

**Cadmium and Manganese in the Hudson River Estuary:
Interannual and Seasonal Variability**

Final Report

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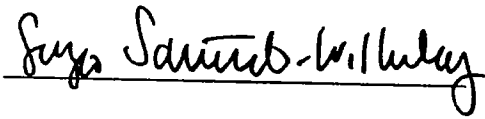
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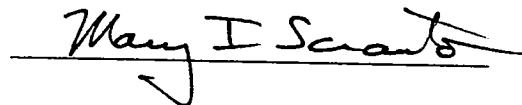
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**Phase Speciation of Cadmium and Manganese in the Hudson River Estuary:
Interannual and Seasonal Variability**

A Thesis Presented

by

Min Yang

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in Partial Fulfillment of the

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in

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at Stony Brook

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Abstract of the Thesis

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The size distribution of Cd and Mn was examined in surface waters of the Hudson River estuary. Water samples were collected in four cruises between 1995 and 1997 along the entire Hudson River estuary under different river discharge conditions, and fractionated into particulate ($>0.45 \mu\text{m}$), "dissolved" ($<0.45 \mu\text{m}$), colloidal (10 kDa- $0.45 \mu\text{m}$) and low molecular weight ($<10 \text{ kDa}$) phases. While most of the cadmium ($>70\%$) was found in the traditionally defined "dissolved"

phase, manganese showed a wide range of distributions between the dissolved and particulate fractions. From the river to the ocean, the percentage of dissolved manganese increased from 10% to 90% suggesting a transfer from the particulate phase to the dissolved along the salinity gradient. However, because most of the $<0.45 \mu\text{m}$ dissolved fraction of Cd ($>90\%$) and Mn ($>80\%$) consisted of low molecular weight ($<10 \text{ kDa}$) species, this transfer is apparently not mediated by colloidal sized particles. The low affinity of these two metals for particle surfaces and humic substances explains the low percentage of Cd and Mn found in association with colloidal particles and macromolecules.

The dissolved ($<0.45 \mu\text{m}$) Cd levels within the estuary (which ranged from 0.11 to 1.19 nM) revealed an order of magnitude decline when compared to the initial measurements of Klinkhammer and Bender (1981) over a 23 year period. Although this decline reflects improvement in sewage treatment and the elimination of industrial sources (e.g., Foundry Cove) to the Hudson River estuary, the levels of dissolved cadmium in the estuary are still higher than those reported in other urban estuaries. In contrast to Cd, dissolved manganese levels (range: 0.033-1.46 μM) were comparable to levels reported in other estuaries and have remained relatively constant over the last 20 years, suggesting that anthropogenic sources have very limited impact on Mn concentrations in the estuary.

Metal-salinity plots and mass balance calculations indicated that sewage inputs and diagenetic fluxes from contaminated sediments are the current major sources of Cd to the estuary. However, under low river flow conditions, the mass balance model could not account for about 40% of the export of Cd out of the estuary, suggesting that inputs from other watersheds (e.g., Long Island Sound/East River and Newark/Raritan basin) should be considered. Finally, this study suggests that elimination of point sources within the estuary may not be reflected in corresponding reductions of trace metal concentrations in the water column of the estuary. As exemplified for Cd, diagenetic remobilization from contaminated sediments may now represent a very important source of toxic metals to the Hudson River estuary.

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1. Introduction

Estuaries are both chemically and physically dynamic systems that, because of their location at the river-ocean interface, act as buffers between the land and the ocean. The net flux of riverine materials to the open ocean depends on their estuarine reactivity. However, anthropogenic processes have the potential to modify the riverine compositional signal to the ocean. This is especially true in urban estuaries such as the Hudson River estuary. This estuary receives about $70 \text{ m}^3 \text{ sec}^{-1}$ of wastewater from more than 30 sewage treatment facilities serving approximately 10 million people in New York and New Jersey (Brosnan and O'Shea, 1996). The magnitude of the sewage input to the Hudson River estuary is comparable to the combined sewage flux from the cities of Los Angeles, San Diego and Orange County to the Southern California Bight (SCB) ($47 \text{ m}^3 \text{ sec}^{-1}$; SCCWRP, 1994). However, the anthropogenic perturbation caused by those discharges is expected to be more severe in the Hudson River estuary than in the SCB. While the wastewater from New York City is discharged directly into the estuary, sewage from the cities bordering the SCB is released between 2-10 km offshore at 60 m depth in the Pacific ocean. This mode of disposal in the open ocean guarantees a 1:100 to 1:200 fold effluent dilution within minutes (Bascom, 1982). In contrast, the input from sewage treatment plants into the Hudson River

estuary can account for up to 40% of the total freshwater budget to the estuary, under conditions of low runoff (Clark et al., 1995).

