U.S. DEPARTMENT OF THE INTERIOR

U.S. GEOLOGICAL SURVEY

Trace metal concentrations in sediments from eastern Long Island Sound

by

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Open-File Report 94-620

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ABSTRACT

Herein we present data on the concentrations of the trace (Ag, Ba, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn) and major (Al, Fe, Mn, and Na) metals in 21 sediment samples from northeastern Long Island Sound, offshore from the Thames River estuary.

The data show a positive correlation between the amount of silt and clay in a sample and the amounts of various trace metals. The highest concentrations of metals were consistently found in the muddier sediment from the northeastern section of the study area. Low concentrations were more commonly found in the southwestern section which is generally characterized by moderately sorted, sandy sediments that have unimodal distributions and contain very little silt and clay. A few notable exceptions to these generalizations occur. For example, sample M-41, which is located in the southeastern region, has a higher levels of both trace metals and silt and clay.

INTRODUCTION

The results of chemical analyses reported here were generated as part of the U.S. Geological Survey/State of Connecticut Cooperative, which is part of a long-standing program to study the marine and terrestrial geology of Connecticut and Long Island Sound. This cooperative was initially focused on resolving stratigraphic problems in the Sound and integrating them with geologic findings in Connecticut and on Long Island (Needell and others, 1987; Lewis and Needell, 1987; Lewis and Stone, 1991). However, with the bulk of these geologic framework studies complete, the emphasis of present work has now shifted to studies of bottom sediment distribution, sedimentary processes, benthic community structures, and trace metal/pollutant inventories. Sidescan sonar surveys (complete coverage acoustic images and spaced-line reconnaissance surveys) are being completed in areas of critical concern in order to provide a framework for research activities and act as guides for the biological, sedimentological, and geochemical sampling. One such survey is located off the Thames River Estuary (Figures 1, 2, and 3; Appendix A).

Long Island Sound, which is about 182 km long by a maximum of 32 km wide, is bordered on the north by the rocky shoreline of Connecticut and on the south by the eroding sandy bluffs of Long Island, New York. The study area (Figures 1, 2, and 3) lies in northeastern Long Island Sound offshore from the Thames River estuary and covers about 5.4 km^2. Water depths in the study area average about 18 m; maximum depths occur in the central and southwestern parts of the study area.

Strong tidal currents have extensively eroded and reworked the sediments and continue to control sedimentary processes and surficial sediment distributions in eastern Long Island Sound. The irregular bottom topography and extensive lag deposits of boulders reflect this scour, transport, and reworking of the glacial and early post-glacial deposits (Lewis and Needell, 1987; Lewis and

Figure 1. Index map showing the location of the study area (solid polygon) off New London, Connecticut. Map also shows the locations (open polygons) of other areas where detailed studies are planned.

