

EVIDENCE OF URBAN SOURCE METAL CONTAMINANTS IN NY/NJ HARBOR

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ABSTRACT: Sediment cores were collected at three stations in the NY/NJ Harbor in December 1991, May 1992, September 1992, and May 1993 for studying heavy metal contaminants (Ag, Cd, Cu, Pb and Zn). Anthropogenic metal contaminants were present up to a depth of >10 cm of sediments in marginal and depositional areas and in the upper 2 cm sediments in the navigational channel areas. In this study, contaminant concentrations in the Harbor were found 1.4 ± 1.0 ppm for Ag, 1.2 ± 0.6 ppm for Cd, 90 ± 37 ppm for Cu, 102 ± 53 ppm for Pb and 182 ± 45 ppm for Zn. Silver (Ag) is used as an urban source tracer in this study to examine the sources of heavy metal contaminants (Ag, Cd, Cu, Pb and Zn) to the Harbor. It is found that the distributions and variations of anthropogenic Cd, Cu, Pb and Zn were correlated with anthropogenic Ag, suggesting that urban source inputs such as municipal sewage and waste waters are the important sources of these contaminants to the harbor.

INTRODUCTION

With the industrial development in urban areas, pollution becomes a serious environmental problem (Goldberg et al., 1979; Trefry and Shokes, 1981; Bopp and Simpson, 1989; Windom, 1992; Valette-Silver, 1993; Hirschberg et al., 1996; Feng et al., 1998a,b). Sediment contamination in the Hudson River estuary has been studied by a number of researchers since the 1970s because it can provide time-integrated records of contaminations due to urban and industrial development (e.g., William et al., 1978; Olsen et al., 1984; Rohmann, 1988; Bopp and Simpson, 1989; Gibbs, 1994; Hunt et al., 1994; Chillrud 1996; Hirschberg et al., 1996; Feng et al., 1998a,b; 1999a; 2002). Williams et al. (1978) found that anthropogenic Cu, Pb and Zn concentrations in the New York Harbor sediments were apparent to depths >60 cm. Klinkhammer and Bender (1981) found that the discharge of Cd, Cu and Zn with Manhattan/New Jersey sewage was comparable to the riverine flux, and their mass balance calculations demonstrated that anthropogenic Cd and Cu were associated with solids and were deposited in the Harbor. Olsen and his colleagues (1984) found that many chemically reactive

contaminants such as Cu, Pb, Zn, petroleum hydrocarbons and polychlorinated biphenyls have very similar distributions in the sediments, implying the high affinity of these contaminants to particles. Along the Hudson River estuary, the highest sedimental metal contaminant concentrations were found in the New York Harbor and this observation could be attributed to the high metal concentrations in local sources as well as hydrodynamics (Gibbs, 1994). In another study of the metal distributions in New York Harbor, Chillrud (1996) found that most metal contaminants such as Cd, Cu, Pb and Zn in New York Harbor sediments had declined by 50-90% from their maximum levels reached in the 1960s and 1970s and the decreases seemed to continue during the early 1990s. Hirschberg et al. (1996) sampled sediments in the lower Hudson River estuary for natural radionuclides (^{234}Th and ^{210}Pb) and trace metals (Ag, Cd, Cu, Pb and Zn). They found that anthropogenic metals were present at sediment depths corresponding to the presence of excess ^{210}Pb , varying from 5 to >45 cm depending on the sedimentation rate in an area. Fine-grained sediment accumulation rates in the Harbor were estimated between 5 and 20 cm y^{-1} in most depositional areas using reactor- and bomb-produced radionuclides, such as $^{239,240}\text{Pu}$, ^{137}Cs , ^{134}Cs

and ^{60}Co (Oslen et al., 1984). Feng et al. (1998a) estimated that sedimentation rates in the western margin area at kmp ~ 8 (km point 0 is taken at the Battery, southern tip of Manhattan) varied from 6 to 26 cm y^{-1} based on ^{234}Th and ^7Be profiles.

Although the prior work has shown that the lower Hudson River estuary, especially the Harbor area, is heavily contaminated, the sources of these contaminants have not been well characterized. This study presents the results of trace metal (Ag, Cd, Cu, Pb and Zn) distributions in the Harbor sediments and attempts to examine the important sources of trace metal contaminants to the harbor sediments.

