Pb. The low East River Pb inputs may reflect the lack of natural sources of freshwater to the East River, as mentioned previously. Water pollution control facilities (WPCFs) are a significant source of metals, accounting for 5 to 23% of the total input for each metal. Benthic flux of both MMHg (21%) and Ni (19%) are of nearly the same magnitude as WPCF inputs to NY/NJ Harbor (Figure 12).

The major sinks for metals in NY/NJ Harbor include estuarine exchange with the continental shelf and burial in sediments, the latter calculated by difference (not for MMHg) from the other terms in the mass balances (Table 5). Burial in sediments was the largest sink for Hg, Pb, Ni, Cu, and Zn in the Harbor, ranging from 58 to 95% of the total sinks (Figure 13). In contrast, estuarine exchange was the major sink for Cd (73%). As discussed earlier, Cd is mainly (>75%) in the dissolved phase in the saline waters of the Harbor, making this trace metal

more available for advection in the water column. Unlike the other metals, the burial flux of MMHg ($4 \pm 3 \text{ mol y}^{-1}$) was estimated by Balcom et al. (2008) from the burial flux of Hg, assuming that MMHg is 0.5% of Hg in sediments (Hammerschmidt et al., 2008). Additional sinks for MMHg include (photo)demethylation (discussed in section 3.5.6) and a “biological processes” term. Balcom et al. (2008) argued that bioaccumulation and subsequent demethylation and/or removal by bioadvection (e.g., fish migration) is an important sink for MMHg in NY/NJ Harbor. The “biological processes” loss term ($17 \pm 11 \text{ mol y}^{-1}$) was estimated by difference from the other terms in the MMHg mass balance, and was the largest sink for MMHg (46%) in the Harbor. The uncertainty associated with the closing terms was calculated as the geometric mean of the errors associated with the other terms in each mass balance.

3.6.1.1 Calculation of fluvial metals flux from sediment loadings

Rivers, as shown, are an especially important source of metals to NY/NJ Harbor, and an independent estimate of these fluxes provides a means of validating and constraining our biogeochemical mass balances for the Harbor. Wall et al. (2008) used an Acoustic Doppler Current Profiler (ADCP) to measure suspended sediment concentrations and discharge at a site located 3.7 km south of Poughkeepsie (116 km north of the Battery), and found a 4-year (2002-2006) mean annual sediment discharge of 7.37×10^5 metric tons. Abood et al. (1999) also estimated sediment loadings from the Hudson River to the Harbor at about 7.37×10^5 metric tons y^{-1} (based on a number of assumptions), but stated that loads are locally variable, and are approximate. HydroQual (2003) used an empirical method for estimating suspended sediment loads in rivers that is based on analysis of sediment discharge and general characteristics from a variety of rivers. Their estimate of mean total sediment discharge (1988 to 2000, $n = 4$) for the Hudson and Mohawk Rivers (3.29×10^5 metric tons y^{-1}) was lower than the other estimates, but

the variance (about 40% RSE) associated with the HydroQual (2003) estimate was a useful constraint because it is based on a longer-term record, and is likely representative of natural variability. The Wall et al. (2008) mean sediment load estimate for the lower Hudson (Poughkeepsie) was assigned an error of 40% ($8.12 \pm 3.25 \times 10^{11} \text{ g y}^{-1}$) to estimate metals fluxes from the lower Hudson to NY/NJ Harbor. This estimate of sediment load overlaps the estimate ($3.62 \pm 1.38 \times 10^{11} \text{ g y}^{-1}$) from HydroQual (2003). Using the approach presented earlier, the Hudson sediment flux was scaled by a factor of 1.1 to represent the flux from all major rivers entering NY/NJ Harbor. No attempt has been made to estimate sediment loadings within separate region of the Harbor, or sediment transport among regions.

Estimates of the fluxes of metals from rivers were calculated using the sediment delivery flux ($8.12 \pm 3.25 \times 10^{11} \text{ g y}^{-1}$) and the mean suspended particle metals concentrations in the waters of the Hudson. Suspended particle concentrations of Hg ($3.54 \pm 0.54 \text{ nmol g}^{-1}$; $n = 4$; collected 1999 to 2001; CARP, 2006) and Cd ($10.16 \pm 2.98 \text{ nmol g}^{-1}$; $n = 7$; collected 1995 to 1997; Yang and Sañudo-Wilhelmy, 1998) were from the lower Hudson River (25 to 100 km north of the Battery). NYS DEC SWMS (2007) suspended particle concentrations of Pb ($0.58 \pm 0.14 \text{ } \mu\text{mol g}^{-1}$), Ni ($0.90 \pm 0.28 \text{ } \mu\text{mol g}^{-1}$), Cu ($1.96 \pm 0.35 \text{ } \mu\text{mol g}^{-1}$), and Zn ($4.72 \pm 0.48 \text{ } \mu\text{mol g}^{-1}$) at Poughkeepsie ($n = 16-17$; collected 1999 to 2001) were used to calculate river fluxes of those metals. The calculated fluxes were $2900 \pm 1200 \text{ mol y}^{-1}$ for Hg, $8.2 \pm 4.1 \text{ K mol y}^{-1}$ for Cd, $470 \pm 220 \text{ K mol y}^{-1}$ for Pb, $730 \pm 370 \text{ K mol y}^{-1}$ for Ni, $1600 \pm 700 \text{ K mol y}^{-1}$ for Cu, and $3800 \pm 1600 \text{ K mol y}^{-1}$ for Zn. All these fluxes overlap (\pm SE) the fluxes calculated from water column metals concentrations and river volume fluxes (Table 5), adding support to our mass balances for NY/NJ Harbor.

3.6.2 Atmosphere-watershed contributions

Although direct atmospheric deposition to the surface of NY/NJ Harbor is a small source of Hg to the Harbor, atmospheric deposition and subsequent leaching from the watershed is estimated to be a significant source of Hg to rivers (e.g., Balcom et al., 2004). The atmospheric wet deposition of Hg to the watershed of NY/NJ Harbor averaged $0.054 \pm 0.008 \mu\text{mol m}^{-2} \text{y}^{-1}$ (MDN, 2006; 2000 to 2005), which equates to $2270 \pm 340 \text{ mol y}^{-1}$ for the whole watershed ($4.2 \times 10^{10} \text{ m}^2$; Balcom et al., 2008). Since the watershed delivery factor for Hg has been estimated to range from 25 to 30% of wet atmospheric fluxes (Engstrom et al., 1994; Lamborg et al., 2002; Fitzgerald et al., 2005), watershed Hg yields were estimated to range from 0.011 to $0.019 \mu\text{mol m}^{-2} \text{y}^{-1}$, resulting in delivery of 480 to $780 \text{ mol Hg y}^{-1}$ to the major rivers surrounding the Harbor (Balcom et al., 2008). Therefore, watershed fluxes are estimated to account for 23 to 37% of the Hg flux from rivers to NY/NJ Harbor ($2100 \pm 820 \text{ mol y}^{-1}$) in the current study. The range of watershed Hg yields given above is similar to the $0.011 \mu\text{mol m}^{-2} \text{y}^{-1}$ estimated by Driscoll et al. (1998) from measurements of fluxes for a small wetland in the Adirondack region of New York. Additionally, these watershed Hg yields fall within the range of values reported for other areas of the U.S., including 0.007 to $0.11 \mu\text{mol m}^{-2} \text{y}^{-1}$ for Maryland (Lawson et al., 2001), 0.004 to $0.051 \mu\text{mol m}^{-2} \text{y}^{-1}$ for Wisconsin (Hurley et al., 1995; Krabbenhoft et al., 1995) and 0.001 to $0.032 \mu\text{mol m}^{-2} \text{y}^{-1}$ for Minnesota (Balogh et al., 2005).

As discussed earlier (section 3.5.5), the atmospheric deposition of MMHg was estimated to be 3% of the HgT flux ($0.0016 \pm 0.0002 \mu\text{mol m}^{-2} \text{y}^{-1}$), based on the average MMHg:HgT ratio for coastal precipitation (Hammerschmidt et al., 2007). Assuming that the watershed yield of MMHg is also 3% of the HgT flux, watershed MMHg yields are estimated to range from 3.4 to $5.6 \times 10^{-4} \mu\text{mol m}^{-2} \text{y}^{-1}$, resulting in delivery of 14 to 23 mol y^{-1} to rivers. This indicates that

watershed delivery may account for the majority of the MMHg flux from rivers to NY/NJ Harbor ($23 \pm 9 \text{ mol y}^{-1}$) estimated in the current study. Similarly, the watershed MMHg yield of $8.5 \times 10^{-4} \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$ calculated from measured fluxes by Driscoll et al. (1998) indicates that as much as $36 \text{ mol MMHg y}^{-1}$ may be delivered to rivers. These findings imply that there may be limited net in-situ production and input of MMHg from river sediments. This is a very testable hypothesis. Lawson et al. (2001) reported that there was significant production of MMHg in Maryland watersheds, that MMHg was less strongly retained by the watersheds than other metals, and that watershed yields were often 100% of the atmospheric deposition of MMHg. The watershed Hg yields reported above fall within the range of values reported for other areas of the U.S., including $1.5 \text{ to } 8.0 \times 10^{-4} \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$ for Maryland (Lawson et al., 2001), $2.5 \text{ to } 9.5 \times 10^{-4} \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$ (Hurley et al., 1995; Krabbenhoft et al., 1995) and $15.0 \times 10^{-4} \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$ (Watras et al., 2005) for Wisconsin, and $1.6 \text{ to } 4.5 \times 10^{-4} \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$ for Minnesota (Balogh et al., 2005).

Since watershed export factors are not available for all metals, watershed yield is sometimes estimated as the fraction of total atmospheric deposition (wet + dry) that is accounted for by stream export (fluvial) flux. As noted by Lawson et al. (2001), however, calculating yield in this manner ignores contributions from the leaching of metals from watershed soils, and, for many metals, natural weathering is important and should be included in the estimate of watershed yield. The estimated watershed yield of Hg (river flux normalized to watershed area) is 41% of our estimate of bulk (wet + dry) atmospheric Hg deposition ($0.12 \text{ } \mu\text{mol m}^{-2} \text{ y}^{-1}$; Sakata et al., 2006) to the NY/NJ Harbor region. Lawson et al. (2001) also reported that Hg was strongly retained in Maryland watersheds (7 to 37% yield). Watershed yields calculated in the same manner for Cd (15%), Pb (23%), Ni (20%), Cu (45%), and Zn (6%) were all quite low,

however. In contrast, yields for Cd, Ni, and Cu reported by Lawson et al. (2001) indicated that these metals were not strongly retained by watersheds. River fluxes do not seem to be an accurate indicator of watershed yield in the Hudson River, and there may be sinks (e.g., sedimentation) that account for the reduced yields in the Hudson.

3.6.3 Comparison with NY/NJ Harbor metals budgets in the literature

Klinkhammer and Bender (1981) produced seasonal budgets for total Cd, Ni, Cu, and Zn in NY/NJ Harbor based on sampling conducted in April 1994 and October 1975 (Table 6). They included rivers, sewage, and the Bight (oceanic input) as source terms, and estuarine exchange as the sink term. The imbalance between the total of the sources and estuarine exchange (sink) has been included as a closing term similar to the sediment burial closing term used in the budgets in the current study (Table 6). Under low-flow conditions (October), sewage input was the largest source term (37 to 67% of total inputs), while ocean input was the smallest (<24%). During the high-flow (April) survey, river inputs were nearly equal to sewage inputs and were the largest source term for Zn (56 to 65%). Ocean input was the smallest term again in April.

Total metals inputs in the budgets of Klinkhammer and Bender (1981) were much higher than in the mass balances produced in the current study. Inputs of Cd (8 to 24x), Ni (2 to 5.5x), Cu (1.5 to 3.5x) and Zn (1 to 4x) were all higher during 1974 and 1975 (Table 7). The elevation in total inputs was generally greater for all metals during the April high-flow period (Table 6). As discussed previously, Sañudo-Wilhelmy and Gill (1999) reported a decrease of similar magnitude in dissolved metal concentrations in surface waters of the Hudson River estuary for the mid-1970 to mid-1990 time period. Total inputs would have been even higher in the Klinkhammer and Bender budgets if all rivers had been included (their rivers input term is for the Hudson only) as well as source terms for atmospheric deposition and benthic flux. While

Klinkhammer and Bender found that WPCFs were typically the largest source of metals to the harbor, river inputs (38 to 88% of total) were considerably larger than WPCF inputs in the current study, indicating a significant reduction in sewage contamination with metals over the past 25 to 30 years.

Yang and Sañudo-Wilhelmy (1998) produced budgets for total Cd in NY/NJ Harbor from sample collections made in October 1995 and April 1996 (Table 6), and Balcom et al. (2008) constructed contemporary budgets from seasonal analyses (2002-2004) of Hg and MMHg. Both studies included rivers, sewage, and atmospheric deposition as source terms, and estuarine exchange and sediment burial as sinks. Yang and Sañudo-Wilhelmy included oceanic input and benthic flux as additional sources, and Balcom et al. used the same Hg and MMHg source and sink terms (with the exception of benthic flux) as the current study. All source and sink terms were measured or calculated in the Yang and Sañudo-Wilhelmy (1998) study, so there were no closing terms calculated by difference. Similar to the Klinkhammer and Bender (1981) budget for Cd, Yang and Sañudo-Wilhelmy reported that sewage (57% of total inputs) and ocean inputs (33%) were the largest source terms under low-flow conditions (October). River inputs (31%) exceeded sewage inputs (25%) during April, although ocean inputs (44%) remained high. Although sediment burial of Cd nearly equaled estuarine exchange during October, as expected, estuarine exchange was the dominant sink term (88%) during April high-flow conditions. The total input of Cd to the Harbor in April 1996 (23.7 Kmol y^{-1} ; Table 6) in the Yang and Sañudo-Wilhelmy (1998) budget is roughly the same as that calculated in the present study (25 Kmol y^{-1}). However, river (0.9 Kmol y^{-1}) and oceanic Cd inputs (3.3 Kmol y^{-1}) were much lower in October 1995, resulting in lower total inputs (10.1 Kmol y^{-1}). Overall, total Cd inputs in the current study and in the Yang and Sañudo-Wilhelmy budgets are considerable smaller than

reported by Klinkhammer and Bender (1981) for the mid-70s ($190\text{-}590 \text{ Kmol y}^{-1}$), with the largest decrease resulting from lowered sewage inputs (Tables 5 and 6). The Balcom et al. (2008) Hg and MMHg budgets are quite similar to the mass balances produced in the current study (Table 5) as several of the source and sink terms reported were obtained from the earlier study. Total loadings of Hg and MMHg ($3100 \pm 900 \text{ Hg mol y}^{-1}$ and $37 \pm 10 \text{ mol MMHg y}^{-1}$) in the current study compare very well with Balcom et al. (2008), and river inputs are the dominant sources in these mass balances.

The oceanic input term used by Yang and Sañudo-Wilhelmy (1998) and Klinkhammer and Bender (1981) is based on salinity measurements and water column metals concentrations in the lower Hudson River and Upper NY/NJ Harbor, and the input flux estimated is for the Narrows. This does not correspond to the region used for estuarine exchange estimates in the current study (Rockaway-Sandy Hook transect), and, therefore, a corresponding oceanic input term has not been included in the current mass balances.

3.6.4 Modern and historic Hg sedimentary accumulation in NY/NJ Harbor

Dated lake sediments have been the primary source of secular data for reconstructing Hg accumulation/depositional patterns associated with preindustrial periods to the modern era. Globally, lake sediment archives from remote locations (182 sediments cores from 90 lakes where localized human-related impact is small) show that the accumulation ratio or “anthropic global increase” relative to preindustrial levels, is remarkably uniform at 3 ± 1 (Fitzgerald et al., 2008). Localized enhancements are evident in urban areas (i.e., Minneapolis/St. Paul, MN) with peaks in the 1960-1970 period (Engstrom et al., 2006). We have reported new and detailed historical data for Hg accumulation in a well studied, scrupulously dated, varved sediment core (Lima et al., 2003; 2005) from the Pettaquamscutt River Estuary (PRE, RI; Fitzgerald et al.,

2008). This system is relatively remote from point sources with a watershed that can be characterized as rural/residential. Accordingly, it provides a potentially valuable analog for assessing anthropic impact and temporal changes in Hg accumulation/inputs in the Harbor Estuary over the past half century. The PRE results are striking and show that the ratio (actual/preindustrial Hg accumulation) peaked in 1950 and 1960 at value of 12. The ratio in 1997 was 4, representing a substantial decline in Hg inputs by about a factor of 3.

What do the sedimentary Hg accumulation data from the Harbor indicate? Unfortunately, sediment accumulation fluxes for Hg are not available. However, and using the summaries provided by Bopp et al. (2006) for Hg concentrations in sediments at a variety of sites in the Harbor Estuary, an approximate accumulation ratio can be estimated (assuming no change in sediment depositional fluxes). Thus, in the mid-1960s the actual/preindustrial Hg concentration ratio was ca. 60 at a station in upper Newark Bay, > 100 in the Arthur Kill, 13 in Jamaica Bay, and 19 in the Upper Harbor. Results from the early to mid 1990s suggest that these approximate measures of anthropogenic Hg impact declined over the intervening three decades. The concentration ratios were respectively, about 20, 27, 3, and 9 in sediment samples obtained in 1995 and 1996. The impact (with the exception of Jamaica Bay) is much greater than observed for the PRE where the 1997 ratio was 4. Although, there has been a decline in contaminant Hg inputs to the Harbor Estuary since the 1960s and 70s, it is difficult to provide a quantitative estimate. However, a factor of 3-5 is likely, which is comparable to the PRE where the decline was about 3. Nevertheless, and not unexpectedly, there is substantially more contaminant Hg accumulating per unit area in the Harbor Estuary (ca. 2-7, ignoring the Jamaica Bay site) as compared to the PRE, whose watershed is rural/residential.