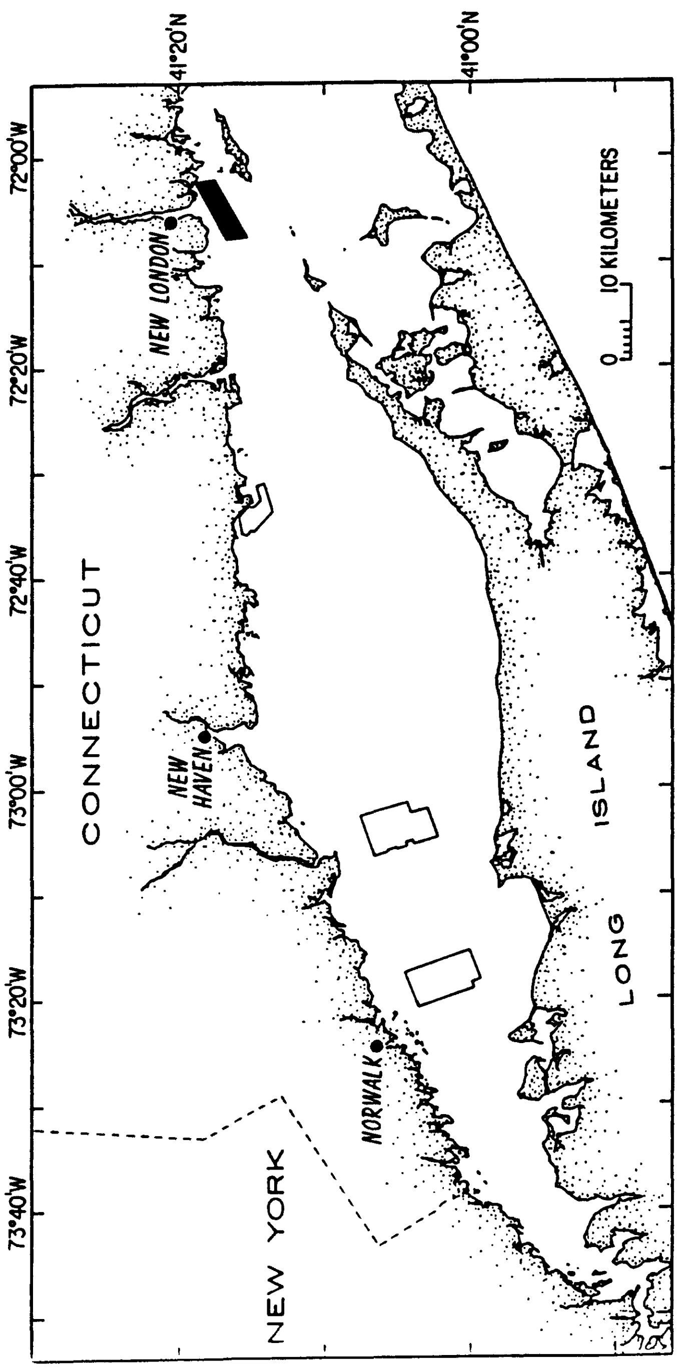


Figure 2. Map of eastern Long Island Sound showing the sample locations and outlines of the study area and a dredge-spoil dumpsite. Solid circles designate stations with both chemical and textural data. Open circles represent stations with textural data only.

