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Contaminant Distribution and Accumulation in the Surface Sediments of Long Island Sound

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ABSTRACT

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The distribution of contaminants in surface sediments has been measured and mapped as part of a U.S. Geological Survey study of the sediment quality and dynamics of Long Island Sound. Surface samples from 219 stations were analyzed for trace (Ag, Ba, Cd, Cr, Cu, Hg, Ni, Pb, V, Zn and Zr) and major (Al, Fe, Mn, Ca, and Ti) elements, grain size, and *Clostridium perfringens* spores. Principal Components Analysis was used to identify metals that may co-vary as a function of common sources or geochemistry. The metallic elements generally have higher concentrations in fine-grained deposits, and their transport and depositional patterns mimic those of small particles. Fine-grained particles are remobilized and transported from areas of high bottom energy and deposited in less dynamic regions of the Sound. Metal concentrations in bottom sediments are high in the western part of the Sound and low in the bottom-scoured regions of the eastern Sound. The sediment chemistry was compared to model results (SIGNELL *et al.*, 1998) and maps of sedimentary environments (KNEBEL *et al.*, 1999) to better understand the processes responsible for contaminant distribution across the Sound. Metal concentrations were normalized to grain-size and the resulting ratios are uniform in the depositional basins of the Sound and show residual signals in the eastern end as well as in some local areas. The preferential transport of fine-grained material from regions of high bottom stress is probably the dominant factor controlling the metal concentrations in different regions of Long Island Sound. This physical redistribution has implications for environmental management in the region.

ADDITIONAL INDEX WORDS: *Metals, trace metals, major elements, grain size, texture, estuaries, multivariate statistics.*

INTRODUCTION

Long Island Sound is a major urban estuary along the east-coast of the United States, bordered on the north side by the State of Connecticut and on the southern shore by Long Island, NY (Figure 1). The western end narrows and connects to the New York metropolitan area through the East River. The eastern end is bounded by Block Island and Fishers Island Sounds.

Semi-enclosed estuaries, such as Long Island Sound, are typically subject to enhanced anthropogenic impacts due to the restricted transport and dispersal of contaminants (O'CONNOR and EHLER, 1991). Contaminants are introduced into the Sound from sewage effluent, disposal of dredged material, industrial discharge, urban and agricultural runoff, atmospheric deposition, and combined inputs from major rivers. These contaminants, with their low solubility, are then scavenged from the water column by adsorption onto sediment particles. Knowledge of the magnitude of contaminant concentration in sediments is important for regulation of contaminant discharges as well as management of the natural resources throughout the Long Island Sound watershed.

A geochemical study of Long Island Sound was undertaken to understand the regional concentrations, distribution, and fates of contaminants in sediments as a component of a larger study by the U.S. Geological Survey. In this paper, we present the results of the metal analyses in the surface sediments of the Sound. Concentration distributions were mapped and multivariate statistical analysis was used to identify metal co-variances that imply common sources or behaviors. We also discuss the regional distribution of contaminants and their possible transport and dispersal paths.

Previous studies of contaminant geochemistry in Long Island Sound sediments: (1) documented impacts of industrialization and urbanization in the 20th century (GREIG *et al.*, 1977; BRICKER *et al.*, 1992; BROWNAWELL *et al.*, 1992); (2) showed local areas where metal concentrations occurred at levels above background (ROBERTSON *et al.*, 1991; MOFFETT *et al.*, 1994; VAREKAMP, 1996; VAREKAMP and SCHOLAND, 1996; KREULEN *et al.*, 1998; BENOIT *et al.*, 1999); and (3) measured higher anthropogenic metal concentrations near dredge material dumpsites (SCHUBEL *et al.*, 1979; BOOTHMAN, 1988; FREDETTE *et al.*, 1992). Other studies have examined the grain-size distribution (MCCRONE, 1966; POPPE and POLLONI, 1998), organic-carbon distribution (HUNT, 1979; HARRIS, 1997), the hydrogen and nitrogen distributions

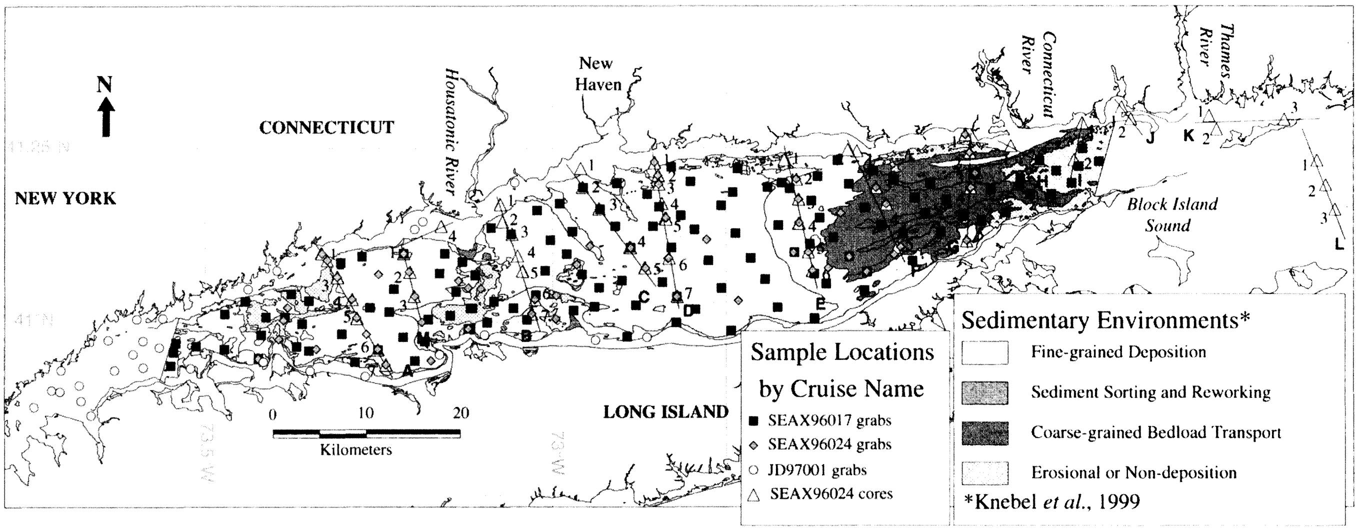

Figure 1. Locations of surface sediment samples taken on three cruises to Long Island Sound aboard the R/V Seaward Explorer and the R/V John Dempsey. Stations were selected to representatively sample the different sedimentary environments, sediment types, and proximity to potential metals sources in the Sound. Sedimentary environments from KNEBEL *et al.* (1999) have been superimposed.

(POPPE *et al.*, 1996), and have discussed diagenesis and anoxia in sediments (ALLER, 1980a,b; HULTH *et al.*, 1999). This work offers a regional view of metal contaminants and the processes responsible for their observed distributions.

STUDY AREA

This section highlights those aspects of the geography, topography, and hydrodynamics of Long Island Sound which pertain to the interpretation of geochemical data. A more extensive account of the geomorphology of the Sound is presented by KNEBEL and POPPE (this volume), while details of Long Island Sound hydrodynamics can be found in SIGNELL *et al.* (this volume).

Geography

The northern shoreline of Long Island Sound is characterized by numerous bays, inlets, populated urban areas, and major river systems. In contrast, most of the shoreline on the Long Island, NY side is characterized by bluffs with relatively few embayments and little riverine input (KOPPELMAN *et al.*, 1976). The western end has both urbanization and communication with the Hudson River estuary. The major watersheds along the Connecticut coastline include the Thames River, the Connecticut River, the Quinnipiac River, and the Housatonic River (Figure 1), which contribute large volumes of sediment to the Sound (ZIMMERMAN *et al.*, 1996; LEWIS and DIGIACOMO-COHEN, this volume). The total watershed area is 4.41×10^4 km^2 and is dominated by the Connecticut River, which flows through urban, agricultural, and forested areas in New Hampshire, Vermont, Massachusetts, and Connecticut (WOLFE *et al.*, 1991).

In addition to watershed sources, the sediment geochemistry in Long Island Sound is affected by urban runoff, atmospheric transport, and direct industrial discharge (FARROW *et al.*, 1986). There are 313 direct industrial and municipal sewage sources along both the Connecticut and New York shorelines (STRATEGIC ASSESSMENTS BRANCH, 1990). The total volume of this sewage is estimated to be 1.5×10^9 m^3/yr where 85% is discharged to the western basin, 11% to the central basin, and 4% to the eastern basin (FARROW *et al.*, 1986). Lead (Pb) is the contaminant most often associated with atmospheric transport and urban runoff. Copper (Cu), chromium (Cr), cadmium (Cd), mercury (Hg), and zinc (Zn) are derived primarily from industrial and municipal wastewater discharge. Heavily populated, industrial cities along the Connecticut coast (such as New Haven, Bridgeport, and Norwalk) can potentially impact the Long Island Sound ecosystem (LANGSTAFF, 1990). The western end of Long Island is also densely populated with potential contaminant sources in the cities of Port Washington, Port Jefferson, the borough of Brooklyn, and waters from the East River, which pass through New York City.

Bottom Topography

Long Island Sound is a complex geological system best described by KNEBEL and POPPE (this volume). The general feature that affects the sedimentation is the division of the Sound into areas that have distinct patterns of sedimentary environments. The easternmost part of the Sound is relatively narrow, and the bottom is scoured by tidal currents. The bottom topography near the Connecticut River is quite irregular and includes a series of tidal ridges and channels trending east-northeast to west-southwest (FENSTER *et al.*, 1990; LEWIS and STONE, 1991; FENSTER, 1995; KNEBEL *et al.*, 1999). Towards the west, the width of the Sound increases, tidal scour decreases, and the irregular topography generally disappears (LEWIS and STONE, 1991; KNEBEL *et al.*, 1999). The central and western basins are characterized by smooth bottom topography and depositional sedimentary environments (KNEBEL *et al.*, 1999).

The central and western basins are demarcated by large shoal complexes that are located off of the cities of Stratford and Norwalk, Connecticut. The shoal complexes trend north-south across the Sound and are comprised of topographic highs and lows with a maximum relief of about 40 m (KNEBEL and POPPE, this volume). In addition, the smooth topography of the central and western basins is cut by an axial depression that is about 77 km long and about 50–60 m deep where it cuts across the shoal complexes (KNEBEL and POPPE, this volume).

Sediments with high percentages of fine-grained sediment (clay <4 μm + silt <63 μm) were found in the deeper central and western portions of the Sound that are characterized by KNEBEL and POPPE (this volume) and KNEBEL *et al.* (1999) as depositional environments. Sediments with the lowest percentages of fine material appear in regions where winnowing by currents is a factor in their removal (SIGNELL *et al.*, 1998, this volume; KNEBEL and POPPE, this volume).

Hydrodynamics in the Sound

The Sound has a mean water depth of 20 m and a mean residence time of 166 days (STRATEGIC ASSESSMENTS BRANCH, 1990). Semidiurnal tides dominate the circulation and cause currents which flow nearly parallel to the trend of the Sound (RILEY, 1956; GORDON and PILBEAM, 1975; BOKUNIEWICZ and GORDON, 1980; IANNIELLO, 1981; KENEFICK, 1985; SIGNELL *et al.*, 1998, this volume). Tidal circulation is especially vigorous in the constricted areas at the eastern end of the Sound where current speeds can reach 80 cm/s (SIGNELL *et al.*, 1998). Wind- and wave-driven circulation, resulting from storms, can cause residual bottom currents as well. Wind-driven bottom currents are strongest when storm winds blow parallel the axis of the basin and have maximum fetch. The effects of wave action on the bottom are mainly limited to water depths of 20 m or less. Nontidal, or density-driven, estuarine circulation is present within the Sound throughout the year, but plays a lesser role in the overall transport of sediment (GORDON and PILBEAM, 1975).