The Hudson River estuary also receives the waste generated by several industrial operations. For example, Foundry Cove, a tidal embayment located about 100 km north of Manhattan, was severely contaminated by the manufacturing of Cd-Ni batteries between 1952 and 1979 (Wallace, 1996). As a result, Cd concentrations in the Cove's sediments formerly exceeded 1 g/100 g of sediment by weight and sometimes reached 25% by weight near the factory outfall (Knutson et al., 1987). While Foundry Cove was subject to a \$90 million remediation project during 1992-1994, which extracted about 12 of the original 22 metric tons of Cd discharged (Kneip and Hazen, 1979; Wallace, 1996), the impact of the clean-up project on metal concentrations in the water column of the Hudson River estuary has never been determined.

While the preceding information indicates that the Hudson River estuary could be one of the most contaminated estuaries in the United States, there has been very limited data collected on metal concentrations in the water column of that system. The only previous dissolved metal concentrations along the estuary were reported by Klinkhammer and Bender (1981), from samples collected in the mid-1970s during the peak of metal contamination. Anthropogenic metal fluxes into the estuary have declined dramatically since then as a result of improvements

in wastewater treatment technologies. However, the impact of those reductions on metal concentrations in the water column of the estuary has not yet been quantified.

The riverine transport of materials to the ocean is modified not only by anthropogenic processes but also by biogeochemical reactions within the estuary. These reactions are driven by changes in the metal sorption-desorption equilibria in response to the mixing of fresh and seawater, and those reactions can explain the nonconservative removal or excess observed in estuaries. Laboratory experiments have shown that Cd and Mn should be desorbed from riverine suspended particles during estuarine mixing (Sholkovitz, 1976; Li et al., 1984). For Cd, speciation calculations suggest that the desorption process is due to the formation of chloro-complexes (Comans and Van Dijk, 1988). Dissolved Mn concentrations appear to be also influenced by diffusion from interstitial water (Crerar et al., 1981; Sundby et al., 1981; Klinkhammer and Bender, 1981; Keeny-Kenicutt and Presley, 1985; Hammond et al., 1985; Morris, 1986; Aller, 1994). Therefore, desorption processes and benthic fluxes have been invoked to explained the non-conservative excesses of those two metals observed in several estuaries (Edmond et al., 1985; Elbaz-Poulichet et al., 1987; Shiller and Boyle, 1991; Flegal et al., 1991; Sañudo-Wilhelmy et al., 1996; Zwolsman et al., 1997).

The reported excesses of Cd and Mn along the salinity gradient of several estuaries have been observed in the traditionally defined $<0.45 \mu\text{m}$ “dissolved” fraction. However, apparent non-conservative excesses could also be caused by the deflocculation of colloidal aggregates and/or the fragmentation of large particles through the formation of colloidal particles. Although the existence of these mechanisms is supported by the significant concentration of colloidal Cd reported in several estuaries (up to 38% of the dissolved; Dai et al., 1995; Martin et al., 1995), the colloidal fraction in these studies has not been directly determined, but rather has been calculated as the difference between the dissolved and the permeate, or “truly dissolved”, fraction. The importance of the colloidal pool for the cycling of this element cannot be confirmed until metal concentrations are determined simultaneously in the permeate and retentate fractions, and realistic mass balances are obtained.

This project was designed to determine the effect of recent reductions in Cd loading to the Hudson River estuary. This was accomplished by comparing our dissolved ($<0.45 \mu\text{m}$) data with the initial study of metal contamination in surface waters of the estuary conducted by Klinkhammer and Bender (1981) using samples collected in the mid-1970s. Because metal levels may reflect both temporal variability in environmental conditions within the estuary and the effect of emission

controls, samples were collected under distinctly different river flow conditions in two consecutive years.

The processes affecting the distribution of Cd were also elucidated by comparing its concentrations with those of Mn. Mixing experiments using seawater and Hudson River waters showed that these elements appear to be affected by similar desorption processes during estuarine mixing (Li et al., 1984). However, in contrast to Cd, Mn distributions in some estuaries appear to be also primarily influenced by internal cycling rather than by anthropogenic inputs (Crerar et al., 1981; Sundby et al., 1981; Klinkhammer and Bender, 1981; Keeny-Kenicutt and Presley, 1985; Hammond et al., 1985; Morris, 1986; Aller, 1994). Finally, the high molecular weight colloidal fractions of Cd and Mn were measured to determine whether the non-conservative excesses of these two elements observed in the $<0.45 \mu\text{m}$ "dissolved" fraction in several estuaries is mediated by the deflocculation of and/or desorption from colloids.

2. Study Area

The Hudson River estuary is a partially mixed estuary with a surface area of approximately $35,000 \text{ km}^2$ (Abood, 1974). The estuary extends from the

Narrows (mp -8 from the southern tip of Manhattan or the Battery) to Green Island (mp +154) (Figure 1). The estuary connects with the Atlantic ocean in the Upper Bay through the Narrows, and several tidal channels, such as Kill Van Kull and the East River, link the estuary with other drainage basins (Newark Bay and the Long Island Sound). The mean depth of the estuary is 10 meters, although in some areas it can be shallower than 3 meters or deeper than 35 meters.

