



Tracing water and suspended matter in Raritan and Lower New York Bays using dissolved and particulate elemental concentrations

Anthony J. Paulson *

*NOAA-Fisheries, James J. Howard Laboratory, 74 Magruder Road, Highlands, NJ, United States
USGS/Washington Water Science Center, Environmental Hydrology and Geochemistry Section, 1201 Pacific Ave.,
Suite 600, Tacoma, WA 98402, United States*

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Abstract

Geochemical tracers were used to examine the mixing of water and particles in Lower New York and Raritan Bays in August 1999 during low-flow conditions. Four brackish water masses ($20 \leq S \leq 28$) originating in the Raritan and Shrewsbury Rivers, Arthur Kill, and Upper New York Bay were characterized by their dissolved metals concentrations. The mixing lines of dissolved Cu, Ni, and Pb in Lower New York Bay were similar to those in Upper New York Bay, the source of most of the freshwater to the system. Dissolved Cd and Mn seemed to have been removed by particles in several regions of the study. Dissolved Cu, Ni and Pb in the Raritan River fell below the mixing lines of the Lower New York Bay. In contrast, the concentrations of dissolved Co and Mn in the Raritan River were distinctly higher than those in the Lower New York Bay, while dissolved Cu and Ni were elevated in the Arthur Kill. A plot of dissolved Co versus dissolved Ni clearly differentiated among three water masses: (1) Upper and Lower New York Bays and Sandy Hood Bay, (2) the Raritan River, and (3) Arthur Kill–Raritan Bay–Shrewsbury River.

The concentrations of 22 elements also were measured in the suspended matter of Raritan and Lower New York Bays and brackish water sources. The elemental composition of the suspended matter in surface and bottom waters was correlated with Fe concentrations, which ranged between 50 and 900 $\mu\text{mol g}^{-1}$. Statistical differences among the geographical regions were detected in the relationships of Ti, Ni, Co, As, and U with Fe, with particulate As being an especially strong geochemical indicator of Raritan River particles. The geochemical signatures of Lower New York Bay particles were similar to those of Upper New York Bay. The geochemical signatures of Raritan River particles were distinctly different than those of the Upper New York Bay, but the influence of Raritan River particles appeared to be limited to only inner Raritan Bay. This study illustrates the utility of trace elements for characterization of physical processes in complex estuaries.

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* Present address: USGS/Washington Water Science Center, Environmental Hydrology and Geochemistry Section, 1201 Pacific Ave., Suite 600, Tacoma, WA 98402, United States. Tel.: +1 253 428 3600x2681.

E-mail address: apaulson@usgs.gov.

1. Introduction

The transport of suspended matter from the Hudson River to the New York Bight has been studied for over 30 years (Biscaye and Olsen, 1976; Young et al., 1985, Darby, 1990). In particular, contamination of water and particles by metal pollutants has been of particular interest (Williams et al., 1978; Klinkhammer and Bender, 1981). Toxicity identification evaluations suggest that cationic metals were partially responsible for the toxicity of ambient brackish water from the East River and Newark Bay (Thursby et al., 2000). The Comprehensive Conservation and Management Plan (CCMP) of the New York–New Jersey Harbor Estuary Program (U.S. Environmental Protection Agency, 1996) was developed to address the overall health of the estuary (Fig. 1) including the biological effects of contaminants and the increased costs of disposal of dredge spoils.

Tracking down the sources of metals of concern (i.e., the Contaminant Assessment and Reduction Project; Litton, 2003) and developing mass balances for metals using a system-wide physical model of water transport are tasks identified in the CCMP. The special attention given to transport of particles and contaminants within the turbidity maximum of the Hudson River by several investigators (Hirschberg et al., 1996; Geyer et al., 2001, Feng et al., 2002) has contributed to our understanding of this estuarine system. In contrast, Lower New York and Raritan Bays have received little attention.

This study focused on the Lower New York and Raritan Bays, and complements more landward research supported by the New York–New Jersey Harbor Estuary Program. In August of 1999, dissolved metals concentrations were measured throughout Lower New York and Raritan Bays to determine how the brackish water sources (the Arthur Kill, Upper New York Bay, Raritan River, and Shrewsbury River) mixed with coastal waters. The elemental composition of suspended particles also was examined to identify geochemical tracers that might differentiate particles supplied by the Raritan and Hudson Rivers. Some fraction of the suspended matter load from these rivers settles in the shipping channels of Lower New York and Raritan Bays and periodically requires removal by dredging. Data on dissolved and particulate metals were examined for evidence of geochem-

ical reactions that might concentrate metals onto particles that settle into shipping channels. Samples for the project were collected during low-flow conditions so that manifestations of geochemical reactions would not be masked by strong advective transport (Paulson and Curl, 1993). Although sampling during low-flow conditions maximized the possibility of detecting geochemical reactions and distinguishing between sources of particles, data on suspended matter compositions and concentrations acquired solely during periods of low flow should not be used to calculate annual fluxes between estuaries and coastal waters. In this study, geochemical tracers were identified that could enhance physical models of water and suspended matter transport in this complex estuarine system, especially at the three-endmember junction of the Arthur Kill and the Raritan River with Raritan Bay.

2. Study area

The Upper New York Bay (UNYB) receives the flows of the Hudson River, the Kill Van Kull and the East River (Fig. 1). Much of the East River freshwater flow during the summer originated as effluent from sewage treatment plants. The Kill Van Kull receives a portion of the net flow from Newark Bay, which in turn receives freshwater from the Passaic and Hackensack Rivers. After some degree of mixing among Kill Van Kull, the Hudson River, and the East River, brackish water from UNYB flows into the Lower New York Bay (LNYB). Raritan Bay (RB) receives water from the Raritan River (RR), and flow from Arthur Kill (AK) which is derived in part from Newark Bay. The Shrewsbury River (SB) flows through Sandy Hook (SH) Bay and enters Raritan Bay from the south. Deep shipping channels, such as the Ambrose Channel, allow salty coastal water to flow landward. During the week prior to August 27, 1999 (the last day of sampling for this study), freshwater discharge from the major gauged watersheds of the UNYB, Raritan River and Newark Bay were stable, averaging 74, 6.2 and 4.8 m³/s, respectively (U.S. Geological Survey, 2003a,b). Freshwater flow from the dam on Shrewsbury River was negligible.

The Lower New York and Raritan Bays are surrounded by a residential population of 13.5 million