METHODS AND ANALYSIS

Field Operations

Surface sediments were collected using a Van Veen grab sampler equipped with a video and still camera system. The R/V *Seaward Explorer* was used on two cruises in 1996 to collect 191 samples from 130 stations within Long Island Sound (Figure 1). The first cruise (SEAX96017) selected sample sites to verify the sidescan sonographs that were used to interpret the sedimentary environments (KNEBEL and POPPE, this volume). Samples on the later cruise in 1996 (SEAX96024) were taken in a series of north-south transects from the Connecticut shoreline towards Long Island to measure the spatial distribution of contaminants across the Sound. A third cruise (JD97001), aboard the R/V *John Dempsey* in 1997 (POPPE and POLLONI, 1998), collected surface sediment samples from the westernmost end of Long Island Sound. The combined samples from all of the cruises provided an even sample distribution throughout the Sound. Samples were obtained only from those grabs that appeared minimally disturbed and had visible interface features. The upper 2-cm of sediment were removed from the Teflon-coated grab using acid-washed and methanol-rinsed tools to prevent sample contamination. Sediment was placed in acid-washed, polyethylene containers, sealed, and those destined for chemical analysis were stored frozen. Salinity in the bottom water was also measured at selected stations during each cruise.

Laboratory Sample Analysis

Aliquots of the wet sediment were sampled in the laboratory using acid-washed, titanium tools. Samples for chemical analysis were freeze-dried to constant weight and the water content was calculated from mass lost. A total acid digestion was performed on 0.1200 g (± 0.0005 g) of the dried sample using hydrofluoric, nitric, perchloric, and hydrochloric acids under microwave-induced pressure (MURRAY and LEINEN, 1996). Analysis of major and trace metals in solution followed standard procedures of inductively coupled plasma atomic emission spectroscopy (ICP-AES) and graphite furnace atomic absorption spectroscopy (GFAAS). Concentrations of 16 elements were reported in μg/g dry sediment for the trace metals (silver (Ag), barium (Ba), Cd, Cr, Cu, Pb, manganese (Mn), nickel (Ni), vanadium (V), Zn, and zirconium (Zr)) and in weight percent (dry sediment) for the major elements (aluminum (Al), calcium (Ca), iron (Fe), and titanium (Ti)). Hg concentrations were reported in μg/kg dry sediment after strong acid leach and elemental analysis (see VAREKAMP *et al.*, this volume). *Clostridium perfringens* concentrations were reported in spores/g dry sediment (see BUCHHOLTZ TEN BRINK *et al.*, this volume).

Experimental and procedural yields and variability from the ICP-AES and the GFAAS were determined by simultaneously extracting and analyzing Standard Reference Materials (SRMs) along with a high-concentration sediment sample in triplicate. The SRMs and the method blanks were also analyzed in triplicate; results for each SRM analysis were within 10% of the accepted value. Sample replicates were within 5% of the mean value. Maximum salt content was calculated by measuring the salinity and the mass of water lost from representative samples. The salt calculation was performed to assess the effects on mass and metal content from the salts. The mass of salt remaining was determined to be less than 5% of the total mass of the sample. The mass difference and the resulting metal concentrations from the salts were within the error of analysis for all samples.

The grain-size distributions were measured on wet sample aliquots from each surface sample site using the method reported in POPPE and POLLONI (1998). Samples were disaggregated and wet sieved to separate the fine- and coarse- size fractions. The fine (silt and clay) fractions were analyzed on a Coulter Counter and the coarse fraction (>63 μm) by sieving and a rapid sediment analyzer. The grain-size data were corrected for salt and reported as weight percent of the total sample.

Data Analysis

Two methods were employed to assess the regional metal distribution in Long Island Sound. These were: (1) surface mapping and geographic information system (GIS) analysis using spatial contouring by triangulation techniques; and (2) multivariate statistics by Principal Components Analysis (PCA) (GRANT, 1990; BUCKLEY and WINTERS, 1992; BUCKLEY *et al.*, 1995; DAVIES, 1997). Contoured maps of contaminant distributions in Long Island Sound were used to subjectively classify the metals into groups based on known geochemical behaviors and common sources. PCA was used to objectively identify groups of elements that statistically covaried.

When comparing geochemical parameters, it is common to do regression analysis to examine the correlation of one variable to another. However, each variable may be correlated with several other variables and this multiple-variable correlation can be accomplished using PCA. In this statistical technique, the interrelations between a large set of variables are reduced to a number of factors containing related variables. The structure of these factors, or the variables contained in them, is the basis for identifying common characteristics by objective grouping of the parameters.

The data set used for the PCA contained 18 measured parameters and 219 samples from Long Island Sound. This raw data matrix was imported to StatView (SAS INSTITUTE INC., 1998) where the PCA was performed. A series of eigenvalues were identified; four of which were >1 and thus considered to represent statistically significant groups of parameters (KAISER, 1960). A VARIMAX orthogonal rotation was then performed on the factor/analysis matrix to further define the magnitudes of the variables in each factor. An orthotrans rotation was also applied, which reduced the statistical requirement that each factor grouping be unrelated to one another. The results define the underlying structure of the data set by further differentiating large and small variables in each factor. Large (>0.7) coefficients, or loadings, of each parameter in the factor were significantly related to the other elements in the factor. Loadings between 0.35 and 0.7 were considered to be more weakly associated with the other parameters represented by the factor. Coefficients of <0.35 were not considered significant and were not included in the final results (BUCKLEY and WINTERS, 1992; WINTERS and BUCKLEY, 1992; BUCKLEY *et al.*, 1995; MAHON *et al.*, 1998).

Means, medians, and standard deviations were calculated for all 219 samples taken in Long Island Sound to establish Sound-wide statistics. The same calculations were done for each parameter after grouping them by their sedimentary environment. Enrichment factors were then used to evaluate the magnitude of metal concentrations in Long Island Sound sediments relative to a standard, such as naturally-occurring background values. Average Long Island Sound enrichment factors were calculated by dividing the mean concentration for each metal by the natural background value for the same element. These natural background values were determined from the concentrations at depth in 4 sediment cores from Long Island Sound (Figure 1; BUCHHOLTZ TEN BRINK and MECRAY, unpublished data) where the metal profiles indicated pre-anthropogenic conditions. These values were constant with depth, were typically below a core depth of 30 cm, and were from muddy, depositional locations. Background values in each core were averaged, and the mean of the 4 cores was used as a representative background concentration for the metals in further calculations. Metals were considered enriched when the mean concentration exceeded the background value, resulting in an enrichment factor greater than 1.

Parameters that are indicative of the composition, or lithology, of the sediment substrate can be used to normalize contaminant data in order to assess the variability in a data set independent of sediment type. The percent fine-grained material, mean grain size, Al concentration, Fe concentration, and organic carbon are commonly used. Mean grain size and the percentage of fine-grained material (POPPE *et al.*, this volume) are used to characterize sediment properties including surface area and, in most coastal locations, mineralogy. A ratio of metal concentration to Al is calculated to normalize for Al-rich clay particles and reduce the dilution effect from carbonates and other contaminant-poor sediments. Fe concentrations are similar to Al trends in many environments and frequently co-vary with grain size distributions; hence, they are used to elucidate contaminant trends (BOTHNER *et al.*, 1998). Differing amounts of organic matter (POPPE *et al.*, this volume) can influence contaminant metal concentrations in sediments and may also be used to normalize data. Organic matter in modern sediments may, however, come from a variety of sources which complicates the interpretation of the resulting ratios. In this study, we divided the metal concentrations by each of these parameters to yield a ratio which, when mapped and plotted by longitude, shows patterns and trends (such as source proximity or chemical behaviors) independent of grain-size or lithology.

RESULTS AND DISCUSSION

Sample locations and the suite of metal concentrations measured in the surface sediments of Long Island Sound are documented in BUCHHOLTZ TEN BRINK and MECRAY (1998). In this paper, we highlight the bulk metal concentration distributions for Pb, Cu, Mn, and Fe in Figures 3–6 and normalized Pb concentrations in Figures 9 and 10. Tables 1–3 and Figures 2, 7 and 8 present the results of the statistical and normalization analyses for the entire data set.

Anthropogenic Enrichment of Metals in Surface Sediments

The ranges and means of all metal concentrations measured in Long Island Sound surface sediments are provided in Table 1. Results of the ratio between metal concentration and natural background show overall enrichment in Ag, Ca, Cr, Cu, Mn, Pb, and Zn. Some of these elements have average concentrations that are significantly (2–4 times) higher than background values. Silver concentrations are 3–4 times, Cu is 5 times, and Mn and Pb are 2 times higher than background values. The other metals analyzed in this study (Al, Ba, Cd, Fe, Ti, V, and Zr) had mean values below the natural background concentration and were not considered enriched. Some of these metals, however, had maximum values that

Table 1. *Summary statistics for 16 metals (concentrations in units of µg/g dry sediment, weight %, or ppb), grain size (weight % fine fraction), and Clostridium perfringens spores in the surface sediments of Long Island Sound.*

Measured Parameter (µg/g dry sed. unless noted)	n	Median	Arithmetic Mean	Std. Dev. (% of mean)	Max	Min#	Natural Background	Enrichment Ratio*
C. perfringens (spores/g dry sed.)	216	385	831	180	15000	0		
% fines (wt %)	220	44.8	47.4	80	99	0		
Ag (silver)	216	0.16	0.27	102	3	0	0.05	**5.40**
Al (aluminum) wt %	218	5.27	5.06	34	10	0.07	6.69	0.76
Ba (barium)	217	330	326	35	1180	5.04	377	0.86
Ca (calcium) wt %	218	1.22	1.27	60	5	0	1.06	**1.20**
Cd (cadmium)	218	0.11	0.16	132	2	0	0.18	0.90
Cr (chromium)	218	66.7	67.9	58	231	0	59	**1.15**
Cu (copper)	217	32.9	39.1	93	275	0	8	**4.89**
Fe (iron) wt %	218	2.85	2.77	46	9	0	3.57	0.78
Hg (mercury) ppb	183	120	119	71	388	0		
Mn (manganese)	218	861	977	59	4627	64.46	544	**1.80**
Ni (nickel)	218	23.0	24.8	74	212	0	25	0.99
Pb (lead)	218	31.8	36.1	60	147	2.87	23	**1.57**
Ti (titanium) wt %	218	0.37	0.37	57	2	0	0.41	0.89
V (vanadium)	218	72.8	68.4	41	129	0	90	0.76
Zn (zinc)	218	95.4	103	59	294	0	68	**1.52**
Zr (zirconium)	218	112	112	78	1145	4.70	132	0.84

Zeros in the minimum value represent measured concentrations reported as below the detection limit.

* The enrichment factor is calculated as the ratio of the mean to the background. Bold type indicates enrichment.

exceeded background, which indicated some localized enrichment.