4.0 Summary

There is a need for high quality time series measurements of filtered and suspended particle metals concentrations, as well as important ancillary parameters (e.g., POC), in the waters of the Hudson River and NY/NJ Harbor. The water column data available for the middle and upper Hudson encompass about 15 years, but these measurements do not include the significant decline in concentrations and loadings of trace metals over the past 25 to 30 years. In particular, there are limited measurements (1999-2001) of Hg and Cd concentrations in the middle and upper Hudson, and almost no data on suspended particle concentrations of these important trace metals. Filtered and total metals concentrations have been measured in the lower reaches of NY/NJ Harbor during the past 25 years, but information on suspended particle metals is very limited. The decline in metals concentrations in the waters of NY/NJ Harbor since the mid-1970s was established by a comparison between adjacent regions since the time series of measurements is incomplete for any one region of the Harbor. Time series measurements of filtered, total, and suspended particle Hg and Cd are needed for the major regions of the Harbor, including the East River where only filtered data is available for most metals. The sediment-water fluxes of most trace metals has not been measured in NY/NJ Harbor and are needed considering the importance of this source term in some mass balances (e.g., MMHg). Similarly, bulk (wet and dry) atmospheric deposition measurements are limited for most metals in the Harbor region, and although direct deposition to the Harbor is a small component in the mass balances, atmospheric deposition of metals and subsequent yield from watersheds accounts for a substantial portion of the fluxes of metals in rivers. We hypothesize that much of the MMHg in NY/NJ Harbor is likely derived/connected to net production in the Hudson River watershed, and that there is limited MMHg input from river sediments.

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Table 1. Lower Hudson River and estuarine turbidity maximum (ETM) water column trace metal concentrations (mean \pm SD with range in parentheses). Geographic ranges indicated as kilometer-points from the Battery (Manhattan).

Sampling locations and dates	Salinity (ppt)	Cd (nM)	Cu (nM)	Fe (nM)	Ni (nM)	Zn (nM)	Ag (pM)	Hg (pM)	Pb (nM)	Reference
(1) Battery to Ossining, NY										
<i>(kmp 0 to ~55)</i>										
Apr. 1974 and Oct. 1975										
filtered – surface and deep	<1-20	2.31 \pm 1.59 ¹	51.5 \pm 16.3 ¹	492 \pm 505 ¹	49.8 \pm 38.8 ¹	159 \pm 187 ¹				Klinkhammer and Bender, 1981 ¹
total – surface and deep	<1-20	2.94 \pm 1.62 ¹	85.0 \pm 35.4 ¹	14100 \pm 11600 ¹	68.6 \pm 55.0 ¹	233 \pm 162 ¹				
(2) Lower Hudson River, Harlem River to Newburgh, NY										
<i>(kmp ~25 to 100)</i>										
filtered - surface	~0-10 ^{2,4}	0.43 \pm 0.34 ² (0.11-1.12) 0.67 \pm 0.24 ³ (0.32-1.15)	25.0 \pm 4.0 ² (20.6-31.5)	666 \pm 839 ² (20.3-2530)	11.6 \pm 4.0 ² (7.60-20.2)	18.0 \pm 10.3 ² (7.7-32.6)	24.4 \pm 16.3 ² (4.7-45.6)	3.7 \pm 1.8 ² (1.0-6.9) 13.4 \pm 12.6 ³ (2.54-35.1)	0.95 \pm 1.11 ² (0.19-3.43)	Sanudo-Wilhelmy and Gill, 1999 ² CARP, 2007 ³ Yang and Sanudo-Wilhelmy, 1998 ⁴
total - surface		0.81 \pm 0.03 ³ (0.78-0.84) 0.55 \pm 0.30 ⁴ (0.26-1.15)						144 \pm 75.0 ³ (40.0-216)		
(3) Estuarine turbidity maximum										
<i>(kmp ~4 to 25)</i>										
filtered - surface	~2-20 ^{2,4}	0.75 \pm 0.35 ² (0.15-1.2) 0.90 \pm 0.28 ³ (0.49-1.4)	29.0 \pm 6.5 ² (21.6-39.9)	312 \pm 542 ² (16.6-1800)	15.9 \pm 6.0 ² (7.9-26.0)	42.9 \pm 28.0 ² (17.3-106)	94.4 \pm 63.1 ² (23.0-261)	4.3 \pm 1.0 ² (2.8-6.0) 7.98 \pm 4.49 ³ (2.3-12.1) 24.8 \pm 29.4 ⁵ (1.1-58.3)	0.58 \pm 0.76 ² (0.09-2.61)	Sanudo-Wilhelmy and Gill, 1999 ² CARP, 2007 ³ Yang and Sanudo-Wilhelmy, 1998 ⁴ Heyes et al., 2004 ^{5,6,7}
total - surface		0.74 \pm 0.28 ³ (0.35-1.01) 1.15 \pm 0.86 ⁴ (0.34-3.65)						53.9 \pm 21.1 ³ (29.4-72.8) 264 \pm 194 ⁵ (87.4-581)		
filtered – bottom								49.4 \pm 38.4 ⁶ 37.9 \pm 15.9 ⁷		
total – bottom								1112 \pm 499 ⁶ 613 \pm 349 ⁷		

¹ Average of means for Hudson R. and Estuary samples collected Apr. 1974 and Oct. 1975 (Table 3; , $n = \sim 65$). Error reported is the geometric mean of the standard deviations associated with means; ^{2,4} Oct. 1995/1996 and Apr. 1996/1997, $n = 8-20$; ³ Feb. 1999 to Oct. 2001, $n = 3-8$; ⁵ Oct. 2000 and Feb./June 2001, $n = 5-6$; ⁶ 0.5 m off bottom, range not given, Nov. 2001 tidal cycle study, $n = 6$; ⁷ 1.5 m off bottom, range not given, Nov. 2001 tidal cycle study, $n = 6$.

Table 2. Lower Hudson River and estuarine turbidity maximum (ETM) suspended particle and sediment metals concentrations (mean \pm SD with range in parentheses). Geographic ranges indicated as kilometer-points from the Battery (Manhattan).

Sampling locations and dates	TSS (mg l ⁻¹)	Cd (nmol g ⁻¹)	Cu (μ mol g ⁻¹)	Fe (mmol g ⁻¹)	Ni (μ mol g ⁻¹)	Zn (μ mol g ⁻¹)	Ag (μ mol g ⁻¹)	Hg (nmol g ⁻¹)	Pb (μ mol g ⁻¹)	Reference
(1) Lower Hudson River										
<i>Harlem River to Newburgh, NY (kmp ~25 to 100)</i>										
particulate – surface	8.3 – 27.7 ²	5.45 \pm 1.0 ¹ (4.31-7.43) 10.16 \pm 7.89 ² (0.53-19.5)						3.54 \pm 0.54 ¹ (2.48-4.98)		CARP, 2007 ¹ Yang and Sanudo-Wilhelmy, 1998 ²
(2) Estuarine turbidity maximum										
<i>(kmp ~4 to 25)</i>										
particulate – surface	1.7 - 219 ² 4.0 – 110 ³	6.55 ¹ (2.03-7.43) 12.59 \pm 9.51 ² (0.14-27.22) 8.27 \pm 3.04 ³ (3.11-12.99)	2.72 \pm 0.51 ³ (1.90-3.51)	0.92 \pm 0.08 ³ (0.80-1.09)	--	11.92 \pm 12.07 ³ (3.76-38.9)	0.053 \pm 0.007 ³ (0.041-0.062)	2.20 \pm 0.48 ¹ (1.30-2.96)	1.74 \pm 0.33 ³ (1.37-2.39)	CARP, 2007 ¹ Yang and Sanudo-Wilhelmy, 1998 ² Feng et al., 2002 ³ Heyes et al., 2004 ^{4,5}
particulate – bottom	25.3 – 490 ³ ~50 – 600 ^{4,5}	15.95 \pm 7.04 ³ (8.10-32.3)	3.09 \pm 0.41 ³ (2.58-4.00)	0.97 \pm 0.07 ³ (0.91-1.11)	--	11.34 \pm 11.79 ³ (3.55-35.56)	0.062 \pm 0.007 ³ (0.048-0.072)	4.62 \pm 1.66 ⁴ 3.17 \pm 1.07 ⁵	1.75 \pm 0.23 ³ (1.35-2.13)	
sediment		5.52 \pm 0.89 ⁶ (0.53-12.63)	1.48 \pm 0.76 ⁶ (0.32-2.28)	0.64 \pm 0.10 ⁶ (0.38-0.73)	--	2.58 \pm 0.87 ⁶ (1.10-3.66)	0.03 \pm 0.02 ⁶ (0.002-0.06)	4.69 \pm 1.02 ⁷ 4.71 \pm 2.19 ⁷ (2.50-10.0)	0.86 \pm 0.32 ⁶ (0.21-1.19)	Feng et al., 2002 ⁶ Heyes et al., 2004 ⁷

¹Feb. 1999 to Oct. 2001, $n = 2-4$; ²Oct. 1995/1996 and Apr. 1996/1997, $n = 7-15$; ³Nov. 1994 and Aug. 1995 tidal cycle study, $n = 10-11$; ⁴0.5 m off bottom, range not given, Nov. 2001 tidal cycle study, $n = 6$; ⁵ 1.5 m off bottom, range not given, Nov. 2001 tidal cycle study, $n = 6$; ⁶Nov. 1994 and Aug. 1995, $n = 14$; ⁷Oct. 2000, Feb., Mar., and June 2001, $n = 14$

Table 3. New York/New Jersey Harbor and NY Bight water column trace metal concentrations (mean \pm SD with range in parentheses). Geographic ranges indicated as kilometer-points from the Battery (Manhattan). Additional data for NY/NJ Harbor is plotted in Figure 8.

Sampling locations and dates	Salinity (ppt)	Cd (nM)	Cu (nM)	Fe (nM)	Ni (nM)	Zn (nM)	Ag (pM)	Hg (pM)	Pb (nM)	Reference
(1) Upper Harbor										
<i>Battery to Narrows (kmp -0 to -10)</i>										
filtered - surface	7-28 ^{1,2}	0.60 \pm 0.20 ¹ (0.37-0.81)	22.1 \pm 4.92 ¹ (15.2-28.2)	148 \pm 221 ¹ (31.9-634)	16.3 \pm 6.18 ¹ (8.39-25.4)	57.3 \pm 32.2 ¹ (35.8-124)	104.7 \pm 54.6 ¹ (49.0-214)	3.37 \pm 0.84 ¹ (2.22-4.44)	0.36 \pm 0.20 ¹ (0.11-0.62)	Sañudo-Wilhelmy & Gill, 1999 ¹ Yang & Sañudo-Wilhelmy, 1998 ² Paulson, 2005 ³
	25-29 ³	0.54 \pm 0.25 ³ (0.27-0.80)								
total - surface		0.74 \pm 0.30 ² (0.44-1.22)								
		0.55 \pm 0.25 ³ (0.28-0.80)								
filtered - bottom	25-30 ³	0.62 \pm 0.23 ³ (0.26-0.88)								
total - bottom		0.62 \pm 0.23 ³ (0.26-0.88)								
(2) Lower Harbor										
<i>Narrows to Rockaway-Sandy Hook (kmp ~ -10 to -25)</i>										
filtered - surface	16-28 ^{1,2}	0.49 \pm 0.11 ¹ (0.34-0.61)	16.8 \pm 5.02 ¹ (12.1-23.7)	42.1 \pm 19.8 ¹ (17.0-65.1)	13.6 \pm 2.89 ¹ (9.62-16.0)	34.5 \pm 11.8 ¹ (23.9-51.2)	71.0 \pm 24.7 ¹ (60.5-107)	3.25 \pm 1.58 ¹ (1.84-5.43)	0.19 \pm 0.11 ¹ (0.09-0.34)	Sañudo-Wilhelmy & Gill, 1999 ¹ Yang & Sañudo-Wilhelmy, 1998 ²
total - surface		0.63 ² (0.49-0.76)								
(3) Raritan Bay										
filtered - surface	26-27 ³	0.49 \pm 0.1 ³ (0.39-0.58)								Paulson, 2005 ³
total - surface		0.50 \pm 0.1 ³ (0.39-0.60)								
filtered - bottom	27 ³	0.48 \pm 0.05 ³ (0.4-0.51)								
total - bottom		0.48 \pm 0.05 ³ (0.4-0.51)								
(4) New York Bight										
<i>(kmp > -25)</i>										
filtered - surface and deep	>20 ⁴	2.09 \pm 1.36 ⁴	43.3 \pm 29.9 ⁴	179 \pm 1092 ⁴	80.9 \pm 53.4 ⁴	210 \pm 174 ⁴				Klinkhammer and Bender, 1981 ⁴
total - surface and deep		2.22 \pm 142 ⁴	66.1 \pm 46.6 ⁴	1969 \pm 1253 ⁴	88.6 \pm 55.5 ⁴	234 \pm 188 ⁴				

^{1,2} Oct. 1995/1996 and Apr. 1996/1997, $n = 2-7$; ³ Aug. 1999, $n = 4-15$; ⁴ Bight samples, Apr. 1974 and Oct. 1975 (Table 3), $n = 5-6$

Table 4. Concentrations (mean \pm SE) of total metals (dissolved + particulate) from various sources.

Location	HgT (pM)	MMHg (pM)	Cd (nM)	Pb (nM)	Ni (nM)	Cu (nM)	Zn (nM)
Combined Waterford (NY; Hudson R.) and Cohoes (NY; Mohawk R.) water concentrations	82.7 \pm 31.6 ¹	0.89 \pm 0.35 ²	0.56 \pm 0.25 ¹	29.6 \pm 1.0 ¹	25.0 \pm 13.4 ³	67.1 \pm 25.6 ³	112 \pm 22 ³
Lower East River water concentrations	63.4 \pm 16.9 ¹	0.26 \pm 0.04 ²	0.58 \pm 0.04 ¹ 0.29 \pm 0.04 ⁴	0.86 \pm 0.39 ⁴	38.4 \pm 5.3 ⁴	29.2 \pm 3.2 ⁴	119 \pm 6.2 ⁴
East River Water Pollution Control Facilities^a	97.1 \pm 10.4 ⁵	2.56 \pm 0.24 ⁵	1.47 \pm 0.18 ⁵	17.2 \pm 2.7 ⁵			
Lower Harbor and Raritan Bay water concentrations	36.7 \pm 7.2 ⁶ 43.0 \pm 7.2 ⁷	0.38 \pm 0.05 ⁷	0.50 \pm 0.06 ⁶ 0.40 \pm 0.02 ⁸	4.4 \pm 0.5 ⁸	16.1 \pm 1.3 ⁸	13.1 \pm 1.0 ⁸	10.5 \pm 1.2 ⁸

¹ CARP (2007), 1999-2001, $n = 4-18$, errors are the geometric mean of the SE associated with average concentrations; ² CARP (2007), 1999-2000, $n = 3-9$; Balcom et al., 2008; ³ NYSDEC SWMS (2007), 1999-2001, $n = 35$; ⁴ Buck et al. (2005), Jul. 2000 and Apr. 2001, $n = 4$; Wen et al. (1999); ⁵ CARP (2007), 1998-2001, $n = 3-11$; ⁶ CARP (2007), Mar./July 1999 and May/June 2000, $n = 4-6$; ⁷ Balcom et al. (2008), Aug. 2002, Feb./May/Aug. 2003, Feb. 2004, $n = 12-13$; ⁸ Paulson et al. (2005; Zn concentrations are particulate only), August 1999, $n = 19-20$;
^a volume-weighted concentrations

Table 5. Sources and sinks (fluxes) of heavy metals for New York/New Jersey Harbor (values in parentheses are comparison estimates described in the text).

	Hg (moles y ⁻¹)	MMHg (moles y ⁻¹)	Cd (K mol y ⁻¹)	Pb (K mol y ⁻¹)	Ni (K mol y ⁻¹)	Cu (K mol y ⁻¹)	Zn (K mol y ⁻¹)
Sources							
Rivers ^a	2100 ± 820 ¹	23 ± 9.0 ¹	14 ± 6.4 ¹	750 ± 70 ¹	630 ± 340 ²	1700 ± 660 ²	2800 ± 610 ²
East River	700 ± 200 ¹	2.9 ± 0.5 ^{1,7}	6.5 ± 0.7 ¹ (3.3 ± 0.5 ³)	9.5 ± 4.4 ³	420 ± 70 ³	320 ± 46 ³	1300 ± 140 ³
Water Pollution Control Facilities	140 ± 15 ^{1,7}	3.7 ± 0.4 ¹	2.1 ± 0.3 ¹	53 ± 2.6 ⁴ (24 ± 3.8 ¹)	260 ± 7.4 ⁴	590 ± 13 ⁴	1600 ± 31 ⁴
Atmospheric Deposition	60 ± 5 ⁵ (30 ± 4 ⁷)	0.9 ± 0.1 ⁷	1.1 ± 0.2 ⁵	38 ± 6.0 ⁵	38 ± 4.0 ⁵	45 ± 8.0 ⁵	560 ⁶
Benthic Flux	60 ± 130 ⁸	8.0 ± 4.0 ⁷ (2.0 ± 3.0 ⁸)	1.1 ± 3.7 ⁸	0.1 ± 0.6 ⁸	310 ± 440 ⁹	160 ± 54 ¹⁰	810 ± 2000 ⁸ (430 ± 40 ⁹)
<i>Total</i>	<i>3100 ± 900 mol</i>	<i>37 ± 10 Mol</i>	<i>25 ± 7.4 Kmol</i>	<i>850 ± 70 Kmol</i>	<i>1700 ± 560 Kmol</i>	<i>2800 ± 660 Kmol</i>	<i>7100 ± 2100 Kmol</i>
Sinks							
Estuarine Exchange	1300 ± 270 ¹ (1600 ± 280 ⁷)	14 ± 2.0 ⁷	18 ± 2.4 ¹ (14 ± 1.1 ¹¹)	160 ± 20 ¹¹	590 ± 58 ¹¹	480 ± 45 ¹¹	380 ± 50 ¹¹
Evasion	60 ± 20 ⁷						
Sediment Burial ^b	1700 ± 900 ^b	4.0 ± 3.0 ⁷	6.7 ± 8.0 ^b	690 ± 73 ^b	1100 ± 560 ^b	2300 ± 660 ^b	6700 ± 2100 ^b
(Photo)demethylation		2.0 ± 1.0 ⁷					
Biological processes ^c		17 ± 11 ^c					
<i>Total</i>	<i>3100 mol</i>	<i>37 mol</i>	<i>25 Kmol</i>	<i>850 Kmol</i>	<i>1700 Kmol</i>	<i>2800 Kmol</i>	<i>7100 Kmol</i>

Errors associated with fluxes are based on the standard error (SE) of means.

¹ CARP (2007); ² NYSDEC SWMS (2007); ³ Buck et al. (2005); Wen et al. (1999); ⁴ NYSDEC Division of Water; ⁵ Sakata et al. (2006); ⁶ Sakata and Marumoto (2004); ⁷ Balcom et al. (2008); ⁸ Mason et al. (2006); ⁹ Warnken et al. (2001); ¹⁰ Riedel et al. (1997, 1999); ¹¹ Paulson et al. (2005).

^a Rivers: Hudson, Raritan, Hackensack, and Passaic (90% flow from Hudson); ^b closing term (not MMHg) – calculated by difference; ^c closing term (MMHg only) – calculated by difference

Table 6. Sources and sinks (fluxes) of heavy metals from seasonal studies of NY/NJ Harbor (percent of total in parentheses).