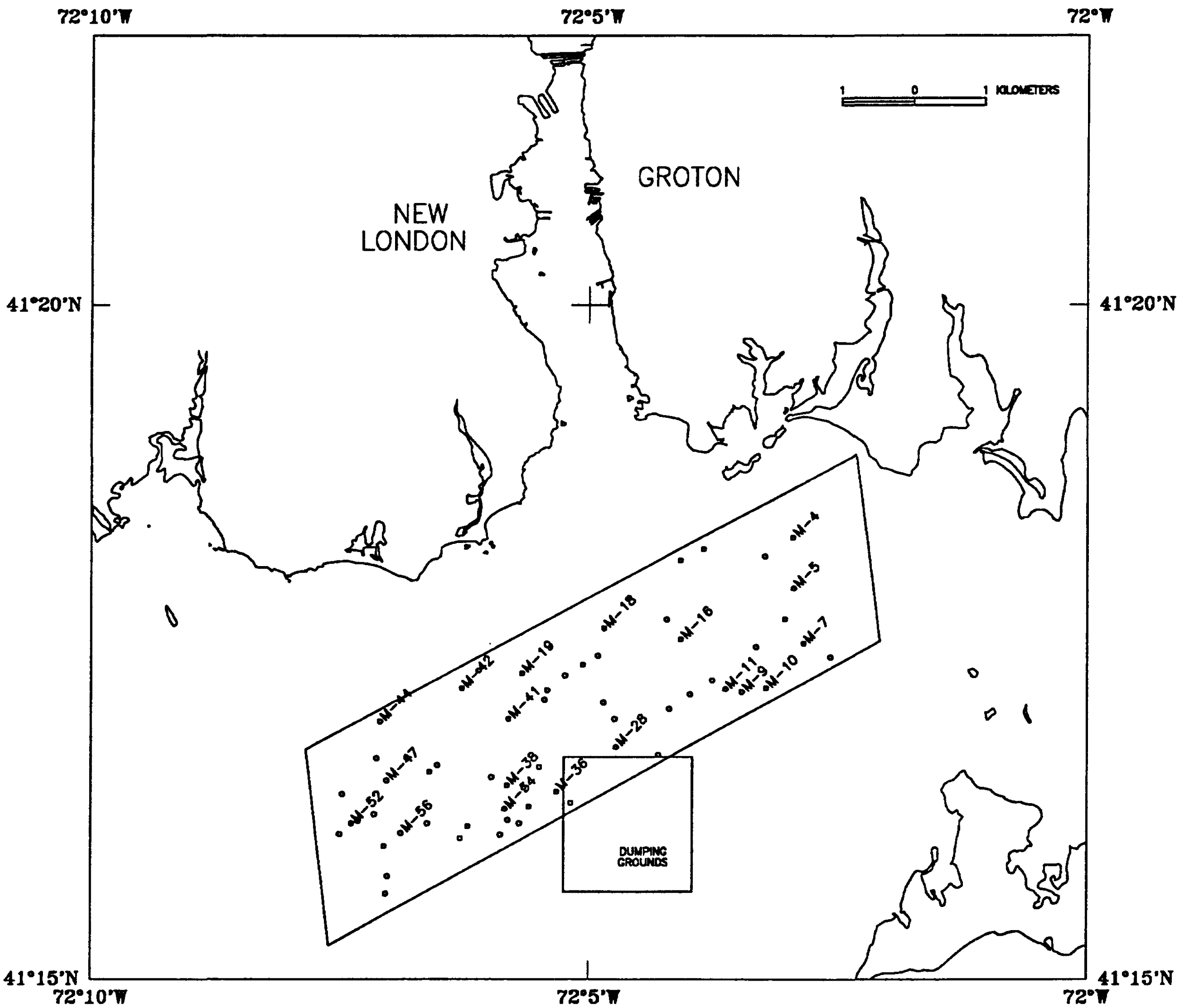
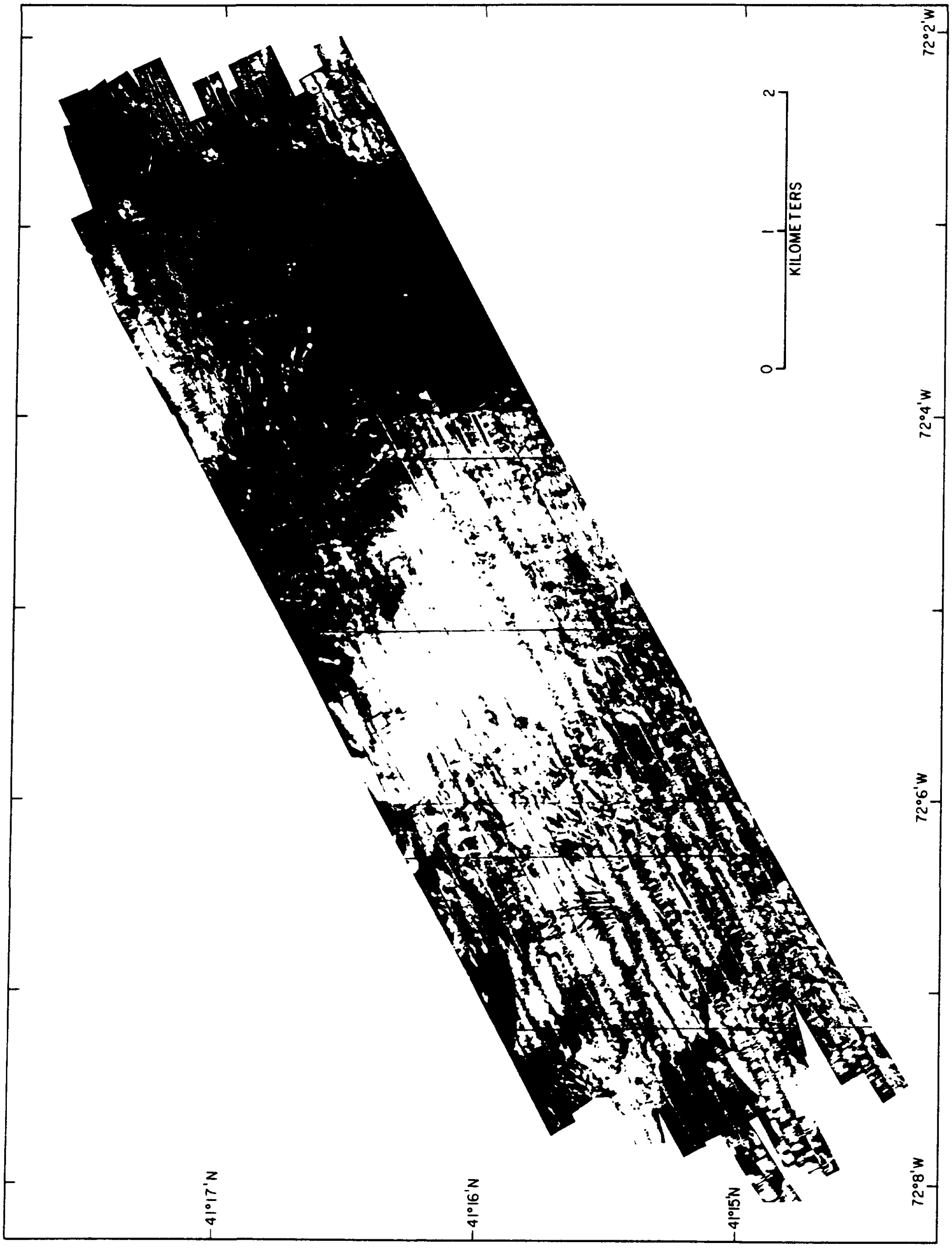