Time trends in surface sediments have been evaluated for other estuaries by sampling stations over several years in order to understand changes in metal concentration within a system over the long-term. Bothner *et al.* (1998) report measurements of decreasing concentrations of Ag, Cr, Cu, Hg, Pb, and Zn in the sediments of Boston Harbor from 1977 to 1993. For this study in Long Island Sound, metal enrichment over time was evaluated by comparing the data with the analyses reported in Greig *et al.* (1977). Of the 12 elements measured in the 1977 study, we compared Ag, Cd, Cr, Cu, Hg, Mn, Ni, Pb, and Zn with the 1996/1997 data in order to evaluate concentration trends with time. Decreasing trends in the mean values were noted for Ag (by 47%), Cd (by 64%), Cr (by 13%), Cu (by 51%), and Hg (by 53%). A comparison of the mean values for Mn, Ni, Pb, and Zn showed increasing trends by 77%, 59%, 20%, and 20% respectively.

This cross-study comparison was complicated by the use of differing analytical methods. Greig *et al.* (1977) used a strong acid leach and cold-vapor process to analyze Hg, neutron activation analysis to measure the concentrations of Ag

Table 2. *Factor analysis matrix after VARIMAX/orthotrans rotation showing correlations and commonalities identified with Principle Components Analysis. Four individual groups are shown that each represent a different chemical behavior, source term, or transport process in sediments.*

Measured Parameter (µg/g dry sed. unless noted) Variance	Factor 1 49.5%	Factor 2 14.4%	Factor 3 6.1%	Factor 4 5.5%
C. perfringens (spores/g dry sed.)	0.43	—	—	0.60
% fines (wt %)	**0.86**	—	—	—
TOC (total organic carbon) wt %	0.61	—	—	0.40
Ag (silver)	**0.94**	—	—	—
Al (aluminum) wt %	0.40	—	0.47	—
Ba (barium)	—	—	**0.80**	—
Ca (calcium) wt %	—	0.52	0.37	—
Cd (cadmium)	**0.75**	—	—	—
Cr (chromium)	**0.84**	—	—	—
Cu (copper)	**0.94**	—	—	—
Fe (iron) wt %	—	**0.89**	—	—
Hg (mercury) ppb	**0.90**	—	—	—
Mn (manganese)	—	**0.96**	—	—
Ni (nickel)	0.53	—	—	—
Pb (lead)	**0.89**	—	—	—
Ti (titanium) wt %	—	**0.97**	—	—
V (vanadium)	0.64	0.44	—	—
Zn (zinc)	**0.93**	—	—	—
Zr (zirconium)	0.61	—	—	—

Notes: (1) Negative factor loadings and loadings <0.35 are not shown. (2) Bold type indicates loadings >0.7; plain type indicates loadings >0.35 and <0.7.

Table 3. *Summary statistics for 16 elements, weight % fine-fraction, and Clostridium perfringens in each of the four sedimentary environments.*

Environment Measured Parameter[&]	Coarse-grained Bedload Transport n = 32						Erosional n = 25					
	Median	Arithmetic Mean	Std. Dev. (% of mean)	Max	Min[#]	Enrichment Ratio[*]	Median	Arithmetic Mean	Std. Dev. (% of mean)	Max	Min[#]	Enrichment Ratio[*]
C. perfringens	23.5	328	500	9300	0		50.0	152	140	840	0	
% fines	1.48	2.90	135	19	0		4.46	14.4	164	96	0	
Ag	0.00	0.02	566	1	0	0.39	0.00	0.09	122	0	0	**1.74**
Al	4.28	4.05	15	5	2	0.61	3.36	3.24	59	7	1	0.48
Ba	286	308	42	824	203	0.82	240	226	56	442	47	0.60
Ca	0.97	1.01	37	2	0	0.95	0.62	0.90	88	3	0	0.85
Cd	0.00	0.02	149	0	0	0.12	0.07	0.08	109	0	0	0.42
Cr	28.0	30.0	56	74	0	0.51	39.6	36.3	82	114	0	0.62
Cu	2.94	3.18	111	14	0	0.40	5.34	13.8	107	56	0	**1.73**
Fe	1.75	2.18	70	9	0	0.61	2.05	2.30	91	9	0	0.64
Hg	15.5	42.5	122	147	1		59.5	64.6	80	170	7	
Mn	686	962	74	3667	125	**1.77**	804	1042	88	4276	64	**1.92**
Ni	12.9	15.9	92	90	5	0.64	13.8	15.5	70	40	0	0.62
Pb	15.7	16.4	37	38	3	0.71	22.8	23.6	53	55	5	**1.02**
Ti	0.24	0.31	91	1	0	0.77	0.25	0.32	95	2	0	0.77
V	40.6	44.5	52	129	4	0.49	48.6	45.0	76	116	0	0.50
Zn	37.9	40.0	46	87	7	0.59	47.0	53.1	69	150	0	0.78
Zr	44.5	68.2	104	407	23	0.52	62.3	66.2	58	168	5	0.50

[&] Parameter names and units are reported in Table 1.

[#] Zeros in the minimum value represent measured concentrations reported as below the detection limit.

[*] The enrichment factor is calculated as the ratio of the mean to the natural background from depositional area (Table 1). Bold type indicates enrichment.

and Cr, and a nitric acid and heat process to partially digest Cd, Cu, Mn, Ni, Pb and Zn from the sediment surfaces. The partial digestion method used by GREIG *et al.* (1977) has been shown to extract a representative fraction of the anthropogenic metals binding to the surfaces of sediment particles; however, elements that are bound in the structure of the sediment are not completely extracted using the nitric acid process (MECRAY *et al.*, 2000). This incomplete digestion method may, therefore, under-represent the lithogenic fraction. The suggested increase in Pb and Zn is not consistent with the results from BOTHNER *et al.* (1998) nor is it consistent with trends observed in sediment cores from the Long Island Sound region (BUCHHOLTZ TEN BRINK and MECRAY, unpublished data).

Factor Analysis

PCA was the factor extraction method employed to reduce the data to a minimum number of factors that represent the maximum amount of variance in a data set. Co-variation of the elements in each factor can result from common sources, transport paths, or chemical processes. The sample matrix consisted of 16 measured elements, the percent fine-grained material (POPPE *et al.*, this volume), the percent total organic carbon (TOC) (POPPE *et al.*, 1998), and the concentration of the sewage tracer, *Clostridium perfringens* (BUCHHOLTZ TEN BRINK *et al.*, this volume). Four factors, representing 75.5% of the total variance in the samples, were identified with the loadings of the variables (Table 2).

Factor 1 contains variables that together represent 49.5% of the total variance of the samples. The components include high loadings (>0.7) for percent fine-grained sediments, Ag, Cd, Cr, Cu, Hg, Pb, and Zn. Municipal and industrial discharges are known sources of the majority of these metals. The grouping of these elements into a single common factor supports the hypothesis that these metals are associated with fine-grained sediments. *Clostridium perfringens,* TOC, Al, Ni, V, and Zr form a second set of parameters within Factor 1 with loadings between 0.35 and 0.7. The component of these parameters that groups them in Factor 1 is their association with fine-grained material. *Clostridium perfringens* and TOC link to fine-sized sediments because of their common sewage source and the small sizes of the spores and the organic particles. Al and Zr are linked by the mineralogy of the fine material. Ni has anthropogenic origins in metal alloys and batteries (Ni-Cd) but, like V, may have other geochemical properties not entirely represented by this factor.

Variables included in Factor 2 account for 14.4% of the total variance. This group includes elements involved in diagenesis (Fe, Mn, Ti, and V) and those present in biogenic sediments (Ca). Fe, Mn, and Ti were strongly correlated variables in this group, while Ca and V exhibited less covariance with elements in this factor.

Elements grouped in Factor 3 account for 6.1% of the total variance. Ba showed strong loading in this factor while Al and Ca are also identified. Elements in this factor are related to sediment composition. Al is a major element in silicates, which dominate the mineral structure of clays. Ca is primarily associated with carbonates, which form the structures of shells and forams. Ba is enriched in fecal pellets, but it also varies in trace amounts with different source rock types. This factor has both biogenic and source rock significance in terms of the parameter loadings.

Clostridium perfringens and TOC were the only variables in Factor 4, which represents 5.5% of the total variance. Each of these parameters also correlated with fine-grained material and anthropogenic contaminants in Factor 1 (*Clostridium*

Table 3. *Extended.*

Sediment Sorting and Reworking n = 64						Depositional n = 98					
Median	Arithmetic Mean	Std. Dev. (% of mean)	Min[#]	Max	Enrichment Ratio[*]	Median	Arithmetic Mean	Std. Dev. (% of mean)	Max	Min[#]	Enrichment Ratio[*]
270	522	155	4500	3		890	1382	130	15000	14	
19.3	30.2	85	97	0		88.6	81.7	23	99	0	
0.13	0.21	107	1	0	**4.12**	0.42	0.44	73	3	0	**8.79**
4.70	4.67	36	10	0	0.70	6.26	6.10	19	10	0	0.91
296	298	29	456	5	0.79	374	375	25	1180	225	0.99
1.20	1.28	68	5	0	**1.21**	1.32	1.44	51	5	0	**1.36**
0.09	0.14	126	1	0	0.77	0.17	0.25	104	2	0	**1.37**
48.7	59.9	55	145	5	**1.01**	88.4	93.3	33	231	26	**1.58**
26.0	35.0	117	275	0	**4.37**	56.9	59.5	48	146	4	**7.44**
2.33	2.42	39	6	0	0.68	3.29	3.31	26	8	0	0.93
84.5	93.8	70	294	0		173	176	39	388	0	
815	900	51	2913	82	**1.66**	903	1011	48	4627	286	**1.86**
18.9	21.7	66	90	2	0.87	29.1	32.2	64	212	12	**1.29**
27.8	33.2	61	135	4	**1.44**	42.0	47.7	43	147	17	**2.07**
0.34	0.37	57	2	0	0.90	0.39	0.39	32	1	0	0.96
56.2	58.9	36	103	4	0.65	91.9	88.5	17	119	22	0.98
70.8	90.0	58	268	12	**1.32**	144	146	32	294	31	**2.14**
104	124	112	1145	22	0.94	124	129	24	241	44	0.98

perfringens- 43.4% and TOC- 60.7%), however 60.4% of the variance of *Clostridium perfringens* and 40.0% of the variance of TOC is explained by Factor 4. These values do not sum to 100% due to the rotation and transformation of the matrix to yield distinctive high and low loadings. Factor 4 represents the organic component of *Clostridium perfringens* bacteria and TOC; both of which have sewage as a primary source in Long Island Sound. Since the variances of *Clostridium perfringens* and TOC attributed to fine-grained material are represented in Factor 1, their presence in Factor 4 may indicate the influence of source location in the Sound.

Metal Concentration Distributions

Maps of anthropogenic metal concentrations show regional distribution patterns of high concentrations in the western Sound with low concentrations measured in the eastern Sound and on the shoal complexes that divide the basins within the Sound. These patterns are similar to those of sedimentary environments (see KNEBEL and POPPE, this volume) and current-generated bottom-stress (SIGNELL *et al.*, this volume). This similarity reflects the common observation that fine-grained sediments dominate in areas of high metal concentrations and in depositional regions. In order to utilize the sedimentary environment data for evaluating the metal distributions in the region, samples were categorized by the sedimentary environment in which they are located (Figure 1). Statistical means, medians, and ranges were calculated to elucidate regional patterns (Table 3) similar to those calculated for the entire Sound (Table 1). The anthropogenic metals, Ag, Cd, Cr, Cu, Hg, Pb (Figure 2), and Zn all have values that increase as sedimentary environment changes from coarse-grained bedload transport, erosional, and reworked areas to the depositional environments where the highest concentrations are measured. The lithogenic elements and those involved in diagenesis, Al, Ba, Fe, Ni, Ti, V, and Zr, do not show a consistent trend when the maps, and the statistics, were compared to the sedimentary environments. The enrichment values observed in the erosional and transport environments that are <1 may be a result of using natural background concentrations that were determined from cores taken in depositional environments. Natural background concentrations are less in areas dominated by coarse-grained sediment than areas of mostly fine-grained sediment. The enrichment factors in the transport and erosional environments would be higher if the appropriate background values were available and applied to the calculations.