METHODS

Three sites (designated as 79th St. mid-channel (79M) and west bank (79W), and Governors Island (GI)) in the lower Hudson River estuary within the Harbor were chosen to study sources of heavy

metal contaminants (Fig. 1). The sediments at most sites were found to be contaminated by heavy metals, PCBs and other contaminants (Williams et al., 1978; Olsen et al., 1984; Bopp and Simpson, 1989; Hunt et al., 1994; Gibbs, 1994; Chillrud, 1996). Detailed morphological and physical descriptions of these sites have been given by Hirschberg et al. (1996). In brief, stations 79M and 79W (kmp 8) are located off the 79th Street of Manhattan and within the turbidity maximum zone (Geyer, 1993; Feng et al., 1999b). Station 79M is near the mid-channel and station 79W is on the west side of the river margin near the New Jersey side. Sediment accumulation rates in this area were measured $<1 \text{ mm y}^{-1}$ to 20 cm y^{-1} based on ^{210}Pb , ^{234}Th and ^7Be profiles, varying from mid-channel to the channel margin on the New Jersey side (Olsen et al., 1984; Feng et al., 1998a). Station GI is near Governors Island (kmp -3). From ^{210}Pb and ^{137}Cs profiles, the sediment accumulation rates were estimated ranging from 1 to 5 cm y^{-1} with an average of $\sim 3 \text{ cm y}^{-1}$ in non-dredged areas, and from 4 to 70 cm y^{-1} with an average of $\sim 9 \text{ cm y}^{-1}$ in dredged areas (Olsen et al.,

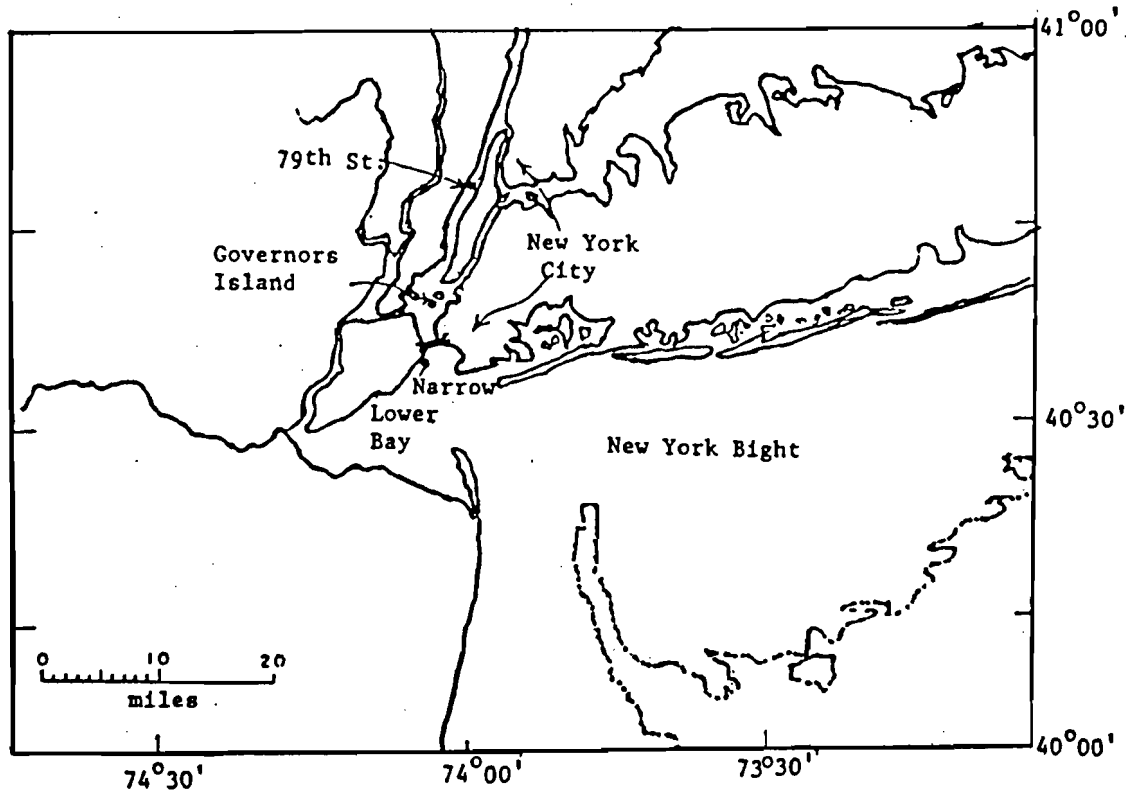


Figure 1. Map showing the study sites in the Inner Harbor.

