Distribution of Heavy Metal and PCB Contaminants in the Sediments of an Urban Estuary: The Hudson River

Huan Feng, J. Kirk Cochran, Honoratha Lwiza, Bruce J. Brownawell and David J. Hirschberg

Marine Sciences Research Center, State University of New York, Stony Brook, New York 11794-5000, USA

(Received 1 September 1996; revised version received 20 June 1997; accepted 5 July 1997; published January 1998)

ABSTRACT

Surficial sediments obtained from sediment cores were collected over 100 km along the axis of the lower Hudson River in June 1994, November 1994, May 1995 and April 1996 and showed the presence of anthropogenic Ag, Cd, Cu, Pb, Zn, PCBs in all samples. Contaminant distributions in the Hudson River estuary show two types of trends: Ag, Cu and Pb show an increasing trend down-estuary with maximum values in New York Harbor sediments; in contrast, Cd, Zn and total PCBs display a decreasing trend toward New York Harbor where urban sources are also apparent. Silver is a useful tracer of urban sources of contaminants in the Hudson River estuary and polychlorinated biphenyls (PCBs) are useful source indicators of upriver sources. Correlations of Cu and Pb with Ag suggest that Ag, Cu and Pb are dominated by down-estuary sources such as wastewater effluent. The history of their inputs suggests that they have been progressively transported downstream. Correlations of Cd and Zn with total PCBs indicate that these contaminants are dominated by upriver sources, where they are removed and diluted downstream along with the sediment transport.

© 1998 Elsevier Science Ltd. All rights reserved

Keywords: heavy metals, polychlorinated biphenyl, contamination, sediments, New York City metropolitan area, Hudson River estuary.

INTRODUCTION

Rivers and estuaries can serve as important sources of metal and organic contaminants to coastal marine environments. Estuaries also often act as sinks for fine-grain sediment and associated particle-reactive contaminants. Due to the two-directional nature of estuarine circulation and extensive resuspension caused by tidally-driven bottom currents, it can be
difficult to trace sources of contaminants to estuaries based on their distribution in surficial sediments. A number of studies (Goldberg et al., 1979; Trefry and Shokes, 1981; Olsen et al., 1984; Bopp and Simpson, 1989) have shown that transport, distribution and accumulation of these particle-reactive metals and polychlorinated biphenyls (PCBs) in sediments are controlled to a great extent by fate of fine-grained sediments.

In this study, we seek to explain the sediment distributions of trace metals and PCBs along a 100 km stretch of the lower Hudson River estuary. The highly populated urban center around New York Harbor (km point -11 to 18, with km point 0 is defined at the Battery—southern tip of Manhattan) provides a unique opportunity to examine the impacts of contaminant releases at the mouth of a river–estuarine system.

The Hudson River estuary is a partially mixed estuary (Abood, 1978; Klinkhammer and Bender, 1981; Cooper et al., 1988) in which the distance of salt water intrusion upriver varies from ~30 km from the Battery during high freshwater discharge in spring to ~100 km during low discharge season in the fall (Abood, 1978). The net flow in the Hudson River estuary is dominated by tidal flow even during times of high freshwater flow, with the former being 10–100 times greater than the latter (Cooper et al., 1988). As in many estuarine systems, trace metals and polychlorinated organic contaminants (e.g. PCBs) are introduced into the Hudson River system from both point and non-point sources (William et al., 1978; Olsen et al., 1978, 1984; Klinkhammer and Bender, 1981; Rohmann, 1988; Gibbs, 1994; Chillrud, 1996; Hirschberg et al., 1996). From a recent study of the lower 50 km of the Hudson River estuary, Gibbs (1994) found that distributions of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the bottom sediments showed metal concentration maxima in New York Harbor. Chillrud (1996) found that metal contaminants in surficial fine-grained sediments (0–2 cm) had high concentrations throughout much of New York Harbor over the last decade. Olsen et al. (1978) found that contaminant profiles in sediments differed from one area to another in the Hudson River estuary, leading these workers to hypothesize that the sediment surface in rivers and estuaries tends toward a local dynamic equilibrium with respect to fresh water discharge, tidal current and wave activity, and the state of this equilibrium determines the sediment and associated contaminant accumulation rates and distributions in a given area (Olsen et al., 1993).

An additional important factor governing contaminant distributions in sediments is differences in sources. Such differences are well documented for many contaminants in the Hudson River estuary. For example, upriver releases and transport of PCBs from the General Electrics facility at Glen Falls to the Fort Edwards area (km point ~300 km) dominate the distributions of most PCB congeners throughout much of the estuary, although the importance of inputs of a more highly chlorinated mixture of PCBs into the region of New York Harbor has been documented (Turk, 1980; Bopp et al., 1981; Bopp and Simpson, 1989; Chillrud, 1996). Upriver sources of Cd also existed in the contaminated sediments of Foundry Cove (~80 km upstream of the Battery) (Valette-Silver, 1993; Wallace, 1996), which had Cd concentration > 7000 ppm (Wallace, 1996). To remove the estimated 12 metric tons of Cd (of the original 22 metric tons) remaining in Foundry Cove, a major remediation project for Cd was initiated in the fall of 1993 (Wallace, 1996). Based on information available at the time, Mueller et al. (1982) estimated that municipal wastewater effluent, concentrated in the New York/New Jersey metropolitan area, was a major source of all trace metals to the entire Hudson/Raritan Bay estuary. However, even if the trace metal data from that time period were reliable, there have been substantial
decreases in loads of trace metals coming from wastewater treatment plants due to both regulated source controls and to upgrades in many treatment plants from primary to secondary treatment (Brosnan et al., 1994). Chillrud (1996) found a good correlation between a number of trace metals with Cu in recent sediments in the New York Harbor region. Arguing that copper is a good tracer of municipal wastewater effluent, he concluded that waste water treatment plant effluent was still the major source of metals to that region of the lower Hudson River estuary. Hudson River contamination caused by non-point and point source emissions of hazardous chemicals has also been documented by Rohmann (1988) and Interstate Sanitation Commission (ISC) reports (ISC, 1994, 1995).