The GREIG *et al.* (1977) data was also categorized by sedimentary environment in order to note time-trends that might be dependent on sediment distribution and hydrodynamic regime. The 1977 data also show a concentration gradient between the sedimentary environments, with the highest values for Ag, Cd, Cr, Cu, Hg, Ni, Pb, and Zn in the depositional environment. Comparison of the 1977 and the 1996/1997 data sets within the depositional environment shows concentrations of Ag, Cd, Cr, Cu, and Hg decreasing (by 58%, 68%, 19%, 35%, and 59% respectively) to the present, and a slight decrease in Pb (by 8%). Mn, Ni, and Zn increased in concentration (by 68%, 53%, and 6% respectively) within the depositional environment from 1977 to 1996.

Spatial Variability of Anthropogenic Elements

Spatial distributions of the anthropogenic elements, Pb (Figure 3), Cu (Figure 4), Cr, Cd, Ag, Zn, and Hg (VAREKAMP *et al.*, this volume) are very similar in the surface sediments of Long Island Sound. High concentrations of these elements were measured in sediments from the central and western basins of the Sound. The concentrations measured in the eastern Sound were low and indistinguishable from natural background. Low concentrations were also measured in the

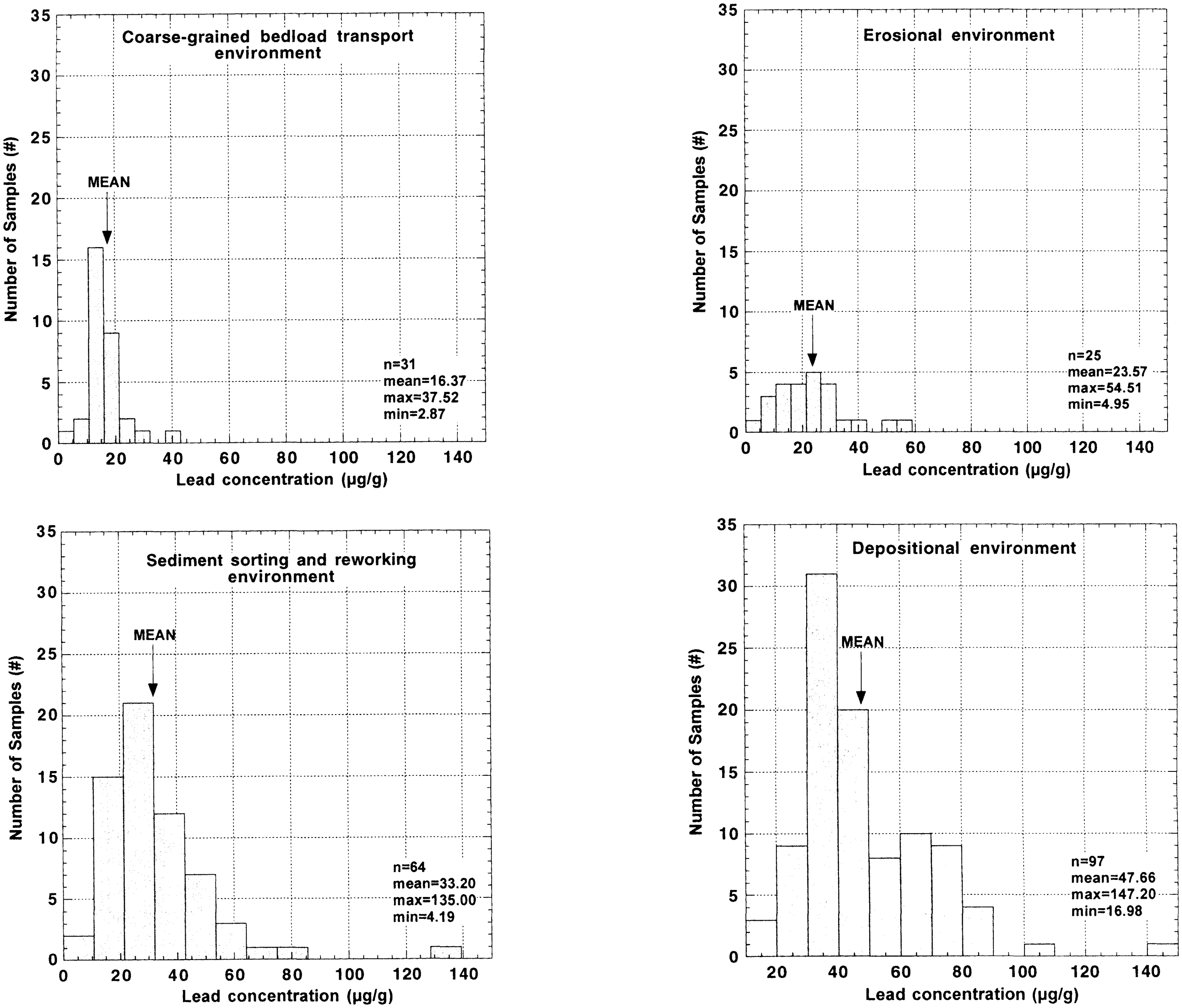

Figure 2. Histograms of lead (Pb) concentrations in the surface sediments of Long Island Sound grouped by sedimentary environment (see KNEBEL and POPPE, this volume). Note the increase in Pb concentrations in each environment with the highest values in the depositional areas (see Table 3).

sediments collected from the shoal complexes and the axial depression.

The anthropogenic metal concentrations for Pb (Figure 3) and Cu (Figure 4) are grouped into ranges defined by the natural background values, which were measured in regional sediment cores (see Tables 1 and 3), and by the potential to induce toxic effects in macro benthos (LONG *et al.* (1996, 1998). LONG *et al.* (1996, 1998) use two toxicity criteria: the Effects Range-Low (ER-L) and the Effects Range-Medium (ER-M) which define the potential for the metal concentrations in sediments to induce toxicity. The concentration ranges outlined by the toxicity criteria also reflect the degree of metal enrichment (Table 1). Pb and Cu are enriched in the whole Sound and have mean concentrations that exceed their ER-Ls. The high anthropogenic metal concentrations in the western and central basins of the Sound generally exceed these sediment criteria, which provide a warning of potential toxic effects in macro benthos.

Statistical analysis using PCA showed that the anthropogenic elements, Ag, Cd, Cr, Cu, Hg, Pb, and Zn, contained in Factor 1 have loadings of 0.7 or greater. Maximum, minimum, and enrichment values were calculated for Pb, Cu, and all of the other metals analyzed in this study (Tables 1 and 3). These statistical comparisons by sedimentary environment (Table 3) and for the whole Sound (Table 1) supported the qualitative appraisal of the similar anthropogenic metal distributions.

Throughout the Sound, higher values were found in sam-

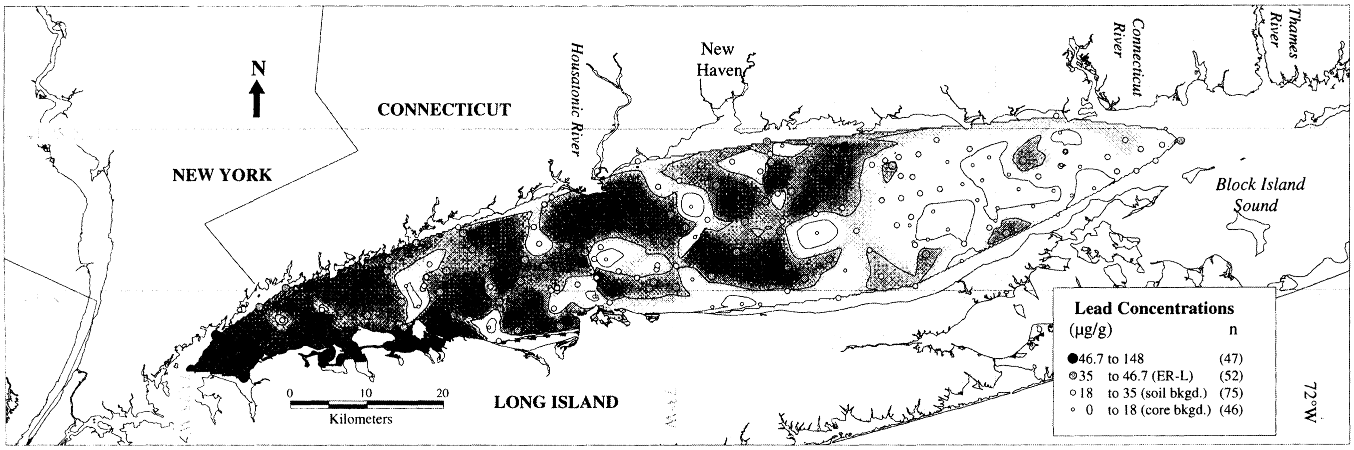

Figure 3. Lead (Pb) concentrations (µg/g dry sediment) in the surface sediments (0–2 cm) of Long Island Sound. The upper divisions on the legend are defined by the Effects Range-Low (ER-L) and Effects Range-Medium (ER-M) toxicity values of LONG *et al.* (1996, 1998). Large dots and darkest areas represent samples above the ER-L for lead. Smaller, dark gray dots are concentrations below the ER-L, but above the background concentration found in natural soils. Light gray, small dots represent Pb concentrations above natural background concentrations in sediment cores, and the smallest circles are concentrations that are below naturally-occurring values for Pb measured in fine-grained, regional sediment cores (see Tables 1 and 3).

ples with a high percentage of fine-grained sediment when compared to samples in sandier regions (SALOMONS and FORSTNER, 1984; BUCKLEY and CRANSTON, 1991; MOFFETT *et al.*, 1994; VISSER, 1999; MECRAY *et al.*, 2000). The high concentrations of metals in the central and western basins, and the absence of enrichment in the sandy eastern Sound and the axial depression, indicate that fine-grained sediments, and the contaminants associated with them, are focused in the basins by current activity. The concentration distributions of these elements follow patterns that correlate with the sedimentary environments (KNEBEL and POPPE, this volume), the sediment texture and TOC (POPPE *et al.*, this volume), and the *Clostridium perfringens* spore concentrations (BUCHHOLTZ TEN BRINK and MECRAY, 1998; BUCHHOLTZ TEN BRINK *et al.*, this volume). The distributions of Pb (Figure 3) and Cu (Figure 4) are also similar to the patterns of bottom stress generated by the hydrodynamic regime in that areas of high concentration are found in basins where winnowing by current and tidal activity is minimal (SIGNELL *et al.*, this volume).