The only natural freshwater source to the estuary is the Hudson River. Monthly mean freshwater discharges reach a maximum of $1000-1500 \text{ m}^3 \text{ s}^{-1}$ during the spring high flow and a minimum of $150-300 \text{ m}^3 \text{ s}^{-1}$ during the summer low flow at the Battery (mp 0) (Clark et al., 1995). Salt water intrudes between 40 km and 110 km into the estuary under high or low flow conditions respectively (Malone, 1977). Freshwater replacement times (total equivalent volume of freshwater in the salt-intruded reach divided by mean freshwater discharge at the Battery) are typically between 45 and 60 days, although they can be greater than 75 days during extreme dry periods (Clark et al., 1992). The effect of anthropogenic inputs as well as first-order geochemical reactions on the water quality of the estuary are expected to be more significant under periods of low riverine flow and long replacement time.

The lower estuary, which extends from the Narrows northward to the upstream limit of saline water, receives the sewage from more than 30 wastewater

treatment facilities serving the New Jersey/New York City metropolitan area (Brosnan and O'Shea, 1996; Clark et al., 1995). Most of the wastewater (>90%) is discharged near Manhattan, and although about 90% of the sewage receives secondary treatment, these facilities still discharge a considerable amount of trace metals into the estuary (e.g., 1.8 kg of Cd, 217 kg of Cu and 285 kg of Zn per day; Chillrud, 1996). The magnitude of those fluxes are similar to the combined input from all the treatment plants to the Southern California Bight (e.g., 1.6 kg of Cd, 123 kg of Cu, 225 kg of Zn per day; SCCWRP, 1995). Therefore, sewage inputs appear to be responsible for the high concentration of toxic metals found in surficial sediments of the New York Harbor (Chillrud, 1996; Feng, 1997).

3. Sampling and Analysis

Surface water samples were collected along the whole salinity gradient during four cruises over a two year period under different riverine runoff conditions (low-flow: October, 1995 and 1996; high-flow: April, 1996 and 1997). Another reason for collecting samples in those months was to facilitate the comparison between our results and those of Klinkhammer and Bender (1981), who collected samples in April 1974 and October 1975. While our sampling

locations were established with the aim of covering the entire salinity gradient rather than by specific geographical location, our most seaward end-member was located at Sandy Hook (Figure 1).

Water samples were collected from the R/V ONRUST at 1 m below the surface using a peristaltic pumping system equipped with acid-washed C-Flex tubing in the pump head. Water was drawn through acid-washed Teflon tubing attached to a stainless steel pole which was oriented 5 m upstream of the ship's drift. All sampling protocols have been detailed elsewhere (Flegal et al., 1991; Sañudo-Wilhelmy et al., 1996). At each location, unfiltered and filtered water (<0.45 μm) samples (1 L) were collected for measurements of the total and the traditionally defined "dissolved" metal concentrations respectively. The particulate metal levels were obtained as the difference between the total and "dissolved" fractions. Additional samples were also obtained at each station to measure salinity, dissolved phosphate and total suspended solids (Strickland and Parsons, 1972). Finally, 20 L of filtered (<0.45 μm) water was collected to be used for ultrafiltration.

These latter samples were collected in dark acid-washed fluorinated carboys, and ultrafiltered within 24 hrs of collection in a Filtron cross-flow filtration system (10 kDa). This tangential-flow ultrafiltration system was modified for trace metal analysis (Whitehouse et al., 1990; Buesseler et al., 1996; Sañudo-

Wilhelmy et al., 1996), and was used to isolate the high molecular weight colloids (10 kDa-0.45 μm) from the low molecular weight fraction (<10 kDa). The ultrafiltration system was cleaned between samples by recirculating 10% methanol for 30 minutes, 0.1 N of hydrochloric acid for at least 60 minutes, after which 20 liters of Milli-Q water was flushed through the system followed by 5 liters of sample through the filtrate and retentate ports. The membrane was conditioned with each sample for 30 minutes. A constant small concentration factor of 7.5 was used in all the samples to eliminate the break-through of colloids and/or diffusion of metals into the ultrafiltrate solution (Buessler et al., 1996; Sañudo-Wilhelmy et al., 1996). Ultrafiltration recoveries, calculated by making a mass balance between the <0.45 μm dissolved, and the sum of colloidal and low molecular weight phases (Sañudo-Wilhelmy et al., 1996), were >90% (Figure 2).