In this paper, we present data of two years (1994-1996) field work on the distributions of trace metals and total PCBs in surficial bottom sediments (< 3 cm) along the length of the Hudson River estuary, and examine the distribution of trace metal and PCB contaminants in the system. Our goal is to determine whether the sources of these contaminants are reflected in their distributions in bottom sediments of the estuary. A multivariate statistical analysis of the data is also used to support interpretations based on tracer distributions.

METHOD

Study area

The study area covers ~100 km in distance along the low reach of the Hudson River estuary from New York Harbor (km point -3) to Newbough (km point 93) (Fig. 1). This includes the full salinity range of the estuary, the turbidity maximum zone (km point 8 to 20) and the metropolitan area of New York City. There are more than 20 sewage treatment plants situated on the both sides of the Hudson River within this area (ISC, 1994, 1995). Waste water discharge from these secondary treatment units ranges from 0.005 to 8.1 m$^3$ s$^{-1}$, with the highest discharge from the North River Plant at Manhattan (ISC, 1994, 1995). There are even larger discharges of municipal wastewater into the East River, some of which is ultimately released into New York Harbor (ISC, 1994, 1995). In an earlier study in the Hudson River estuary and New York City metropolitan area, Thomann et al. (1989) reported that there were 25 sewage treatment plants in the New York City metropolitan area, discharging 96 m$^3$ s$^{-1}$ of treated wastewater—65 m$^3$ s$^{-1}$ of which flowed south to New York Bight through the lower portion of New York Harbor and 31 m$^3$ s$^{-1}$ to Long Island Sound. Thomann et al. (1989) also reported that the treated wastewater flows from New York City metropolitan area were 10 times greater than those from upstate New York municipal plants discharging into the Hudson river. Although wastewater discharges from the sources to the Hudson River estuary may have varied over time, the dominant discharge from New York City metropolitan area is not expected to have changed significantly from the previous decade. It has been documented that seasonally extreme monthly-averaged fresh water discharges recorded at the Battery are 150–250 m$^3$ s$^{-1}$ during late summer and 1000–1500 m$^3$ s$^{-1}$ during spring (Chillrud, 1996). Hence, municipal wastewater discharges most certainly have an influence on the Hudson River water quality, especially during the low river flow season.

In the field observations, we found that sediment compositions varied from sandy mud, mostly present in the lower estuary, to muddy sediments in the margin area of the upriver
Fig. 1. Map showing sampling sites in the Hudson River. Distance at the Battery, the southern tip of Manhattan, is defined as zero km.
stations. Variations in sediment substrates along the estuary can be related to differences in compositions of soil and vegetation of watershed and variations of fresh water discharge and tidal currents which can sort and redistribute the sediments (Ullman and Wilson, 1997). In the turbidity maximum zone off 79th Street, Manhattan (km point ~8 km), sediment substrates change from fine mud at the western margin of the river to shell hash, bricks and debris at the mid-channel area (Feng, 1997). Spatial variations in concentrations of metal contaminants in the surficial sediments of the marginal depositional area of this zone are less than 10% (Ag, Cu, Pb and Zn) except for Cd (29%) (Feng, 1997). Vertical variations in trace metal (Ag, Cd, Cu, Pb and Zn) concentrations and metal/Fe ratios in the surficial sediments (0–3 cm) in the lower Hudson River estuary are <10% for all metals except Cd (<20%), based on the analysis of sediment samples from 5 stations (km point -3 to 55) in the estuary (Feng et al., 1997).

**Sediment Sampling**

Sampling stations were spaced ~5–10 km along the axis of the Hudson River in order to measure the distributions of contaminants (Fig. 1). The sites were usually chosen in the depositional area of the west margin. To ensure the recovery of a well preserved sediment–water interface, sediment samples were collected using a 625 cm² Soutar-type box corer at all stations. Subsamples for surface sediment analysis were obtained from the box cores by a specially designed 25 cm × 8.5 cm × 35 cm plastic subcorer. The subcorer was gently inserted into the sediment so that the integrity of the sample was preserved. Sediment samples from the box cores were sectioned in the laboratory of the R/V Onrust immediately after collection. Because this study was coupled with other studies of natural radionuclide sampling, segments representing surface sediments were chosen to be 0–3 cm in June 1994 and November 1994 and 0–0.5 cm in May 1995 and April 1996. This sampling strategy should not significantly affect the representation of metal contaminant concentrations in surficial bottom sediments because vertical variations in concentration gradients (0–3 cm) in the lower Hudson River estuary are <10% for Fe, Ag, Cu, Pb and Zn and <20% for Cd (Feng et al., 1997).