1984).

Sediment samples were collected at the three stations using a Soctour box corer in December 1991, May and September 1992, and May 1993. Subsamples of ~10 cm long were obtained from the box corer using a 8.5 cm x 25 cm x 30 cm rectangular plastic box. These sub-samples were either carefully sectioned at 1 to 3 cm interval increments on board, or carefully sealed, stored in a freezer and sectioned in the laboratory upon return from the field. All sediment samples were dried at ~80°C in an oven in the laboratory after sectioning for physical and chemical analysis. The oven-dried sediments were then ground to a powder with a mortar and pestle.

Total digestion of an aliquot of ~0.4 g of the dried sediments was carried out in acid pre-cleaned 100 ml Teflon beakers using HNO₃-HClO₄-HF in a three step procedure as described by Feng et al. (1998b) to determine metal concentrations. The completely dissolved samples were diluted to 25 ml with Ultrex 2% HNO₃ solution. Sample solutions and reagent blanks were analyzed for Ag, Cd, Cu, Fe, Pb and Zn using a Hitachi Model Z-8100 Polarized Zeeman Atomic Absorption Spectrophotometer. Background correction and matrix interference were monitored throughout the analyses. To ensure the quality of the trace metal data, BCSS-1 sediment standard reference material issued by the National Research Council, Canada, was analyzed along with the samples by the same technique to monitor the accuracy of the analytical procedures and to ensure

the data quality. All analytical results for BCSS-1 reference material were within the certified values (Table 1). Triplicate digestion and analyses of one sample out of every 10 samples were performed to check the analytical precision. The analytical precision expressed by the coefficient of variation was <10% for Ag and Cd, and <5% for Cu, Fe, Pb and Zn.

RESULTS AND DISCUSSION

Sediment Ag, Cd, Cu, Fe, Pb and Zn concentrations at the three stations ranged from 0.02 to 3.66 ppm for Ag, 0.09 to 4.30 ppm for Cd, 15 to 186 ppm for Cu, 16 to 200 ppm for Pb and 79 to 346 ppm for Zn (Figs. 2-4). As shown in Figs. 2-4, excess metal contaminants, which are defined as greater than the background values that are ~80 cm deep in a core (see Hirschberg et al., 1996), were found present in, at least, the upper 10 cm of surface sediments in marginal and depositional areas and in the upper 2 cm sediments in the navigational channel area. In comparison of our data with those from other studies in the Hudson River estuary (e.g., Gibbs, 1994; Chillrud, 1996), our metal data are in general agreement with others (Table 2).

The results of trace metals from the box core samples collected in the different time period suggest

Table 1 Results of BCSS-1 standard reference material analysis

Element	Analytical Value (ppm)	Certified Value (ppm)
Ag	0.094 ± 0.023	0.103 ± 0.068
Cd	0.23 ± 0.02	0.25 ± 0.04
Cu	18.0 ± 1.0	18.5 ± 2.7
Fe	3.32 ± 0.19	3.28 ± 0.14
Pb	23.4 ± 1.6	22.7 ± 3.4
Zn	113 ± 4	119 ± 12