All samples (unfiltered, <0.45 μm filtered, colloidal (0.45 μm -10 kDa), and low molecular weight (<10 kDa)) were acidified with sub-boiling quartz-distilled Q-HCl and stored for at least one month prior to analysis. Cadmium concentrations were determined by graphite furnace atomic absorption spectroscopy (GFAAS) after preconcentration with an ammonium 1-pyrrolidinedithiocarbamate/diethylammonium diethyldithiocarbamate (APDC/DDDC) organic extraction (Bruland et al., 1985). Manganese was determined by direct injection in a Hitachi Zeeman-8100 atomic absorption

spectrophotometer. The technique of standard additions was used in all the analyses. The procedural blank for Cd was $2.6 \text{ pM} \pm 1.14$ ($x \pm 1 \text{ s.d.}$, $n=27$) and the detection limit, defined as 3 times the 1-sigma s.d. of the procedural blanks, was 3.4 pM .

4. Results

Autumn distributions (October 1995 and 1996)

Autumn cruises were characterized by low river flow conditions ($104 \text{ m}^3 \text{ sec}^{-1}$ in October 1995 and $254 \text{ m}^3 \text{ sec}^{-1}$ in October 1996 at the Green Island Dam, US Geological Survey, personal communication). In the first cruise, low concentrations of $<0.45 \text{ }\mu\text{m}$ filtered “dissolved” Cd (0.29 nM) and Mn ($0.057 \text{ }\mu\text{M}$) were found at the river end-member and reached a first maximum (1.12 nM for Cd and $1.12 \text{ }\mu\text{M}$ for Mn) downcurrent from Foundry Cove (salinity 7; Table 1, Figures 3 and 4). Further downstream, dissolved Cd and Mn continued to increase and reached another maximum (1.19 nM for Cd and $1.46 \text{ }\mu\text{M}$ for Mn) at the station near the New York City Sewage Treatment Plant (NYCSTP; salinity 20). While dissolved Mn declined linearly from the NYCSTP to the Atlantic Ocean

(Figure 4), another small excess in Cd concentrations was present in the New York Harbor (Figure 3).

In contrast to autumn 1995, the fluvial discharge in October 1996 was more than 2 times higher, and dissolved Cd and Mn levels were 2-3 times lower (Figures 3 and 4). These low metal levels are probably due to the short residence time of the water within the estuary and/or a rapid flushing to the ocean. Low concentrations of “dissolved” Cd (0.12 nM) and Mn (0.033 μ M) were also found in the incoming river water (Table 1). Well-defined peaks were again detected by the NYCSTP (0.60 nM for Cd and 0.23 μ M for Mn) and the NY Harbor (Figures 3 and 4). Because the zero-salinity end member was located about 35 miles north of the Battery, instead of 70 miles as in October 1995, the sampling range in this cruise was in the lower estuary and Foundry Cove in the upper estuary was not sampled.

Spring distributions (April 1996 and 1997)

The spring cruises were conducted under high river discharge conditions (864 $\text{m}^3 \text{sec}^{-1}$ in April 1996 and 684 $\text{m}^3 \text{sec}^{-1}$ in April 1997). The profile of $< 0.45 \mu\text{m}$ filtered Cd in April 1996 was very similar to the autumn profile of 1995 described above. The highest levels of “dissolved” Cd were detected downriver from Foundry Cove (salinity 6; 1.02 nM; Table 1) and by the NYCSTP (salinity

20.6; 0.97 nM). A secondary peak was also observed at the NY Harbor (salinity 24; 0.78 nM). Although relatively high concentrations of Cd were also measured by the NYCSTP and the Harbor in the spring 1997, the average Cd concentration along the estuary (average = 0.28 nM) was less than half of the levels found in the previous spring (average = 0.72 nM; Figure 3).

In contrast to the case for the autumn cruises, Cd and Mn profiles were very distinct in the spring (Figures 3 and 4). In both high flow cruises, Mn concentrations showed a gradual increase with increasing salinity, leading to a well-defined peak by the NY Harbor (Figure 4). The relatively high concentrations of “dissolved” Mn observed upriver and by the NYCSTP in the autumn cruises were not detected in the spring. The average dissolved Mn level (0.18 μM) in the spring of 1997 was also less than half of the mean value measured (0.46 μM) in the spring 1996, as previously noted for Cd.

Size-fractionated cadmium and manganese concentrations

The concentrations among the operationally defined size classes of Cd and Mn measured in the four cruises are also listed in Table 1. The traditionally defined “dissolved” (<0.45 μm) cadmium ranged from 0.11 to 1.19 nM, and accounted for 70-80% of the total cadmium at most of the sampling locations. The contribution of particulate (>0.45 μm) Cd to the total pool was between 3-

30% (from 0.01 to 0.46 nM) with the exception of the sample collected at the turbidity maximum (station 7; 2.7 nM) in April 1996 where particulate Cd accounted for 75% of total metal concentration (Table 1). The relatively low contribution of particulate Cd to the total Cd pool has previously been reported in the Hudson River estuary (Klinkhammer and Bender, 1981) as well as in other estuaries (e.g., Yeats and Bowers, 1982). This finding is consistent with the relatively low particle reactivity that this element exhibits in laboratory experiments and in sediments (Turner et al., 1992; Turner, 1996).