**Trace metal analysis**

Subsamples for trace metal analysis were dried at ~80°C and then ground to a powder with a mortar and pestle. Total digestion of each sediment sample was carried out to determine the amount of metal present. Digestion of ~0.4 g of dried sample was performed in Teflon beakers using HNO₃-HClO₄-HF in a three-step process (Windom et al., 1989). The completely dissolved samples were then diluted to 30 ml with 2% Ultrex HNO₃. Sample solutions and reagent blanks were analyzed for Cu, Fe, Pb and Zn by flame atomic absorption spectrophotometer (AAS) and Ag and Cd by graphite furnace atomic absorption spectrophotometer (GFAAS). Background correction and matrix interference were monitored throughout the analyses. Sediment reference material, BCSS-1 issued by National Research Council of Canada, was analyzed along with the sediment samples as a reference for the accuracy of metal analysis. Our analytical values for BCSS-1 reference material are within the certified values. The precision for Ag and Cd are less than 10% expressed by coefficient of variance and the precisions for other metals are less than 5%.
PCB analysis

PCB analyses of sediments for this study followed a modification of the method of Brownawell and Farrington (1986) and is detailed in Achman et al. (1996). All glassware and other apparatus used for PCB analysis was rinsed prior to the analysis with acetone followed by hexane and finally methylene chloride. An aliquot of 10–15 g dry wt of sediment samples was soxhlet extracted for 48 h with acetone/hexane (50:50). PCB congeners IUPAC No. 29 (2, 4, 5-trichlorobiphenyl) and No. 143 (2, 2', 3, 4, 5, 6'-hexachlorobiphenyl) were added to the samples prior to extraction to act as internal standards and to monitor recovery efficiency. The acetone/hexane extracts were back extracted with water to remove the acetone, dried with sodium sulfate (precombusted at 450°C for 8 h to destroy organic substances) and concentrated on a Kuderna Danish evaporating apparatus to about 1 ml left. The concentrated organic samples were eluted through a column packed with anhydrous sodium sulfate to remove water, with copper to remove elemental sulphur and with 10 g of Florisil (Supelco, 60/100 mesh combusted at 450°C, 2.5% deactivated with water) to separate a PCB-containing fractions. Two micro-liters of PCBa-containing fraction were injected and analyzed on a high resolution capillary gas chromatography (Hewlett-Packard 5840 gas chromatography) equipped with an electron capture detector (ECD). Total PCB concentrations were estimated by comparing a mixture of 15 prominent congeners in a standard consisting of 1:1:1 Aroclors 1242:1254:1260 to that in the sample. Relative responses to recovery standards were employed. In a related Hudson River estuary study, it was found that this method of quantification compared well, 30 ± 29%, higher than another method in which 46 major peaks were quantified separately and summed. Recoveries of PCB congeners 29 and 143 were 98 ± 16 and 91 ± 12%, respectively; precision of the PCB analysis was better than 15%.

Organic carbon analysis

Prior to analysis, ~1 g of homogenized wet sediment was sieved through a 250 μm screen to remove large detritus and coal particles. The sieved wet sediments were then treated with 0.1 M HCl in a glass beaker to remove carbonates. The mixture was left in the hood until the production of gas bubble (CO₂) ceased. The treated samples were evaporated to dryness on hot plates at ~40°C. The dried samples were finely ground and dried in a oven at ~60°C overnight. Organic carbon analysis was performed on 10 mg of the dried sediment sample using Carlo-Erba model EA 1108 CHNS-0 analyzer equipped with a four filament thermal conductivity detector (Lwiza, 1996). Sulfanilamide standards (C = 41.84%, N = 16.27%, S = 18.62%) was used to ensure the accuracy of the analysis. The precision of the analysis is < 5% for sediments containing 2% organic carbon.

RESULTS AND DISCUSSION

We analyzed Fe, Ag, Cd, Cu, Pb and Zn concentrations on all samples collected in all samplings, Al concentrations on samples collected in May 1995 and April 1996, and PCB and organic carbon concentrations on samples collected in June 1994 and on a portion of samples collected in November 1994. The analytical results show that the concentrations
of trace metals and total PCBs in the sediments vary from site to site (Table 1). Sediment Fe concentration ranges from 2.03 to 4.28 %, Ag from 0.20 to 6.38 ppm, Cd from 0.18 to 2.29 ppm, Cu from 18 to 149 ppm, Pb from 24 to 177 ppm, Zn from 101 to 257 ppm, total PCBs from 0.08 to 1.41 ppm, and organic carbon from 1.06 to 5.15 % (Table 1).