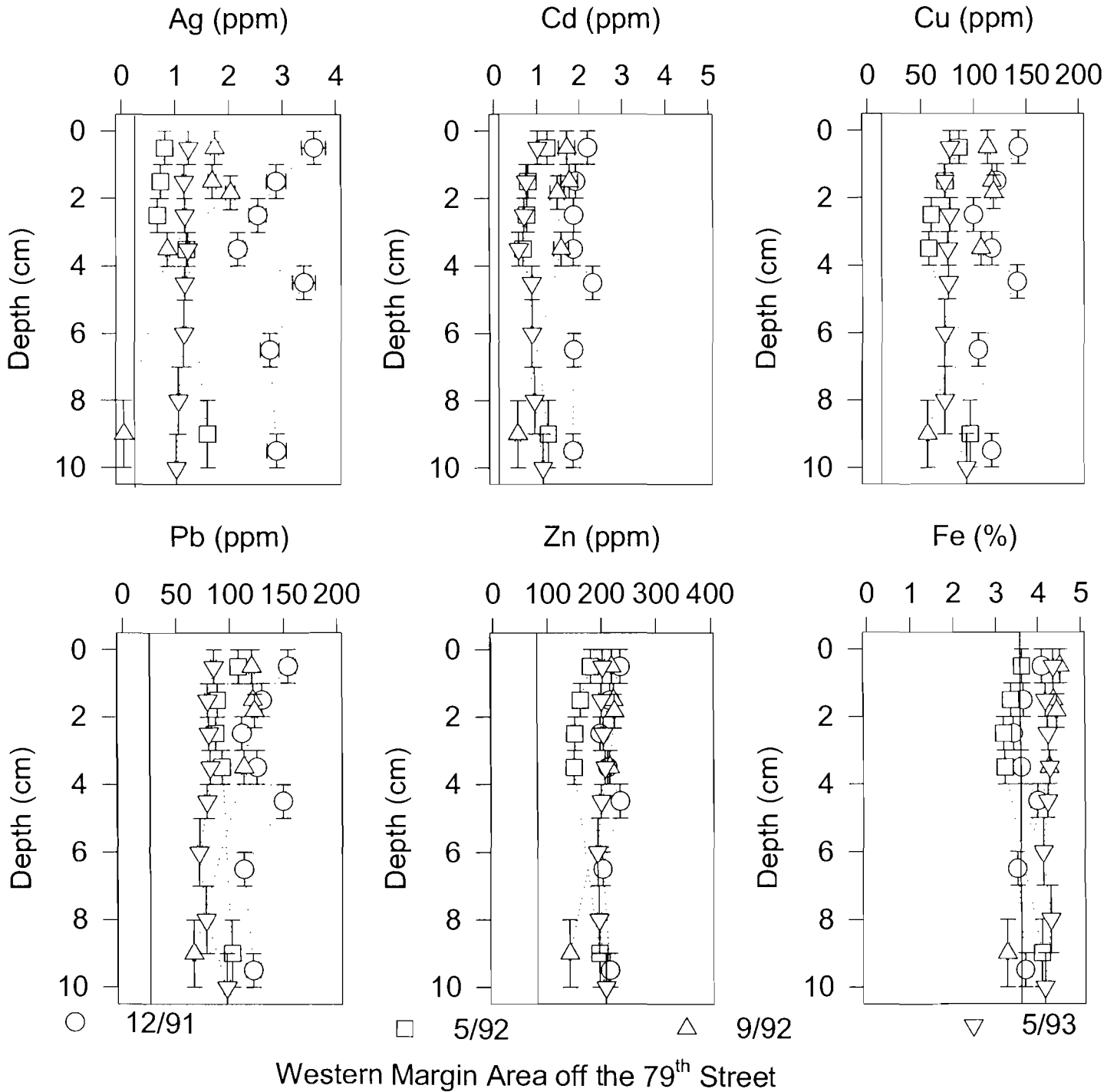


Figure 2. Vertical profiles showing Ag, Cd, Cu, Pb, Zn and Fe concentrations in sediments from station 79W. Sediment box core samples were collected in December 1991 (○), May 1992 (□), September 1992 (Δ) and May 1993 (▽). Vertical line in each graph indicates the background value of the metal in the Hudson River sediments (Hirschberg et al., 1996).