Most of the “dissolved” (<0.45 μm) Cd throughout the Hudson River estuary consisted of <10 kDa species (>94% of total dissolved; Table 1). High molecular weight (10 kDa-0.45 μm) colloidal Cd accounted for <6% upriver and <1% at high salinities. The presence of colloidal species of Cd along the estuary appears to be associated with the river flow. This is suggested by the fact that the high molecular weight Cd was mostly detected in the spring cruises (April 96 and 97) under high river discharge conditions (Table 1). The relatively small contribution of colloidal Cd to the <0.45 μm “dissolved” pool observed in the Hudson River estuary agrees with other results obtained in the San Francisco Bay estuary, and it has been attributed to the low affinity of this metal for humic substances and for particulate surfaces (Sholkovitz, 1978; Sañudo-Wilhelmy et al., 1996).

Dissolved (<0.45 μm) and particulate (>0.45 μm) Mn concentrations along the estuary were in the range of 0.033-1.46 μM and 0.02 to 4.08 μM respectively (Table 1). Contrary to the predominance of “dissolved” Cd over the particulate phase at all salinities, there was a redistribution of Mn between the two pools during estuarine mixing. The contribution of the <0.45 μm fraction to the total pool of Mn increased from about 10% in the river to 90% in the seawater end-member (Table 1). Similar fractionation of Mn has been previously reported in the Hudson (Klinkhammer and Bender, 1981) and in other estuaries as well (e.g., Moore et al., 1979).

In contrast to the results for Cd, high molecular weight colloidal Mn was detected in all of our cruises. In the low-salinity region of the estuary, colloidal Mn accounted for approximately 12-25% of the “dissolved” manganese, and this percentage rapidly decreased with increasing salinity to <4% of the <0.45 μm phase (Table 1). The decline of colloidal Mn with salinity observed in the Hudson River estuary has also been observed in other estuaries and seems to be due to mixing and not to flocculation (e.g., San Francisco Bay; Sañudo-Wilhelmy et al., 1996).

Dissolved (<0.45 μm) Cd and Mn concentrations in the Hudson River estuary also appear to strongly depend on the season and on river discharge (Figures 5A and 5B). The concentrations of Cd and Mn tend to decrease as river

flow increases. The exception to this trend was the spring cruise of 1996, in which sampling was conducted after a winter of record snow accumulation. Therefore, in this case, high metal levels could be related to the high run-off volume of melt waters. This suggests that external loading from tributaries could also have a significant effect on metal levels along the estuary, as previously suggested for organic carbon (Howarth et al., 1992).

5. Discussion

Historic variations of cadmium and manganese concentrations in the estuary

Our results revealed an order of magnitude decline in average “dissolved” surface water Cd concentrations from 2.27 nM to 0.28 nM over a period of 23 years (Figure 6A), when compared to the initial measurements of Klinkhammer and Bender (1981). This decrease paralleled the order of magnitude decline in Cd fluxes from sewage into the area of study (from 51.8 kg day⁻¹ to 1.8 kg day⁻¹; Klinkhammer and Bender, 1981; Chillrud, 1996), and is consistent with the 90% diminution of Cd levels detected in surficial sediments from the 1960s to the 1990s along the estuary (Chillrud, 1996; Feng, 1997).

In contrast to the decrease observed in Cd concentrations, there was no decline in Mn levels in surface waters of the estuary during the same period (Figure 6B). The average concentrations measured in the 1970s ($0.50 \mu\text{M}$; Klinkhammer and Bender, 1981) and in the 1990s ($0.58 \mu\text{M}$; Table 1) were essentially the same. This comparison suggests that anthropogenic inputs have a limited impact on Mn levels in surface waters of the estuary. Several studies have provided evidence that internal natural processes such as desorption from suspended particles, reductive solubilization and sediment fluxes control the distribution of this element in estuaries (Evans and Cutshall, 1973; Elderfield and Hepworth, 1975; Graham et al., 1976; Evans et al., 1977; Sanders, 1978; Bewers and Yeats, 1978; Duinker et al., 1979; Morris and Bale, 1979; Moore et al., 1979; Knox et al., 1981; Morris et al., 1982).

The dominance of natural processes in controlling Mn distributions was further indicated by the high dissolved Mn levels measured in the cruise of autumn 1995 under low fresh water flow (Figure 4). Because water discharge is inversely correlated with the residence time of the water ($T = 41.8 \exp(-0.00435 \text{River flow})$; Pilson, 1985), the freshwater replacement time in the estuary was substantially longer in 1995 (27 days) than in the 1996-1997 cruises (1-14 days) and even in the 1974-1975 (< 2 days) sampling of Klinkhammer and Bender (1981). Therefore, high metal levels in the water column were detected in the autumn months, when

long water residence times allow a major build-up of metals in solution. The influence of river discharge on Mn levels in the Hudson River estuary is further illustrated in Figure 6B. The Mn profiles obtained in cruises with comparable river flow conditions (October 1975; $760 \text{ m}^3 \text{ sec}^{-1}$; and April 1996 and 1997; 864 and $684 \text{ m}^3 \text{ sec}^{-1}$) were very similar, despite the fact that they were carried out more than 20 years apart.