Iron is an abundant element in the structure of clay minerals and is also associated with particle surfaces as oxide coatings. Sediment Fe concentration in the study area does not vary greatly (3.43 ± 0.56 %; Fig. 2). Indeed, the concentrations are close to values (3.58 ± 0.15 %, Hirschberg et al., 1996) determined from deep sections in sediment cores, implying that there is little additional Fe input in this area and Fe in the estuarine sediment is mainly from natural weathering processes. Any variation in Fe concentrations

### TABLE 1
Heavy Metal, Total PCBs and Organic Carbon Concentrations in Surface Sediments of the Hudson River Estuary

<table>
<thead>
<tr>
<th>Location</th>
<th>Sampling date</th>
<th>Depth (cm)</th>
<th>Fe (%)</th>
<th>Ag (ppm)</th>
<th>Cd (ppm)</th>
<th>Cu (ppm)</th>
<th>Pb (ppm)</th>
<th>Zn (ppm)</th>
<th>PC (ppm)</th>
<th>Z.C. (%)</th>
<th>Distance (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP 56.4 W</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.32</td>
<td>0.64</td>
<td>1.57</td>
<td>51</td>
<td>52</td>
<td>188</td>
<td>0.99</td>
<td>2.05</td>
</tr>
<tr>
<td>MP 52.5 EC</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.70</td>
<td>0.89</td>
<td>1.73</td>
<td>58</td>
<td>61</td>
<td>256</td>
<td>1.16</td>
<td>2.73</td>
</tr>
<tr>
<td>MP 49.5 W</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>4.05</td>
<td>1.22</td>
<td>2.29</td>
<td>72</td>
<td>70</td>
<td>227</td>
<td>1.40</td>
<td>2.41</td>
</tr>
<tr>
<td>MP 44</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.80</td>
<td>2.56</td>
<td>2.16</td>
<td>70</td>
<td>86</td>
<td>210</td>
<td>1.41</td>
<td>2.33</td>
</tr>
<tr>
<td>MP 36</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.43</td>
<td>3.12</td>
<td>1.13</td>
<td>59</td>
<td>59</td>
<td>180</td>
<td>0.86</td>
<td>1.81</td>
</tr>
<tr>
<td>MP 30.8</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>4.23</td>
<td>1.32</td>
<td>0.46</td>
<td>58</td>
<td>68</td>
<td>189</td>
<td>0.62</td>
<td>2.27</td>
</tr>
<tr>
<td>MP 25.5</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.59</td>
<td>2.08</td>
<td>73</td>
<td>65</td>
<td>71</td>
<td>173</td>
<td>0.76</td>
<td>1.74</td>
</tr>
<tr>
<td>MP 96</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.93</td>
<td>3.32</td>
<td>0.51</td>
<td>58</td>
<td>69</td>
<td>177</td>
<td>0.62</td>
<td>2.27</td>
</tr>
<tr>
<td>MP 92</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>2.03</td>
<td>1.17</td>
<td>0.53</td>
<td>42</td>
<td>62</td>
<td>116</td>
<td>0.32</td>
<td>1.06</td>
</tr>
<tr>
<td>MP 2</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.25</td>
<td>1.58</td>
<td>0.49</td>
<td>44</td>
<td>58</td>
<td>111</td>
<td>0.23</td>
<td>1.74</td>
</tr>
<tr>
<td>GI</td>
<td>6/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>4.02</td>
<td>6.38</td>
<td>1.47</td>
<td>149</td>
<td>166</td>
<td>257</td>
<td>0.88</td>
<td>2.15</td>
</tr>
<tr>
<td>MP 15</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.42</td>
<td>2.82</td>
<td>0.76</td>
<td>80</td>
<td>72</td>
<td>177</td>
<td>0.84</td>
<td>2.02</td>
</tr>
<tr>
<td>MP 12</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>4.03</td>
<td>3.35</td>
<td>0.96</td>
<td>94</td>
<td>87</td>
<td>209</td>
<td>1.26</td>
<td>2.20</td>
</tr>
<tr>
<td>125 St.</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>2.98</td>
<td>0.28</td>
<td>0.18</td>
<td>18</td>
<td>24</td>
<td>101</td>
<td>0.08</td>
<td>1.42</td>
</tr>
<tr>
<td>90W</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>2.86</td>
<td>3.53</td>
<td>0.85</td>
<td>83</td>
<td>82</td>
<td>166</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>79W</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>2.75</td>
<td>1.38</td>
<td>0.66</td>
<td>58</td>
<td>85</td>
<td>133</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pier 12</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.09</td>
<td>2.11</td>
<td>0.37</td>
<td>68</td>
<td>82</td>
<td>166</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Pier 9</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.03</td>
<td>3.99</td>
<td>1.19</td>
<td>91</td>
<td>99</td>
<td>193</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>MP 2.5</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>2.59</td>
<td>2.19</td>
<td>0.57</td>
<td>68</td>
<td>93</td>
<td>151</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>GI</td>
<td>11/94</td>
<td>0-3</td>
<td>n.a.</td>
<td>3.67</td>
<td>5.25</td>
<td>1.66</td>
<td>148</td>
<td>177</td>
<td>250</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>G. W. Bridge</td>
<td>5/95</td>
<td>0.5</td>
<td>5.35</td>
<td>3.43</td>
<td>0.82</td>
<td>0.28</td>
<td>62</td>
<td>84</td>
<td>147</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Grant Tomb</td>
<td>5/95</td>
<td>0-0.5</td>
<td>4.85</td>
<td>3.88</td>
<td>4.32</td>
<td>0.66</td>
<td>123</td>
<td>103</td>
<td>207</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>79W</td>
<td>5/95</td>
<td>0-0.5</td>
<td>4.83</td>
<td>3.57</td>
<td>2.05</td>
<td>1.15</td>
<td>129</td>
<td>127</td>
<td>231</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>GI</td>
<td>5/95</td>
<td>0-0.5</td>
<td>4.1</td>
<td>3.04</td>
<td>1.50</td>
<td>0.77</td>
<td>120</td>
<td>110</td>
<td>131</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Newburgh Bridge</td>
<td>4/96</td>
<td>0-0.5</td>
<td>5.24</td>
<td>3.51</td>
<td>0.20</td>
<td>1.43</td>
<td>50</td>
<td>45</td>
<td>170</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Foundry Cove</td>
<td>4/96</td>
<td>0-0.5</td>
<td>6.32</td>
<td>4.06</td>
<td>0.64</td>
<td>1.85</td>
<td>61</td>
<td>55</td>
<td>197</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Haverstraw Bay</td>
<td>4/96</td>
<td>0-0.5</td>
<td>5.68</td>
<td>3.42</td>
<td>0.68</td>
<td>1.09</td>
<td>51</td>
<td>43</td>
<td>161</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Piermont</td>
<td>4/96</td>
<td>0-0.5</td>
<td>5.09</td>
<td>3.84</td>
<td>1.16</td>
<td>0.70</td>
<td>58</td>
<td>43</td>
<td>160</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>G. W. Bridge</td>
<td>4/96</td>
<td>0-0.5</td>
<td>5.44</td>
<td>4.28</td>
<td>2.25</td>
<td>0.73</td>
<td>78</td>
<td>59</td>
<td>192</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Grants Tomb</td>
<td>4/96</td>
<td>0-0.5</td>
<td>5.04</td>
<td>3.57</td>
<td>3.90</td>
<td>1.51</td>
<td>118</td>
<td>115</td>
<td>210</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Governors Island</td>
<td>4/96</td>
<td>0-0.5</td>
<td>4.45</td>
<td>3.11</td>
<td>2.26</td>
<td>0.53</td>
<td>96</td>
<td>91</td>
<td>160</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td>Hudson River sediment</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