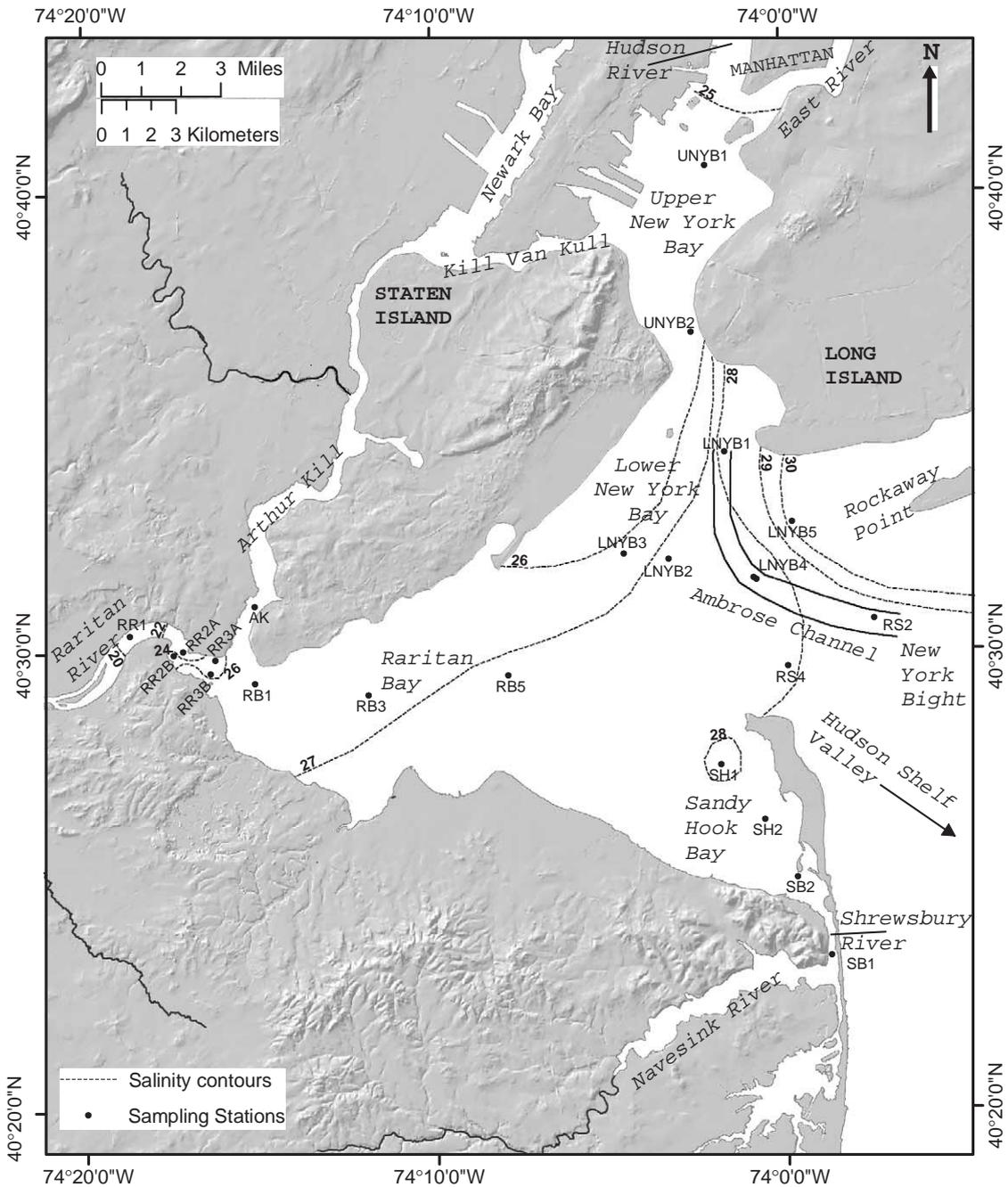


Fig. 1. Study area and contours of surface salinity. Sampling stations are located in the brackish waters of Upper New York Bay (UNYB), Arthur Kill (AK), Raritan River (RR), and Shrewsbury River (SB) and in Lower New York Bay (LNYB) that includes two stations along the Rockaway–Sandy Hook (RS) transect, Raritan Bay (RB) and Sandy Hook Bay (SH).

that generates 9100 million L of effluent per day from 31 sewage treatment plants (Litton, 2003). With the seasonal decrease in Hudson River flow, the concentrations of dissolved Ag, Ni, Pb and Cu increase in the vicinity of Manhattan (Sanudo-Wilhelmy and Gill, 1999). Additionally during low-flow conditions, it is suspected that tidal currents move suspended matter with elevated Pb concentrations upriver from the Upper New York Bay to the Hudson River (Feng et al., 2002). Although sewage treatment plants contribute a significant portion of the flux of metals, such as Cd, to the Upper New York Bay, the rates of advective outflow and sedimentation of metals from Upper New York Bay suggest that other significant sources have yet to be identified (Yang and Sanudo-Wilhelmy, 1998).

In August 1999, the salinities of surface waters (0–0.5 m depth) in Lower New York, Raritan and Sandy Hook Bays ranged from 26 to 28, except for the sample at LNYB 5 that had a salinity of 30.2 (Fig. 1). The higher salinities on the eastern side of LNYB were consistent with observations of net flow across the Rockaway–Sandy Hook (RS) transect (A. Kao, State University of New York, Stony Brook, as referenced in Oey et al., 1985). The water was generally well mixed vertically, with differences in salinity between surface and bottom water generally not exceeding 2.0 at any given station. Deeper (>17 m) water in the Ambrose Channel had salinities between 29.8 and 30.2, indicating landward flow into the estuary from New York Bight. The water column was well oxygenated, with minimum dissolved oxygen concentrations in bottom waters ranging between 310 μM (LNYB1) and 440 μM (LNYB5). Surface temperatures were 23 °C, while the bottom water temperature in the Ambrose Channel was 22.5 °C.

The surface water samples representing the brackish water sources from the Upper New York Bay, the Arthur Kill, the Raritan River, and Shrewsbury River had salinities of 25.23, 26.37, 20.73 and 27.47, respectively. The largest vertical difference in salinity in this study (3.2) was found in the Raritan River. When deep samples are included, the salinities of the UNYB and the Raritan River overlap between 25 and 26. The dissolved oxygen in the bottom waters of the Raritan River (275 μM) was lower than that of the UNYB.

3. Methods

3.1. Sampling and filtration

In 1999, samples from the Raritan River (August 24), the Upper New York Bay (August 25), and the Shrewsbury River (August 26) were collected in the landward direction during an ebbing tide. Due to a 4-h delay caused by a malfunctioning CTD, sampling inside the Upper New York Bay (UNYB1 and UNYB2) was performed nearer slack tide. Lower New York Bay was sampled on August 27 between higher high tide and higher low tide. Upon arrival on station in a 20-ft fiberglass boat (R.V. Harvey), collection of a surface water sample in an acid-cleaned, 1-L HDPE bottle using clean sampling techniques was followed by CTD measurements. Subsurface samples (>1 m) were collected in a single 5-L Go-Flo bottle (General Oceanics, Miami, FL) that was equipped with Teflon stopcocks. The Go-Flo bottle was lowered manually on a Kevlar line over the side of the fiberglass boat. All bottles and apparatus used for sample collection, filtration and metal analysis were cleaned in 4 M trace-metal-grade nitric acid (A509-212, Fisher, Pittsburgh, PA). Bottles containing samples for the analysis of metals and particulate organic carbon were bagged in plastic, packed in ice, and transported to the laboratory for filtration within 8 h.

Within the laboratory laminar flow hood, seawater from each 1-L HDPE bottle was withdrawn into an all-plastic, ink-free, 30-mL Luer syringe (Air-Tite, Vineland, NJ). The syringe contents were then filtered through a 25 mm, 0.25 μm in-line syringe Teflon filter (Spartan T-#72140, Schleicher and Schuell, Keene, NH) and collected into a 60-mL HDPE bottle after discarding the first 10 mL aliquot. Only syringe–filter combinations that delivered filtered deionized, distilled water (DDI) with Zn concentrations less than 1.5 nM were accepted for use. Filtered samples were then acidified to pH 1.5 with Optima-grade nitric acid (Fisher, A671-1). Particles from well-mixed 1-L HDPE bottles were filtered onto a pre-weighed, acid-cleaned Teflon filter (47 mm, 0.45 μm) (TE-36, Schleicher and Schuell, Keene, NH). Particles for analysis of organic carbon were filtered onto a pre-combusted Whatman glass fiber filter supported by a polypropylene filter holder, and were then frozen until analysis.