Concentrations are low in the eastern Sound, the axial depression, and the shoal areas despite their proximity to contaminant sources near shore. These low values are associated with the occurrence of predominantly coarse-grained sediment (POPPE *et al.*, this volume), non-depositional environments (KNEBEL and POPPE, this volume), and high bottom stress generated by the local hydrodynamic regime (SIGNELL *et al.*, 1998, this volume). Low metal concentrations are mea-

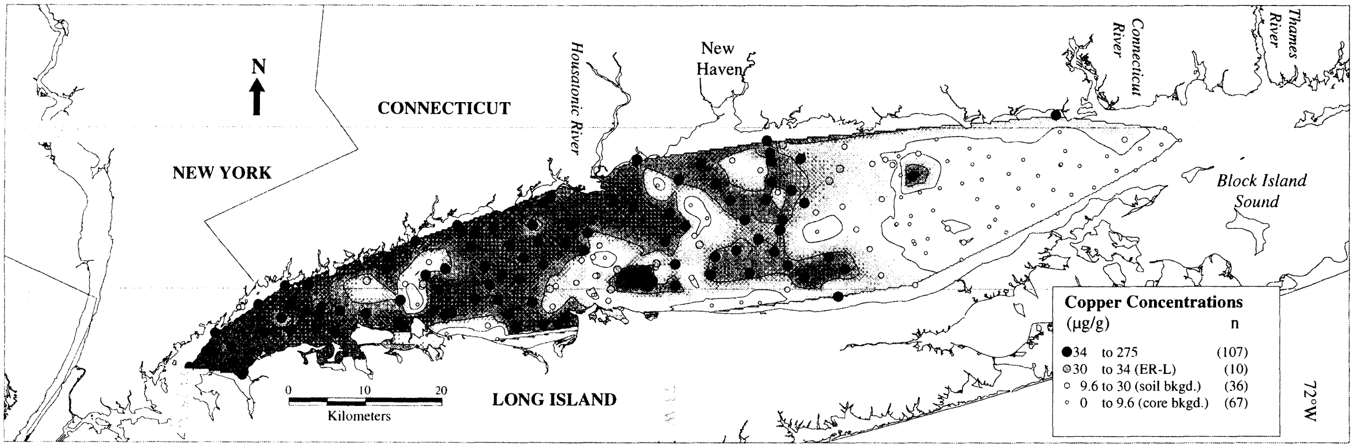

Figure 4. Copper (Cu) concentrations (µg/g dry sediment) in the surface sediments (0–2 cm) of Long Island Sound. Concentration ranges used on the map are determined by the same toxicity criteria and natural background values as in Figure 3. The distributions of silver (Ag), cadmium (Cd), chromium (Cr), and mercury (Hg), are similar to this Cu distribution (maps not shown).

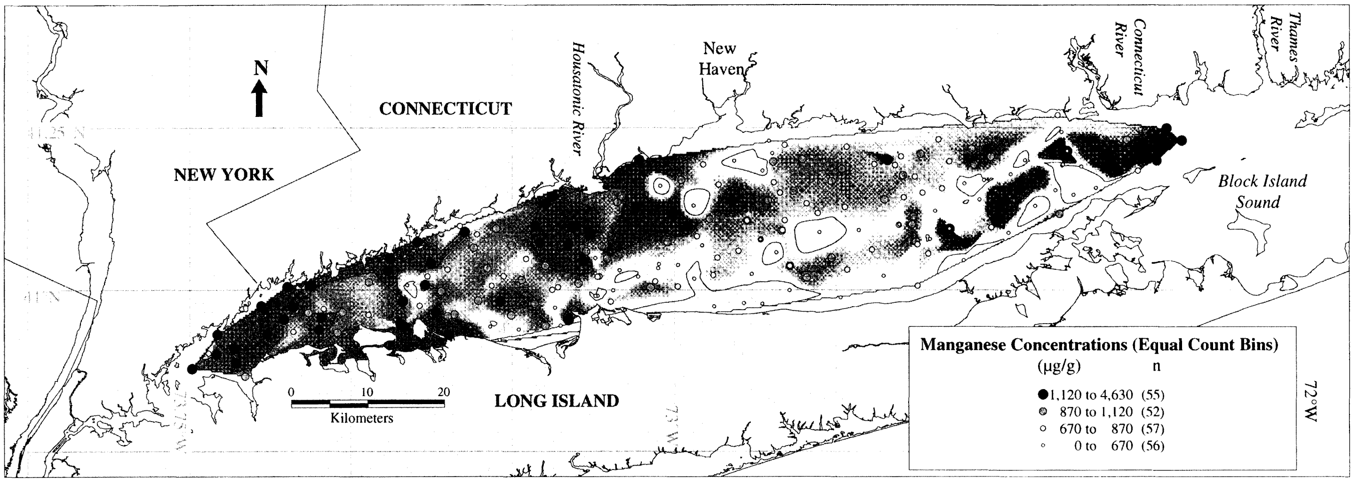

Figure. 5. Manganese (Mn) concentrations (µg/g dry sediment) in the surface sediments (0–2 cm) of Long Island Sound. Fe (Figure 6) and V distributions are similar to that of Mn.

sured on the shoal complexes and in the axial depression where, when winds blow parallel to the axis of the Sound, the currents are stronger which winnows the fine-grained, metal-bearing particles and deposits them in the relatively quiescent basins (Signell *et al.*, this volume).

In addition to the sedimentary environment and the hydrodynamic regime, the distribution of anthropogenic metal concentrations in Long Island Sound surface sediments is also affected by the proximity to contaminant sources. Within the Sound, particulates and associated contaminants exist as suspended material which becomes homogenized and dispersed (Kim and Bokuniewicz, 1991). After solids and associated metals sink towards the bottom, they are transported by the net westerly bottom flow (Signell *et al.*, this volume), which traps the sediments in the western end. Anthropogenic sources of metals are greater in the central and western regions than elsewhere in the Sound (Greig *et al.*, 1977; Strategic Assessments Branch, 1990; Breault and Harris, 1997). Metal loadings in the western Sound originate from direct discharge and industrial effluent from the largest metropolitan region of the United States (Farrow *et al.*, 1986; Benoit *et al.*, 1999). The combined effects of population density in the western Sound, point and non-point sources in the region, the general transport of contaminant-bearing fine-grained material, and the location of depositional areas yield the contaminant concentration patterns that are observed in the Sound.

Spatial Variability of Major Elements

The elements, Al, Ba, Ca, Fe, Mn, Ti, and V were grouped by PCA in Factors 2 and 3. These elements are associated with source rocks, fine-grained mineral structure, and biogenic sediments. High concentrations of Mn (Figure 5) and Fe (Figure 6) were found in the western basin of the Sound; however, elevated levels were also measured east of the Connecticut River mouth where strong bottom currents dominate and the sediments are predominantly sandy. The spatial distributions observed for these elements in Long Island Sound are more variable than the anthropogenic metal distributions with regard to sedimentary environments, hydrodynamic regime, and source proximity. Enrichment values, across both the whole Sound (Table 1) and the different environments (Table 3), do not show anthropogenic impacts for Al, Ba, Fe, Ti, and V. Ca and Mn enrichment values; however, show mean concentrations for the whole Sound that are above natural background (Table 1) and their concentrations increase from the coarse-grained sedimentary environment to the fine-grained, enriched, depositional environment (Table 3).

An explanation for the concentration distributions of Mn, Fe, V, and Zn in the Sound may be local sources or lag deposits of these elements. Major elements, particularly Fe and Mn, are found in steel manufacturing (Farrow *et al.*, 1986). Zn is used in the metal industry as well as in rubber tires (Nriagu, 1980). Both point and non-point sources are likely to affect the distribution of these elements over a broad area of the Sound. Metals, such as Fe, Mn, Ti, and V, may accumulate in the sediments as oxide crusts formed in the presence of high water volumes flowing across the surface sediments in the eastern Sound. Such oxide crusts may be a recent addition to the Sound from diagenesis, or they may be the result of a lag deposit causing an apparent enrichment.

Four samples from the scoured, eastern Sound had concentrations of Mn (Figure 5), Fe (Figure 6), vanadium (V), titanium (Ti), and zinc (Zn), that were more than ten times greater than elsewhere in the Sound. These values in coarse-grained material suggest that oxide coatings rich in these elements (Poppe *et al.*, 1985; Jenne, 1998; Visser, 1999) might be present in this area. Scanning electron microscopy was performed on selected samples and the results verified the existence of oxide coatings and stains on grains of feldspar and quartz. The coatings had relatively high abundances (area under the peaks) of Mn, Fe, and Ti; however, V and Zn

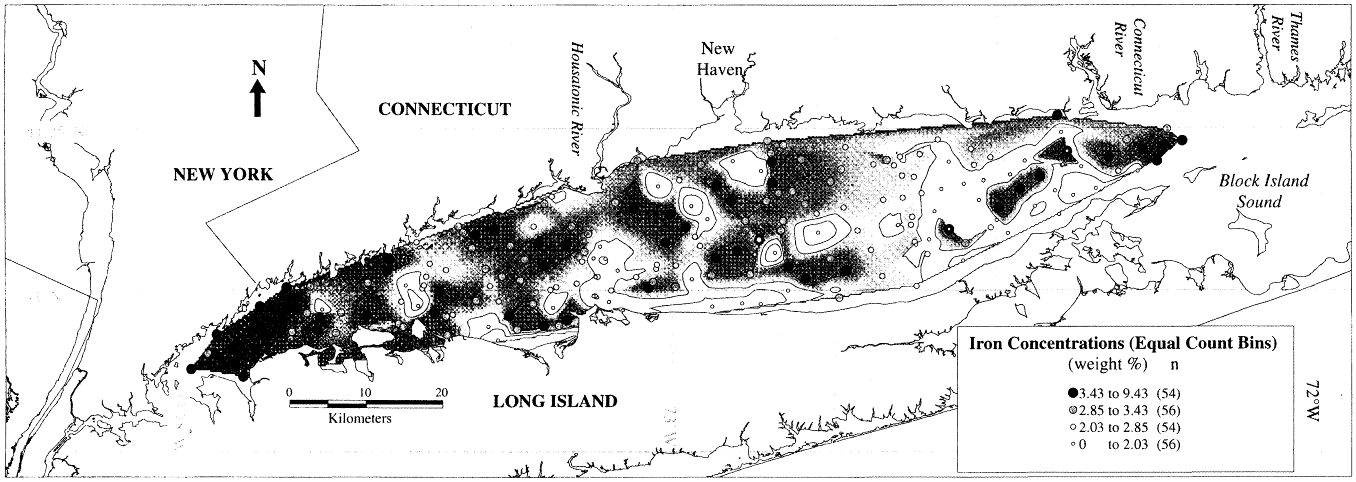

Figure 6. Iron (Fe) concentrations (weight %) in the surface sediments (0–2 cm) of Long Island Sound. The elevated concentrations in the eastern Sound are samples that contain oxide coatings.

are trace elements that were not recorded as abundant in the samples analyzed for oxides.

An important geochemical implication of the presence of Mn and Fe is their impact on the accumulation of anthropogenic metals. Fe and Mn oxides, in particular, provide a reactive surface area for the adsorption of anthropogenic elements (JENNE, 1998; POTTER and YONG, 1999). Their high sorption capacity provides an additional medium for the accumulation of the other metals identified in this study. Thus, the elevated concentrations of Fe and Mn oxides in the west may contribute to the high Factor 1 metals sequestered in the western Sound where source proximity and fine-grained sediment focusing provide anthropogenic metals to the sea floor.