*aDistance = 0 at the Battery, the southern tip of Manhattan.

*b.n.a. = not analyzed.

'Hirschberg et al. (1996).

Concentration units: % = g 100 g⁻¹ dry wt, ppm = μg g⁻¹ dry wt.
Fig. 2. Distributions of (a) Fe in the sediments along the axis of the Hudson River estuary in the study area (the horizontal line through the data represents the Fe concentration at depth in Hudson River sediments; Hirschberg et al., 1996) and (b) organic carbon concentrations in the sediments along the axis of the Hudson River estuary in the study area. The segments of surface sediment samples are 0–3 cm in June 1994, 0–3 cm in November 1994, 0–0.5 cm in May 1995 and 0–0.5 cm in April 1996, respectively. Symbols are designated as (○) for June 1994, (□) for November 1994, (△) for May 1995 and (▽) for April 1996.

thus can be explained by particle grain size differences, with fine-grained sediments having high Fe concentrations.

Except for sediments in New York Harbor (km point -3), organic carbon concentrations in sediments vary between 1.06 to 2.73% (Table 1), showing a decrease tendency down-estuary with scattered distributions (Fig. 2). Mueller (1982) reported that approximately half of organic carbon input to the Hudson River estuary was due to wastewater. The variations of organic carbon concentration also can be caused by differences in particle grain size and lability of carbon with respect to microbial degradation. We took available Fe and organic carbon data from two out of four samplings to examine the particle grain size effect and found a correlation between Fe and organic carbon ($r^2 = 0.625$), excluding one sample taken in New York Harbor (Fig. 3).

In order to exclude variations due to physical properties of particles such as grain size differences and to better compare site-to-site variations in the trace metal concentrations in the sediments, we use Fe to normalize the trace metal contaminants because Fe has a great abundance in natural crust and has a reactive fraction associated with particle surfaces like other contaminants (Trefry, 1977; Trefry et al., 1983; Gibbs, 1994; Daskalakis and O'Connor, 1995). A concern with this approach is that Fe is susceptible to rapid reduction and oxidation and its distribution can be affected by non-steady state chemical and physical processes associated with organic carbon input (diagenesis) (e.g. Berner, 1982, 1984). This is especially true for dissolved Fe in interstitial water (Aller, 1980). To
Distribution of heavy metal and PCB contaminants

Fig. 3. Fe vs organic carbon concentrations in Hudson River sediments. Data are from this study and Feng (1997).

Fig. 4. Fe vs Al concentrations in Hudson River suspended and bottom sediments. Data are from this study and Feng (1997).
eliminate these problems, Al is often used for metal normalization (Windom et al., 1989; Shropp et al., 1990). We did not analyze Al on all samples in this study, but our available Al and Fe data in sediments and suspended particles show a good correlation ($r^2 = 0.925$) between Fe and Al (Fig. 4; Feng, 1997), which permits us to use Fe for normalization. Moreover, in cases in which sediments are composed of quartz sand, Al concentration will be nearly zero because of no silt and clay material. In contrast, Fe concentrations tend not to reach zero because of its presence on particle surfaces. PCB concentrations are known to be affected more by organic carbon content than the particle grain size (Choi and Chen, 1976; Means et al., 1980), and we normalize total PCB concentration to organic carbon for site-to-site comparison.

Comparison of the measured metal/Fe ratios with the background values of the Hudson estuary sediments shows that the metals to Fe concentration ratio exceed the background metal/Fe ratios of the Hudson estuary sediment by factors of 2 to 10 (Fig. 5), implying that all sites sampled have elevated concentrations of Ag, Cd, Cu, Pb and Zn.