3.2. Analysis of water

Dissolved trace metals were determined using an off-line buffering adaptation of Willie et al. (1998) and Arslan and Paulson (2002). Acidified samples were partially neutralized with small aliquots of concentrated trace metal grade NaOH (Fisher A470-250). Each sample that had a pH of 2.3 was then buffered with 1 M Fisher Optima-grade acetic acid ammonium acetate buffer. The pH of each sample with 0.01 M total acetate was checked to ensure values between 5.0 and 5.5. The 5-port unit and the tubing on the Perkin–Elmer flow injection analysis system (FIAS) 400 system were then rinsed with the buffered sample. Metals in 3.2 mL of the buffered sample were then chelated by Toyopearl AF-Chelate 650 M (Tohahaus, Montgomeryville, PA) contained in a 100- μ L polyethylene miniature column (Global FIA, Gig Harbor, WA). The column was then rinsed with DDI before being backflushed with 2.4 mL of 5% (v/v) HNO₃ spiked with 10 μ g/L ¹⁰³Rh as an internal standard. The 5% HNO₃ solution that was used to elute the column was injected directly into the cross-flow nebulizer of a Perkin–Elmer Elan 5000 inductively coupled plasma mass spectrometer (ICP-MS) equipped with standard ICP torch and platinum sampler and skimmer cones. The counts of ⁵⁹Co, ⁶²Ni, ⁶³Cu, ¹¹³Cd and ²⁰⁸Pb were normalized to the Rh internal standard and calibrated against multi-element standards that had been diluted with DDI to appropriate concentration ranges. Mn was measured by direct injection after dilution to a salinity of 2.3 (10% of the salinity of CASS-2). Mn calibrations utilized a standard curve prepared from NASS-3 diluted to a salinity of *S*=2.3.

Quality-control analyses included use of daily instrument blanks during the 4 days of analyses, filtration blanks each day in the field, and measurement of standard reference materials. Sample concentrations were corrected for the instrument blank concentrations, which ranged between 0.08 nM for Co and 0.3 nM for Ni. Only in the case of Pb were the instrumental (0.024 nM) and filtration method (0.029 nM) detection limits within a factor of 3 of the lowest sample concentration. The results of the analyses of Cu, Pb, and Cd were within 15% of the certified values for CASS-2 (*n*=8) and SLEW-1 (*n*=7). The

average Ni concentrations of CASS-2 and SLEW-1 were 91% and 80% of the certified values, respectively. The average recoveries of Co in CASS-2 and SLEW-1 were 130% and 147% of the certified concentrations (0.48 nM and 0.78 nM, respectively), with the maximum discrepancy between reported and certified values being 0.34 nM. SRM concentrations were low compared to those in most of the samples analyzed in this study and were comparable only for the Co concentration of New York Bight water (*S*=30). The high recoveries for low-Co concentration SRMs were probably a result of interferences (⁴³CaO⁺ and ⁴²CaOH⁺) from Ca in seawater that was not rinsed off the column before acid backflushing. Because calibrations were performed using metals dissolved in DDI standard solutions, Ca interferences in seawater samples would result in positive errors. The effect of such interferences would be greatly diminished at the lower salinities and higher Co concentrations of the Raritan River (8.74 nM). Recovery values were not used to adjust sample concentrations. The detection limit for Mn by direct injection was 0.005 μ M, and the recoveries for CASS-2 and SLEW-1 were 114% and 107%, respectively. The relative standard deviation (RSTD) of replicate sample and SRM analyses was generally less than 10% (1 std. dev.).

3.3. Analysis of suspended matter

After each filter for particulate elemental measurements was dried in a desiccator, total suspended matter (TSM) measurements were determined gravimetrically by reweighing the filters on a Cahn 29 electrobalance (Cerritos, CA). The suspended matter on each filter (typically about 2 mg) was dissolved using 95% Optima-grade nitric acid (Fisher A671-1) and 5% Ultrex-grade hydrofluoric acid (#4804-04, Baker, Jackson, TN) in a CE-123 digestion system (40% microwave power) with care to minimize destruction of the filter. The acid solutions in the digestion bombs were transferred to 15-mL Teflon centrifuge tubes, and the filters and bombs were thoroughly rinsed with DDI resulting in a total volume of approximately 10 mL.

Standards for analyses of suspended matter on the Elan 5000 ICP-MS, delivered directly by peri-

staltic pump, were matched with the acid matrix containing dissolved aluminosilicates. A 1.73 mM Si solution in a 9.5% HNO₃/0.5% HF acid matrix was used to prepare Fe (0.018–0.09 mM) and Al (0.074–0.37 mM) standards. Likewise, trace metal standards (10–100 µg/L) were prepared from 10 mg/L #2, #3, #4 Spex multi-element standards (Metuchen, NJ) in a matrix containing 1.73, 0.37 and 0.090 mM Si, Al and Fe, respectively. The calibration of the ICP-MS was verified by frequent recalibrations using both the Fe and Al standards and trace metal standards.

For 15 elements, the recoveries of all three standards were within 20% of the certified values, and recoveries of two of the three standards were within 12% (Table 1). The recoveries of Cd in MESS-2 and the 1999 NOAA/NIST intercalibration SRMs were low, and the RSTD was 45% for these two SRMs

with low Cd concentrations near the detection limit (~0.0012 µmol g⁻¹). In contrast, the recovery of PACS-2 at a Cd concentration of 0.019 µmol g⁻¹, which was within the concentration range of the samples in this study, was 104% and the RSTD was 23%. Concentrations of Be, Ni, Ag, Sb, and Tl in more than 10% of the field samples were below the detection limit of the method. Particulate metal concentrations were corrected based on the blank levels listed in the first column of Table 1 but were not corrected for recoveries. The precision of the replicate analyses was generally between 10% and 15% for the standard 2 mg aliquot used in this study, due primarily to physical inhomogeneity of the standard. When the procedure was scaled up using 10 mg SRM aliquots (same solid to liquid ratio and detection limits), the RSTD decreased to less than 5% (last column of Table 3).

Table 1
Quality assurance data for particulate metals

	DL ^a		Recovery (%) ^b			Relative standard deviation	
	µmol g ⁻¹	No. of samples <DL	PACS-2 (n=6)	MESS-2 (n=6)	NOAA/NIST (n=5)	Average of 3 SRM (~2 mg)	MESS-2 (10 mg)
²⁷ Al	6.3	0	109	95	102	27	13
⁵⁸ Fe	5.4	0	92	90	89	14	5
⁷ Li	0.045	0	110	105		12	3
⁹ Be	0.047	17			99	14	<DL
²⁴ Mg	1.1	0	105	89		18	4
⁴⁷ Ti	0.25	0	83			19	2
⁵¹ V	0.019	0	102	94		10	2
⁵² Cr	0.33	3	82	96	89	12	2
⁵⁵ Mn	0.055	0	104	96	88	12	2
⁵⁹ Co	0.004	0	109	107		8	2
⁶⁰ Ni	0.2	11	109	93		12	
⁶⁴ Zn	0.12	0	111	100	98	13	4
⁶⁵ Cu	0.02	0	110	104	99	16	4
⁷⁵ As	0.0045	0	116	89	93	15	3
¹⁰⁹ Ag	0.011	29	79		117	30	1
¹¹¹ Cd	0.0012			82^c	95 ^c	45	1
¹¹¹ Cd	0.0012	1	104 ^d			23	
¹¹⁷ Sn	0.0051	0	112	101	100	17	1
¹²³ Sb	0.026	21	151	107	98	10	4
²⁰⁵ Tl	0.0013	52		107		11	2
²⁰⁶ Pb	0.0012	0	110	118	100	10	1
²⁰⁹ Bi	0.0029	17	69			25	2
²³⁸ U	0.0005	0	92	70		11	2

^a Detection limit values in regular font are based on the instrumental detection limit. Values in bold font are reported as three times the standard deviation of the filter blanks (n=6).

^b Recoveries in bold are outside the 88% to 112% range.

^c Cd concentration of standard near detection limit of 0.0012 µmol/kg.

^d Cd concentration of standard is ten times the detection limit and near sample concentrations.

The particulate C and N captured by the glass fiber filters were analyzed by combustion at 1020 °C, and reduction of NO_x to N₂ at 670 °C, with a Carlo Erba EA1108 elemental analyzer equipped with an AS 128 autosampler. Standardization was performed by comparison with the integrated peak of acetanilide standards. The results of the C analyses for PACS-1 were 3.12 mmol/g (std. dev.=0.27 for *n*=16), which is within the certified tolerance value of 3.08±0.09 mmol/g. The glass fiber filters were not weighed and only particulate C and N concentrations in millimoles per liter were directly determined. The organic content of the particles was estimated by assuming that the sample volume filtered for analysis of particulate organic carbon contained the same TSM as the sample volume filtered onto the Teflon filter that was drained from the same Go-Flo bottle. Dissolved and particulate elemental data are available upon request to the author.