	Cd (K mol y⁻¹)	Cd (K mol y⁻¹)	Ni (K mol y⁻¹)	Cu (K mol y⁻¹)	Zn (K mol y⁻¹)
	Yang and Sanudo-Wilhelmy (1998)		Klinkhammer and Bender (1981)		
Sources	October 1995		October 1975		
Rivers	0.9 (9%)	39.3–75.8 (13–14%)	967-1343 (18-29%)	1687-2233 (26-43%)	2749-4582 (30-39%)
Sewage	5.8 (57%)	135–393 (49–67%)	1612-4835 (48-64%)	1786-5459 (45-65%)	2605-7718 (37-51%)
Atmospheric deposition	0.04 (0.4%)				
Benthic flux	0.05 (0.5%)				
Oceanic input	3.3 (33%)	16.8–30.9 (5–6%)	806-1343 (18-24%)	496-744 (9-13%)	1640-2846 (19-23%)
<i>Total</i>	<i>10.1</i>	<i>191–500</i>	<i>3385-7521</i>	<i>3969-8436</i>	<i>6994-15146</i>
Sinks					
Estuarine exchange	10.0 (56%)	56.1–168 (29-34%)	2095-3331 (44-62%)	2283-4317 (51-58%)	5306-11094 (73-76%)
Sediment burial/ Closing term ^a	7.9 (44%)	135-331 ^a (66-71%)	1289-4190 ^a (38-56%)	1687-4119 ^a (43-49%)	1688-4052 ^a (24-27%)
<i>Total</i>	<i>17.9</i>	<i>191-500</i>	<i>3385-7521</i>	<i>3969-8436</i>	<i>6994-15146</i>
<i>Imbalance</i>	<i>-7.8</i>				
Sources	April 1996		April 1974		
Rivers	7.4 (31%)	126-157 (27-46%)	2364-3223 (34-53%)	3027-3325 (33-58%)	7235-15918 (56-65%)
Sewage	5.8 (25%)	135-393 (49-67%)	1612-4835 (36-51%)	1786-5459 (34-54%)	2605-7718 (23-27%)
Atmospheric deposition	0.04 (0.2%)				
Benthic flux	0.05 (0.2%)				
Oceanic input	10.4 (44%)	14.0-39.3 (5-7%)	484-1450 (11-15%)	397-1241 (8-12%)	1254-4630 (11-16%)
<i>Total</i>	<i>23.7</i>	<i>275-589</i>	<i>4459-9509</i>	<i>5210-10024</i>	<i>11094-28266</i>
Sinks					
Estuarine exchange	18.1 (88%)	140-224 (38-51%)	1719-6984 (39-73%)	4069-6451 (64-78%)	11576-21223 (75-104%)
Sediment burial/ Closing term ^a	2.4 (12%)	135-365 ^a (49-62%)	2525-2740 ^a (27-61%)	1141-3573 ^a (22-36%)	-482-7042 ^a (-4-25%)
<i>Total</i>	<i>20.4</i>	<i>275-589</i>	<i>4459-9509</i>	<i>5210-10024</i>	<i>11094-28266</i>
<i>Imbalance</i>	<i>3.3</i>				

^a Closing term for each metal calculated as the difference between total inputs and estuarine exchange (Klinkhammer and Bender data only).

Table 7. Comparison of total metals inputs to NY/NJ Harbor in the mid-1970s with post-2000 inputs (\pm SE).

Reference	Sampling period	Cd (K mol y ⁻¹)	Ni (K mol y ⁻¹)	Cu (K mol y ⁻¹)	Zn (K mol y ⁻¹)
This study	~2000 to 2006	25 \pm 7.4	1700 \pm 560	2800 \pm 660	7100 \pm 2100
Klinkhammer and Bender (1981)	April 1974	280 – 590	4500 – 9500	5200 – 10000	11100 - 28300
	(enhancement)	(11 to 24x)	(2.5 to 5.5x)	(2 to 3.5x)	(1.5 – 4x)
	October 1975	190 – 500	3400 – 7500	4000 – 8400	7000 – 15100
	(enhancement)	(8 to 20x)	(2 to 4.5x)	(1.5 to 3x)	(1 – 2x)

Figure Captions

Figure 1. The Hudson River watershed with NYSDEC SWMS and CARP sampling sites indicated for the middle (Newburg to Albany, NY) and upper (north of dam at Troy, NY) Hudson, and regions of NY/NJ Harbor with primary rivers (adapted from Geyer and Chant, 2006). NYSDEC SWMS sampling sites were at Waterford (42.786 °N, 73.671 °W), Cohoes (42.774 °N, 73.691 °W), Glenmont (42.590 °N, 73.757 °W), and Poughkeepsie (41.734 °N, 73.936 °W). CARP sites were at Waterford (42.787 °N, 73.671 °W), Cohoes (42.780 °N, 73.694 °W), Kingston-Poughkeepsie (41.818 °N, 73.948 °W), and Poughkeepsie (41.701 °N, 73.947 °W).

Figure 2. Middle and upper Hudson River total and filtered metal concentrations, total suspended solids (TSS), and percent of metals in the particulate fraction (surface waters). Hg and Cd (mean ± SD) are from CARP (2007; $n = 3-16$; collected 1999-2001), and Pb, Cu, Ni, Zn, and TSS concentrations are from NYSDEC SWMS (2007; mean ± SD; $n = 51-74$; collected 1993-2006). Filtered Zn is from 1993-1996 only ($n = 11-14$), so percent particulate Zn was not plotted. Kingston-Poughkeepsie TSS was 12.3 ± 10.0 (mean ± SD).

Figure 3. Middle and upper Hudson River suspended particle metal concentrations and Fe-normalized suspended particle metal concentrations (mol/mol). Metals data from NYSDEC SWMS (2007; mean ± SE; $n = 37-74$; collected 1993-2006).

Figure 4. Poughkeepsie, Cohoes, and Waterford total Hg and Cd (mean ± SE; CARP, 2007; $n = 3-16$; collected 1999-2001) plotted against TSS (NYSDEC SWMS, 2007; $n = 17-18$; collected 1999-2001). Estimates of average suspended particle and Fe-normalized suspended particle concentrations are presented in the text.

Figure 5. Mean concentrations (±SE) for filtered and total Hg (a) and Cd (b) at sampling sites in the estuarine turbidity maximum (ETM), lower, middle, and upper Hudson River. Seasonal concentrations (SE shown when there were data available for multiple samples at a site; $n = 3-5$) of filtered Hg (c), filtered Cd (d), total Hg (e), and total Cd (f) plotted against approximate distance from the Battery (Manhattan) between the estuarine turbidity maximum (ETM) and Waterford (NY; collected 1999-2001; CARP, 2007). Data are plotted for spring (March through May; includes February collections), summer (June through August), and fall (September through October). Individual data points not included in averages are circled. The plot includes CARP data from Waterford, Kingston-Poughkeepsie, and Poughkeepsie (coordinates given in caption to Fig. 1), the lower Hudson R. (between Tappan Zee Bridge and Harlem River; 40.954 °N, 73.911 °W), and the ETM (south of Harlem River; 40.786 °N, 73.993 °W).

Figure 6. Average (±SE) Fe-normalized suspended particle concentrations (mol/mol) of Cu (a), Pb (b), and Zn (c) in the estuarine turbidity maximum (ETM) and the middle and upper Hudson River. Data are plotted for two sites in the ETM (collected 1994/1995; Feng et al., 2002; $n = 9-12$) and for four sites (Waterford, Cohoes, Glenmont, and Poughkeepsie [coordinates given in caption to Fig. 10]) in the middle and upper Hudson (collected 1999 to 2001; NYSDEC SWMS, 2007; $n = 14-18$).

Figure 7. Mean concentrations (\pm SE) of filtered, total, and suspended particle Hg and Cd at sampling stations on the major rivers entering NY/NJ Harbor (CARP, 2007; $n = 2-8$). CARP sampling sites were at the mouth (40.727° N, 74.099° W) and mid-tidal (40.807° N, 74.061° W) on the Hackensack R., at the mouth (surface and bottom; 40.716° N, 74.120° W) and mid-tidal (40.811° N, 74.139° W) on the Passaic R., upstream of the mouth in the lower reaches of the Raritan R. (surface and bottom; 40.508° N, 74.290° W), and in the lower East R. (40.745° N, 73.964° W [between the Brooklyn Bridge and Hell Gate]).

Figure 8. Total and filtered metals, total suspended solids (TSS), and percent of metals in the particulate fraction in surface and bottom waters of major regions of NY/NJ Harbor. Hg and Cd (mean \pm SD) from CARP (2007; collected 1999 to 2001, $n = 3-4$; surface water only), Hg and MMHg from Balcom et al. (2008; collected 2002 to 2003, $n = 8-11$), and Pb, Cu, Ni, Zn (particulate only for Zn) from Paulson (2005; collected 1999, $n = 8-15$). Cd data from Paulson and additional NY/NJ Harbor data are given in Table 3. TSS is plotted separately for the CARP, Balcom et al. (circled value not included in average), and Paulson data.

Figure 9. Average (\pm SD) filtered and total concentrations of Cd, Cu, Ni, and Zn (surface and deep waters) in the NY Bight (Klinkhammer and Bender, 1981; collected 1974/1975; $n = 5-6$) and at the Rockaway-Sandy Hook transect (Paulson, 2005; collected 1999; $n = 9-10$).

Figure 10. Average (\pm SD) suspended particle concentrations of Hg and Cd in surface waters (CARP, 2007; collected 1999 to 2001; $n = 3-4$), Hg and MMHg in surface and bottom waters (Balcom et al., 2008; collected 2002 to 2003; $n = 8-11$), and Pb, Cu, Ni, and Zn in surface and bottom waters (Paulson, 2005; collected 1999; $n = 8-15$) plotted with surface sediment concentrations of the same metals in major regions of NY/NJ Harbor. Sediment concentrations plotted with CARP and Paulson data are from EMAP (2008; collected 1998, $n = 11-28$), except that surface sediment Cu concentrations and NY Bight data for all metals are from Adams et al. (1998; collected 1993 to 1994; $n = 13-27$). Sediment Hg and MMHg data from Hammerschmidt et al. (2008; collected 2002 to 2003, $n = 5-7$) are plotted with Balcom et al. (2008) data. Data points not included in averages are plotted for each metal.

Figure 11. Average (\pm SE) Fe- and Al-normalized suspended particle concentrations (mol/mol) of Hg (sediment only), Cd, Pb, Cu, Ni, and Zn in NY/NJ Harbor (Paulson, 2005; collected 1999; $n = 8-15$) and the estuarine turbidity maximum (ETM; Feng et al., 2002; collected 1994/1995; $n = 9-12$), and surface sediment concentrations (mol/mol) in the Harbor (EMAP, 2008; collected 1998; $n = 11-28$; Adams et al., 1998; collected 1993 to 1994; $n = 13-27$) and the ETM (Feng et al., 2002; collected 1994/1995; $n = 7-14$). Sediment Al-normalized Cu concentrations, all Fe-normalized sediment concentrations, and sediment silt/clay and total organic carbon (TOC) are from Adams et al. (1998). Water column particulate organic carbon (POC) is from CARP (2007; collected 1998 to 2000; $n = 5-10$).

Figure 12. Average percent inputs (\pm SE) for major sources of heavy metals to NY/NJ Harbor.

Figure 13. Average percent export (\pm SE) for major sinks of heavy metals in NY/NJ Harbor. Photodemethylation and biological processes terms are for MMHg only, and evasion is for Hg only.

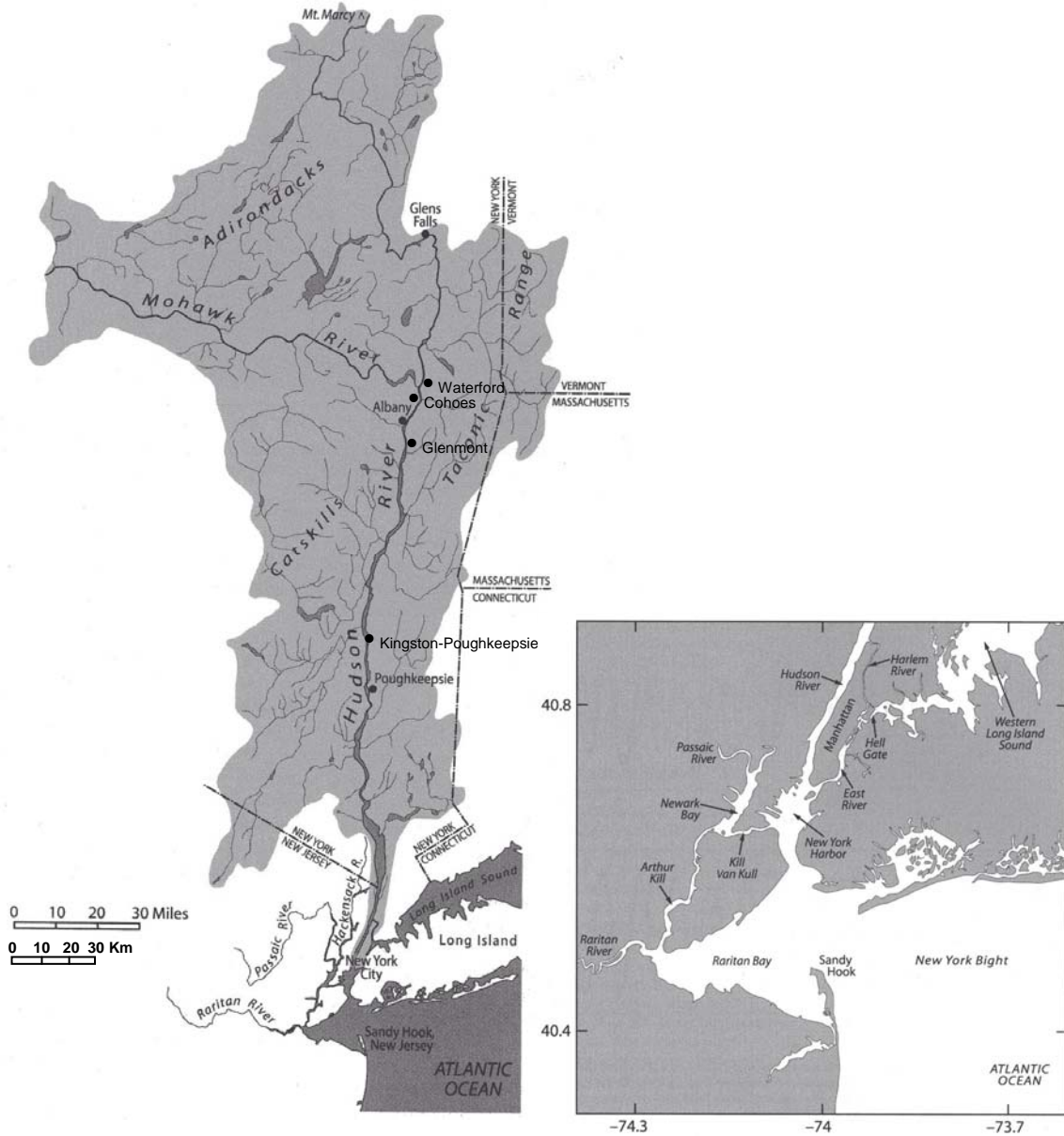


Figure 1 – Balcom et al.

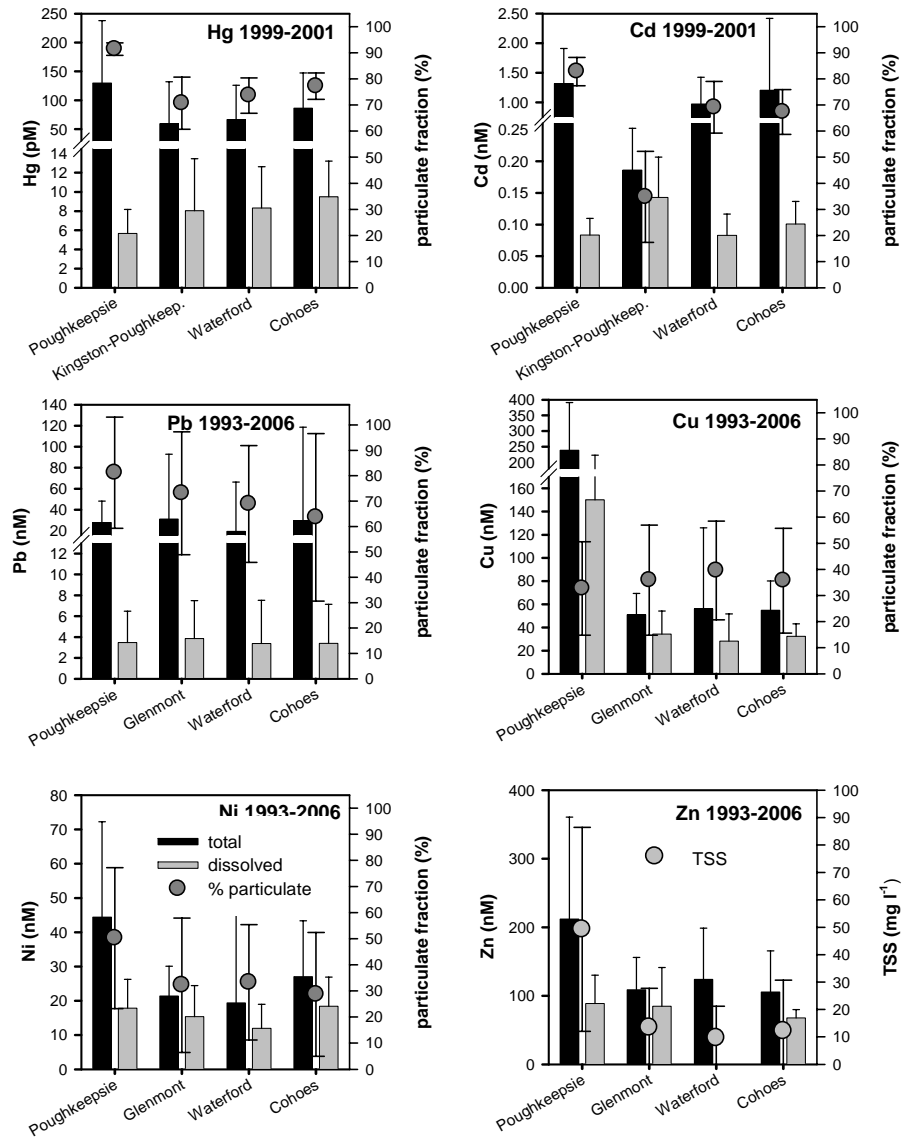


Figure 2 - Balcom et al.