The normalized trace metal and PCB concentrations show different trends down the estuary. Two patterns are evident: the ratios of Ag/Fe, Cu/Fe and Pb/Fe in the sediments show increases downstream while total PCBs/organic carbon, Cd/Fe and possibly Zn/Fe show a decreases downstream, although high values of Cd/Fe and Zn/Fe are also found in sediments near New York Harbor (Fig. 5). It is important to note that these observations of relative differences among the trace metals are likely to be valid even if there are spatial variations at any single location. We have evaluated the small-scale spatial variation in a depositional area off 79th Street of Manhattan (km point ~8) and found them to be <10% for Fe, Ag, Cu Pb and Zn and <29% for Cd (Feng, 1997).

In this study, the increases of sediment Ag/Fe, Cu/Fe and Pb/Fe ratios down-estuary toward New York Harbor (Fig. 5) suggest that these trace metals are mainly input from urban runoff or municipal wastewater treatment effluents and the New York City metropolitan source influence is not clearly evident in the estuary at or above km point ~40. Silver has been used in recent years as a tracer of municipal wastewater effluent because of its low crustal abundance and because many of the major sources of Ag (e.g. dentistry; photoprocessing) are added to wastewater discharges (Saudio-Wilhelm and Flegal, 1992; Smith and Flegal, 1993; Ravizza and Bothner, 1996). In this study, significant correlations of Cu and Pb with Ag ($r^2 = 0.636$ and $0.637$, respectively; Fig. 6) suggest that the wastewater can be a significant source delivering Cu and Pb to the Hudson River system along with Ag. Significant correlations of Cd and Zn with Ag inside New York Harbor ($r^2 = 0.630$ and $r^2 = 0.727$, respectively; Fig. 6) also suggest municipal wastewater inputs. There is much poorer correlations of Cd and Zn with Ag on the whole estuarine system-wide basis, presumably due to the other upstream sources of these two metals. Outside of New York Harbor, relatively high Cd (>1 ppm) and Zn (>150 ppm) concentrations corresponding to low Ag concentrations (<1 ppm) can be reflective of the upriver sources along the axis of the Hudson River estuary (Fig. 6).

The down-estuary decreases in total PCB/organic carbon and Cd/Fe and Zn/Fe (from km point 100 to 40) suggest the importance of upriver sources of these contaminants (Fig. 5). In fact, the upper Hudson River is one of the most PCB-contaminated rivers in the USA (Sanders, 1989). Prior to 1976, wastewater discharge from two plants of General Electric Company and downstream transport of PCB-contaminated sediments contributed to down-river supply of PCBs. A settlement between New York State and the General Electric Company in 1976 resulted in cessation of PCB discharges and initiation of effort
to rehabilitate the upper Hudson River. The amount of PCBs discharged into the lower
Hudson River has decreased from ~2 ton y⁻¹ in the late 1970s to 1 ton y⁻¹ or less in the
1980s (Sanders, 1989).

Unlike the other trace metal contaminants, Cd has had a significant up-estuary source.
For many years, there was a Cd source in Foundry Cove (km point ~80) due to the
presence of a Ni-Cd battery factory between 1953 and 1979 (Sanders, 1989; Wallace,
Fig. 6. Cu, Pb, Cd and Zn vs Ag for the surficial bottom sediment samples collected from all sites in the Hudson River. Regression lines of Cu and Pb with Ag are for all samples collected along a 100 km of the estuary and regression lines of Cd and Zn with Ag are for samples collected in New York Harbor only (kmp -11 to 18). Symbols are designated as (○) for June 1994, (□) for November 1994, (△) for May 1995 and (▽) for April 1996. Filled symbols stand for stations inside New York Harbor (kmp -11 to 18) and open symbols for stations outside New York Harbor (kmp > 18).

Prior to remediation, sediments of Foundry Cove contained up to 500 ppm of Cd, and concentrations in the most polluted area reached as high as 225 000 ppm Cd (Knutson et al., 1987; Klerks and Levinton, 1989). Remediation efforts in 1994 have led to the removal of much of this material, but our data demonstrate the importance of this source, at least in the past.

A fairly good correlation of Cd and Zn with PCBs ($r^2 = 0.548$ and 0.663, respectively, Fig. 7) implies an up-estuary source of Cd and Zn. The distributions of Cd, Zn and PCBs contaminants thus reflect down-estuary transport by natural sediment transport governed by river water discharge (Turk, 1980). In New York Harbor, Cd/Fe and Zn/Fe ratios, and very limited data for total PCBs and organic carbon concentrations show increases (Fig. 5; Table 1), suggesting the importance of the local New York/New Jersey metropolitan area input of Cd, Zn, total PCBs and organic carbon (Bopp and Simpson, 1989; Brosnan et al., 1994; Chillrud, 1996). In the case of Cd, additional sources to the lower estuary include discharges of municipal wastewater treatment plant from electroplating and metal finishing industries (Brosnan et al., 1994). Loading of Cd from New York City wastewater was estimated to be 2 kg d$^{-1}$ in 1993 with a 88% decrease comparing to 14 kg d$^{-1}$ in 1985 (Brosnan et al., 1994). Regarding input of PCBs, Bopp et al. (1981) estimated that, from 1971 to 1976, about 75% of PCBs deposited in New York Harbor sediments were transported from the upriver sources and the remainder were delivered from local New York/New Jersey metropolitan area. About a decade later, Bopp and Simpson (1989) estimated
Fig. 7. Cd and Zn vs total PCBs for the surficial bottom sediment samples collected from the sites in the Hudson River estuary. Symbols are designated as (○) for June 1994 and (□) for November 1994. Filled symbols stand for stations inside New York Harbor (km p = 11 to 18) and open symbols for stations outside New York Harbor (km p > 18).