Figure 3. Sidescan sonar (100 kHz) mosaic of the study area produced by the University of Rhode Island for the Long Island Sound Resource Center. Darker areas represent areas of lower reflectivity, typically characterized by sediments of finer grain size. Lighter areas represent areas of higher reflectivity, typically characterized by sediments of coarser grain size.



Stone, 1991).

The fundamental objectives of this study were to accurately measure selected trace and major metal distributions in surficial sediment samples from northeastern Long Island Sound and to comment on the processes controlling these distributions.

METHODS

A total of 60 surficial sediment samples (0 to 2 cm in the sediment) were collected using a Teflon-coated Van Veen grab sampler while aboard the RV Asterias during June, 1992 (Poppe and others, 1992; Figure 2; Appendix A). Positioning of the ship at each sampling location was by differential GPS.

One-half of the sediment recovered in the grab sampler from twenty-one of these samples was collected with trace metal clean procedures (Bothner and others, 1982), placed in nitric acid-washed polyethylene containers and frozen immediately for storage. Field replicates were collected as three grabs from station M-38; all replicates were less than 20 m apart.

After thawing, any visible organisms, large stones, and shells were manually removed from the sample. The samples were then dried for 48 hours at 60 ^{o}C in an oven purged with N_2. Subsequently, the samples were then ground to less than 62 μm with a clean agate mortar and pestle, homogenized and stored until the analyses were conducted.

Analysis of trace and major metals, except for Hg, were performed after complete digestion of the homogenized sample in nitric, perchloric and hydrofluoric acids. V, Ni, Cr were analyzed by flameless atomic absorption spectrophotometry following suitable dilution of the acid solutions with ultra pure (Q) water (Arbogast, 1990). The analysis of Zn was performed using a flame atomic absorption spectrophotometer and analysis of Cd, Cu, Ag and Pb was performed using a Perkin Elmer 4100 ZL Graphite furnace AAS with Zeeman splitting background correction. Analysis of Hg was performed using the same Perkin Elmer instrument equipped with a cold vapor attachment. Analysis of Ba, Fe, Na and Al were performed on an optical emission inductively coupled plasma spectrometer (ICP). The limits of detection for these analyses (ppm) are reported in Tables 1 and 2. Analyses of five laboratory replicates from a single sieved sediment sample gave acceptable relative standard deviations for most elements (Tables 1 and 2). The relatively poor reproducibility (higher standard deviations) obtained for Ag and Cd, however, are probably due to these values being close to detection limits.