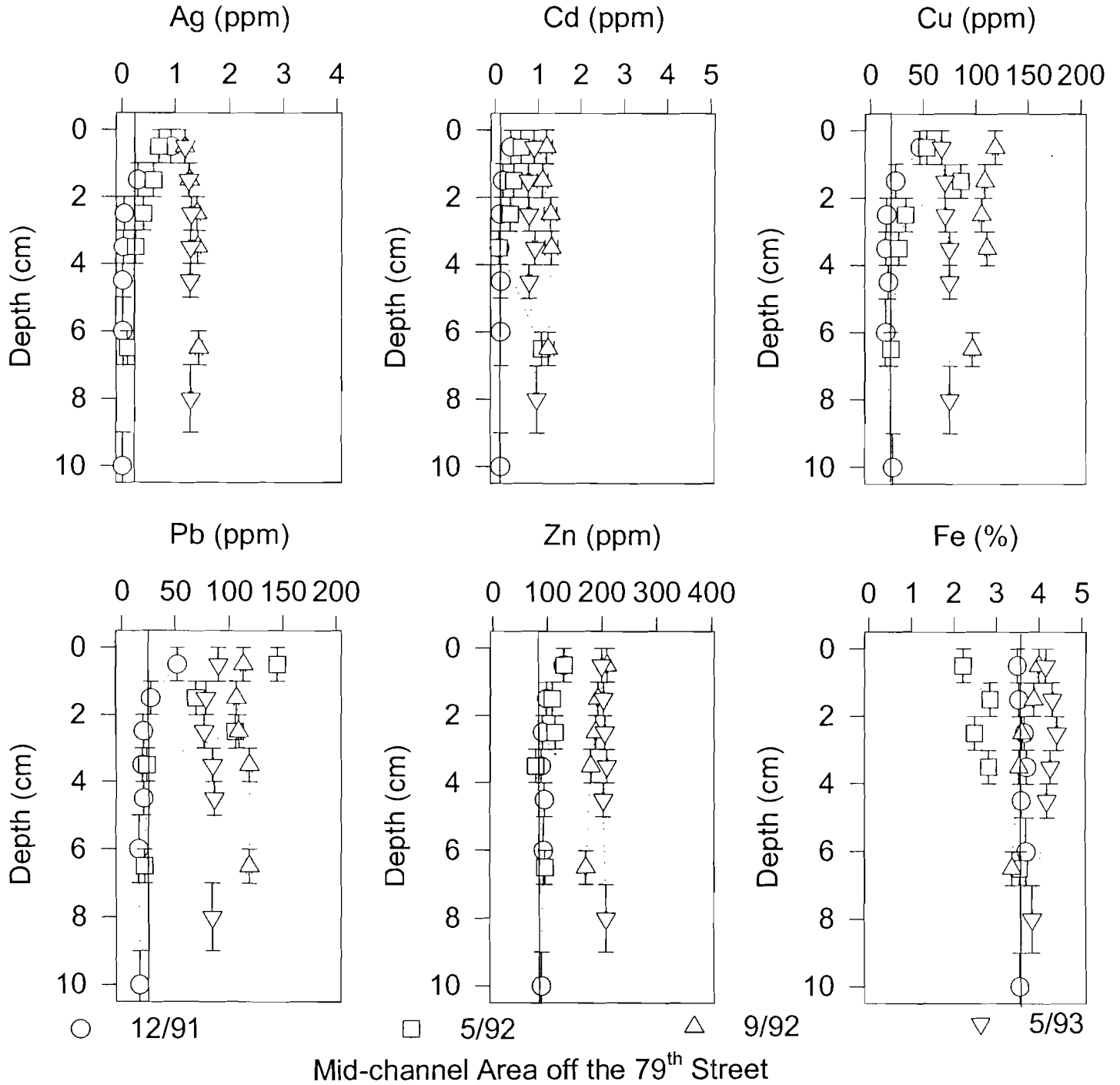


Figure 3. Vertical profiles showing Ag, Cd, Cu, Pb, Zn and Fe concentrations in sediments from station 79M. Sediment box core samples were collected in December 1991 (O), May 1992 (□), September 1992 (Δ) and May 1993 (∇). Vertical line in each graph indicates the background value of the metal in the Hudson River sediments (Hirschberg et al., 1996).