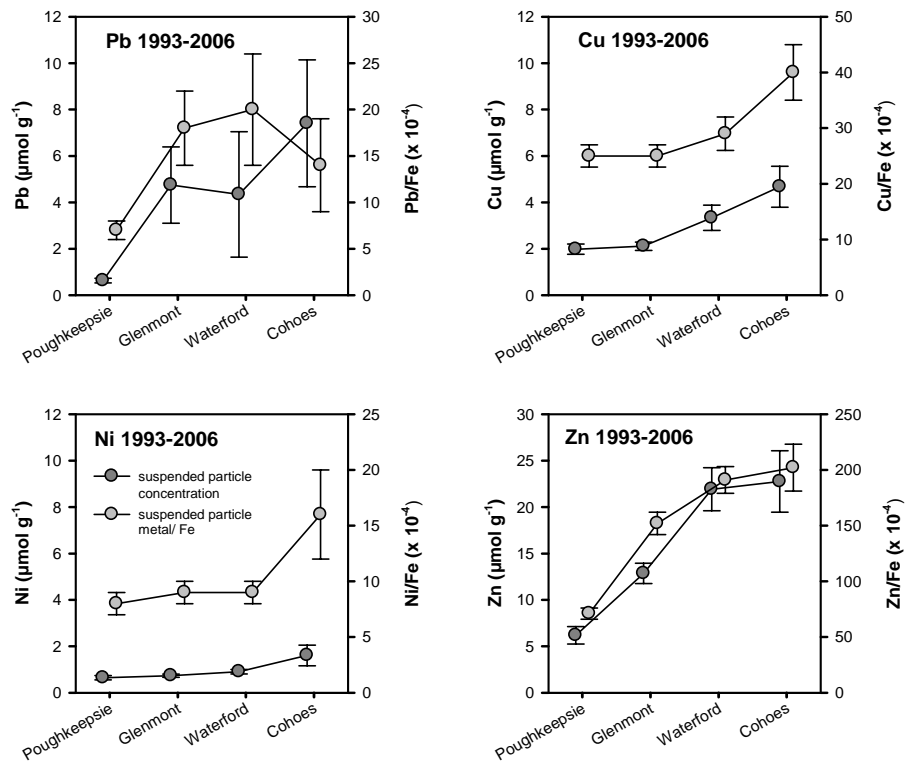


Figure 3 - Balcom et al.

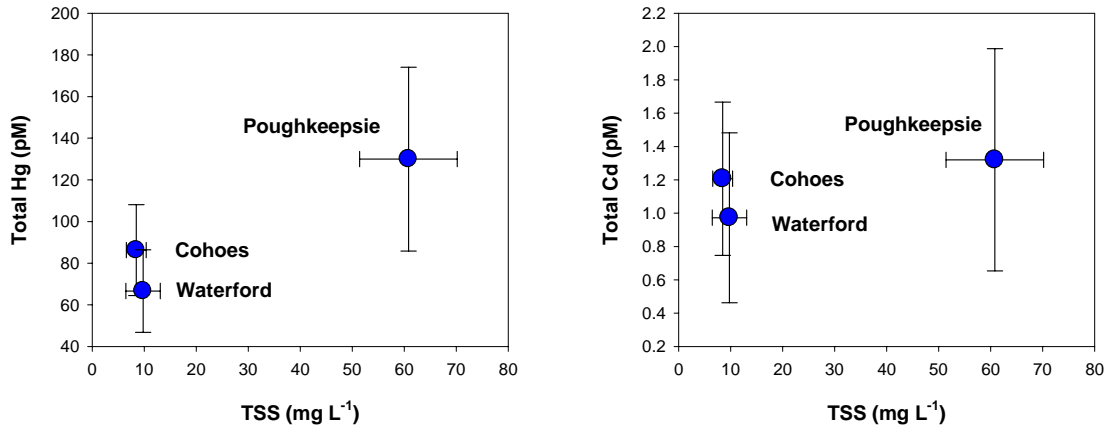


Figure 4 – Balcom et al.

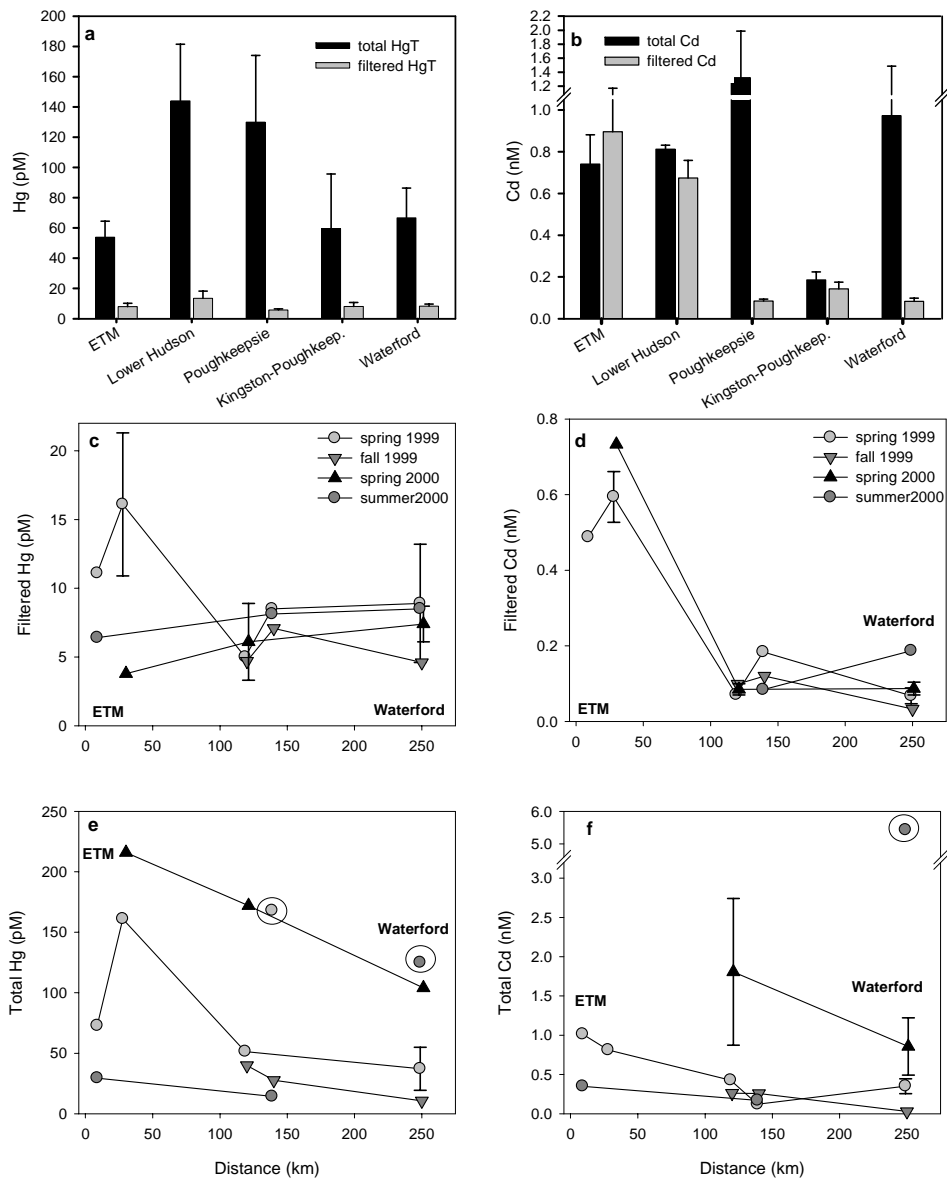


Figure 5 – Balcom et al.

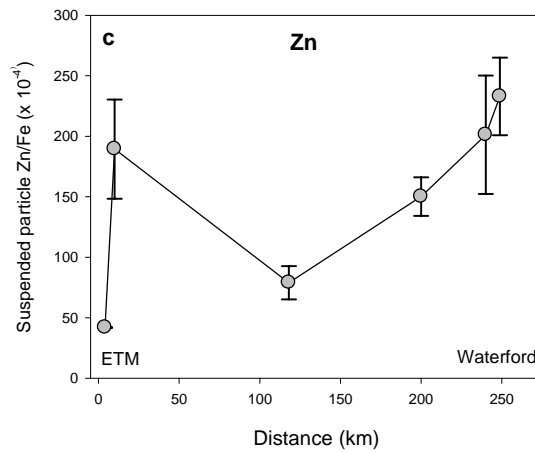
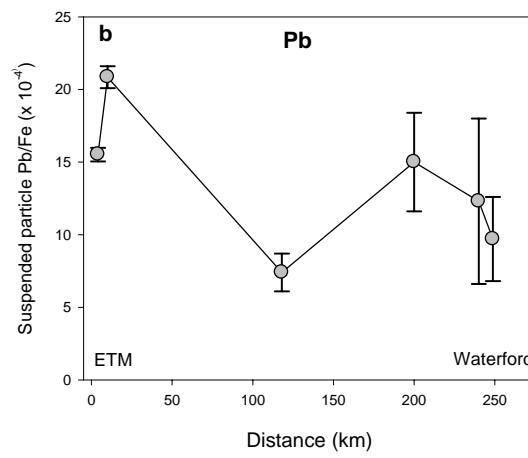
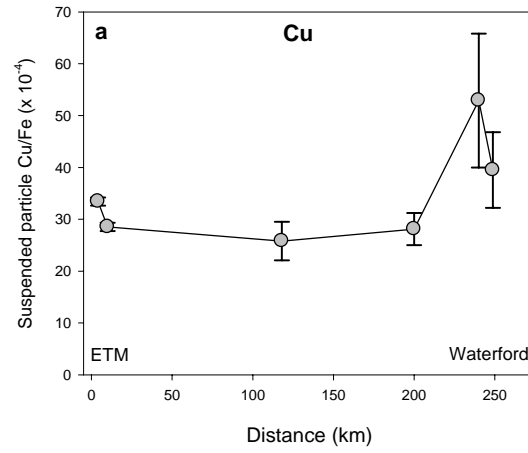


Figure 6 – Balcom et al.

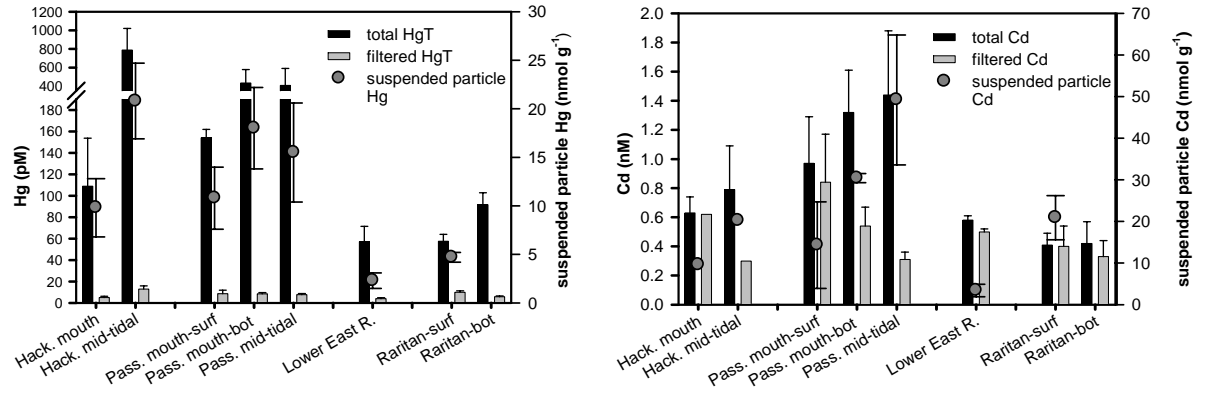


Figure 7 – Balcom et al.

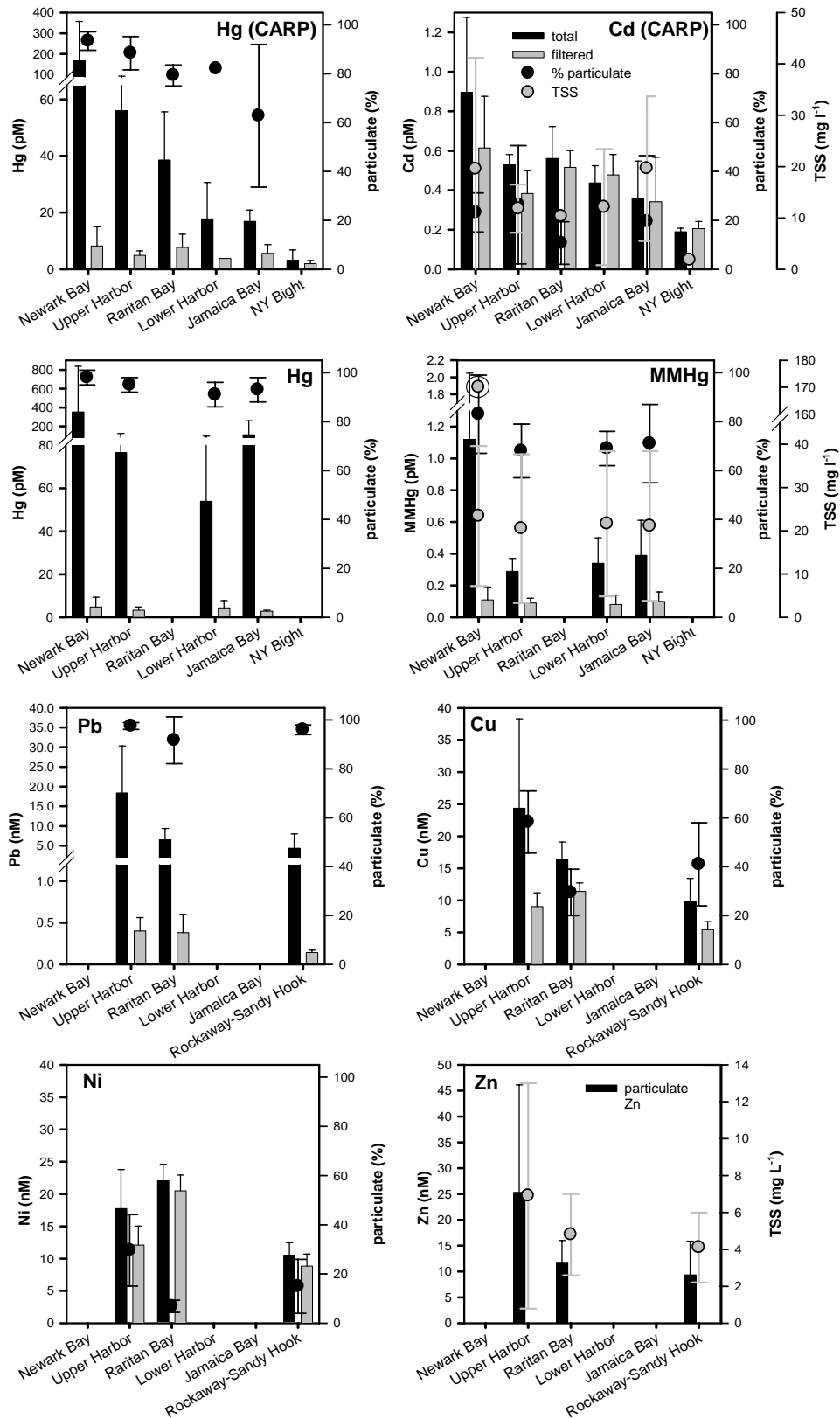


Figure 8 – Balcom et al.

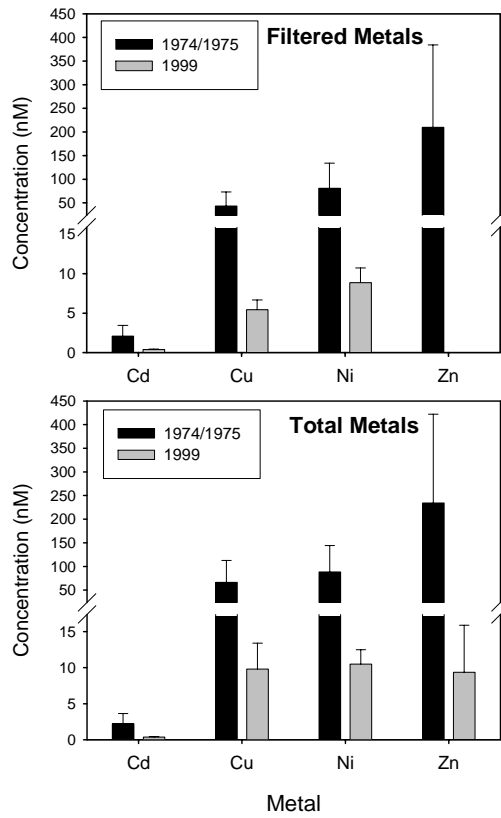


Figure 9 – Balcom et al.

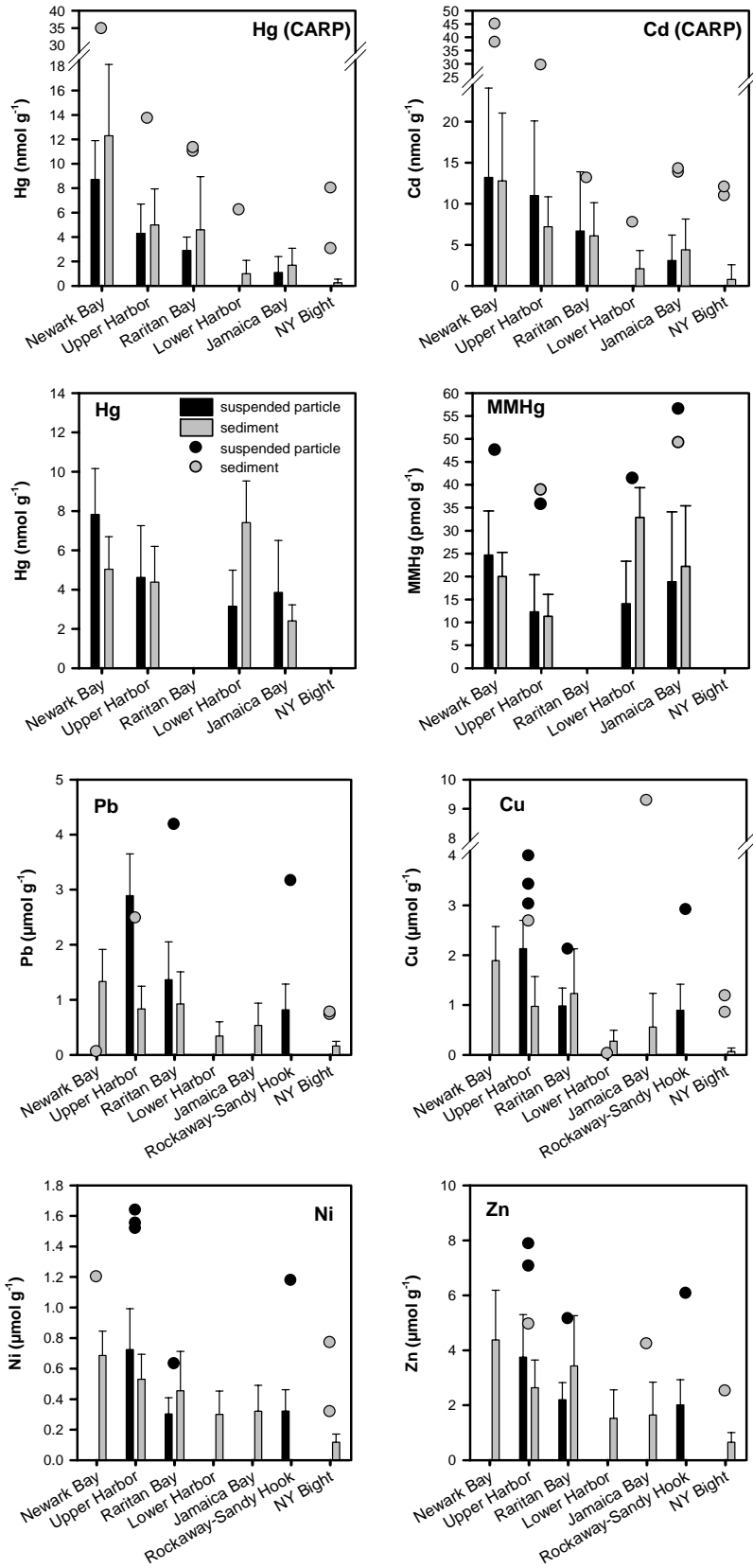


Figure 10 – Balcom et al.