For a more complete discussion of the techniques employed during this study see Bothner and others (1988).

RESULTS AND COMMENTS

The trace and major metal concentrations from the sediment samples collected in northeastern Long Island Sound, and related statistics, are reported in Tables 1 and 2. Zinc concentrations were the highest (mean = 54 ppm) among the 8 trace metals studied. Vanadium concentrations were the second (mean = 49 ppm). Chromium and copper ranked third (mean = 38 ppm) and fourth (mean = 21 ppm) respectively, followed closely by lead (mean = 8.5 ppm). For both cadmium (mean = 0.081 ppm) and mercury (mean = 0.051 ppm) mean concentrations remained below 0.1 ppm. Similar trace metal concentrations were reported at the marine (southern) end of a transect down the Thames River estuary (National Oceanographic and Atmospheric Administration, 1977). Greig and others (1977) also reported similar values for trace metals in surficial sediments collected from Long Island Sound. When adjusted for textural differences (i.e. values for sandy samples are equated to published values for sandstone), the trace metal concentrations at the stations in the study area are similar to or higher than the published values for average world rock types (Krauskopf, 1967). This suggests that the sediments in the study area are enriched in trace metals by natural processes or by industrial contamination (Bother and others, 1988).

Three field replicates were obtained for sample M-38. The variability in these field replicates is larger than the analytical standard deviation, indicating that there is some small scale intra-station variability, which is probably related to changes in sediment texture and bioturbation (Turekian and others, 1980).

The boundaries of the study area are in close proximity to the Thames River estuary and a dredge spoil dumpsite (United States Naval Oceanographic Office, 1973; National marine Fisheries Service, 1974; Reid and Frame, 1977; Brown, 1980; Fig. 2). However, there is no evidence in our data, such as spatial trends of trace metal concentrations, that suggest either of these regions are point sources of trace metals to our study area. Furthermore, there seems to be no strong correlation between the concentration of Fe or Mn and other metals, which supports the hypothesis that most of the trace metals (such as Cu, Cr, Ni, Pb, V, and Zn) are derived from anthropogenic sources (Lyons, 1980).

However, there are systematic spatial trends in the concentrations of most of these elements as a function of percent fines (silt and clay) in the sediment samples (Figures 4, 5, 6, and 7; Appendix B). Although little or no correlation exists between the concentrations of Ba, Cd, Fe, Hg, and Mn and the grain size of the sediments, concentrations of Ag, Al, Cr, Cu, Na, Ni, Pb, V, and Zn are directly proportional to the amount of fines in the grain size distribution of the sediments. This positive relationship, coupled with the lack of other identifiable spatial trends, indicates that the primary control on most of the trace metal concentrations within the study area is clearly the grain size of the host sediment, rather than proximity to any point sources of metals. For example, the northeastern part of the study area is characterized by very poorly sorted sediments that have bimodal distributions and elevated concentrations of silt and clay (Poppe and others, 1992). Sediment samples from this area (such as M-4, M-5, M-10 and M-16) have high silt and clay contents, show relatively greater concentrations of metals, and show up as darker areas in

Figure 4. Plots of Ag, Al, Ba, and Cd concentrations versus percent fines (silt and clay) in the sediments from eastern Long Island Sound. Textural data from Poppe and others (1992).