4. Results and discussion

4.1. Dissolved elements

Overall, the concentrations of dissolved metals determined in this study were similar to concentrations reported in recent publications that used ultra-clean methods for which analytical results were verified with low-concentration standard reference materials (Table 2). The maximum dissolved Cu, Cd and Pb concentrations found in Upper New York Bay samples, which had salinities near 25, were within 10% of the maximum of two samples (*S*=24–25) reported by Sanudo-Wilhelmy and Gill (1999). The low minimum values found in this study were probably a result of sampling bottom waters of the shipping channels that had higher salinities. Likewise, the minimum dissolved metal concentrations found in LNYB and Raritan Bays

Table 2
Ranges of concentrations of dissolved trace metal reported in various studies

Sampling date(s)	<i>n</i>	Salinity	nM				Reference
			Cu	Ni	Cd	Pb	
<i>Upper New York Bay</i>							
01/1991	2	24–25	23–28	18–25	0.78–0.80	0.26–0.53	Sanudo-Wilhelmy and Gill, 1999 Litton, 2003 Litton, 2003
	3				0.25–0.44	0.42	
	1						
08/1999	10	25–28	16–24	12–17	0.67–0.89	0.37	This Study
<i>Lower New York and Raritan Bays</i>							
01/1991	2	20–26	16–27	10–19	0.45–0.66	0.47–1.30	Battelle Ocean Sciences, 1991
10/1996 and 4/1997	4	25–30	12–19	16–20	0.61–0.81	0.09–0.62	Sanudo-Wilhelmy and Gill, 1999
11/1998 to 05/2000	8				0.36–0.60	0.48	Litton, 2003
08/1999	27	26–28	1.9–15	6–22	0.19–0.36	0.07–0.31	This study
<i>Arthur Kill</i>							
01/1991	2	18–21	39	31–37	1.42	1.3–2.1	Battelle Ocean Sciences, 1991
08/1999	3	26	16–24	24–28	0.60–0.85	0.40–0.53	This study
09/1998 to 06/2000	4				0.42–1.01		Litton, 2003
12/2000 to 11/2001	5				0.38–1.65	0.47–13.0	Pecchioli, 2003
<i>Shrewsbury River</i>							
08/1999	4	27	7.6–19	20–22	0.27–0.41	0.07–0.31	This study
<i>Raritan River</i>							
08/1999	8	21–26	7.6–15	17–22	0.80–1.03	0.22–0.77	This study
04/2001–03/2002	4				0.37–1.29	0.44–14.6	Pecchioli, 2003
<i>Coastal Water</i>							
01/1991	1	32	8.0	36	0.30	0.34	Battelle Ocean Sciences, 1991
08/1999	5	29–30	4.6	7	0.23	0.14	This study
12/1998–03/2000	3				0.17–0.24		Litton, 2003

were a result of both sampling higher salinity water and a larger sample population over a greater geographical area.

Dissolved Cu, Ni, Pb, Cd, Co and Mn in UNYB were correlated with salinity (correlation coefficients ranging between 0.74 for Cu and 0.94 for Ni as shown in Table 3), even within the narrow (3 units) salinity range. It was not surprising that the mixing lines for the higher salinity samples ($S=26\text{--}30$) from the LNYB were similar to the mixing lines for the UNYB because freshwater flow to the Lower New York Bay is dominated by Hudson River input passing through Upper New York Bay. The term “mixing line” is used in the general sense to denote the least-square linear regression of the metal with salinity and does not preclude the influence of geochemical reactions. When plotted against salinity, dissolved Cu and Ni from UNYB samples fell on the mixing line of the Lower New York Bay (Fig. 2a–b). An analysis of covariance indicated that there were no significant differences between the mixing lines of the Upper and Lower Bays for dissolved Cu and Ni (Table 3). Dissolved Pb in UNYB samples plotted slightly above the LNYB mixing line (Fig. 2c), but the slopes of the mixing lines were not significantly different. In contrast, the slope of the mixing line of dissolved Cd in UNYB was significantly different from the LNYB mixing line ($p=0.036$), and the UNYB mixing line plotted well above the LNYB mixing line (Fig. 2d). This discontinuity in the relationship between Cd and salinity was due either to geochemical reactions that removed Cd once the UNYB water mass entered the LNYB or incomplete mixing of the waters of the Hudson and East Rivers within the UNYB. As a result of the

mentioned CTD malfunction, samples were collected in UNYB near slack water. Thus, samples may have contained a disproportionately high percentage of water from the East River and may not have been representative of water that flowed into the LNYB over a complete tidal cycle. This explanation is plausible because, in order to avoid ship traffic, the UNYB samples were collected on the east side of the channel downstream of the junction with the East River. The significant input of freshwater into the East River from sewage treatment plants may explain the high Cd concentrations. The limited number of samples collected for nutrient analyses (Daniel Wieczorek, personal communication, NOAA-Fisheries, 2003) indicated that nitrate, and to a lesser extent ammonia, also exhibited mixing line discontinuity between the Upper and Lower New York Bays.

While the brackish water of the UNYB dominates the mass balances of water and salt to the LNYB, the Raritan River and the Arthur Kill are the dominant sources of brackish water to Raritan Bay. To determine the portion of a brackish water source and coastal seawater in a parcel of water in any simple estuary requires solution of mass balance equations for water and salt. Salinity in mixing plots is an implicit measure of the seawater endmember in a specific sample. However, one additional conservative tracer must be identified for each additional brackish water source in progressively more complex estuaries. In order for a dissolved metal in the waters of the Raritan River or the Arthur Kill to be useful as a chemical tracer, the dissolved metal’s relationship with salinity must be distinct from its metal–salinity relationship in the Upper and Lower New York Bays. The metal also must be

Table 3
Differences in the correlations of dissolved metal concentrations with salinity between Upper and Lower New York Bays

	Upper New York Bay ($n=10$)			Lower New York Bay ($n=21$) ^a			Difference in Slopes between Lower and Upper New York Bays
	Intercept (nM)	Slope (nM/S)	<i>R</i>	Intercept (nM)	Slope (nM/S)	<i>R</i>	
Cu	53.6	– 1.67	0.74	45.3	– 1.37	0.79	NS
Ni	71.8	– 2.17	0.94	79.2	– 2.43	0.92	NS
Pb	2.56	– 0.0794	0.89	2.82	– 0.0924	0.83	NS
Cd	3.15	– 0.0912	0.84	1.74	– 0.0508	0.87	$p=0.036$
Co	11.7	– 0.368	0.90	6.9	– 0.205	0.74	NS
Mn	2990	– 97	0.90	- -	- -	0.02	

- -: Slope and intercept of dissolved Mn with salinity in Lower New York Bay were not statistically significant.

NS—slopes not significantly different at the $p=0.05$ level.

^a LNYB includes the two Rockaway–Sandy Hook (RS) transect stations shown in Fig. 1.