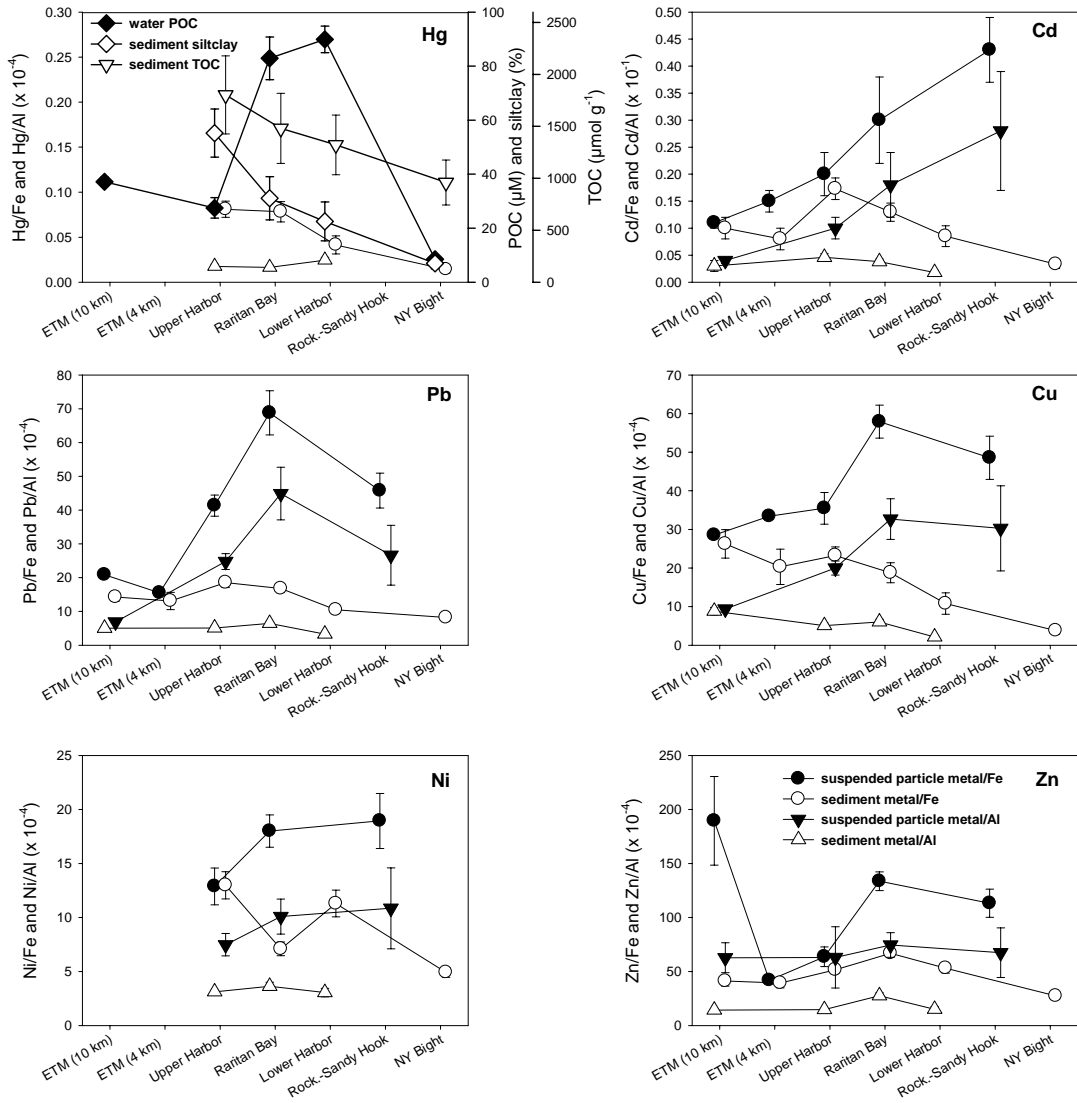


Figure 11 – Balcom et al.

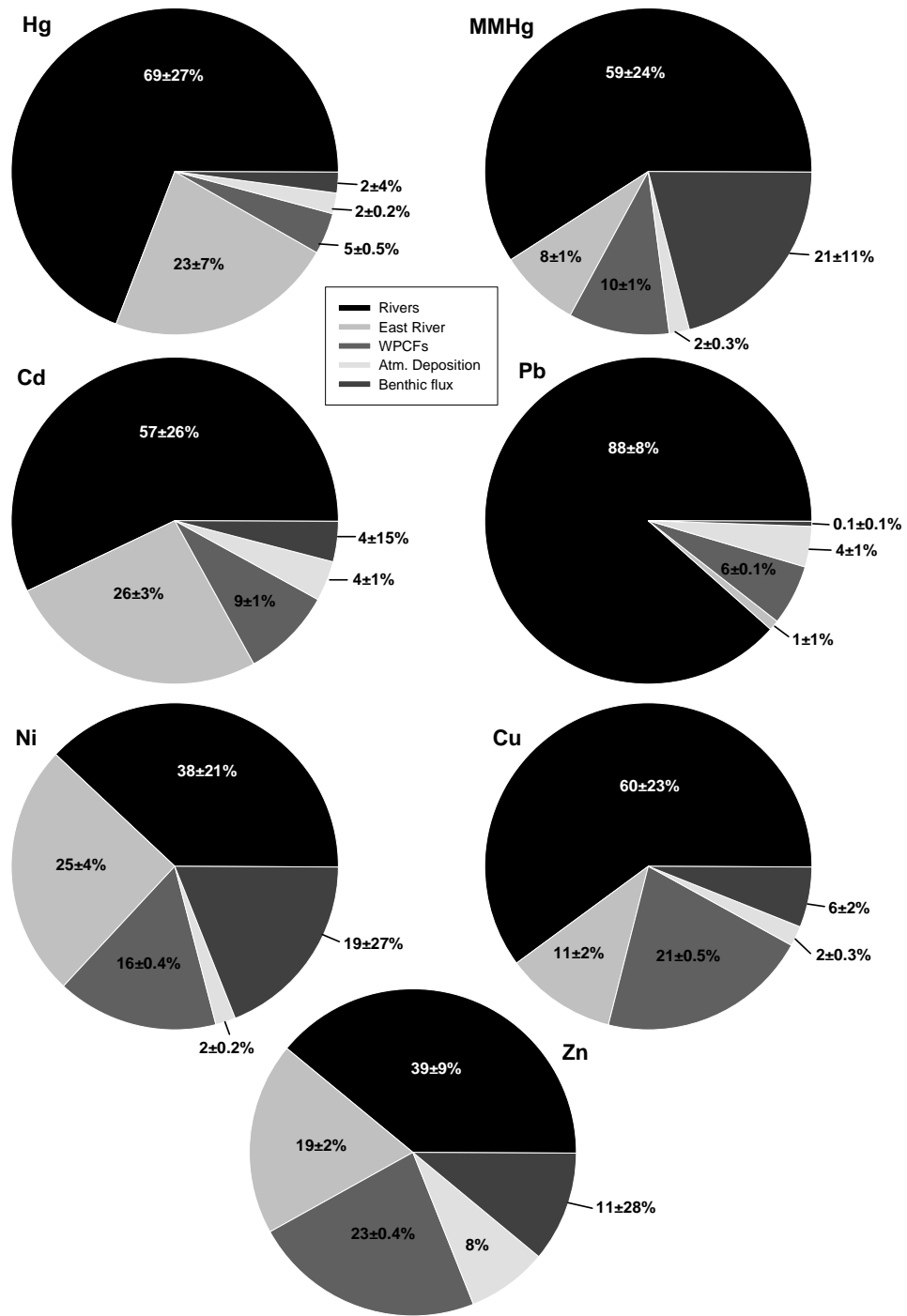


Figure 12 – Balcom et al.

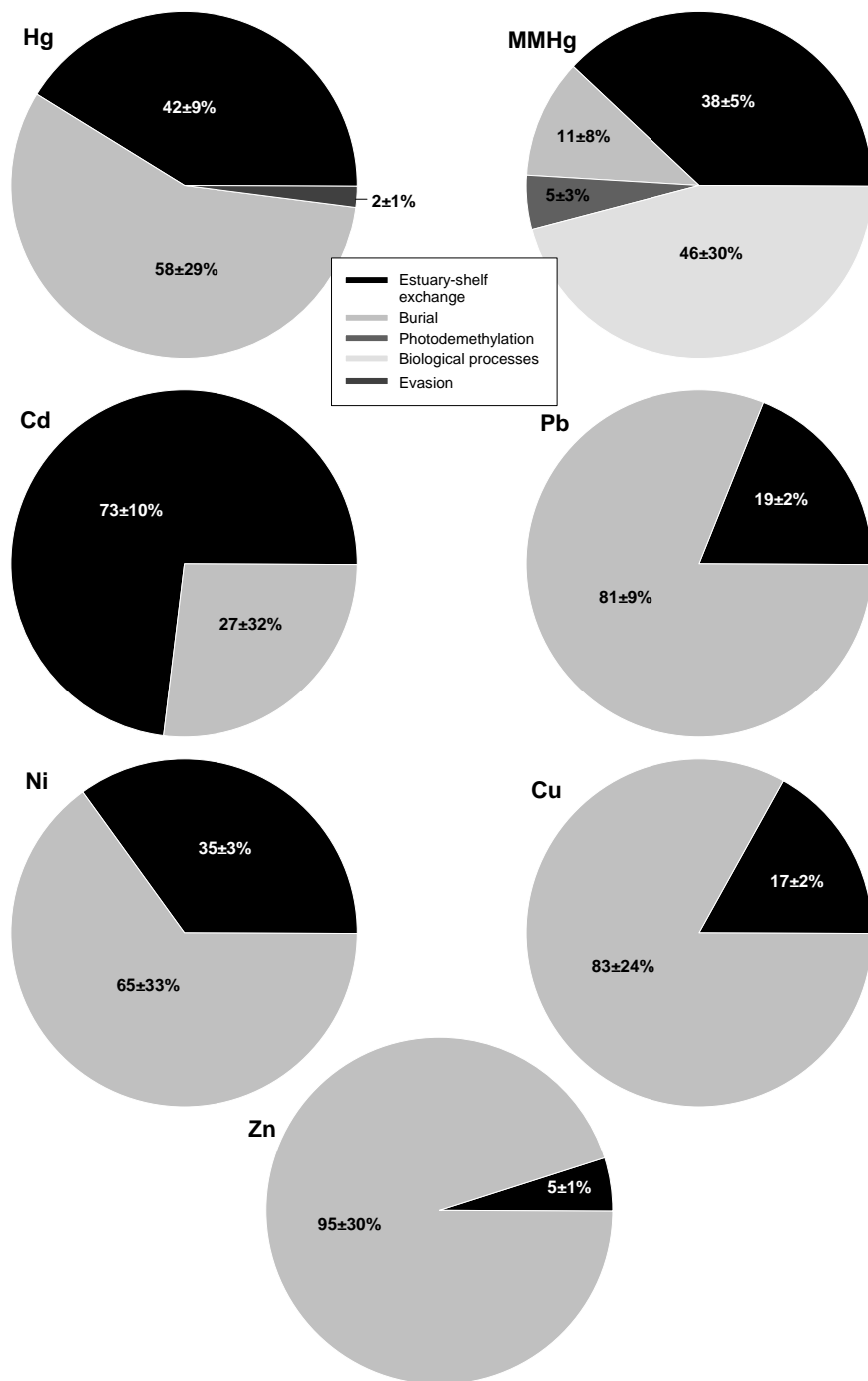


Figure 13 – Balcom et al.

Synthesis and Assessment of Heavy Metal Contamination in the Hudson River and New York/New Jersey Harbor Estuary

Prentiss H. Balcom, William F. Fitzgerald, Robert P. Mason
*Department of Marine Sciences, University of Connecticut, 1080 Shennecossett Road,
Groton, CT USA*

Supporting Information

This manuscript will be submitted to a peer-reviewed journal. The information and data contained in this document, including associated supporting materials, are proprietary, and should not be used publicly until the manuscript is published. Contact the authors if there are requests or questions related to this research.

Supporting Information

Figures Captions

Figure S1. Annual mean (\pm SE; 1993 to 2006; SWMS, 2007; $n = 3-6$) filtered and suspended particle concentrations of selected trace metals in the Hudson River at Waterford and Poughkeepsie, NY.

Figure S2. Annual mean (\pm SE; 1993 to 2006; SWMS, 2007; $n = 3-6$) total concentrations of selected trace metals in the Hudson River at Waterford and Poughkeepsie, NY.

Figure S3. Concentrations of total Pb, Ni, Zn, and Al as a function of total Fe (1993 to 2006; SWMS, 2007) in the Hudson River at Waterford and Poughkeepsie, NY.

Figure S4. Suspended particle concentrations of Pb, Ni, Zn, and Al as a function of Fe (1993 to 2006; SWMS, 2007) in the Hudson River at Waterford and Poughkeepsie, NY.

Figure S5. Concentrations of total Pb, Ni, Zn, and Al plotted against total suspended solids (TSS; 1993 to 2006; SWMS, 2007) in the Hudson River at Waterford and Poughkeepsie, NY.

Figure S6. Seasonal concentrations (mean \pm SE) of suspended particle and total Pb, Cu, Ni, and Zn at Waterford (1993-2006; SWMS, 2007; $n = 16-26$). Data are plotted for spring (Mar. to May), summer (June to Aug.), and fall (Sept. to Nov.). Stream flow data (mean \pm SE) are for the Hudson River at Stillwater (USGS, 2008) on the same dates that metals were sampled.

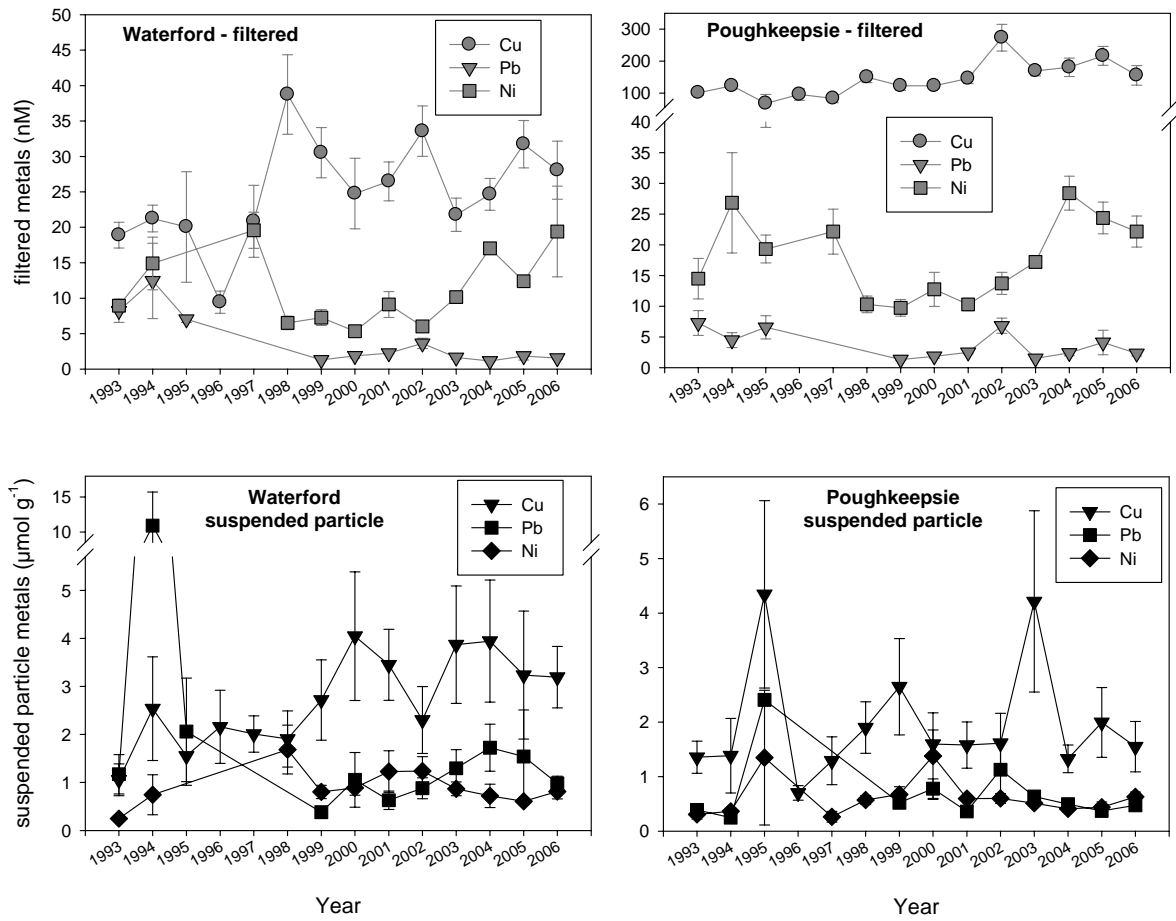
Figure S7. Seasonal concentrations (mean \pm SE) of suspended particle and total Pb, Cu, Ni, and Zn at Poughkeepsie (1993-2006; SWMS, 2007; $n = 20-26$). Data are plotted for spring (Mar. to May), summer (June to Aug.), and fall (Sept. to Nov.). Stream flow data (mean \pm SE) are for the Hudson River at Green Island (USGS, 2008) on the same dates that metals were sampled.