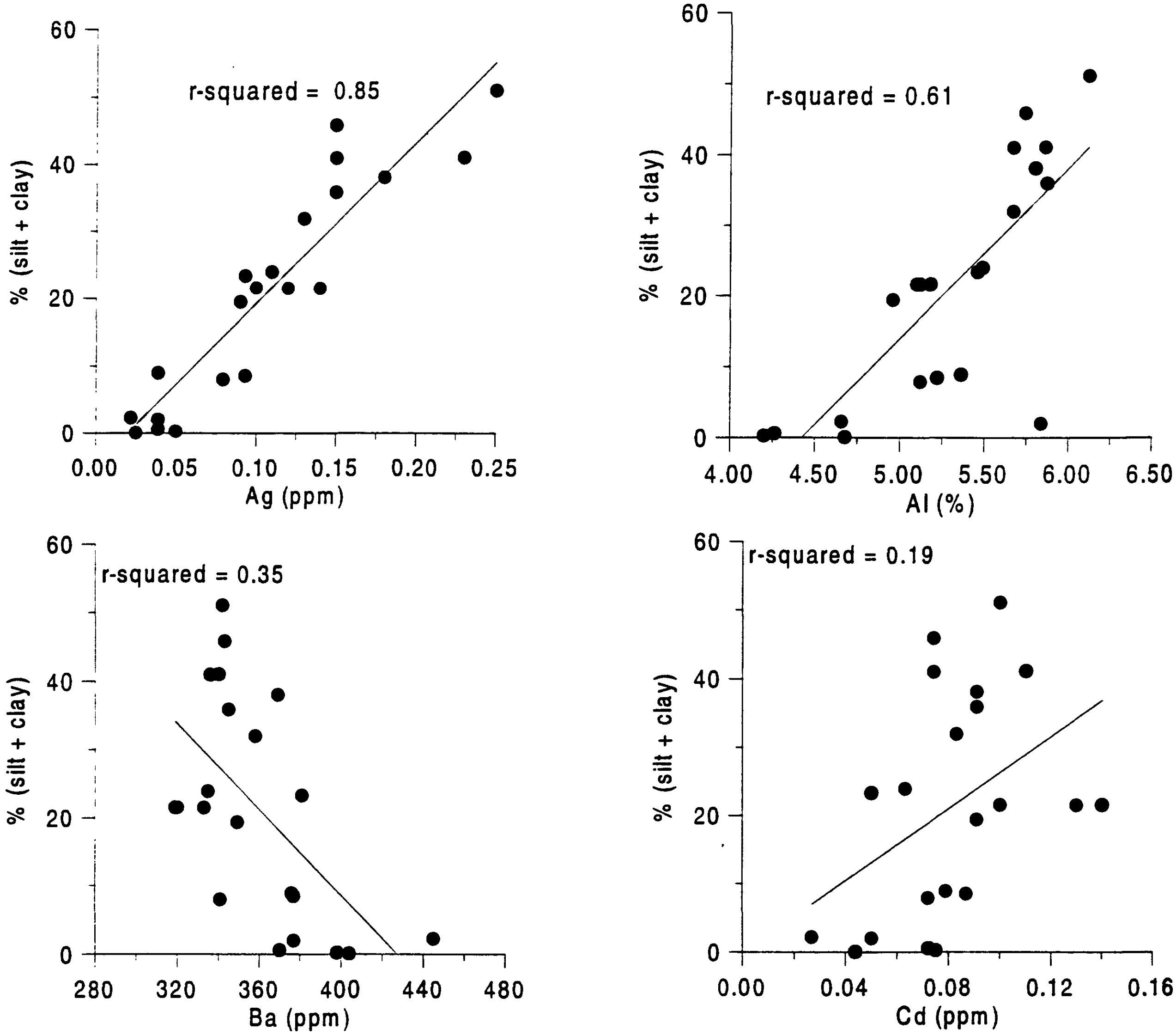


Figure 5. Plots of Cr, Cu, Fe, and Hg concentrations versus percent fines (silt and clay) in the sediments from eastern Long Island Sound. Textural data from Poppe and others (1992).