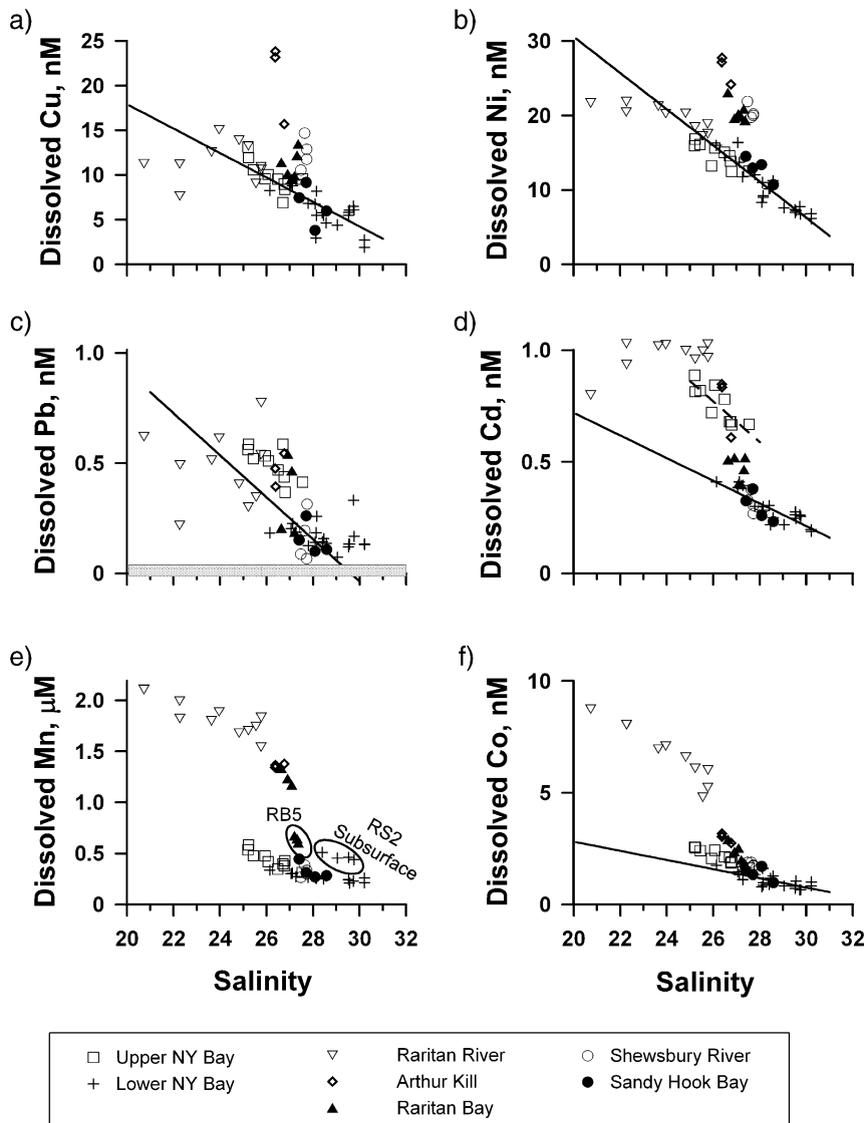


Fig. 2. Concentration of dissolved metal as a function of salinity for (a) Cu, (b) Ni, (c) Pb, (d) Cd, (e) Mn, (f) Co. The open symbols represent the sources of brackish water (Upper New York Bay, Arthur Kill, Raritan River and Shrewsbury River) entering the Lower New York–Raritan–Sandy Hook Bays system (plus sign and filled symbols). The solid lines are the linear regressions of the metals with salinity in the Lower New York Bay (Table 3), except for dissolved Mn that was not statistically correlated with salinity. The dotted line for Cd is the regression for the Upper New York Bay. Dissolved Pb concentrations in the high salinity water were near the detection limit, which is shown as the shaded area.

conservative over the period that the water mass flows through the estuarine system. In the following discussion, the utility of Cu, Ni, Pb, Cd, Co and Mn as chemical tracers for water masses emanating from the Raritan River and the Arthur Kill is examined.

Dissolved Ni, Cu, Pb and Cd in the Raritan River and Bay, Arthur Kill, Sandy Hook Bay, and the

Shrewsbury River deviated from the LNYB mixing lines in a variety of ways (Fig. 2a–d). Dissolved Cu and Ni in the Raritan River were both slightly below the LNYB mixing lines at salinities less than 23 (Fig. 2a–b) but were indistinguishable from the LNYB mixing lines for S between of 23 and 25. However, dissolved Ni and Cu concentrations in the Arthur Kill

and the Shrewsbury River showed elevated concentrations relative to the LNYB mixing line. For the entire data set, dissolved Cu and Ni were correlated ($r=0.82$) with no Cu:Ni data outside the general scatter of the plot. Therefore, both Ni and Cu are good candidates for a chemical tracer for the Arthur Kill and/or Shrewsbury River, but neither Ni nor Cu is chemical tracers for the Raritan River.

Dissolved Pb concentrations in the Raritan River were generally less than 0.63 nM, except for one sample along the shore adjacent to industrial facilities. Like Cu and Ni, dissolved Pb in the Raritan River generally plotted below the LNYB mixing line for salinities less than 24. Above salinity 24, however, Pb became indistinguishable from the LNYB mixing line (Fig. 2c). Dissolved Pb concentrations from the Arthur Kill samples were about 0.5 nM and were not distinguishable from UNYB samples. Dissolved Pb in samples from Sandy Hook Bay and the Shrewsbury River ranged between 0.09 and 0.31 nM and were scattered around the LNYB mixing line.

In contrast to Ni, Cu and Pb, the concentrations of dissolved Cd in the Raritan River plotted significantly above the LNYB mixing line (Fig. 2d). The curvature of the dissolved Cd relations with salinity in the Raritan River suggested an additional input, either through direct discharge, contaminated runoff or release from sediments. Like Cu and Ni, dissolved Cd concentrations indicated that either the Arthur Kill or the Raritan River was influencing the water chemistry of samples well into Raritan Bay. However, because the concentrations of dissolved Cd in the Arthur Kill samples fell between those in the Raritan River and in the Raritan Bay, it is impossible to use Cd to distinguish the influences of the Raritan River from those of the Arthur Kill.

Dissolved Mn and Co concentrations in the Raritan River were clearly distinguishable from those in samples collected in LNYB, thereby allowing the influence of the Raritan River to be followed into Raritan Bay (Fig. 2e–f). Strong correlations between Co and Mn have been known since early investigations on oceanic manganese modules were undertaken (Calvert and Price, 1977; Moorby and Cronan, 1981). Concurrent release of Mn and Co from estuarine sediments has also been observed (Sunby et al., 1986). Dissolved Mn and Co concentrations in inner Raritan Bay (RB1 and RB3) and southern Arthur Kill plot

between the metal's concentration in LNYB and the Raritan River. Although dissolved Co in inner Raritan Bay (RB5) fell along the LNYB mixing line, dissolved Mn in outer Raritan Bay was elevated relative to concentrations in most of LNYB. When dissolved Co was plotted against dissolved Mn (not shown), only samples from RB5 and subsurface samples from RS2 (Ambrose Channel) deviated from a tight correlation suggestive of local sedimentary inputs of dissolved Mn. In another study, high concentrations of porewater Mn were found in Raritan Bay (Luther et al., 1999), indicating that diffusion from the sediments was probably the cause of this deviation in Mn:Co relationships. Dissolved Co provided a distinct geochemical signature for the Raritan River and seemed to be a better tracer of mixing within Raritan Bay because of non-conservative Mn behavior.

When dissolved Co was plotted against dissolved Ni (Fig. 3), three water masses were clearly distinguishable. Raritan River water was observed at high dissolved Co and moderate dissolved Ni concentrations. In contrast, high Ni concentrations and above average Co concentrations set the Arthur Kill, Raritan Bay and the Shrewsbury River apart from the LNYB and the Raritan River. All Raritan Bay and Shrewsbury River samples exhibited chemical characteristics distinct from the Lower New York Bay and clearly exhibited significant contributions from the Arthur Kill. It is not clear if the high Ni concentrations in Raritan Bay and the Shrewsbury River originated directly within the Arthur Kill or were a result of sedimentary diagenic processes within Raritan Bay. If dissolved Mn was released into the water column of the Raritan Bay, it is possible that Ni was also released from the Ni-enriched Raritan Bay sediments (Greig and McGrath, 1977). Numerical mixing calculations based on Ni should be used with caution because the conservative nature of Ni in this system is in question. It appears that Raritan Bay and Shrewsbury River samples originated as a mixture of waters from Arthur Kill and Lower New York Bay. Biogeochemical models, such as the system-wide eutrophication model being developed for the New York/New Jersey Harbor area and the New York Bight, are built upon the numerical models of water transport. Just as the GEOTRACES program is proposing to use geochemical tracers to characterize ocean water masses (Frank et al., 2003), dissolved Ni and Co determinations allow