Normalization of the Metals Data

The concentration of metals in sediments is dependent on the amount added by human activity, the amount naturally present, and the capacity of the sediment to adsorb or sequester metals that are introduced to the system. In order to identify spatial, or temporal, trends in metal sources or anthropogenic enrichment, it is necessary to remove the effects of other factors. Metal concentrations can vary with differences in the sediment composition, the percentage of total organic carbon (TOC), the concentration of Al, and the concentration of Fe in the sediments. In this study, we evaluate which normalization parameters are most effective in reducing grain size variability, and what the resulting normalized metals indicate about contamination in Long Island Sound.

A linear correlation of the TOC to the percent fine-grained (% fines) material (POPPE *et al.*, this volume) results in a correlation coefficient of 0.87, illustrating that either parameter may be used to normalize metal concentrations to account for small particles and organic matter (Figure 7a). The % fines were selected for normalization in this study because of the diverse sources of TOC in natural systems (BOTHNER *et al.*, 1998). Fe and Al concentrations were also compared to establish normalization criteria (Figure 7b). The regression coefficient of Fe and Al was 0.68, which again illustrates that either parameter may be used to normalize the metals data for the abundance of fine-grained material in sediments based on lithology. Al concentrations vary widely in glacially-derived source rocks (BOTHNER *et al.*, 1998). Fe is a better proxy for the abundance of fines (BENOIT *et al.*, 1999) and for its covariance with sewage signals in coastal systems (BOTHNER *et al.*, 1998). The mean grain size (MGS) and % fines (Figure 7c) may be interchangeable as normalization parameters if there is a normal distribution of size ranges. The regression coefficient for MGS plotted against % fines was 0.90, which suggests that either parameter may be used in a normalization of grain sizes. The regression of Fe and % fines resulted in a coefficient of 0.43 (Figure 7d), which indicates the need to normalize to both parameters for the best representation of metal concentrations independent of the lithology and the dilution from fines.

In this study, we selected the Pb data to illustrate the effects of normalization by both fine-grained material and Fe. The normalized Pb concentrations were evaluated by plotting against longitude (Figure 8) and by contoured maps (Figures 9 and 10) to show distribution patterns from east to west across the Sound. Pb concentrations that were normalized to the % fines measured in the same samples showed a general decrease from west to east, but higher values in the shoal areas and in the scoured eastern Sound (Figures 8a and 9). Normalizing the Pb to Fe concentrations showed a general decrease from west to east as well, but a marked decrease is noted in the eastern Sound (Figures 8b and 10).

Pb concentrations normalized to % fines, illustrated using contoured maps (Figure 9), show reduced variance within each sedimentary environment relative to the non-normalized data (Figure 3). This is manifested in a constant metal/fines ratio within each basin and within the various sedi-

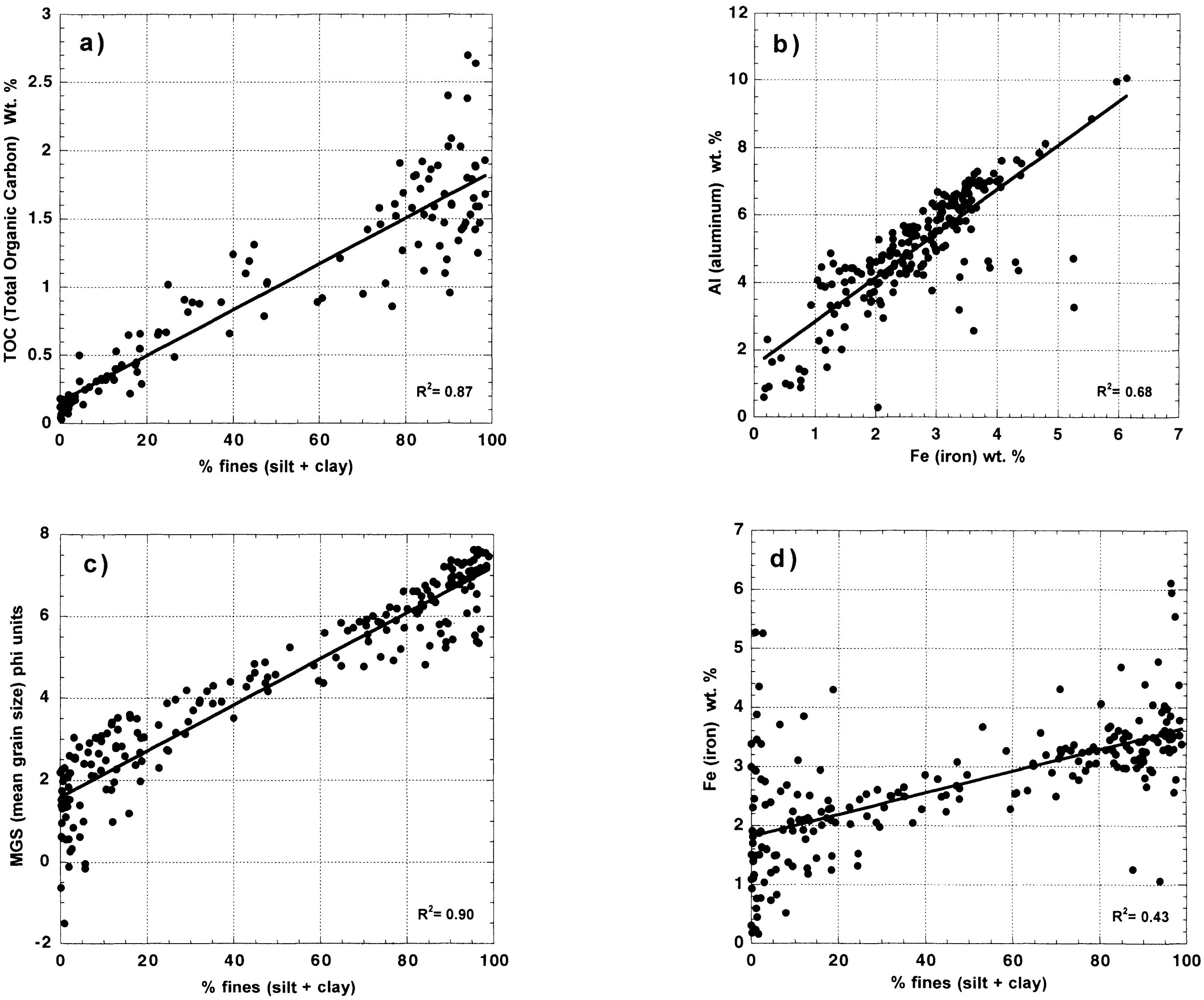

Figure 7. Parameters and relationships that are useful for normalizing metal concentrations. Plots and linear regressions for (a) total organic carbon (TOC) vs. percent fine-grained material (% fines); (b) aluminum (Al) vs. iron (Fe) concentrations; (c) mean grain size (MGS) vs. % fines; and (d) Fe concentration vs. % fines.

mentary environments (see Table 3), which supports the theory that fine-grained sediments are fairly well-mixed prior to deposition (KIM and BOKUNIEWICZ, 1991). The much higher Pb/fines ratio in the east is opposite from the western enrichments in Pb concentrations for the bulk sediment. Also, the Pb concentrations measured on separated fine-grained material from the scoured eastern Sound are higher that those measured for fine-grained material extracted from depositional areas in the central and western Sound (VISSER, 1999). This spatial difference in Pb concentration may be due to a Pb source in the east, more effective scavenging by particles in the eastern Sound, or dilution of the Pb-bearing fine-grained material with other particles in the remainder of the Sound. Efficient scavenging is effected by the volume of Pb introduced in the region, by the amount and the lithology of the scavenging sediments, or by the greater exposure of the particles to water allowing time for sorption to occur.

Normalizing Pb concentrations by Fe, and by TOC, allows the Pb spatial distribution to be evaluated for the lithology of the sequestering sediment. As noted earlier, Pb, and other anthropogenic metals, may be scavenged and sequestered by fine-grained material, TOC, or Fe- and Mn-oxide coatings. The increase in the Pb to fines ratio in the east shows that fines can effectively scavenge the Pb introduced to the Sound; however, this fine-grained fraction may contain TOC and Fe as specific scavenging agents. The distribution of TOC (POPPE *et al.*, this volume) is similar to Pb and to % fines in that the concentrations are less in the eastern basin. When TOC is normalized to % fines the distribution is similar to the Pb and % fines showing greater values in the eastern Sound. The fact that Pb normalized to TOC and to % fines increases, and the Pb to Fe decreases in the eastern basin, relative to the central and western basins, strongly suggests that TOC, rather than Fe, is the predominant carrier of the Pb load in the scoured eastern Sound.

Regional Management Issues

This study has found that establishing a representative suite of samples in a study area, assessing the level of metal enrichment, and grouping the elements by chemical behaviors may serve as a useful tool for those involved in management of our natural resources. The geochemical data from Long Island Sound reveal patchy contaminant distributions that range from background values to potentially toxic levels (LONG *et al.*, 1998). The distribution of the elements in the Sound demonstrates that the variance in the metal concentrations is low within each of the sedimentary environments. It is possible, therefore, to obtain representative samples at strategic locations to assess the spatial geochemistry of the Sound using knowledge of the sedimentary and physical oceanographic regimes. As such, a regional assessment of sediment contamination can be made by: (1) taking fewer samples in each sedimentary regime; (2) determining elevations in metal concentrations relative to the potential for toxicity; and (3) identifying elements that co-vary and using them as proxy elements. The benefits of such a regional, and multi-disciplinary, assessment would be: (1) reducing the total cost of the study without losing scientific value; (2) improving the accuracy of system predictions used for environmental management decisions; and (3) understanding the scales of contaminant variability and sediment processes to target critical management factors.

SUMMARY

- This study presents a comprehensive assessment of the spatial distribution of metals in Long Island Sound surface samples collected in 1996–1997. It provides data that are used to: (1) establish a regional baseline for temporal studies of contamination in Long Island Sound; (2) identify areas of high contamination in the Sound; (3) elucidate transport and deposition processes affecting contaminant distributions; and (4) generate predictive and assessment tools for regional management in Long Island Sound and elsewhere.
- Metals are grouped by PCA into factors that indicate common anthropogenic sources or chemical behaviors. Factor 1 includes anthropogenic contaminants (*Clostridium perfringens* spores, TOC, Ag, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn), and some compositional parameters (the fine-grained sediment fraction and Zr). Factor 2 includes elements associated with diagenesis (Fe, Mn, Ti, and V). Factor 3 includes those elements derived from source rocks (Ba) and from the composition of the sediment (Al and Ca). The parameters in Factor 4 (*Clostridium perfringens* and TOC) represent non-metal sewage components in the sediments.
- Enrichment values calculated for the whole Sound were greatest for the anthropogenic metals in the depositional environments of the central and western basins. Enrichment on the fine-grained fraction was greater in the eastern basin. For the whole Sound and for the four sedimentary environments, Ag and Cu concentrations were shown to be 4–5 times greater than natural background values. Zn, Pb, and Mn concentrations were enriched by factors of 1.5–2. In contrast, the major elements, Al, Fe, and Ti, and the trace elements, V, Zr, and Ba were not enriched in the surface sediments.