Current status of cadmium and manganese contamination in the estuary

Despite an order of magnitude reduction in Cd concentrations in surface waters of the Hudson River estuary in the last 20 years (Figure 6A), this system may still be one of the most contaminated estuaries of the US (Figure 7A). For example, under high flow conditions, the average dissolved Cd concentrations in the Hudson were comparable to the average concentrations measured in other urban estuaries (e.g., San Francisco Bay; Flegal et al., 1991; Sañudo-Wilhelmy et al., 1996). However, when river discharge was low, dissolved Cd concentrations in the estuary were up to 2 times higher than in San Francisco Bay and 3 times higher than the levels reported for the less-industrialized Savannah River estuary (Windom et al., 1991; Figure 7A). Under similar low flow conditions, Cd concentrations in the Hudson River estuary were as high as those measured in the Seine, one of the most contaminated estuaries of Europe (Chiffolleau et al., 1994).

In contrast to the case for Cd, the levels of dissolved Mn in the Hudson River estuary were similar to the concentrations reported in other urban estuaries (e.g., San Francisco Bay, the Seine, Figure 7B). Relatively high concentrations of dissolved Mn were only measured in our survey of autumn 1995 which was under very low river discharge (see previous section). This comparison substantiates our previous arguments that Mn concentrations in the Hudson River estuary are mainly controlled by natural processes and not by anthropogenic inputs.

Dissolved Cd and Mn distributions exhibited non-conservative excesses across the whole salinity gradient of the estuary, relative to a simple mixing of river water and seawater end-members (Figures 3 and 4). However, the concentrations of $<0.45 \mu\text{m}$ filtrable Cd (0.12-0.15 nM) and Mn (0.049-0.057 μM ; Table 1) upriver (about 60 miles north of the Battery; Cruises 1 and 2) were comparable to or lower than the estimated "world river" average concentrations (0.18 nM and 0.15 μM respectively; Martin and Whitfield, 1983; Owens and Balls, 1997). This indicates that the incoming river water is low in metal concentrations before any estuarine influence. However, different mechanisms appear to be responsible for the high metal levels observed in the upper and in the lower estuary and during different seasons. These various mechanisms are discussed below.

Factors governing the distributions of cadmium and manganese in the estuary

Because the peaks in the traditionally defined “dissolved” phase observed in the lower estuary in the Cd-salinity plot (Figure 3) suggested that sewage may still influence the concentration of this trace element in the estuary, the relative importance of this input to the total Cd budget in the lower estuary was evaluated by mass balance estimates. The different sources and removal processes included in the model are shown in Figure 8. The mass balance also assumes that the estuary is a mixture of three end-members: Hudson River, sewage, and New York Bight ocean water. The first station in the zero-salinity region was used as riverine end-member (station 1; Table 1), while the average of the last two stations (stations 9 and 10; Table 1) were treated as the oceanic end-member. Hammond (1975) demonstrated that salinity is conservative in our study area. Therefore, the following two equations were used to calculate the water exchange from the ocean to the estuary according to Klinkhammer and Bender (1981):

$$Q_E * S_E = Q_O * S_O$$

$$Q_E = Q_R + Q_S + Q_O$$

where Q_E represents the flow leaving the estuary, S_E is the mean salinity in the estuary, Q_O represents the water exchange coming from the ocean, S_O denotes the mean salinity in the incoming ocean water, Q_R is the river discharge, and Q_S is the

freshwater flow from the sewage treatment plants. It is assumed that the salinity of the sewage (S_S) and of the river (S_R) is zero.

The mass balance was calculated only for Cd and for our cruises of autumn 1995 and spring 1996 where we covered the whole salinity range of the estuary. Manganese was not evaluated with the mass balance for two reasons: Mn concentrations in NY City sewage have not been reported, and dissolved Mn appears to be controlled by natural processes instead of anthropogenic ones in the Hudson Rivers estuary (see previous section). The river outflow (Q_R) used in the calculations were $104 \text{ m}^3 \text{ s}^{-1}$ during October 1995 and $864 \text{ m}^3 \text{ s}^{-1}$ during April 1996 (US Geological Survey, personal communication). The sewage flow (Q_S was $64 \text{ m}^3 \text{ s}^{-1}$; Brosnan and O'Shea, 1996) was kept constant in both cruises. The water exchange from the ocean to the estuary (Q_O) was calculated as $158 \text{ m}^3 \text{ s}^{-1}$ and $537 \text{ m}^3 \text{ s}^{-1}$ respectively for 1995 and 1996.