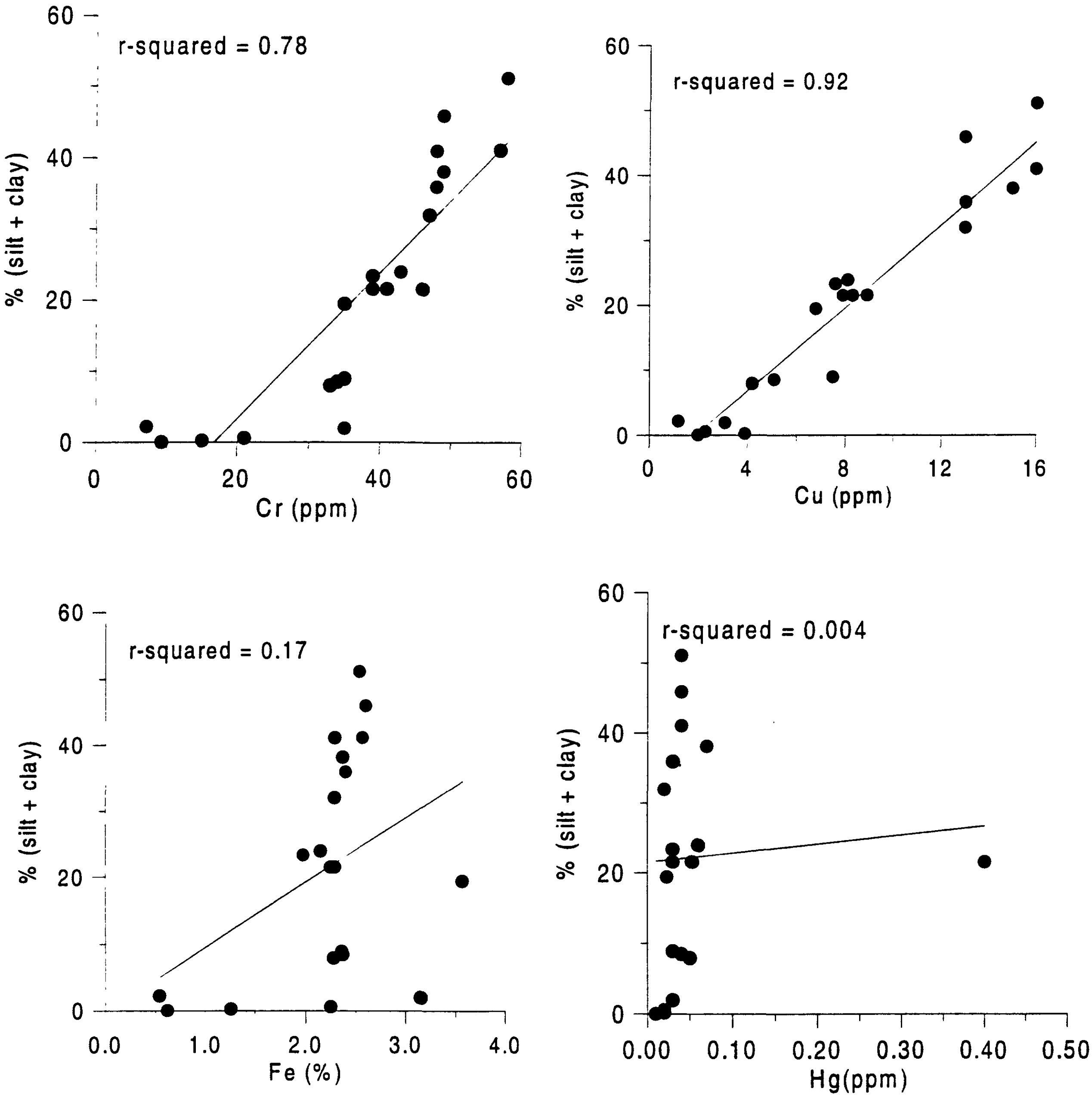


Figure 6. Plots of Mn, Na, Ni, and Pb concentrations versus percent fines (silt and clay) in the sediments from eastern Long Island Sound. Textural data from Poppe and others (1992).