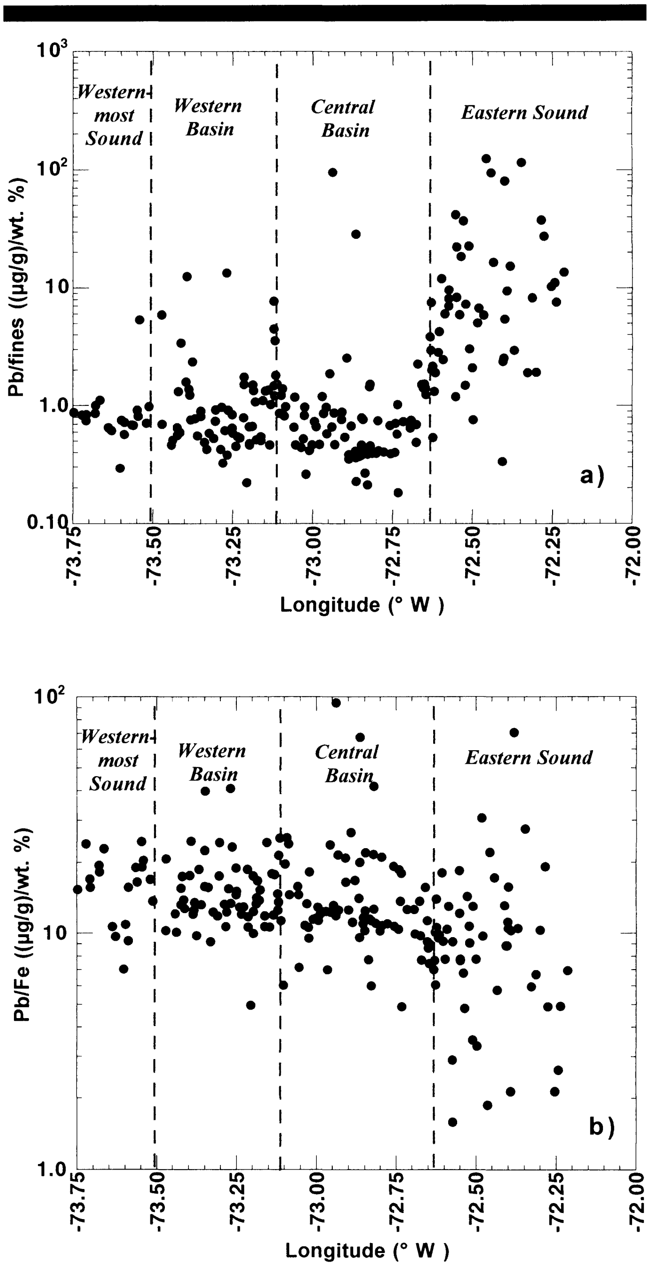

Figure 8. Lead (Pb) concentrations normalized to selected parameters and shown as a function of longitude. (a) Pb concentrations normalized to percent fine-grained material. (b) Pb concentrations normalized to Fe concentrations.

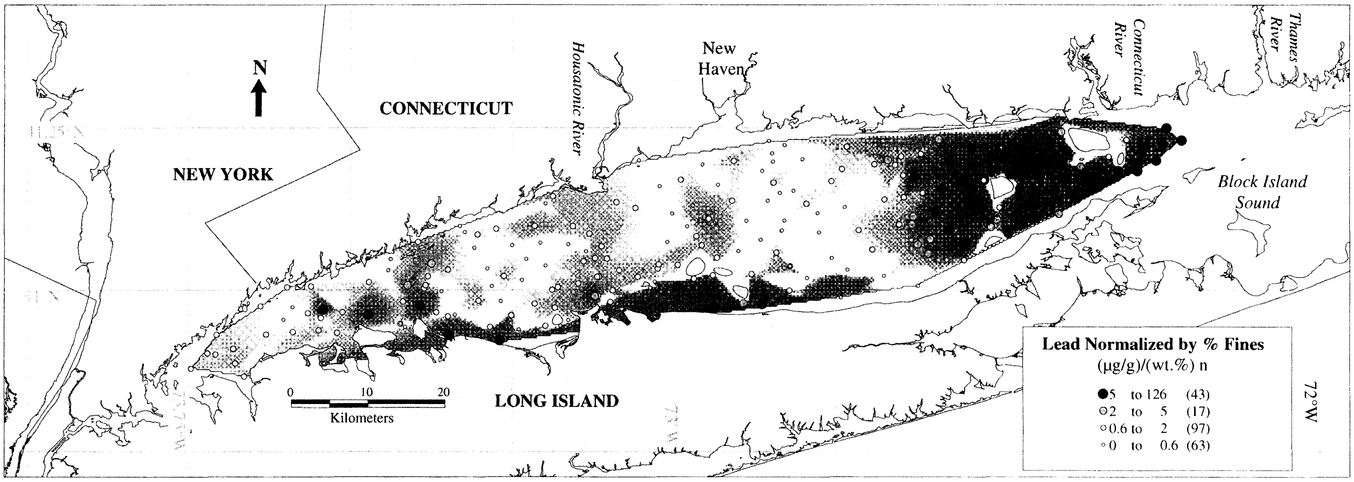

Figure 9. Lead (Pb) distribution in Long Island Sound normalized to fine-grained material. The lead concentration divided by the percentage of fine-grained material (silt + clay) is shown for each sample, and as a contoured surface, to delineate the distribution of lead in the fine-fraction.

- The regional patterns of metal concentrations in Long Island Sound result primarily from variations in bottom energy that result in differing grain sizes and particle lithology for the sedimentary environments. The anthropogenic metals are widely dispersed in Long Island Sound and are subject to redistribution in some regions. Their distributions co-vary with the texture, the sedimentary environments and the lithology of the sequestering material (Fe, Al, or TOC) measured in the sediments.

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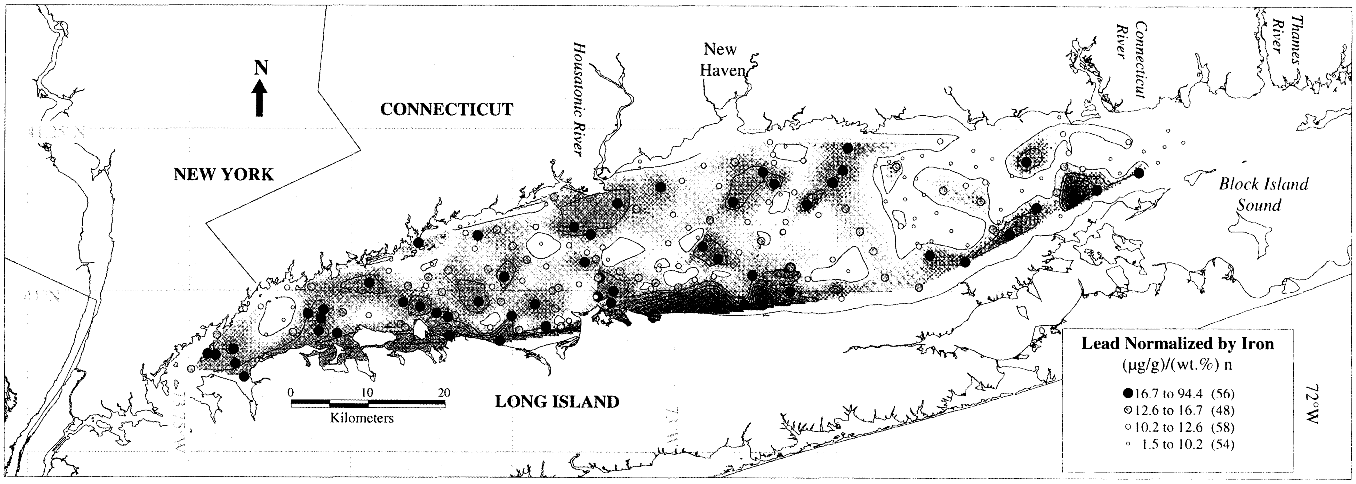

Figure 10. Lead (Pb) concentrations normalized to Fe concentrations illustrated as a contoured surface to show spatial distribution.

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LITERATURE CITED

Aller, R.C., 1980a. Diagenetic processes near the sediment-water interface of Long Island Sound; Part I: Decomposition and nutrient element geochemistry (S, N, P). *Advances in Geophysics,* 22, 237–350.

Aller, R.C., 1980b. Diagenetic processes near the sediment-water interface of Long Island Sound; Part II: Fe and Mn. *Advances in Geophysics,* 22, 351–415.

Benoit, G.; Rozan, T.F.; Patton, P.C., and Arnold, C.L., 1999. Trace metals and radionuclides reveal sediment sources and accumulation rates in Jordan Cove, Connecticut. *Estuaries,* 22, 65–80.

Bokuniewicz, H.J. and Gordon, R.B., 1980. Storm and tidal energy in Long Island Sound. *Advances in Geophysics,* 22, 41–67.

Boothman, W.S., 1988. Characterization of trace metal-particulate matter associations in sediments at a Long Island Sound hazardous material dumping site. *In*: Lichtenberg, J.J; Winter, J.A.; Weber, C.I. and Fradkin, L. (eds.), Chemical and biological characterization of municipal sludges, sediments, dredge spoils, and drilling muds. *American Society for Testing and Materials, Special Technical Publication 976,* 81–92.

Bothner, M.H.; Buchholtz ten Brink, M., and Manheim, F.T., 1998. Metal concentrations in surface sediments of Boston Harbor-Changes with time. *Marine Environmental Research,* 45, 127–155.

Breault, R.F. and Harris, S.L., 1997. Geographical distribution and potential for adverse biological effects of selected trace elements and organic compounds in streambed sediment in the Connecticut, Housatonic, and Thames River Basins, 1992–1994. *U.S. Geological Survey Water-Resources Investigations Report 97-4169,* 24p.

Bricker, S.B.; Wolfe, D.A.; Scott, K.J.; Thursby, G.; Long, E.R., and Robertson, A., 1992. Sediment toxicity in Long Island Sound embayments. *In*: *Long Island Sound Research Conference.* New Haven, Connecticut: Southern Connecticut State University, Connecticut Sea Grant Program, pp. 181–189.

Brownawell, B.; Fisher, N., and Naeher, L., 1992. *Characterization of a Database on Toxic Chemical Contamination in Long Island Sound.* Report to U.S. Environmental Protection Agency, 114p.

Buchholtz ten Brink, M.R. and Mecray, E.L., 1998. Chapter 5 *In:* Poppe, L.J. and Polloni, C. (eds.), Long Island Sound Environmental Studies. *U.S. Geological Survey Open-File Report 98-502,* 1 CD-ROM.

Buchholtz ten Brink, M.R.; Mecray, E.L., and Galvin, E.L., this volume. *Clostridium perfringens* in Long Island Sound sediments: An urban sedimentary record. Thematic Section. *Journal of Coastal Research.*

Buckley, D.E. and Cranston, R.E., 1991. The use of grain size information in marine geochemistry. *In*: Syvitski, J.P.M. (ed.), *Principles, Methods, and Application of Particle Size Analysis.* New York: Cambridge University Press, pp. 311–331.

Buckley, D.E. and Winters, G.V., 1992. Geochemical characteristics of contaminated surficial sediments in Halifax Harbour: Impact of waste discharge. *Canadian Journal of Earth Sciences,* 29, 2617–2639.

Buckley, D.E.; Smith, J.N., and Winters, G.V., 1995. Accumulation of contaminant metals in marine sediments of Halifax Harbour, Nova Scotia: Environmental factors and historical trends. *Applied Geochemistry,* 10, 175–195.

Davies, B.E., 1997. Heavy metal contaminated soils in an old industrial area of Wales, Great Britain: Source identification through statistical data interpretation. *Water, Air, and Soil Pollution,* 94, 85–98.