Figure S8. Sediment concentrations of Hg, Cd, Pb, and Zn plotted against Al (1993 and 1994; EMEP; Adams et al., 1998) with regression lines for regions of NY/NJ Harbor (r^2 values given in Table S2).

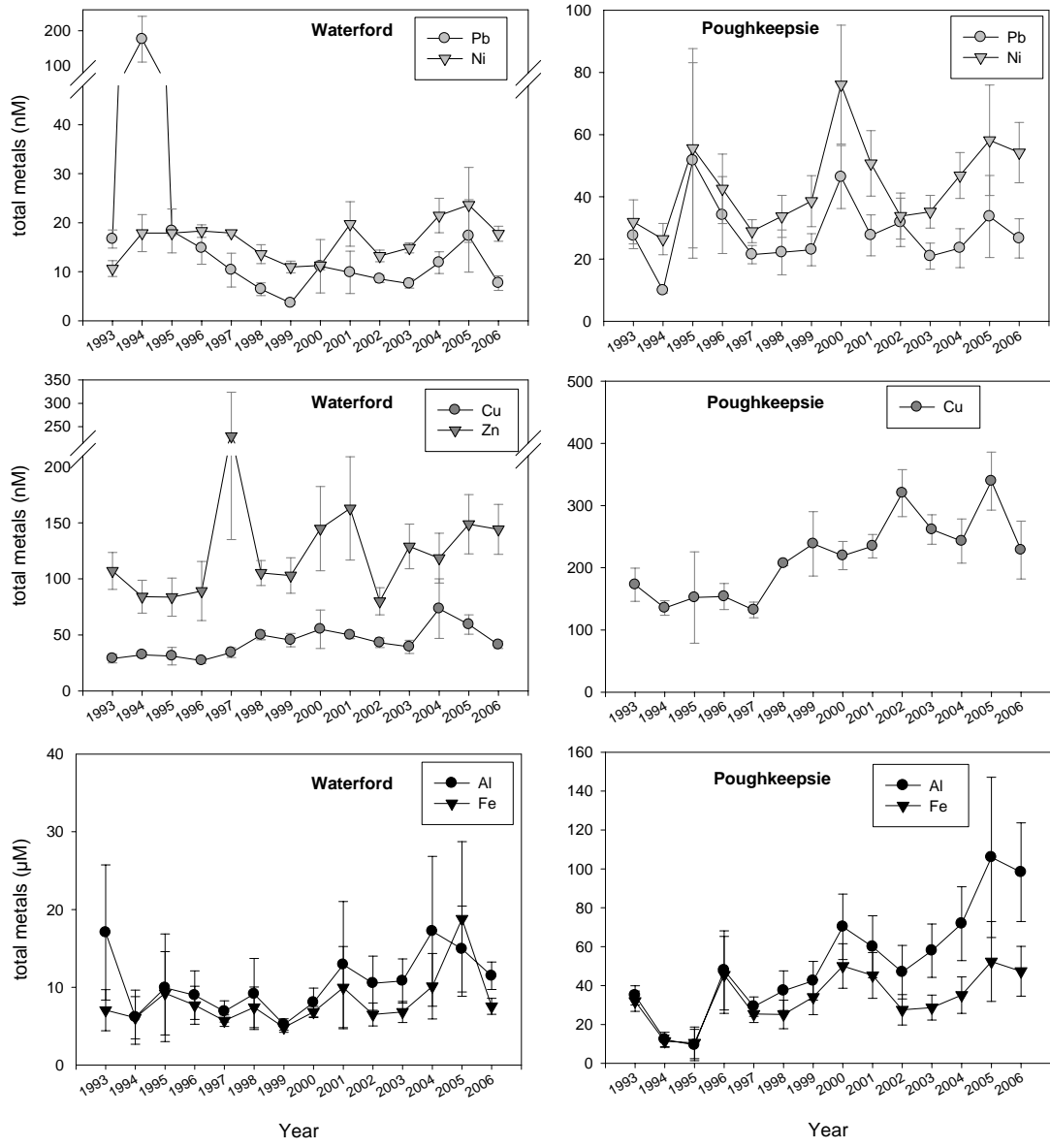
Figure S9. Sediment concentrations of Hg, Cd, Pb, and Zn plotted against siltclay (1993 and 1994; EMEP; Adams et al., 1998) with regression lines for Jamaica Bay and NY Bight (r^2 values given in Table S2).

Figure S10. Sediment concentrations of Hg, Cd, Pb, and Zn plotted against Al (1998; EMAP, 2008) for regions of NY/NJ Harbor (r^2 values given in Table S3).

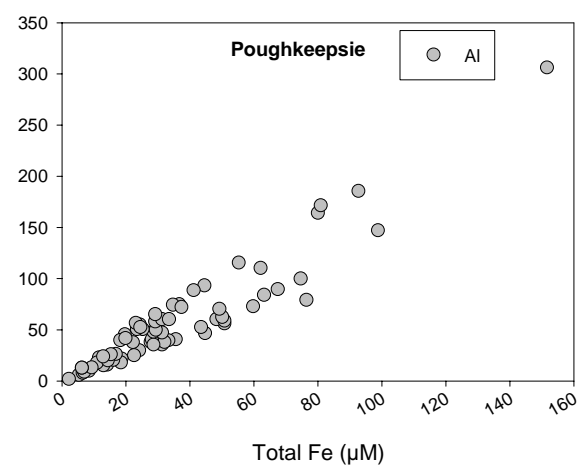
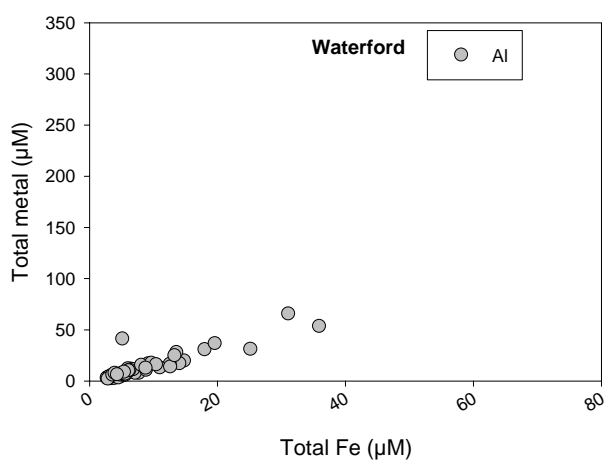
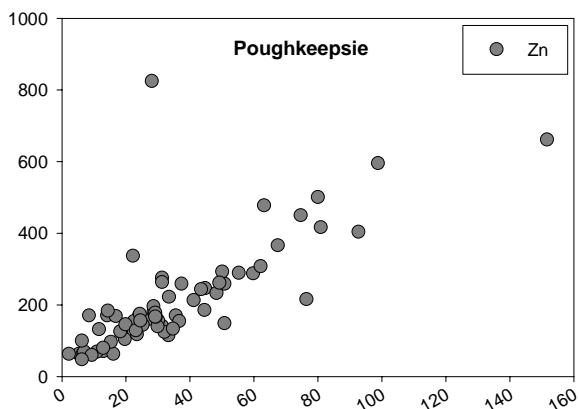
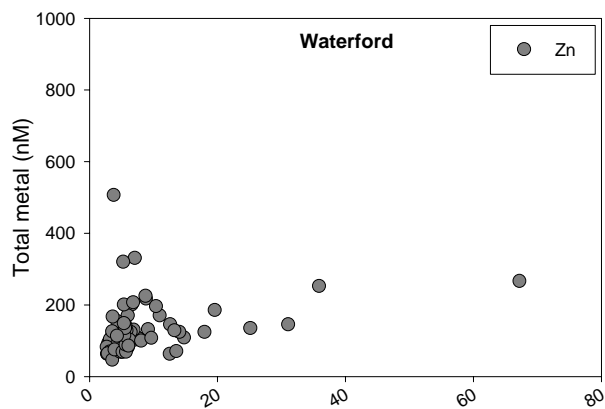
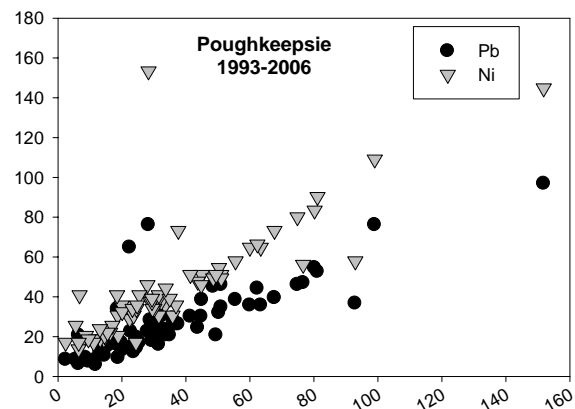
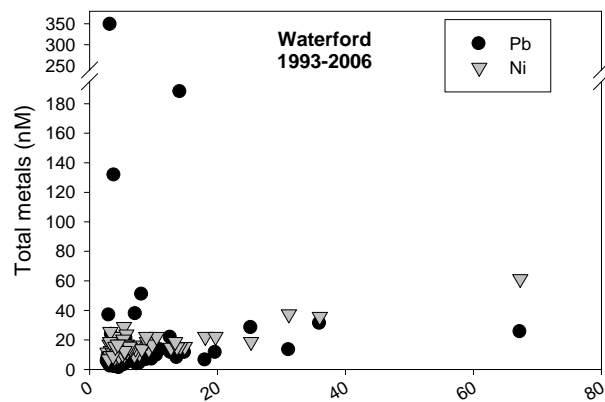
Figure S11. Sediment concentrations of Hg, Cd, Pb, and Zn plotted against siltclay and total organic carbon (TOC; 1998; EMAP, 2008) for Jamaica Bay (r^2 values given in Table S3).



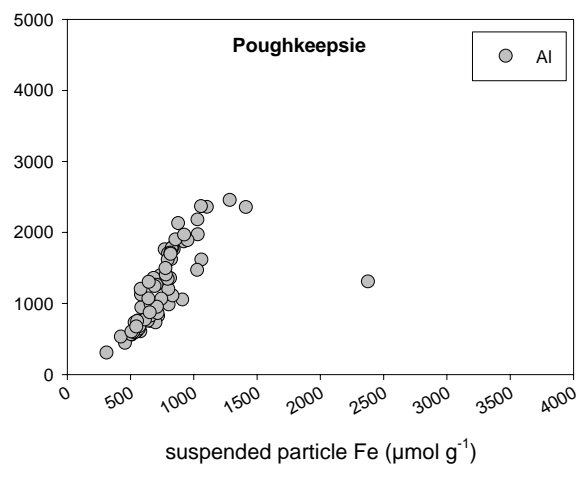
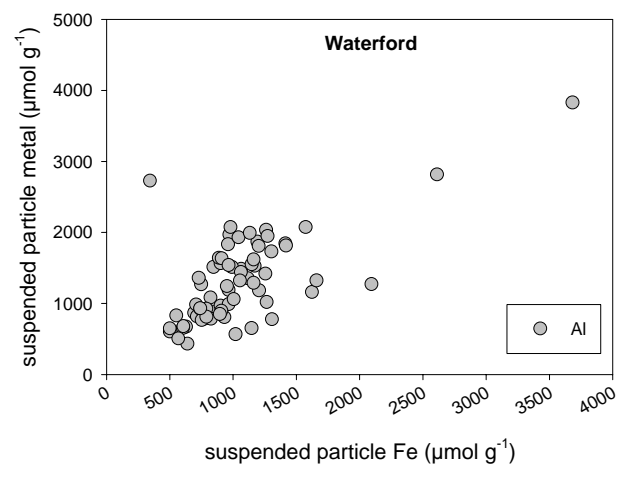
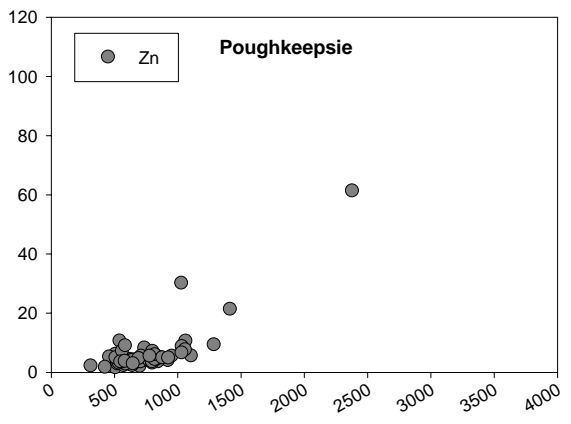
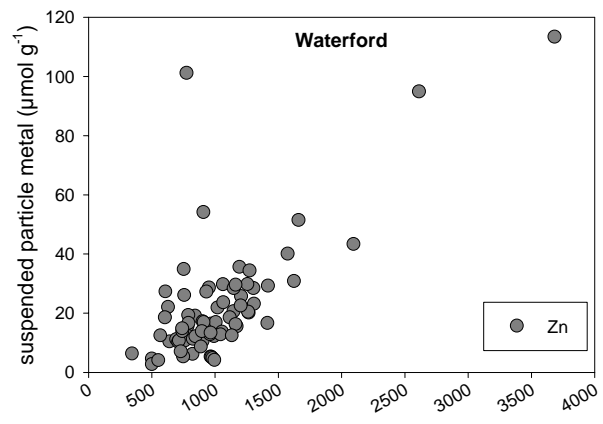
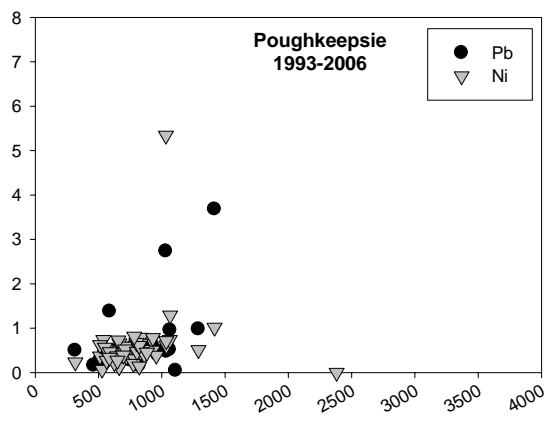
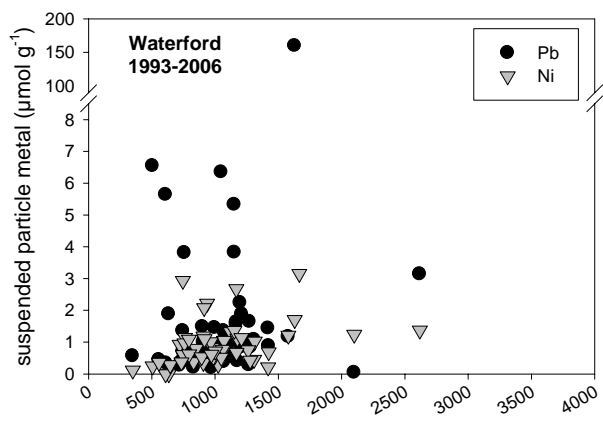
Balcom et al. – Figure S1