Gibbs (1994) also studied sediment metal concentrations along the Hudson River estuary and concluded that concentrations of anthropogenic Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the bottom sediments of the estuary reached a maximum in New York Harbor. However, our trace metal results do not replicate those results. For example, in the same area, our Cd concentration is up to a factor of ~5 lower than his results and our Fe concentration is ~2 orders of magnitude higher than his. In addition, the spatial trends of Cd/Fe and Zn/Fe concentration ratios of our study are also different from the Gibbs' results. The differences may be attributed to different sampling techniques, sample processing procedures and distances covered by the two studies in the Hudson River estuary: (1) our sediment samples were recovered with a box corer which can give a better resolution with depth, while sediment samples of Gibbs' study (Gibbs, 1994) were taken by a pipe dredge and the concentrations represent the average of upper 8 cm of sediments; (2) our sediment samples were analyzed by a HF-H4ClO4-HNO3 total digestion method (Windom et al., 1989) which gives the total amount of trace metals in the sediments, while sediment samples of Gibbs (1994) were processed with acid-leaching method; and (3) our sampling covered a longer distance (> 100 km) along the axis of the Hudson River than that of Gibbs' study (~50 km), which likely influences conclusions related to Cd and Zn distributions.

Chillrud (1996) studied extensively the metal distributions in New York Harbor sediments. Although he did not measure Ag, a general agreement with our results is found for contaminant concentrations and relationships to Cu in the sediments near New York Harbor.
Fig. 8. Pb, Zn, Cd and total PCBs vs Cu in surficial bottom sediments of the Hudson River estuary, based on this study and Chillrud (1996). Symbols are designated as (○) for June 1994, (bfn) for November 1994, (△) for May 1995 and (▽) for April 1996 of this study. Filled symbols stand for stations inside New York Harbor (kmp - 11 to 18) and open symbols for stations outside New York Harbor (kmp > 18). Symbols are designated as (+) for stations inside New York Harbor from Chillrud (1996). Solid lines in the graphs are regressions of Chillrud's data.

It is interesting to note that, although the metal data largely conforms to the mixing lines that describe Chillrud's data, the metal concentrations determined in this study are lower than the earlier measurements (Fig. 8). Lower metal levels found in this study are most likely due either to a decrease in metal loads to the harbor between 1982–1994 (Chillrud’s samples) and 1994–1996 (this study) or to the possibility that some of the recent sediment in our surface sediment samples were diluted with relict sediments containing low trace metal levels. Chillrud minimized this latter problem by only analyzing sediment that contained high $^7$Be specific activities in surface sediments (0–2 cm). We analyzed $^7$Be specific activities on portion of our samples (Feng, 1997) and found no significant correlation between $^7$Be activities and trace metal concentrations because of different source functions. The linear relationship between Cd and Cu in sediment near New York Harbor breaks down at low Cu concentrations (Fig. 8). This behavior is consistent with the generally low particle-reactivity of Cd in seawater (Li et al., 1984) that should cause a point source of Cu to be distributed more broadly than for a more particle-reactive metal like Cu. It could also be the result of a second (low Cu) source of Cd coming from upriver that is evident from the data (Fig. 8). The concentrations of Cd in relationship to Cu are significantly elevated in many samples collected upriver (Fig. 8), consistent with our conclusion of significant upriver sources of this contaminant to the lower estuary. The Pb data of sediment samples collected outside of New York Harbor do not depart significantly from the relationship with Cu determined from New York Harbor.
Distribution of heavy metal and PCB contaminants

This is consistent with our hypothesis that sources of Pb and Cu from the NY/NJ metropolitan area dominate input of these contaminants to the lower Hudson estuary.

Generally, the relationship between total PCB and Cu concentrations in New York Harbor sediments found in this study also agrees well with Chillrud's (1996) data, with the exception of a single sample with higher PCB concentration (Fig. 8). Concentrations of total PCBs are higher in samples farther up the estuary when compared to Cu, consistent with an important upriver source of PCBs. The one sample with higher concentrations of PCBs in the harbor corresponds to one of the samples obtained at km point ~8 on the western margin of the river. Sediments in that area are subject to dynamic depositional and erosional processes at various times of the year (Hirschberg et al., 1996). High PCB concentrations in surficial sediments could be indicative of recent transport of materials from the upriver sources.