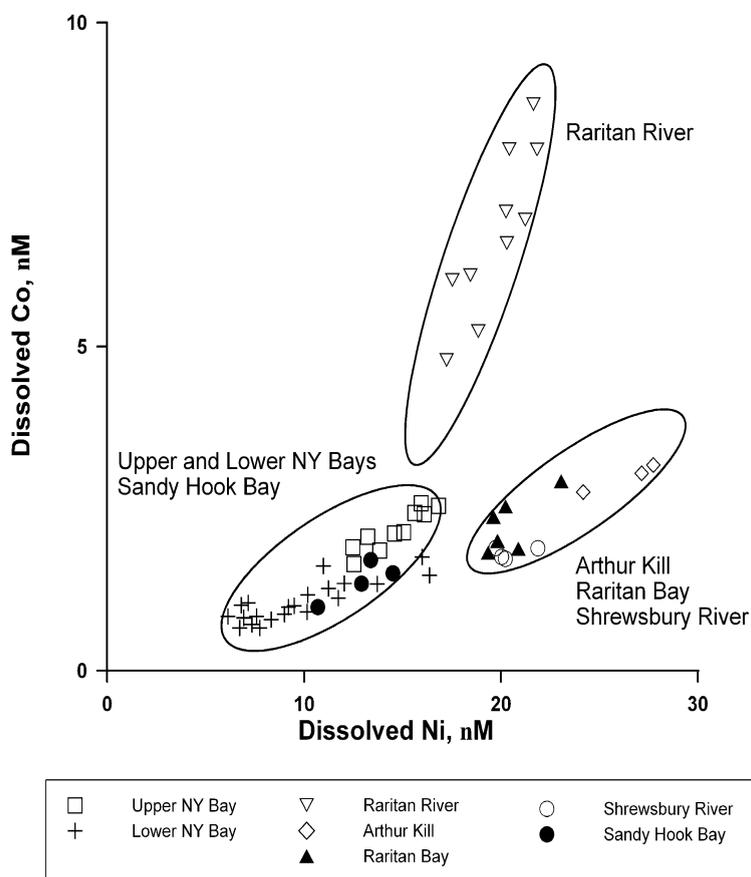


Fig. 3. Relationship of dissolved Ni to dissolved Co showing three groupings of water samples.

identification of distinct water masses in the Raritan Bay. In particular, Shrewsbury River water exhibited a chemical signal similar to that of Raritan Bay water and was distinct from Sandy Hook Bay water. This new insight into the mixing of water of this complex estuary should help constrain physical models of circulation in the entire New York Bight. Dissolved metal determinations should not be limited to environmentally interesting toxic metals (Hg, Cd, and Pb). Other dissolved metals can provide information about transport and biogeochemical processes that control all constituents, natural and anthropogenic.

4.2. Elemental composition of suspended matter

In UNYB, maximum surface total suspended matter (TSM) concentrations were 5.1 mg/L and the bottom boundary layers were more turbid (11.8 and 27.3

mg/L TSM). In the surface waters of LNYB, TSM concentrations were generally between 2 and 4 mg/L and increased slightly with depth to about 5 mg/L. Maximum surface concentrations in the Raritan River were 7.5 mg/L and generally decreased with depth. A large surface TSM concentration in the Raritan Bay at its junction with the Arthur Kill and the Raritan River was the result of a ship passing the station just prior to sampling. Maximum surface concentrations of TSM in the Shrewsbury River and Sandy Hook Bay were 6.2 and 8.1 mg/L, respectively. Bottom TSM concentrations in Sandy Hook Bay were higher (11 mg/L) than those in the Lower New York Bay, possibly due to the influences of the turbid bottom boundary layer in the Shrewsbury River channel (TSM=18.6 and 28.3 mg/L). The correlations of TSM with salinity in all regions were weak, suggesting that settling of particles and resuspension were the dominant trans-

port mechanisms rather than estuarine advection of particles.

Concentrations of Fe in surface suspended matter collected from Lower New York, Sandy Hook and Raritan Bays ranged between 50 and 365 $\mu\text{mol g}^{-1}$, while the two surface samples in the UNYB contained 550 and 575 $\mu\text{mol g}^{-1}$. Dilution of terrestrial inorganic suspended matter by marine particulate organic matter appeared to be the dominant process controlling the metal concentrations of suspended matter. In Lower New York and Raritan Bays, particulate organic carbon concentrations ranged from 23 to 71 μM (with an average of 34.8 μM). The C:N atom ratios of the suspended particles averaged 5.5, suggesting significant marine productivity in this nutrient enriched system. Estimated mean organic carbon content was 9.2 mmol/g, with a maximum of 26 mmol/g. Particulate Fe concentrations generally increased with depth to a maximum of 900 $\mu\text{mol g}^{-1}$, while organic carbon content decreased with depth.

The process of identifying which of the 22 elements might provide a chemical signal for specific sources of suspended matter required a systematic approach. The dilution of metal-rich terrestrial inorganic material by

metal-poor marine organic matter was considered by normalizing all elemental concentrations to Fe concentrations. In the first step, particulate elemental concentrations for the entire set of particulate samples from all geographical regions were regressed against particulate Fe and the resulting correlation coefficients were examined. A high correlation with Fe for the entire sample set indicates that the particulate ratio (element:Fe) was fairly constant throughout the study area. In contrast, lack of a strong correlation with Fe may simply be due to general scatter of the analytical data, especially at concentrations near the detection limit. Significant differences in the element ratios among the seven regions (UNYB, LNYB, Raritan River and Bay, Arthur Kill and Sandy Hood Bay, and Shrewsbury River) would also result in a low correlation coefficient when regressions were performed on the entire data set. The particulate ratios of major elements (>0.001) and minor elements (ratio <0.001) were separately categorized into three groups according to their correlation coefficients with Fe (Table 4). Significant differences in the slopes of the elemental relationship to Fe among the seven regions were then identified by performing an analysis of covariance on the elemental concentrations

Table 4
Correlation coefficients and slopes of elements with Fe in suspended matter

Major elements				Minor elements			
Element	Slope	Regression coefficient	Covariance ^a <i>p</i> values	Element	Slope $\times 10^3$	Regression coefficient	Covariance ^a <i>p</i> values
<i>R</i> < 0.5							
				Sb	0.09	0.174	0.88
				Bi	0.014	0.271	0.71
				Tl	0.003	0.334	0.85
				Ag	0.085	0.482	0.67
<i>0.5</i> < <i>R</i> < <i>0.8</i>							
Mn	0.125	0.514	0.001	U	0.021	0.588	0.031
Pb	0.0021	0.715	0.56	Sn	0.31	0.702	0.44
Al	2.25	0.734	0.092	As	0.65	0.753	0.0004
<i>R</i> > 0.8							
Zn	0.0074	0.883	0.34	Cd	0.029	0.839	0.0051
Cr	0.0059	0.892	0.152	Co	0.43	0.897	0.012
Ni	0.00162	0.894	0.018				
Cu	0.0040	0.904	0.12				
Ti	0.084	0.906	0.074				
V	0.0034	0.942	0.103				

^a Indicated the probability that element:Fe relationships in the different regions were the same.

with Fe concentrations as the confounding factor (SAS Institute, Inc., 1989).

Six major elements (Zn, Cr, Ni, Cu, Ti, and V) were highly correlated with Fe ($R > 0.8$ in Table 4), but only Ni (Fig. 4a) exhibited significant differences in Ni:Fe relationship among regions (Upper New York Bay > Raritan River and Sandy Hook–Shrewsbury River). Particulate Mn concentrations were moderately correlated with particulate Fe concentrations, and analysis of covariance indicated significant differences among regions. The high concentrations of particulate Mn (between 70 and 200 $\mu\text{mol g}^{-1}$) in several samples collected in Raritan Bay and in the Shrewsbury River (Fig. 4b) suggested that dissolved Mn was transferred to suspended matter. Particulate

Pb was moderately correlated with particulate Fe, but analysis of covariance indicates that the variations in the Pb:Fe ratio were not correlated with region.