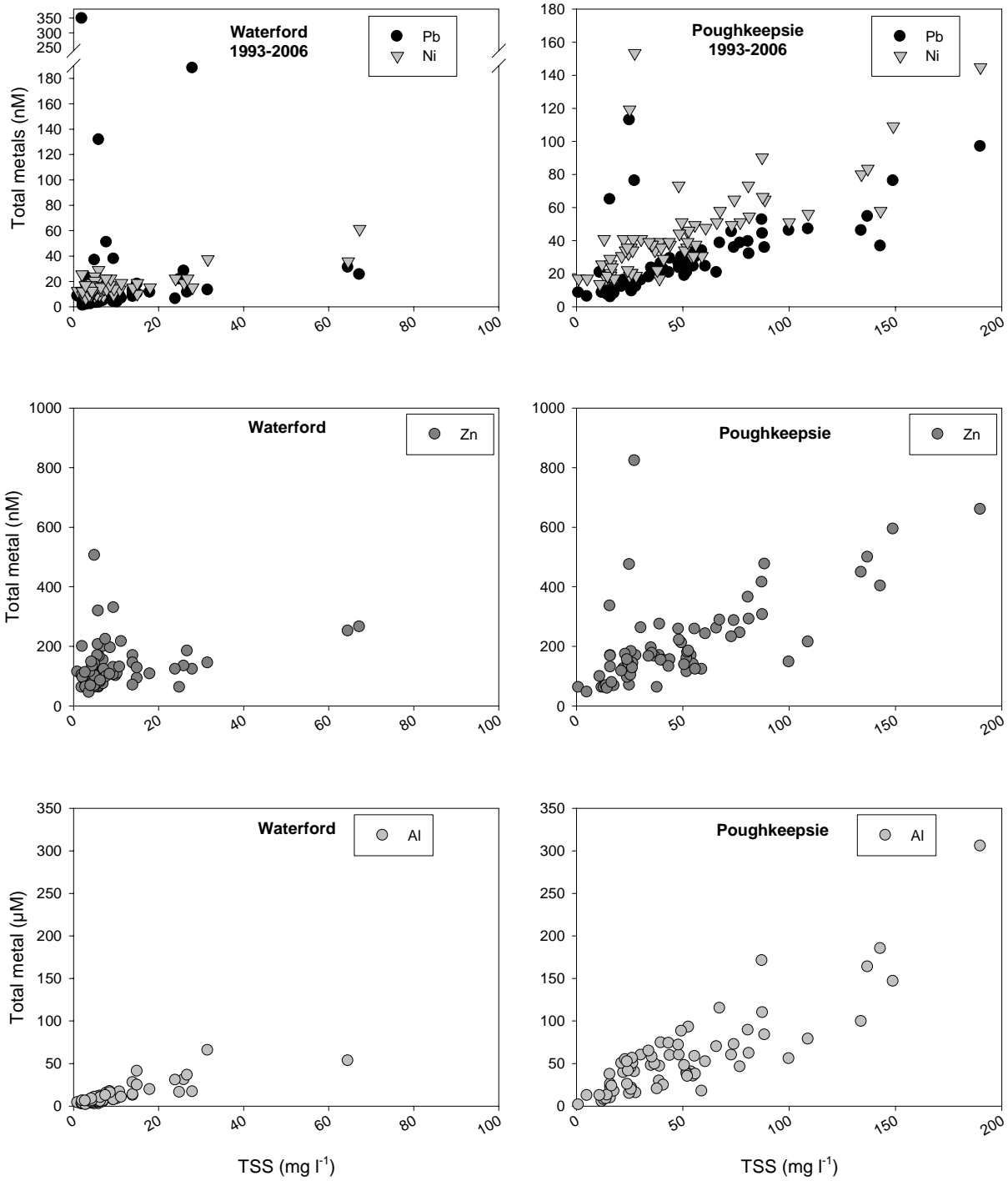
Balcom et al. – Figure S2



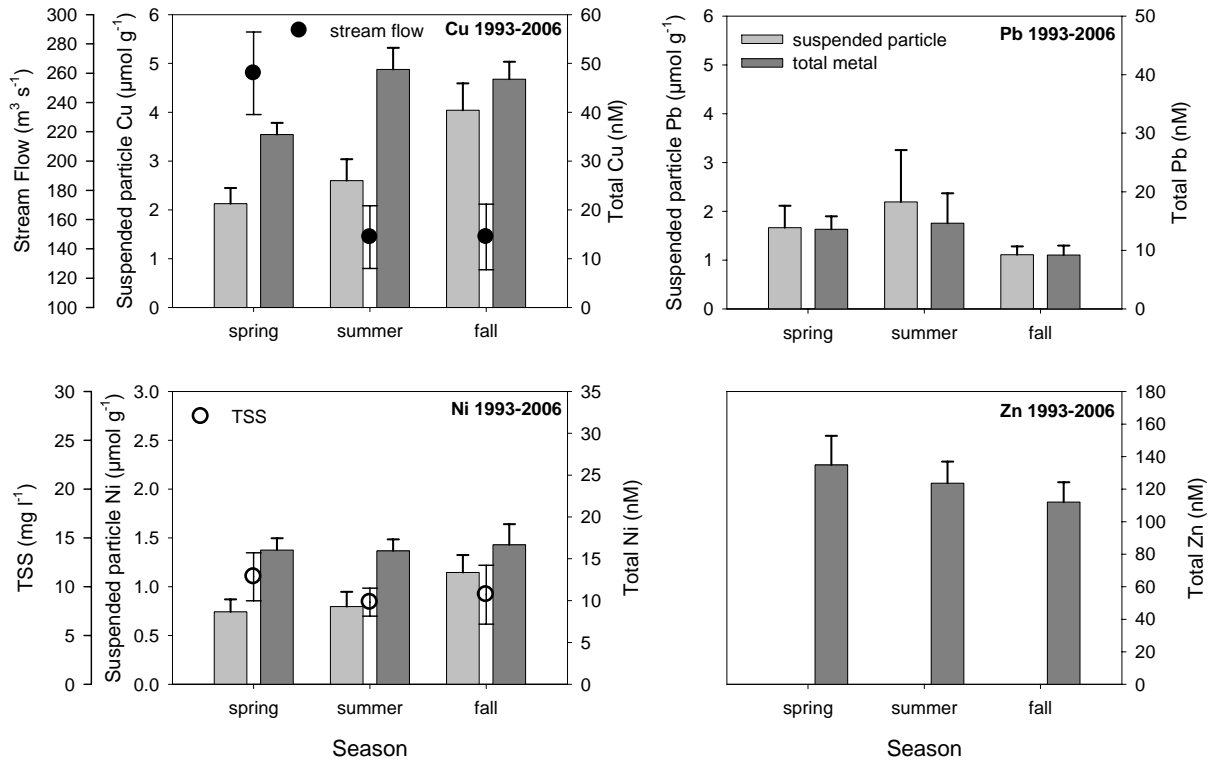
Balcom et al. – Figure S3



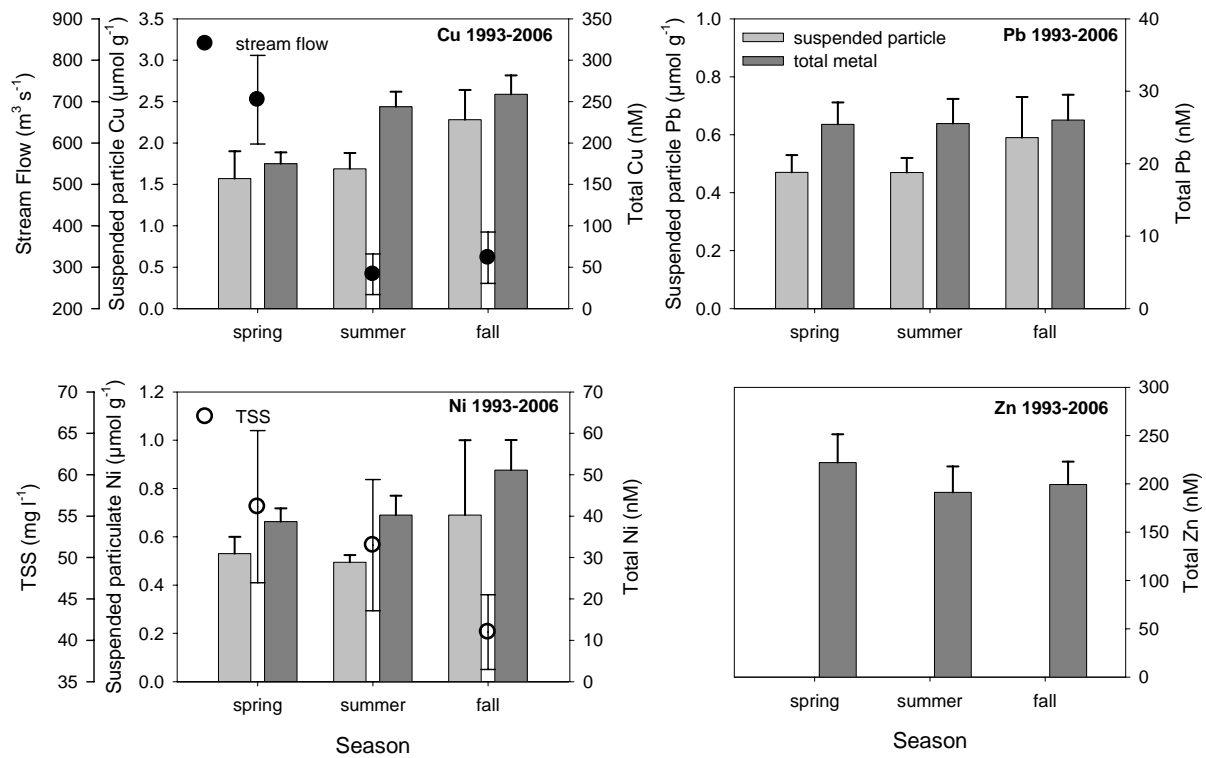
Balcom et al. – Figure S4



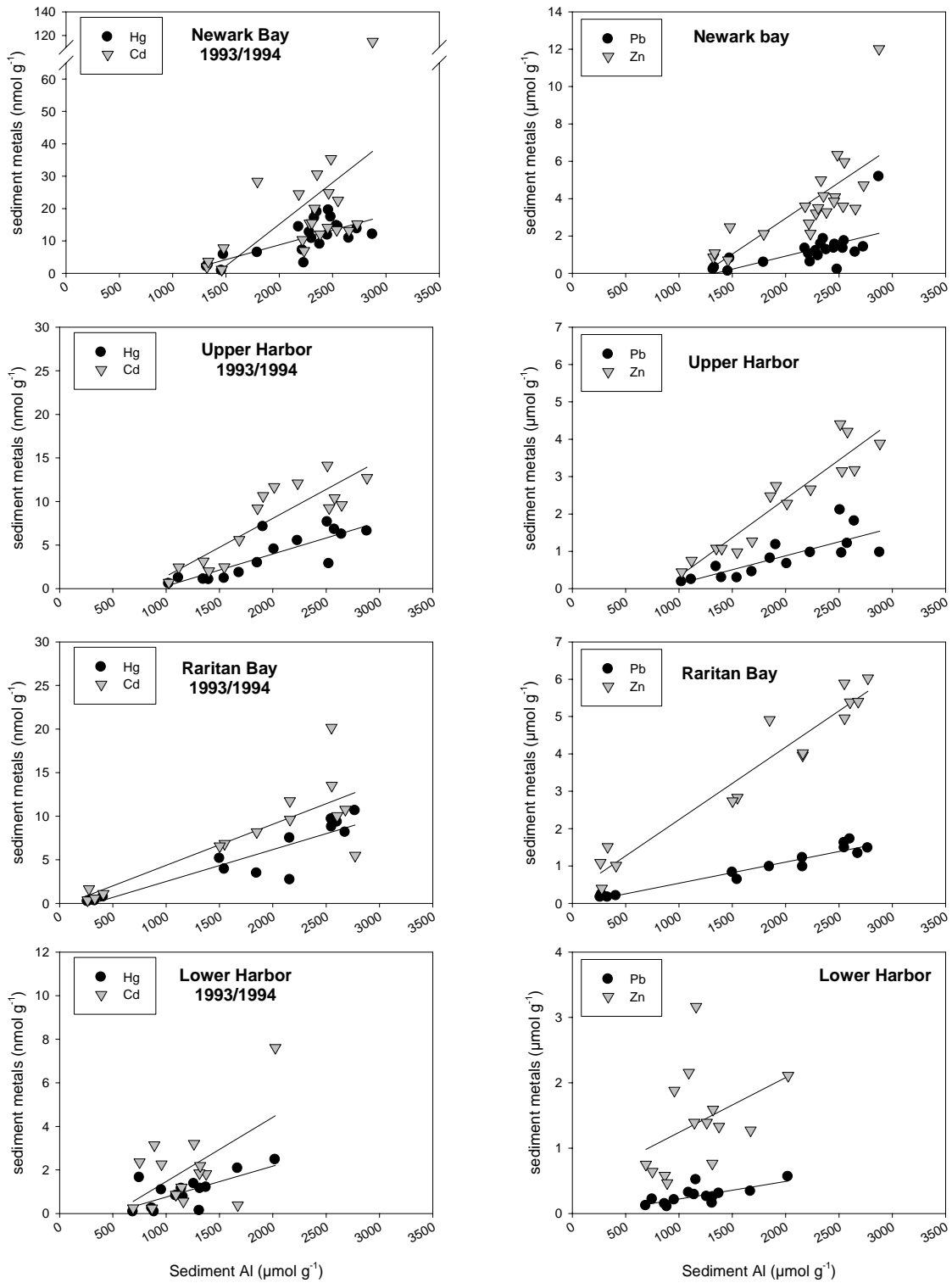
Balcom et al. – Figure S5



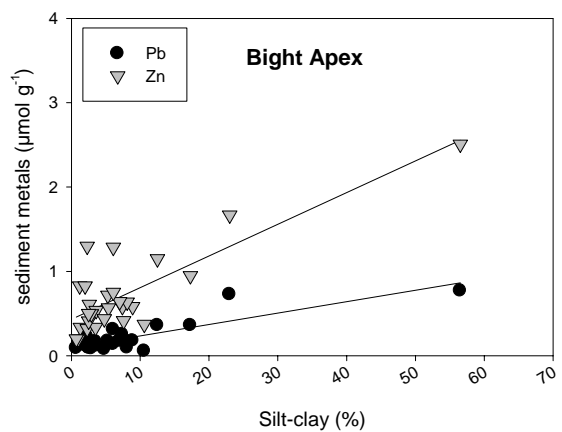
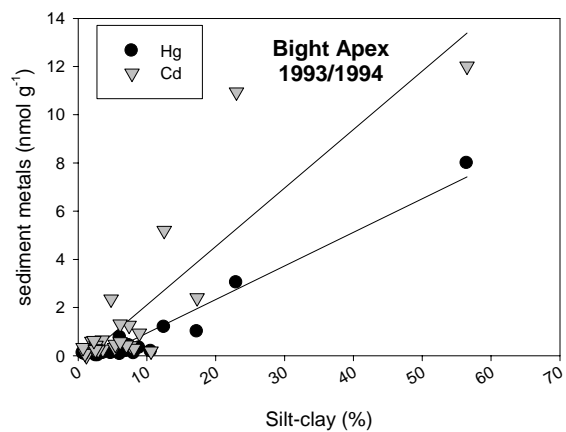
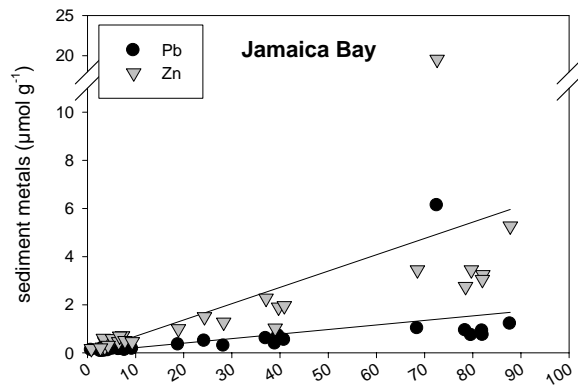
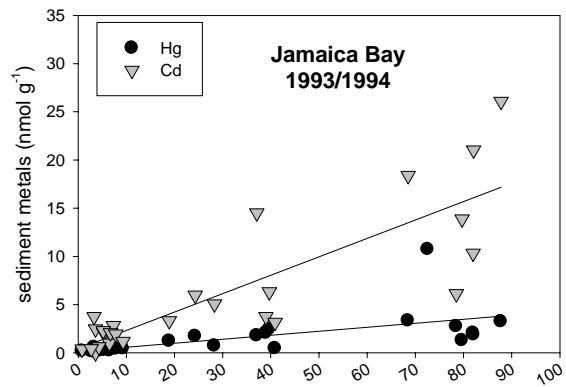
Balcom et al. – Figure S6



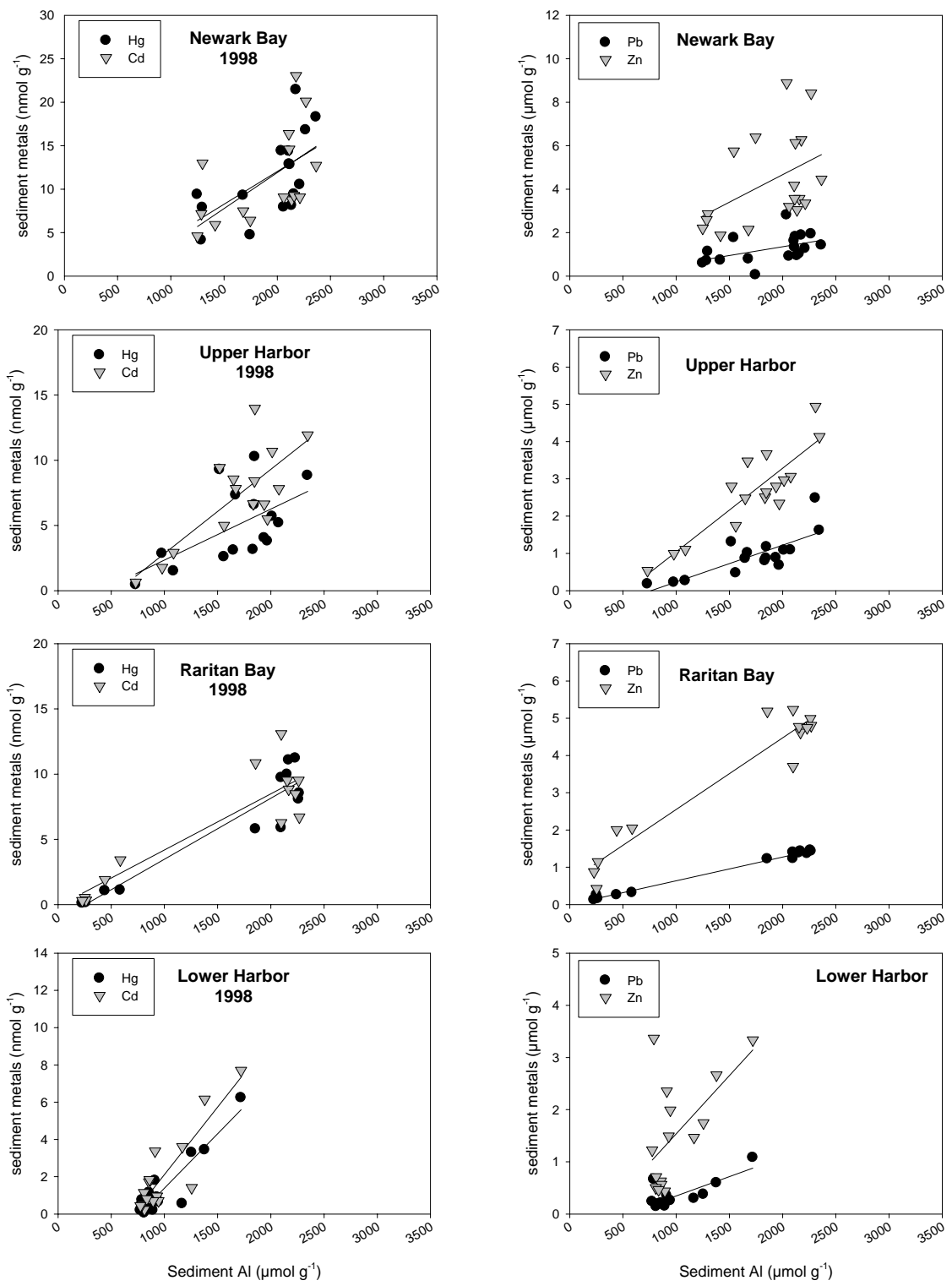
Balcom et al. – Figure S7



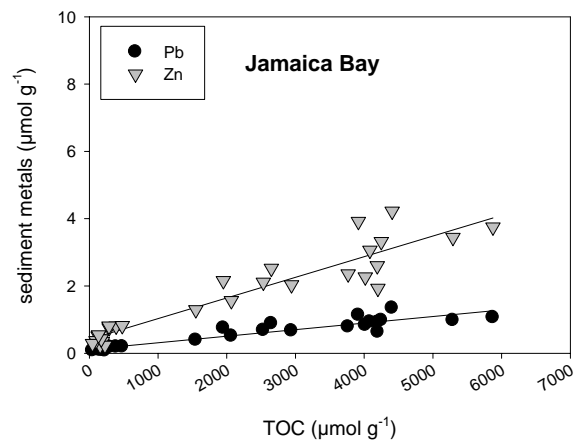
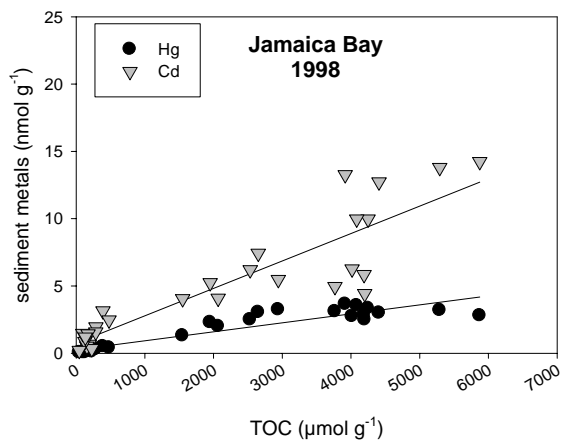
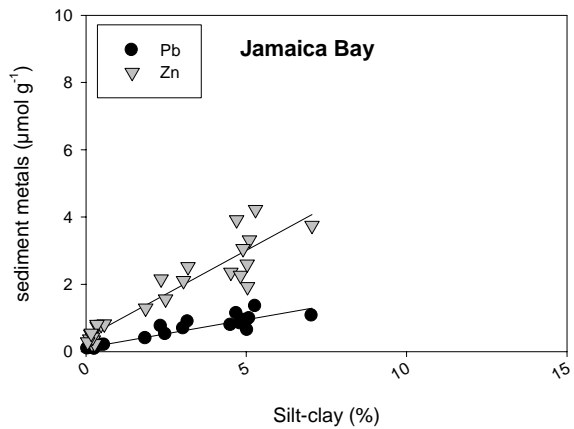
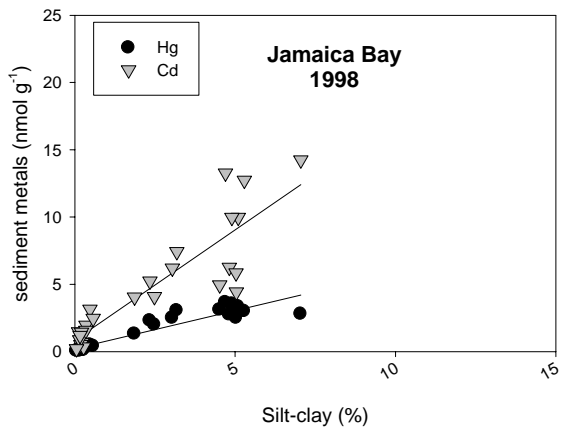
Balcom et al. – Figure S8



Balcom et al. – Figure S9



Balcom et al. – Figure S10



Balcom et al. – Figure S11

Table S1. K_D values (mean with range in parentheses) for trace metals in NY/NJ Harbor and the Hudson River. Geographic location of Lower Hudson River and ETM indicated as kilometers from the Battery (Manhattan).