It is important to note that there are significant changes in the composition of PCB congeners along the axis of the lower estuary (Bopp and Simpson, 1989; Chillrud, 1996; Lwiza, 1996). The relative importance of higher chlorinated congeners increases downestuary. This is especially true of octa-, nona- and decachlorobiphenyl, but also holds for hexa- and heptachlorinated congeners (Lwiza, 1996). These trends have also been found by Bopp and Simpson (1989) and Chillrud (1996), who have argued that the higher molecular weight congeners are characteristic of sources in the metropolitan New York area into the area near New York Harbor. The change in PCB composition favoring more highly chlorinated congeners going downstream could also be due to preferential weathering of more soluble and volatile congeners during down-estuary transport. However, much better correlation of lower chlorinated congeners with Cd, than that observed for more highly chlorinated congeners, supports the premise that there is an important urban source of higher molecular weight PCBs (Lwiza, 1996). Our data for total PCBs are consistent with assessments made by Bopp and coworkers that there are both important upriver sources of PCBs into the lower Hudson estuary and significant local sources of PCBs being added to New York Harbor.

Comparison of the Zn vs Cu relationship in New York Harbor with the Hudson River estuary sediments suggests that Zn may have local sources input into the harbor in addition to upriver sources (Fig. 8). Zn concentrations in upriver sediments tend to fall above the trend line determined from samples taken in the harbor, although to a lesser extent than those of Cd and PCBs. These results suggest that, while Zn has dominant sources in the lower estuary, there are additional sources upriver. Urban sources of Zn from municipal wastewater discharges have been documented by Brosnan et al. (1994), although they estimated that Zn loading from New York City wastewater effluent is 285 kg d⁻¹ in 1993 with a decrease of 68% comparing to 880 kg d⁻¹ in 1985.

To better elucidate the factors governing the metal and PCB contaminant distributions in the estuary, we performed a multivariate statistical analysis (factor analysis) on our data (Meglen, 1992). The approach is strictly statistical and, in order to include PCB, the data used for the analyses are restricted to June 1994 and November 1994 samplings. The eight concentration variables (Fe, Ag, Cd, Cu, Pb, Zn, PCB and OC (organic carbon)) were converted to logarithms and R-mode factor analysis was performed (Meglen, 1992). In the R-mode analysis, three factors account for 93% of the variance, with the first factor accounting for 27%, the second factor for 36% and the third factor for 30% (Table 2). Factor 1, which is essentially an Fe factor with moderate loadings for organic carbon (OC) and Zn, is interpreted as representing the sediment grain size. Factor 2, which has
Fig. 9. Graph showing the results of factor analysis. The factors of urban and upriver sources of contaminants account for 66% of variance, with additional 27% contributed by grain size.

high loadings for Ag, Pb and Cu, is interpreted as representing the urban source input to the lower estuary. Factor 3, whose loadings are high Cd and PCB with moderate Zn, is interpreted as representing the up-river sources.

Figure 9 shows the effect of the urban and upriver source factors on the Hudson River estuary. The influence of these two factors in the Hudson River estuary is distinctive: urban sources (Ag, Pb and Cu) have greater influence on the lower estuary stations and
upriver sources (Cd and PCBs) have greater input on the upper estuary stations (Fig. 9). The station off the 125th Street is anomalous (Fig. 9) due to low concentrations of contaminants at that location (Table 1). This factor analysis is consistent with our observations that Ag, Pb and Cu have dominant urban source input in the lower estuary, and Cd and PCBs are dominantly input from up-river sources and transported down-estuary.

CONCLUSIONS

Surficial sediment samples were collected at four times along the lower ~100 km of the Hudson River estuary to determine the distribution of heavy metal and PCB contaminants. Trace metal and PCB contaminants in surficial sediments (0–3 cm) show two distinctly different trends along the axis of the Hudson River estuary: Ag, Cu and Pb, normalized to Fe to correct for grain size effects, show an increasing trend down-estuary, reaching maximum values in New York Harbor; in contrast, total PCBs and Cd (as well as Zn) show a decreasing trend down-estuary to New York Harbor where the concentrations increase due to local source inputs in the lower estuary. In addition, the axial distributions of Ag, Cu and Pb contaminants shows a distinguishable metropolitan region influence on the metals to less than ~40 km upstream of the Battery at the southern most tip of Manhattan Island. The strong correlation of Ag with wastewater effluent, observed elsewhere, and the upriver discharge of PCBs in the 1970s make these two contaminants effective indicators of urban (down-estuary) and upriver sources of contaminants, respectively. Good correlation of Cu and Pb with Ag throughout the lower 100 km of the Hudson River estuary suggest that these contaminants have urban sources (e.g. urban runoff and wastewater effluent), while the correlations of Cd and Zn with PCBs suggest that the distributions are partly controlled by upriver sources and these contaminants are being transported down-estuary. These conclusions are consistent with the results from the factor analysis which show that particle grain size, urban source input and upriver source input account for 93% of variations in contaminant distributions. The high concentrations of Ag, Cu, Pb, Cd, Zn and PCBs in New York Harbor sediments indicate that these sediments serve as a reservoir for particle-associated contaminants.

ACKNOWLEDGEMENTS

This work was sponsored by the Hudson River Foundation (Grants 00491A, 00494A and 00591A). We have benefited from discussions with Drs Robert Aller, Robert Cerrato and Sergio Sañudo-Wilhelmy. We thank three anonymous reviewers for their constructive comments. Thanks also go to Mark Wiggins, Kim Roberts and the crew members of the R/V Onrust for the assistance in the field samplings, and Ms Eileen Goldsmith for the assistance in preparation of this manuscript.

REFERENCES


Treffry, J. H. (1977) The transport of heavy metals by the Mississippi River and their fate in the Gulf of Mexico. Ph.D. Dissertation. Texas A&M University, College Station, TX.