Several minor elements exhibited significant differences among regions (Table 4). The analysis of covariance indicated significant difference in the Cd:Fe relations among regions, with Sandy Hook Bay having slightly higher Cd:Fe ratios (Fig. 4c). The most significant difference among regions was observed for the minor element As (Fig. 4d), with the Raritan River having significantly higher As:Fe ratios than all other regions. At a particulate Fe concentration of 350 $\mu\text{mol g}^{-1}$, particulate As concentrations in the Raritan River ranged between 0.25 and 0.80 $\mu\text{mol g}^{-1}$, while those in the LNYB aver-

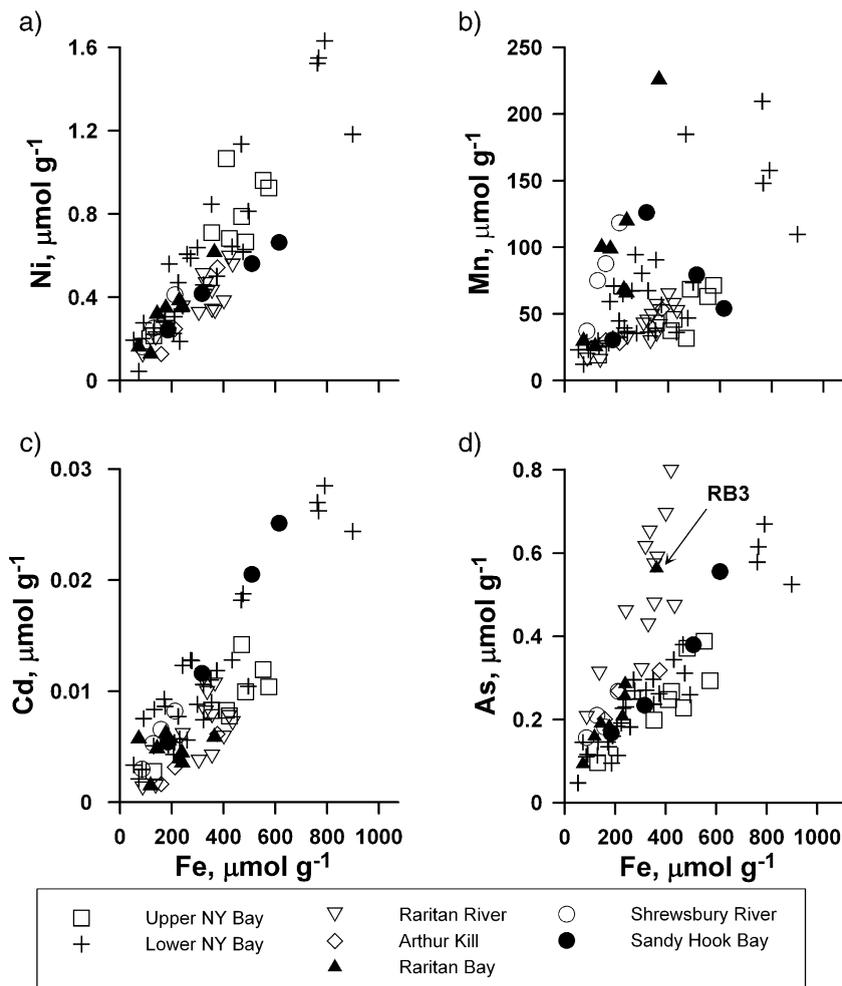


Fig. 4. Relationship of particulate element concentration to particulate Fe concentrations for (a) Ni, (b) Mn, (c) Cd, and (d) As.

aged about $0.25 \mu\text{mol g}^{-1}$. Also, note that one sample in inner Raritan Bay (RB 3) also had a high As:Fe ratio. While the overall correlation (0.90) between particulate Co and Fe was high (Table 4), the analysis of covariance detected significant differences in the Co:Fe relationship among regions ($p=0.012$). Particulate Sn and U exhibited moderate correlations with particulate Fe, but significant differences in the correlations with particulate Fe among regions were detected only for U. The low correlations of particulate Sb, Bi, Tl and Ag with particulate Fe were mainly due the general scatter caused by concentrations at or slightly above detection limits and were not related to geographical distribution.

Principal component analysis (SAS Institute, Inc., 1989) was used to differentiate the chemical signals of particulate matter emanating from Upper New York Bay and from the Raritan River. Elements for which the analysis of covariance detected significant differences ($p<0.05$) in the correlations with Fe (Ni, Co, As and U) were included in the principal component analysis. With the inclusion of Ni, 11 samples were eliminated from the PCA because of concentrations below the detection limit. Since the chemical signals of particulate matter in Lower New York, Raritan, and Sandy Hook Bays are being compared to brackish water sources, elements that were likely enriched in particulate matter due to geochemical reactions (Mn and Cd) were not included in the PCA. Also included in the PCA were Ti, V, Cu, Cr and Al data, for which the probability of significant differences among regions ranged between 0.05 and 0.15.

The plot of principal components (PC) 2 versus 3, both having large eigenvectors for As, clearly distinguished Raritan River from UNYB (Fig. 5). Raritan River particles were clustered in the upper left quadrangle of the plot, whereas UNYB particles clustered along a diagonal line originating in the upper right quadrangle. Most of the particulate samples from inner Raritan Bay were positioned near the Raritan River cluster, but two of the three samples from outer Raritan Bay (RB5) fell near the UNYB cluster. This would suggest that the extent of the As signal from Raritan River particles was limited to inner Raritan Bay. PC 1 had a small eigenvector for As (0.03), and thus was not useful in distinguishing Raritan River particles from those of UNYB. Most of the LNYB particle samples were centered about the UNYB cluster.

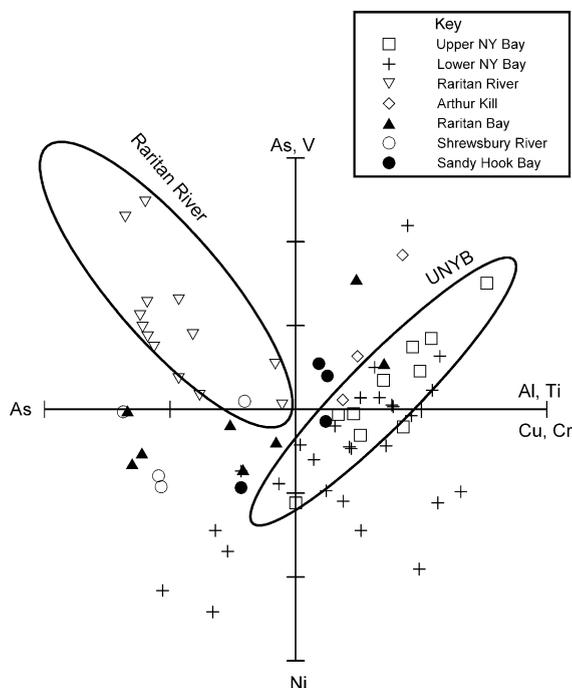


Fig. 5. The elemental composition of suspended matter displayed as component 2 versus component 3 from a principal component analysis using Fe, Ti, Ni, Co, As, U, V, Cu, Cr, and Al concentrations. The elements with the largest eigenvectors for each component are identified at the end of each component axis. The clusters for the Raritan River and the Upper New York Bay are circumscribed with ovals.

ter. The particles from Sandy Hook Bay were located either within or slightly above the UNYB and LNYB cluster. In contrast, particles from the Shrewsbury River were positioned closer to the Raritan River cluster.