Sampling locations and dates	Hg (pM)	Cd (nM)	Pb (nM)	Cu (nM)	Ni (nM)	Reference
(1) Middle and Upper Hudson River; Mohawk River (Cohoes)						
Waterford			5.91 ¹ (4.66-6.45)	5.14 ¹ (3.74-6.04)	5.10 ¹ (4.12-5.70)	NYSDEC SWMS, 2007 ¹
Cohoes			6.17 ¹ (4.15-7.13)	5.16 ¹ (3.38-6.08)	5.12 ¹ (4.01-6.18)	
Glenmont			6.21 ¹ (4.45-7.40)	4.89 ¹ (3.45-5.36)	4.90 ¹ (3.47-5.37)	
Poughkeepsie			5.48 ¹ (4.21-6.32)	4.33 ¹ (3.06-5.63)	4.75 ¹ (3.60-5.88)	
(2) Lower Hudson River (kmp ~25 to ~100)						
	5.79 ² (5.29-6.12)	3.96 ² (3.88-4.01) 4.70 ³ (3.17-5.21)				CARP, 2007 ² Yang and Sañudo-Wilhelmy, 1998 ³
(3) Estuarine Turbidity Maximum (ETM) (kmp ~4 to ~25)						
	5.39 ² (5.07-5.57)	4.10 ² (3.42-4.36) 4.39 ³ (3.43-4.75)				CARP, 2007 ² Yang and Sañudo-Wilhelmy, 1998 ³
(4) New York/New Jersey Harbor						
Newark Bay	6.18 ² (5.72-6.33)	4.33 ² (3.98-4.64)				CARP, 2007 ² Paulson, 2005 ⁴
Upper Harbor	6.01 ² (5.54-6.28)	4.57 ² (3.94-4.93) 4.53 ⁴ (3.52-5.04)	6.99 ⁴ (6.43-7.54)	5.37 ⁴ (4.89-5.58)	4.76 ⁴ (4.16-5.01)	
Lower Harbor	5.46 ² (5.35-5.55)					
Raritan Bay	5.59 ² (5.46-5.69)	4.09 ² (3.73-4.40) 4.01 ⁴ (3.49-4.19)	6.63 ⁴ (6.07-6.98)	4.94 ⁴ (4.59-5.10)	4.23 ⁴ (3.73-4.46)	
Jamaica Bay	5.53 ² (4.32-5.96)	4.17 ² (2.91-4.48)				
Rockaway-Sandy Hook		4.51 ⁴ (3.95-4.87)	6.79 ⁴ (6.40-7.05)	5.30 ⁴ (4.73-5.72)	4.56 ⁴ (4.25-4.76)	

¹ 1993 to 2006, $n = 37-70$; ² Feb. 1999 to Oct. 2001, $n = 2-4$; ³ Oct. 1995/1996 and Apr. 1996/1997, $n = 7-11$; ⁴ Aug. 1999, $n = 7-15$

Table S2. Coefficients of determination (r^2) for linear regressions of sediment heavy metals with independent variables (data collected 1993-1994; EMAP, Adams et al., 1998). Summary of term(s) included in stepwise multiple regressions using all independent variables.

Region	Heavy Metals (nmol g ⁻¹)	Independent Variables					Summary - Stepwise Multiple Regression
		Al (μmol g ⁻¹)	Fe (μmol g ⁻¹)	TOC (μmol g ⁻¹)	Siltclay (%)	Mn (μmol g ⁻¹)	
Newark Bay	Hg	0.544	0.497	0.056	0.701	0.383	siltclay (0.701)
	Cd	0.254	0.315	0.437	0.210	0.117	TOC (0.437)
	Pb	0.381	0.446	0.541	0.289	0.159	TOC, Fe (0.637)
	Ni	0.691	0.694	0.085	0.537	0.580	Fe (0.694)
	Zn	0.534	0.633	0.560	0.480	0.314	Fe, TOC (0.768)
	Ag	0.694	0.626	0.045	0.640	0.624	Al (0.694)
	Cu	0.609	0.717	0.343	0.639	0.426	Fe (0.717)
Upper Harbor	Hg	0.691	0.766	0.043	0.193	0.568	Fe, TOC (0.859)
	Cd	0.759	0.649	0.008	0.156	0.581	Al, TOC (0.858)
	Pb	0.620	0.767	0.093	0.101	0.699	Fe, Mn (0.853)
	Ni	0.515	0.543	0.089	0.239	0.346	Fe (0.543)
	Zn	0.883	0.896	0.134	0.199	0.523	Fe, TOC (0.923)
	Ag	0.730	0.639	0.030	0.101	0.492	Al (0.730)
	Cu	0.712	0.809	0.079	0.178	0.582	Fe, TOC (0.864)
Raritan Bay	Hg	0.850	0.821	0.216	0.097	0.535	Al (0.850)
	Cd	0.666	0.669	0.013	0.009	0.377	Fe, TOC (0.864)
	Pb	0.940	0.937	0.218	0.115	0.489	Al, siltclay, Fe (0.979)
	Ni	0.722	0.708	0.015	0.020	0.457	Al, TOC, Fe (0.908)
	Zn	0.936	0.972	0.306	0.249	0.375	Fe (0.972)
	Ag	0.879	0.872	0.114	0.054	0.534	Al, siltclay (0.956)
	Cu	0.912	0.915	0.178	0.188	0.348	Fe, TOC (0.941)
Lower Harbor	Hg	0.486	0.123	0.013	0.014	0.359	Al, Mn (0.668)
	Cd	0.314	0.013	0.016	0.0001	0.154	Al (0.314)
	Pb	0.512	0.721	0.003	0.068	0.061	Fe (0.721)
	Ni	0.423	0.305	0.045	0.117	0.032	Al, siltclay (0.610)
	Zn	0.161	0.691	0.015	0.208	0.048	Fe (0.691)
	Ag	0.016	0.0001	0.246	0.030	0.134	--
	Cu	0.441	0.070	0.0005	0.003	0.261	Al (0.441)
Jamaica Bay	Hg	0.190	0.269	0.034	0.387	0.005	siltclay, TOC (0.522)
	Cd	0.149	0.248	0.034	0.361	0.002	siltclay, TOC (0.484)
	Pb	0.094	0.182	0.026	0.272	0.001	siltclay (0.272)
	Ni	0.079	0.171	0.029	0.257	0.001	siltclay (0.257)
	Zn	0.118	0.232	0.049	0.331	0.002	siltclay (0.331)
	Ag	0.503	0.762	0.331	0.846	0.035	siltclay (0.846)
	Cu	0.114	0.239	0.051	0.336	0.002	siltclay (0.336)
NY Bight	Hg	0.422	0.031	0.006	0.936	0.001	siltclay (0.936)
	Cd	0.505	0.022	0.021	0.770	0.001	siltclay (0.770)
	Pb	0.543	0.038	--	0.724	0.0001	siltclay, Al (0.768)
	Ni	0.490	0.052	0.006	0.858	0.0004	siltclay (0.858)
	Zn	0.402	0.215	0.025	0.678	0.013	siltclay, Fe (0.822)
	Ag	0.479	0.012	0.004	0.674	0.0003	siltclay (0.674)
	Cu	0.510	0.015	0.006	0.848	0.002	siltclay (0.848)

Table S3. Coefficients of determination (r^2) for linear regressions of sediment heavy metals with independent variables (data collected 1998; EMAP, 2008). Summary of term(s) included in stepwise multiple regressions using all independent variables.

Region	Heavy Metals (nmol g ⁻¹)	Independent Variables					Summary - Stepwise Multiple Regression
		Al (μmol g ⁻¹)	AVS (μmol g ⁻¹)	TOC (μmol g ⁻¹)	Siltclay (%)	Mn (μmol g ⁻¹)	
Newark Bay	Hg	0.406	0.109	0.014	0.003	0.003	Al (0.406)
	Cd	0.310	0.414	0.011	0.024	0.121	AVS, Al, Mn (0.717)
	Pb	0.227	0.279	0.005	0.054	0.260	AVS, Mn (0.446)
	Ni	0.452	0.320	0.122	0.262	0.188	Al, AVS (0.618)
	Zn	0.203	0.241	0.003	0.141	0.321	Mn, AVS (0.466)
	Ag	0.638	0.332	0.003	0.054	0.454	Al, AVS (0.762)
Upper Harbor	Hg	0.342	0.475	0.218	0.026	0.362	AVS (0.438)
	Cd	0.604	0.442	0.331	0.059	0.439	Al (0.547)
	Pb	0.613	0.594	0.433	0.127	0.430	Al, AVS (0.705)
	Ni	0.636	0.345	0.287	0.127	0.364	Al (0.644)
	Zn	0.772	0.460	0.396	0.154	0.552	Al (0.797)
	Ag	0.541	0.132	0.252	0.154	0.376	Al (0.642)
Raritan Bay	Hg	0.901	0.242	0.786	0.745	0.459	Al, Mn, siltclay (0.954)
	Cd	0.804	0.422	0.705	0.625	0.452	Al (0.804)
	Pb	0.991	0.430	0.926	0.885	0.623	Al (0.991)
	Ni	0.988	0.389	0.931	0.894	0.677	Al (0.988)
	Zn	0.921	0.922	0.829	0.809	0.582	Al (0.921)
	Ag	0.929	0.119	0.797	0.774	0.504	Al, AVS (0.974)
Lower Harbor	Hg	0.848	0.367	0.693	0.497	0.028	Al (0.848)
	Cd	0.777	0.663	0.754	0.449	0.001	Al, AVS (0.867)
	Pb	0.608	0.308	0.537	0.261	0.064	Al (0.608)
	Ni	0.200	0.020	0.052	0.044	0.303	Mn (0.303)
	Zn	0.343	0.069	0.163	0.128	0.174	Al (0.343)
	Ag	0.846	0.523	0.794	0.578	0.001	Al, TOC (0.924)
Jamaica Bay	Hg	0.823	0.620	0.836	0.854	0.111	siltclay, Al (0.896)
	Cd	0.674	0.815	0.803	0.785	0.000	AVS, siltclay, Mn, Al (0.939)
	Pb	0.803	0.735	0.880	0.882	0.043	TOC, AVS, Al (0.926)
	Ni	0.911	0.710	0.890	0.887	0.078	Al, siltclay, AVS (0.983)
	Zn	0.798	0.807	0.875	0.868	0.025	TOC, AVS, Al, Mn (0.956)
	Ag	0.795	0.779	0.934	0.928	0.030	siltclay, AVS (0.952)

Table S4. Correlation coefficients (r) for comparisons among sediment heavy metals (collected 1993-1994; EMAP; Adams et al., 1998).

Heavy Metals								
Region	(nmol g ⁻¹)	Hg	Cd	Pb	Ni	Zn	Ag	Cu
Newark Bay	Hg	--	0.365	0.417	0.706	0.579	0.701	0.827
	Cd	0.365	--	0.880	0.368	0.904	0.481	0.671
	Pb	0.417	0.880	--	0.516	0.869	0.509	0.824
	Ni	0.706	0.368	0.516	--	0.582	0.767	0.780
	Zn	0.579	0.904	0.869	0.582	--	0.641	0.851
	Ag	0.701	0.481	0.509	0.767	0.641	--	0.701
	Cu	0.827	0.671	0.824	0.780	0.851	0.701	--
Upper Harbor	Hg	--	0.907	0.862	0.564	0.907	0.800	0.908
	Cd	0.907	--	0.790	0.617	0.907	0.894	0.879
	Pb	0.862	0.790	--	0.620	0.864	0.755	0.894
	Ni	0.564	0.617	0.620	--	0.676	0.806	0.661
	Zn	0.907	0.907	0.864	0.676	--	0.849	0.955
	Ag	0.800	0.894	0.755	0.806	0.849	--	0.833
	Cu	0.908	0.879	0.894	0.661	0.955	0.833	--
Raritan Bay	Hg	--	0.764	0.954	0.795	0.899	0.897	0.860
	Cd	0.764	--	0.844	0.935	0.795	0.920	0.847
	Pb	0.954	0.844	--	0.878	0.953	0.966	0.954
	Ni	0.795	0.935	0.878	--	0.813	0.960	0.897
	Zn	0.899	0.795	0.953	0.813	--	0.904	0.948
	Ag	0.897	0.920	0.966	0.960	0.904	--	0.945
	Cu	0.860	0.847	0.954	0.897	0.948	0.945	--
Lower Harbor	Hg	--	0.528	0.677	0.522	0.350	0.028	0.865
	Cd	0.528	--	0.403	0.610	0.123	ns	0.748
	Pb	0.677	0.403	--	0.608	0.825	ns	0.580
	Ni	0.522	0.610	0.608	--	0.416	ns	0.657
	Zn	0.350	0.127	0.825	0.416	--	ns	0.265
	Ag	0.028	ns	ns	ns	ns	--	ns
	Cu	0.865	0.748	0.580	0.657	0.265	ns	--
Jamaica Bay	Hg	--	0.955	0.969	0.957	0.965	0.788	0.968
	Cd	0.955	--	0.968	0.964	0.985	0.776	0.986
	Pb	0.969	0.968	--	0.998	0.994	0.694	0.991
	Ni	0.957	0.964	0.998	--	0.992	0.677	0.989
	Zn	0.965	0.985	0.994	0.992	--	0.742	0.997
	Ag	0.788	0.776	0.694	0.677	0.742	--	0.760
	Cu	0.968	0.986	0.991	0.989	0.997	0.760	--
NY Bight	Hg	--	0.901	0.874	0.958	0.853	0.835	0.949
	Cd	0.901	--	0.943	0.855	0.839	0.975	0.971
	Pb	0.874	0.943	--	0.867	0.892	0.959	0.960
	Ni	0.958	0.855	0.867	--	0.909	0.787	0.924
	Zn	0.853	0.839	0.892	0.909	--	0.808	0.885
	Ag	0.835	0.975	0.959	0.787	0.808	--	0.953
	Cu	0.949	0.971	0.960	0.924	0.885	0.953	--

Table S5. Correlation coefficients (r) for comparisons among sediment heavy metals (collected 1998; EMAP, 2008).

Trace Metals							
Region	(nmol g ⁻¹)	Hg	Cd	Pb	Ni	Zn	Ag
Newark Bay	Hg	--	0.837	0.747	0.416	0.526	0.739
	Cd	0.837	--	0.901	0.701	0.684	0.818
	Pb	0.747	0.901	--	0.529	0.696	0.753
	Ni	0.446	0.701	0.529	--	0.697	0.828
	Zn	0.506	0.684	0.696	0.697	--	0.828
	Ag	0.739	0.818	0.753	0.823	0.778	--
	Upper Harbor	Hg	--	0.871	0.915	0.893	0.846
Cd	0.871	--	0.911	0.847	0.919	0.818	
Pb	0.915	0.911	--	0.879	0.949	0.555	
Ni	0.893	0.847	0.879	--	0.896	0.780	
Zn	0.846	0.919	0.949	0.896	--	0.812	
Ag	0.573	0.818	0.555	0.780	0.812	--	
Raritan Bay	Hg	--	0.879	0.955	0.952	0.919	0.955
	Cd	0.879	--	0.915	0.879	0.958	0.793
	Pb	0.955	0.915	--	0.990	0.962	0.954
	Ni	0.952	0.879	0.990	--	0.951	0.966
	Zn	0.919	0.958	0.962	0.951	--	0.909
	Ag	0.955	0.793	0.954	0.966	0.909	--
	Lower Harbor	Hg	--	0.839	0.856	0.275	0.666
Cd	0.839	--	0.765	0.410	0.579	0.959	
Pb	0.856	0.765	--	0.389	0.872	0.828	
Ni	0.275	0.410	0.389	--	0.339	0.402	
Zn	0.666	0.579	0.872	0.339	--	0.631	
Ag	0.922	0.959	0.828	0.402	0.631	--	
Jamaica Bay	Hg	--	0.830	0.941	0.947	0.916	0.919
	Cd	0.830	--	0.928	0.905	0.967	0.954
	Pb	0.941	0.928	--	0.969	0.988	0.982
	Ni	0.947	0.905	0.969	--	0.967	0.966
	Zn	0.916	0.967	0.988	0.967	--	0.985
	Ag	0.919	0.954	0.982	0.966	0.985	--