The mass balance equations, assuming steady state conditions, were as follows:

$$\text{Flux in} = Q_R * C_R + Q_S * C_S + Q_O * C_O + F_A * A_E + F_B * A$$

$$\text{Flux out} = (Q_O + Q_R + Q_S) * C_E + F_S$$

$$\text{where } F_S = R_S * (1 - \phi) * \rho * C_P * A_E$$

C_R , C_S , and C_O represent the Cd concentrations in the river, sewage and the ocean. C_E is the average estuarine Cd concentration (from stations 2-8; Table 1). F_A and

F_B are the atmospheric and benthic fluxes to the estuary and A_E is the surface area of the NY Harbor (35.2 km²; Klinkhammer and Bender, 1981). Because the actual atmospheric deposition rate and the diffusive benthic fluxes have never been estimated in the estuary, we used the highest atmospheric deposition rate (140 $\mu\text{g}/\text{m}^2$ year) measured in Bermuda (Church et al., 1984) as well as the mean benthic flux rate of Cd (0.0039 $\mu\text{mol}/\text{m}^2\text{day}$) reported for San Francisco Bay (Rivera-Duarte, 1995). The F_S term represents the burial rate calculated assuming a constant sedimentation rate (R_S) of 1.5 cm/year (Feng, 1997), sediment porosity (ϕ) of 0.82 (Chillrud, 1996; Feng, 1997), dry sediment density (ρ) of 2.65g/cm³ (Chillrud, 1996; Feng, 1997), and the particulate cadmium (C_P) content measured in the suspended solids (Table 1).

These calculations indicated that about 57% of the Cd input to the Harbor is attributable to sewage discharges, and that atmospheric deposition and benthic fluxes can account for <1% of the total input (Table 2). Also, the riverine and oceanic contributions to the metal budget of the estuary were variable and accounted for <9% to 33% depending on the river discharge. Mass balance estimates also suggested that, under high river flow, the sources and sinks considered in the model were nearly balanced (within 15%), and that most of the dissolved Cd is transported out of the estuary (88% versus 12% burial; Table 2). In contrast, under low river discharge, the inputs considered cannot account for

more than 40% of the flux exported out of the lower estuary. In order to balance the model, an additional input, of the same magnitude as that of the sewage input, is needed (Table 2). These preliminary estimates suggest that there may be substantial inputs of contaminants from other sources not considered in our model (e.g., industries) and/or from other tributaries to the Harbor, such as western Long Island Sound/East River and the Newark/Raritan Basin. The suggestion that these areas are possible sources of Cd is supported by the high metal concentrations found in sediments at those locations (Chillrud, 1996). However, in contrast to the extensive information on metal contamination in the sediments, there are no data on dissolved metal concentrations for those places.

Remobilization of dissolved Cd and Mn from riverine particles in response to changes in salinity appears to be another important mechanism affecting the concentrations of these two elements within the estuary (Li et al., 1984). The significance of the desorption process on “dissolved” metal levels in the Hudson River estuary was evaluated by calculating gains or losses in the dissolved and/or particulate phases during estuarine mixing. The changes in concentration for the two metal fractions were calculated as the difference between the theoretical (estimated assuming conservative mixing) and the actual concentration measured in each pool (Table 3; Figure 9). This analysis showed that, under high river flow and from salinity 2 to 13, particulate Mn and Cd decreased by 0.10 μM and 0.09

nM respectively (Table 3; Figure 9). However, this decrease in particulate concentrations only accounted for about 45% and 35% of the increases observed in the $<0.45 \mu\text{m}$ dissolved phase. Furthermore, under low flow conditions, both phases increased with salinity, suggesting that surface reactions were not responsible for the high levels found in the dissolved phase. Therefore, additional processes such as sewage inputs (Cd) and benthic fluxes (Mn) must be considered in the dissolved Cd and Mn budgets.

The seasonal impact of particle dynamics on the “dissolved” Cd and Mn concentrations along the estuary was also illustrated by the distribution of these two metals in the suspended particulate matter (Figure 10). Metal enrichments in the suspended particle load appear to be higher under low flow condition (Figure 10). Therefore, the impact of the desorption process on dissolved metal levels is expected to be higher under high river flow conditions, as observed in our previous model. This type of behavior is also consistent with laboratory experiments indicating that the remobilization of particulate Cd occurs through the formation of chlorocomplexes in solution (Ackroyd et al., 1986; Elbaz-Poulichet et al., 1987; Coman and van Dijk, 1988). Under low flow conditions, resuspended riverine particles are not transported to the high salinity region of the estuary where desorption can readily occur. Furthermore, particles collected near the NYCSTP were up to 4 times more enriched with Cd with respect to particles both up and

downriver (Figure 10). However, no enrichment was evident under high river discharge.