It has been suggested that one of the primary modes of sediment and contaminant transport in the New York Bight is resuspension of particles within the bottom boundary layer (BBL) (Young et al., 1985). This contention can be examined for the transfer of Hudson River particles through Lower New York Bay to the Hudson Shelf Valley. In August 1995, at a time when instantaneous surface TSM concentrations varied between 4 and 91 mg/L (Feng et al., 2002), suspended particles (2-h averages) in surface water from the Hudson River had an average Pb:Fe molar ratio of 0.0011. If Hudson River suspended matter was the sole source of inorganic particles to LNYB and was diluted by organic matter, the

composition of suspended matter would fall along the dotted line in Fig. 6. All the samples of suspended matter samples from UNYB collected in August 1999 and a majority collected from LNYB plotted above this line. This difference may have been due to temporal differences (1995 versus 1999) in the Hudson River conditions, to the mass of Pb discharged into UNYB from New York City sources, or to the much higher suspended matter concentrations in Hudson River surface waters compared to those in the LNYB. In August 2000, samples of suspended matter were collected less than 10 m above the bottom of the Hudson Shelf Valley of the New York Bight (by the Marine Geology and Geophysics Program of the U.S. Geological Survey). Samples were analyzed in a man-

ner identical to the methods described in this study. For Fe concentrations less than $400 \mu\text{mol g}^{-1}$, the regression of Pb versus Fe from particles suspended in the BBL of the Hudson Shelf Valley was 0.0083. Since this Pb:Fe ratio is only slightly lower than the ratio from the Hudson River, the dotted line representing dilution of Hudson River particles by organic matter falls quite near the regression line of Hudson Shelf BBL particles. The suspended matter composition of the particles in the BBL of the Hudson Shelf Valley represents a time-averaged input to the New York Bight, which could include inputs from the sludge dumpsite at the head of the Hudson Shelf Valley. The higher Pb:Fe ratios in UNYB and LNYB during lower flow conditions relative to

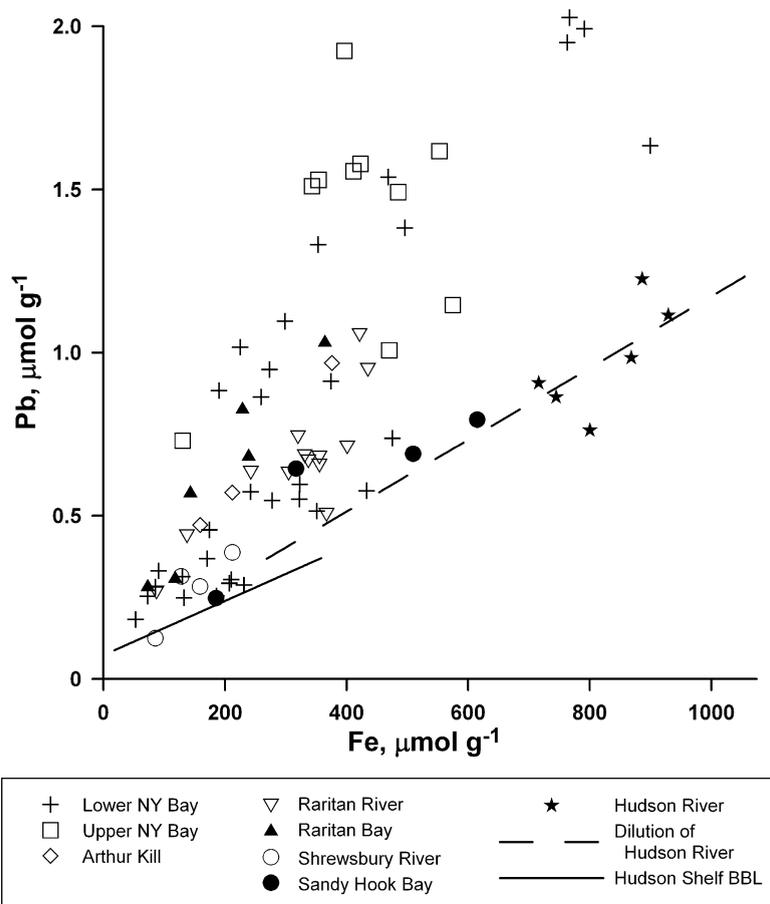


Fig. 6. Particulate Pb versus particulate Fe concentrations for this study, using surface suspended matter collected from the Hudson River in August 1995 (Feng et al., 2002), and particles collected within the bottom boundary layer of the Hudson Shelf Valley by Marine Geology and Geophysics Program of USGS during 2000 (the solid line). The dotted line is the extension of the Pb:Fe relationship in the Hudson River to lower Fe concentrations.

those in the Hudson River or those in the BBL of the Hudson Shelf Valley could be due to differences in either sources or the effects of physical processes. During the low-flow sampling of this study, sewage-derived solids may have contributed a high portion of the suspended matter, and their high metal content may have elevated metal concentrations of suspended matter above the concentrations of terrestrial minerals. In contrast, the particle size of the suspended matter collected in Lower New York Bay at low TSM concentrations (2 mg/L) was probably smaller than that found in the Hudson River at higher suspended matter concentrations. As the larger sized, less enriched suspended matter in the Hudson River settled from the water column, the remaining smaller suspended matter that entered the Upper and Lower New York Bays probably became enriched in metals.

5. Conclusion

Dissolved metal concentrations in the Upper New York Bay (UNYB) and Lower New York Bay (LNYB) in August 1999 were comparable to those found in other recent studies. Cu, Ni, and Pb relationships with salinity in the LNYB ($26 \leq S \leq 30$) were not significantly different than those for the UNYB ($25 \leq S \leq 28$). This observation is consistent with the fact that most of the freshwater flowing into the LNYB originates from the Hudson River via the UNYB. Concentrations of dissolved Cu, Ni and Pb in the Raritan River plotted below the LNYB mixing line, while dissolved Ni and Cu in the Arthur Kill plotted above the LNYB mixing line. Dissolved concentrations of the biogeochemically active elements Mn and Co in the Raritan River were significantly elevated relative to Upper New York Bay. Dissolved Cd concentrations in the UNYB were significantly higher than in the LNYB, suggesting that Cd may have been transferred from the dissolved phase to the particulate phase in LNYB. Correlations of dissolved Mn with salinity and with other dissolved elements also suggest that Mn was diffusing out of Raritan Bay sediments.

Elevated concentrations of dissolved Co and Ni proved to be excellent geochemical signals for water contributions of the Raritan River and the Arthur Kill, respectively, and together allowed water masses from

the Raritan River, the Arthur Kill and the Upper Bay to be easily distinguished. The use of these two tracers should facilitate models of physical mixing at the complex junction of the Raritan River and the Arthur Kill with Raritan Bay.

Total suspended matter concentrations were low (2–4 mg/L) in the surface waters of LNYB, even though inflowing brackish sources had higher surface concentrations (5–8 mg/L). The elemental composition of suspended matter was highly correlated with particulate Fe concentrations. A systematic approach was developed for examining the utility of 22 elements as distinctive geochemical indicators of suspended matter sources. Analysis of covariance highlighted differences in correlations of particulate elements with particulate Fe among geographical regions within the study. Significant differences in the correlations of particulate Mn and Cd with particulate Fe were attributed to geochemical reactions within the study area rather than geochemistry of source particles. The analysis of covariance indicated that the elements commonly associated with pollution were of limited (Cu and Cr) or no use (Zn and Pb) for discrimination among particulate sources. Of the major elements thought not to have undergone geochemical reactions within the study region, only the relationship of Ni with Fe was found to be significantly different among geographical regions. In contrast, minor element relationships with Fe were highly valuable in identifying significant differences among regions. In particular, elevated particulate arsenic (As) concentrations were found in the Raritan River. A principal component analysis (PCA) was conducted using the particulate concentrations of Fe, Al, Ti, V, Cu, Cr, Ni, As, Co and U. A plot of principal components 2 and 3 indicated that LNYB particles had a geochemical signature similar to that of the UNYB, and that the influence of the As signature of the Raritan River was limited to inner Raritan Bay.

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