Farrow, D.R.G.; Arnold, F.D.; Lombardi, M.L.; Main, M.B., and Eichelberger, P.D., 1986. *The National Coastal Pollutant Discharge Inventory: Estimates for Long Island Sound.* Rockville, MD: National Oceanic and Atmospheric Administration, Selected Appendices (II-VIII), 74p.

Fenster, M.S., 1995. The Origin and Evolution of the Sand Sheet Facies: Eastern Long Island Sound. Ph.D. Thesis, Boston University, Boston, Massachusetts, 328p.

Fenster, M.S.; Fitzgerald, D.M.; Bohlen, W.F.; Lewis, R.S., and Baldwin, C.T., 1990. Stability of giant sand waves in eastern Long Island Sound. *Marine Geology,* 91, 207–225.

Fredette, T.J.; Murray, P.M., and Carey, D.A., 1992. Subaqueous containment of contaminated dredged sediments: Trace metal results of sediment cores from "capped" disposal mounds. EOS, Transactions, American Geophysical Union, 73, 166–167.

Gordon, R.B. and Pilbeam, C.C., 1975. Circulation in central Long Island Sound. *Journal of Geophysical Research,* 80, 414–422.

Grant, A., 1990. Multivariate statistical analyses of sediment geochemistry. *Marine Pollution Bulletin,* 21, 297–299.

Greig, R.A.; Reid, R.N., and Wenzloff, D.R., 1977. Trace metal concentrations in sediments from Long Island Sound. *Marine Pollution Bulletin,* 8, 183–188.

Harris, S.L., 1997. Inorganic and organic constituents and grain size distribution in streambed sediment and ancillary data for the Connecticut, Housatonic, and Thames River Basins Study Unit, 1992–1994. *U.S. Geological Survey Open-File Report 96–397,* 39p.

Hulth, S.; Aller, R.C., and Gilbert, F., 1999. Coupled anoxic nitrification/manganese reduction in marine sediments. *Geochimica et Cosmochimica Acta,* 63, 49–66.

Hunt, C.D., 1979. The Role of Phytoplankton and Particulate Organic Carbon in Trace Metal Deposition in Long Island Sound. Ph.D. Thesis, University of Connecticut, Storrs, Connecticut, 282p.

Ianniello, J.P., 1981. Tidally-induced residual currents in Long Island and Block Island Sounds. *Estuarine, Coastal, and Shelf Science,* 12, 177–191.

Jenne, E.A., 1998. *Adsorption of Metals by Geomedia: Variables, Mechanisms, and Model Applications.* Boston: Academic Press, 583p.

Kaiser, H.F., 1960. The application of electronic computers to factor analysis. *Educational and Psychological Measurement,* 20, 141–151.

Kenefick, A.M., 1985. Barotropic M_2 tides and tidal currents in Long Island Sound: A numerical model. *Journal of Coastal Research,* 1, 117–128.

Kim, B.H. and Bokuniewicz, H.J., 1991. Estimates of sediment fluxes in Long Island Sound. *Estuaries,* 14, 237–247.

Knebel, H.J. and Poppe, L.J., this volume. Sea-floor environments within Long Island Sound: A regional overview. Thematic Section. *Journal of Coastal Research.*

Knebel, H.J.; Signell, R.P.; Rendigs, R.R.; Poppe, L.J., and List, J.H., 1999. Seafloor environments in the Long Island Sound estuarine system. *Marine Geology,* 155, 277–318.

Koppelman, L.E.; Weyl, P.K.; Gross, M.G., and Davies, D.S., 1976. *The Urban Sea: Long Island Sound.* New York: Praeger Publishers, 223p.

Kreulen, B.; Varekamp, J.C., and Buchholtz ten Brink, M.R., 1998. Mercury pollution in and around Long Island Sound. *In*: *Fourth Biennial Long Island Sound Research Conference, Program and Abstracts,* p. 5.

Langstaff, L.M., 1990. Demographic and land use trends in the Long Island Sound region. *U.S. Environmental Protection Agency, Long Island Sound Study Technical Report,* 16p.

Lewis, R.S. and Stone, J.R., 1991. Late Quaternary stratigraphy and depositional history of the Long Island Sound basin: Connecticut and New York. *Journal of Coastal Research,* Special Issue No. 11, 1–23.

Lewis, R.S. and DiGiacomo-Cohen, M., this volume. A review of the geologic framework of the Long Island Sound basin, with some observations relating to postglacial sedimentation. Thematic Section. *Journal of Coastal Research.*

Long, E.R.; Robertson, A.; Wolfe, D.A.; Hameedi, J.W., and Sloane, G.M., 1996. Estimates of the spatial extent of sediment toxicity in major U.S. estuaries. *Environmental Science and Technology,* 30, 3585–3592.

Long, E.R.; Field, L.J., and Macdonald, D.D., 1998. Predicting toxicity in marine sediments with numerical sediment quality guidelines. *Environmental Toxicology and Chemistry,* 17, 714–727.

Mahon, R.; Brown, S.K.; Zwanenburg, K.C.T.; Atkinson, D.B.; Buja, K.R.; Claflin, L.; Howell, G.D.; Monaco, M.E.; O'Boyle, R.N., and Sinclair, M., 1998. Assemblages and biogeography of demersal fishes of the east coast of North America. *Canadian Journal of Fisheries and Aquatic Sciences,* 55, 1704–1738.

Mccrone, A.W., 1966. Sediments from Long Island Sound (New York): Physical and chemical properties reviewed. *Journal of Sedimentary Petrology,* 36, 234–236.

Mecray, E.L.; King, J.W.; Appleby, P.G., and Hunt, A.S., 2000. Historical trace metal accumulation in the sediments of an urbanized region of the Lake Champlain watershed: Burlington, Vermont. *Water, Air, and Soil Pollution,* (in press).

Moffett, A.M.; Poppe, L.J., and Lewis, R.S., 1994. Trace metal concentrations in sediments from eastern Long Island Sound. *U.S. Geological Survey Open-File Report, 94–620,* 17p.

Murray, R.W. and Leinen, M., 1996. Scavenged excess Al and its relationship to bulk Ti in biogenic sediment from the central equatorial Pacific Ocean. *Geochimica et Cosmochimica Acta,* 60, 3869–3878.

Nriagu, J.O. (ed.), 1980. Zinc in the Environment, Part I: Ecological Cycling. *In*: Metcalf, R.L. and Stumm W. (eds.), *Wiley Interscience Series of Texts and Monographs,* New York: John Wiley and Sons, pp. 453.

O'Connor, T.P. and Ehler, C.N., 1991. Results from the NOAA National Status and Trends Program on distribution and effects of chemical contamination in the coastal and estuarine United States. *Environmental Monitoring and Assessment,* 17, 33–49.

Poppe, L.J. and Polloni, C. (eds.), 1998. Long Island Sound Environmental Studies. *U.S. Geological Survey Open-File Report 98–502,* 1 CD-ROM.

Poppe, L.J.; O'Leary, D.W., and Commeau, R.F., 1985. Composition and morphology of ferromanganese coatings on glacial erratics in Lydonia Canyon, United States east coast. *Geo-Marine Letters,* 5, 127–133.

Poppe, L.J.; Zajak, R.N.; Lewis, R.S.; Mlodzinska, Z.J.; Pratt, S.E.; Taylor, B.B., and Digiacomo-Cohen, M.L., 1996. Organic carbon, hydrogen, and nitrogen concentrations in surficial sediments from western Long Island, Connecticut, and New York. *U.S. Geological Survey Open-File Report 96-708,* 20p.

Poppe, L.J.; Hastings, M.E.; Digiacomo-Cohen, M.L.; Manheim, F.T., and Mlodzinska, Z.J., 1998. Chapter 3: Surficial sediment database. *In*: Long Island Sound Environmental Studies. *U.S. Geological Survey Open-File Report 98-502,* 1 CD-ROM.

Poppe, L.J.; Knebel, H.J.; Mlodzinska, Z.L.; Hastings, M.E., and Seekins, B.A., this volume. Distribution of surficial sediment in Long Island Sound and adjacent waters: Texture and total organic carbon. Thematic Section. *Journal of Coastal Research.*

Potter, H.A.B. and Yong, R.N., 1999. Influence of iron/aluminum ratio on the retention of lead and copper by amorphous iron-aluminum oxides. *Applied Clay Science,* 14, 1–26.

Riley, G.A., 1956. Oceanography of Long Island Sound, 1952–1954. *Bulletin of the Bingham Oceanographic Collection,* 15, 15–46.

Robertson, A.; Gottholm, B.W.; Turgeon, D.D., and Wolfe, D.A., 1991. A comparative study of contaminant levels in Long Island Sound. *Estuaries,* 14, 290–298.

Salomons, W. and Forstner, U., 1984. *Metals in the Hydrocycle.* New York: Springer Verlag, 349p.

SAS Institute Inc., 1998. *StatView,* v. 5.0.1. SAS Institute Inc., Cary, NC.

Schubel, J.R.; Wise, W.M., and Schoof, J. (eds.), 1979. *Questions about Dredging and Dredged Material Disposal in Long Island Sound.* Stony Brook, New York: State University of New York, Marine Sciences Research Center, 136p.

Signell, R.P.; Knebel, H.J.; List, J.H., and Farris, A.S., 1998. Physical processes affecting the sedimentary environments of Long Island Sound. *In*: Spaulding, M. and Blumberg, A.F. (eds.), *Proceedings of the 5th International Conference on Estuarine and Coastal Modeling.* New York: American Society of Civil Engineers, pp. 400–412.

Signell, R.P.; List, J.H., and Farris, A.S., this volume. Bottom currents and sediment transport in Long Island Sound: A modeling study. Thematic Section. *Journal of Coastal Research.*

Strategic Assessments Branch, 1990. *Estuaries of the United States: Vital statistics of a national resource base.* Rockville, Maryland: National Oceanic and Atmospheric Administration, National Ocean Service, Ocean Assessments Division, 40p.

Varekamp, J.C., 1996. Metal pollution in wetlands around Long Island Sound. *In*: *Proceedings of the Third Biennial Long Island Sound Research Conference,* p. 94.

Varekamp, J.C. and Scholand, S.J., 1996. Metal pollution in coastal and riverine wetlands. *In*: *Proceedings of the Third Biennial Long Island Sound Research Conference,* pp. 95–100.

Varekamp, J.C.; Buchholtz ten Brink, M.R., and Mecray, E.L., this volume. Mercury in Long Island Sound sediments. Thematic Section. *Journal of Coastal Research.*

Visser, K., 1999. Chemical Concentrations in Sediment from Long Island Sound: Relationships to Grain Size. B.S. Senior Thesis, Boston University, Boston, Massachusetts, 55p.

Winters, G.V. and Buckley, D.E., 1992. Factor analyses as a method of evaluating sediment environmental quality in Halifax Harbour, *In*: *Current Research, Part D; Geological Survey of Canada, Paper 92–1D,* pp. 165–171.

Wolfe, D.A.; Monahan, R.; Stacey, P.E.; Farrow, D.R.G., and Robertson, A., 1991. Environmental quality of Long Island Sound: Assessment and management issues. *Estuaries,* 14, 224–236.

Zimmerman, M.J.; Grady, S.J.; Todd-Trench, E.C.; Flanagan, S.M., and Nielsen, M.A., 1996. Water-quality assessment of the Connecticut, Housatonic, and Thames River Basin study unit: Analysis of available data on nutrients, suspended sediments, and pesticides, 1972–1992. *U.S. Geological Survey Water-Resources Investigations Report 95–4203,* 162p.