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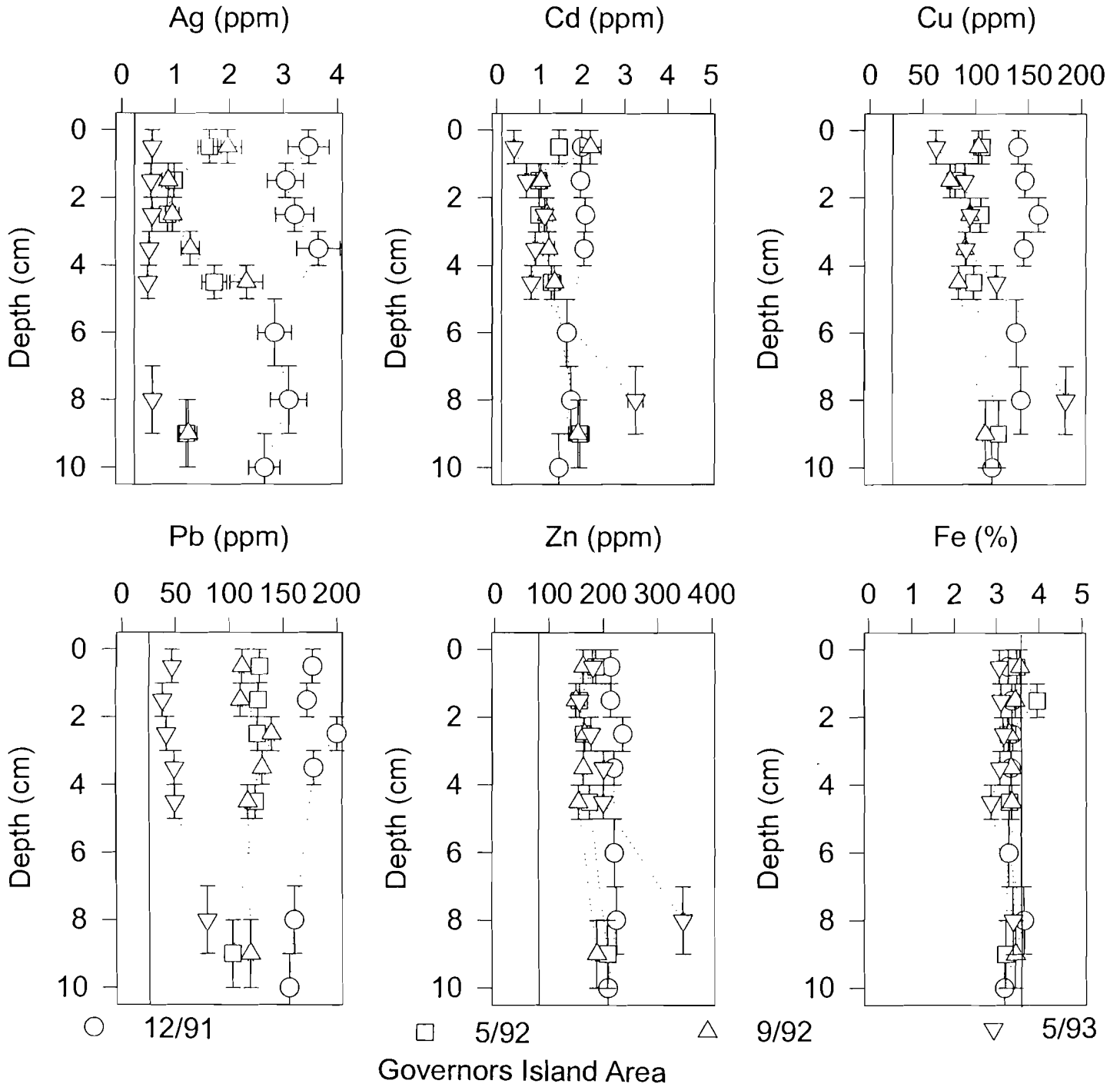


Figure 4. Vertical profiles showing Ag, Cd, Cu, Pb, Zn and Fe concentrations in sediments from station GI. Sediment box core samples were collected in December 1991 (O), May 1992 (□), September 1992 (Δ) and May 1993 (▽). Vertical line in each graph indicates the background value of the metal in the Hudson River sediments (Hirschberg et al., 1996).

Table 2 Comparison of metal contaminant results from this study with those from others in the Harbor

Study area (km point) ⁽¹⁾	Sample size	Ag (ppm)	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)	Source
-5 to 11	n=71	1.4 ± 1.0	1. ± 0.6	90 ± 37	102 ± 53	182 ± 45	This study
-4 to 8	n=5	n.a. ⁽²⁾	4. ± 3.1	55 ± 30	92 ± 36	109 ± 62	Gibbs 1994
-3 to 16 ⁽³⁾	n=5	n.a. ⁽²⁾	1. ± 0.5	135 ± 27	150 ± 31	265 ± 64	Chillrud 1996

(1) km point = 0 is designated as the Battery, southern tip of Manhattan.

(2) n.a. = Not available.

(3) 1989, 1992 and 1994 transects.

some spatial as well as temporal variations in these metal contaminant distributions (Figs. 2-4), resulting from the dynamics of the Hudson River estuary as discussed by Hirschberg et al. (1996), Ullman and Wilson (1998) and Feng et al. (1999a). The processes and mechanisms governing the heavy metal contaminant distributions in the harbor can be explained by their chemically particle-reactive characteristics, estuarine circulation and local hydrological conditions (e.g., Olsen et al., 1993; Ullman and Wilson, 1998; Feng et al., 1999a; 2002). Feng et al. (1999c) estimated that the residence times of ²³⁴Th- and ⁷Be-carrying particles in the Hudson estuary range from <1 to 10 d.