While the preceding discussion indicates that desorption was involved in the transfer from the particulate to the dissolved phase during the mixing of river water and seawater, our phase speciation data indicated that this shift was not mediated by colloidal sized particles. The high proportion of Cd and Mn in the <10 kDa fraction (70-90%; Table 1) were responsible for the nonconservative excesses of these elements (Figures 3 and 4), and this suggests that metal remobilization from particulate matter occurs within the small molecular weight pool. Apparently colloidal particles are not being generated through the disaggregation of large particles during estuarine mixing, but instead that low molecular weight metal species are being released in the desorption processes. The remobilization of small species of Cd and Mn from particulate matter and from sediment in estuaries is consistent with the formation of soluble inorganic complexes with these elements (Windom et al., 1971; Graham et al., 1976; Evans et al., 1977; Sholkovitz, 1978; Comans and van Dijk, 1988).

The limited association of Cd and Mn with colloidal particles found in this study is consistent with laboratory mixing experiment using river and seawater which found that flocculation via colloids could remove only about 25% of the Mn and about 5% of the Cd (Sholkovitz, 1978). The relative abundance of metals in

the colloidal particles (Cd < Mn) found in the Hudson River estuary was the same as the one observed in the macroparticles (>0.45 µm; Table 1), suggesting that the same mechanisms appear to govern the association of metals with the two particle pools. Similar surface chemistry (e.g. organic coating; Balistrieri et al., 1981; Davis, 1984) most likely controls the adsorption properties of colloids and macroparticles. Alternatively large particles may be composed of coagulated colloids. Furthermore, the low association of these two metals with colloidal and macroparticles is consistent with their weak affinity for humic acids and for particulate surfaces (Sholkovitz, 1978; Sañudo-Wilhelmy et al., 1996).

While the decrease in surface water Cd concentrations in the lower part of the Hudson River estuary reflects the reduction in Cd emissions from sewage between 1970s and 1990s, the high Cd levels found in northern sections of the river (30 miles north of Manhattan; Figure 3) indicates that this metal is still being remobilized from contaminated sediments. The high Cd concentrations were found downstream of the Cd-enriched Foundry Cove, suggesting that the dominant source of this metal is previous industrial inputs to the estuary. Although Foundry Cove was subjected to a \$90 million remediation project in 1992-1994, our findings suggest that large amounts of Cd from the Cove were exported downriver during the 25 years (from 1953 to 1979) that the battery manufacturing operation lasted, resulting in widespread sediment contamination.

This is consistent with previous estimates showing that about 0.35 kg of Cd was transported from the Cove to the river in each tidal cycle (Knutson et al., 1987).

Waters enriched in Cd from the lower Hudson estuary could also be transported upriver during tidal incursions. Therefore, the relative contribution of sewage to the high Cd concentrations in the upper estuary was estimated using an apportionment mixing model (Table 4). The fraction of sewage in the upper estuary was calculated using the $<0.45 \mu\text{m}$ “dissolved” phosphate concentrations, which appear to serve as a conservative tracer for the sewage treatment plant (in contrast to dissolved Cd, $<0.45 \mu\text{m}$ filtrable PO_4 exhibits conservative behavior between the river and the NYCSTP; Figure 11). Furthermore, Clark et al. (1992) reported that the NYCSTP was the dominant source of dissolved phosphate to the estuary. The fraction of sewage at each location in the upper Hudson was calculated assuming two scenarios: a) that all the dissolved phosphate measured at station 7 (near the NYCSTP) originated from the sewage discharge, and b) because the salinity at that location was not zero, we also estimated the sewage portions assuming that station 7 was a 50% mixture of sewage and estuarine water. The results are shown in Table 4. Under both circumstances, sewage could explain 50-60% of the high levels of Cd measured at our station downcurrent from Foundry Cove (station 3; Table 4). Therefore, the remaining 40 to 60% may be attributable to contaminated sediments. As the sampling locations approached the

NYCSTP, the non-sewage contribution declined as the sewage increased. The non-sewage contribution to the dissolved Mn concentrations was even more significant (68-84%; Table 4), as expected based on the high rate of diagenetic remobilization observed for this element in estuaries (Sanders, 1978; Morris and Bale, 1979; Duinker et al., 1982; Morris et al., 1982).

Finally, the anomalously high Cd concentrations measured south of Foundry Cove almost 20 years after industrial operations ceased showed the persistent cycling of contaminant Cd within the estuary. These results also showed that, in spite of the elimination of point-source discharges, metal levels in the water column of the estuary may still remain very high due to diagenetic remobilization from contaminated sediments. Sediments may now represent a major source of toxic metals in the Hudson River estuary.

6. Summary

1) Dissolved Cd concentrations in the Hudson River estuary have declined by an order of magnitude since the measurements by Klinkhammer and Bender (1981) in samples collected in the 1970s. That decline is associated with the continuous improvements in sewage treatment facilities. In contrast, dissolved Mn levels have