As described by Hirschberg et al. (1996), surface sediments (<10 cm) showed little permanent sediment accumulation between the Battery and Haverstraw Bay and short time-scale (months) variability in ²³⁴Th deposition occurred in the lower estuary sediments, although excess ²³⁴Th inventories in bottom sediments were on average balanced by local production in the water column. Small-scale spatial variability of contaminant distributions near stations 79M and 79W were discussed in detail by Feng et al. (1998a). They found that the local spatial variability in

metal concentrations could be as high as 50% in that area.

In an urban estuarine system, Ag can be referred to a good indicator of urban waste effluent input (Sañudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993; Feng et al., 1998b) because Ag concentration in natural crust rock and soil is very low (0.008 ppm in rock and 0.005 ppm in soil, Martin and Whitfield, 1983). Therefore, the supply of Ag to the riverine and estuarine systems is mainly from urban anthropogenic sources such as sewage sludge and waste waters (Sañudo-Wilhelmy and Flegal, 1992; Smith and Flegal, 1993). Results from this study show a high excess Ag concentration in most core sediments except two cores from the middle channel area. These two cores could represent either non-depositional sites or dredged for navigational purpose (Figs. 2-4).

In this study, despite the differences in hydrodynamic conditions and sediment accumulation rates in this area as discussed by Olsen et al. (1984), Feng et al., (1998a; 1999b) and Ullman and Wilson (1998), excess Cd, Cu, Pb and Zn concentrations generally show significant correlations ($r^2 = 0.4-0.7$, $n=65$) with excess Ag at depths of the sediments sampled except for a few outliers (Fig. 5). The

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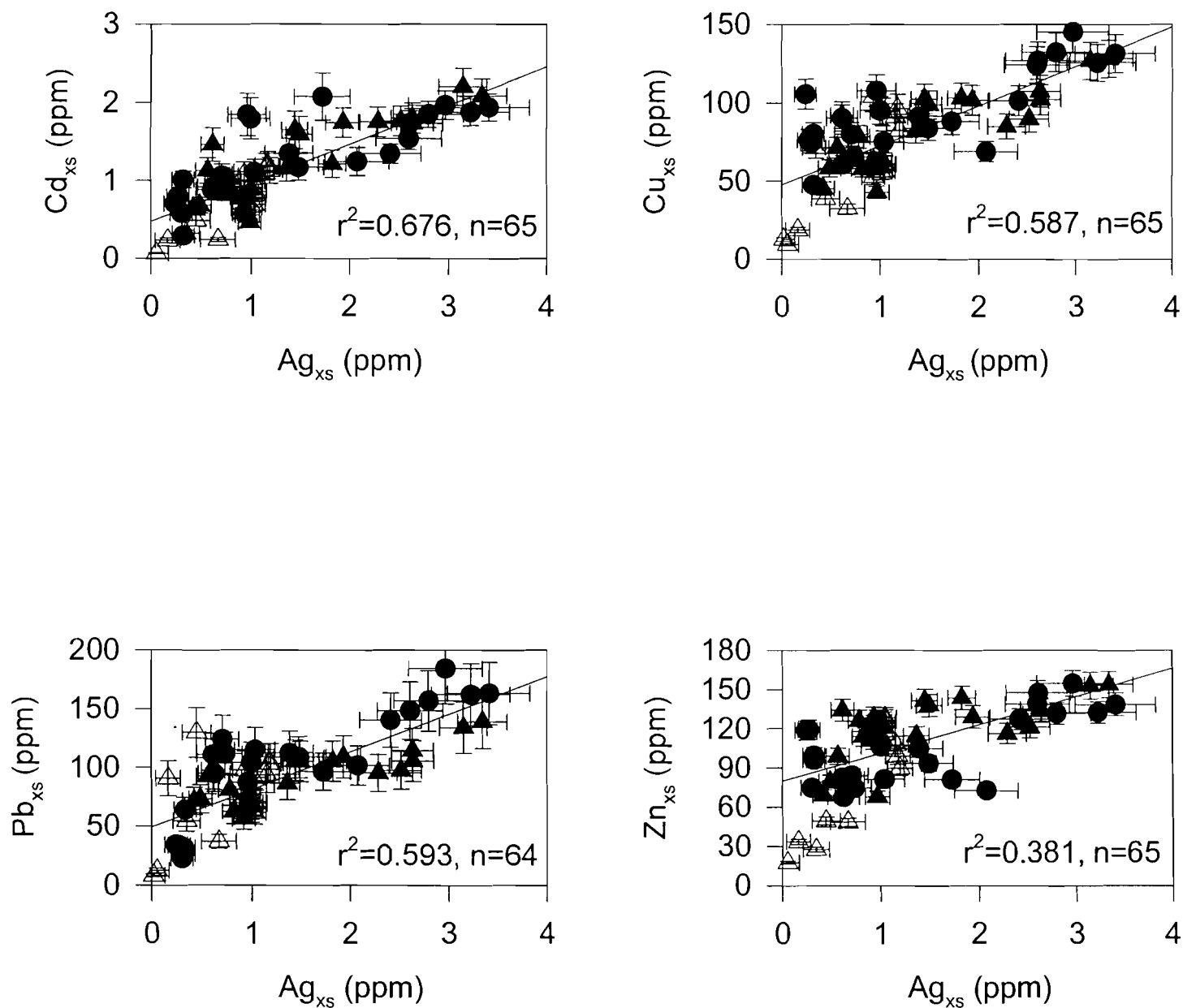


Figure 5. Correlations of excess Cd, Cu, Pb and Zn with excess Ag in the Inner Harbor sediments. The lines are the best-fit linear regression lines. Sediment box core samples were collected in December 1991, May 1992, September 1992 and May 1993. Symbols are designated as (▲) for station 79W and (Δ) for station 79M and (●) for station GI.

evidence of the linear correlation of excess Cd, Cu, Pb and Zn with excess Ag in the sediments strongly suggests that excess Cd, Cu, Pb and Zn have been input to the Harbor along with excess Ag from the urban sources, distributed and accumulated in the Harbor sediments. In fact, a 10-15 km up-estuary transport of sediments during the low river flow and a similar distance of down-estuary transport during the high flow are found by Feng et al. (1999c). It is very likely that a certain amount of heavy metal contaminants are transported and redistributed with sediments due to estuarine circulation (Geyer, 1993; Feng, 1999a; 2002). Some outliers shown in Fig. 5 may imply either a local addition of these contaminants, causing a high concentration of one or more specific metals, or a dredged area (e.g., Station 79M), where the metal contaminant concentrations are usually low. As reported by Klinkhammer and Bender (1981) and Brosnan et al. (1994), the New York/New Jersey waste water from the sewage plants and flood runoff had been historically discharged into the harbor area. Therefore, the general good correlations of trace metal contaminants (Cd, Cu, Pb and Zn) with Ag in the harbor sediments suggest that these contaminants may have the same source function. In addition, as shown in Fig. 5, there are no distinctive distribution clusters among three stations on excess metal vs. excess Ag relationships, implying that the contaminants are transported, mixed and redistributed in the Harbor. As shown in this study, most metal contaminants in New York Harbor sediments showed a strong tendency to vary together as indicated by correlation of metals vs Ag. This agrees with our hypothesis that sources of metal contaminants from the NY/NJ metropolitan area dominate input of these contaminants to NY/NJ Harbor and that fine particles and their associated contaminants are effectively mixed by tidal currents.

CONCLUSIONS

In this study, anthropogenic metal contaminants were found present in >10 cm of surface sediments in marginal and depositional areas and in the upper 2 cm sediments in the navigational channel area. Contaminant concentrations in the NY/NJ Harbor

were found 1.4 ± 1.0 ppm for Ag, 1.2 ± 0.6 ppm for Cd, 90 ± 37 ppm for Cu, 102 ± 53 ppm for Pb and 182 ± 45 ppm for Zn. As shown in this study, Ag can be used as an urban source tracer of contaminants because Ag is mainly from municipal sewage and waste waters. The similar distribution and accumulation patterns of excess metal contaminants vs. excess Ag found in this study suggest that these metal contaminants have the same urban source and are controlled by the same mechanisms and processes, such as hydrodynamics of the Hudson River and sediment dynamics caused by wave and tidal currents.

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