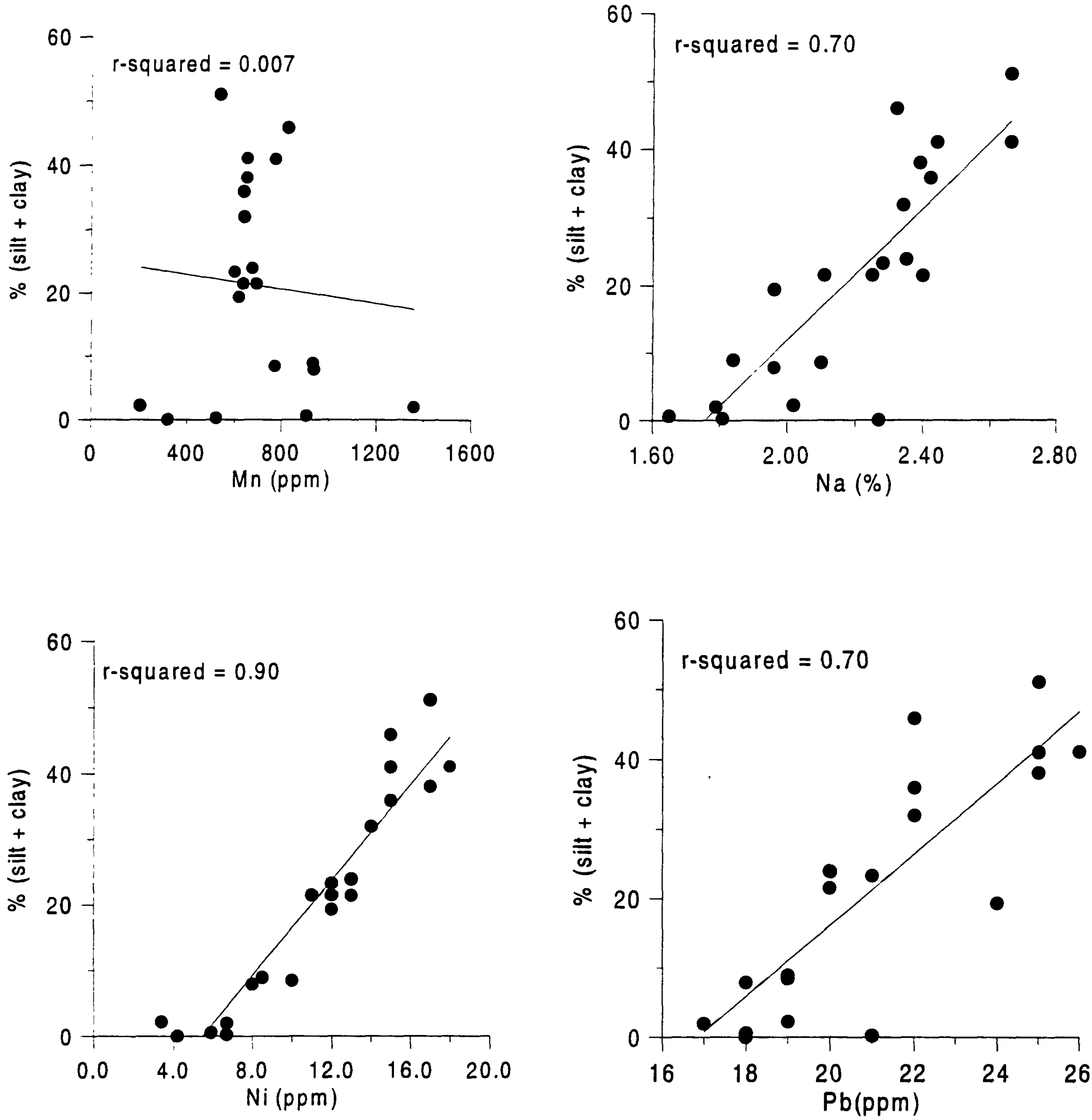
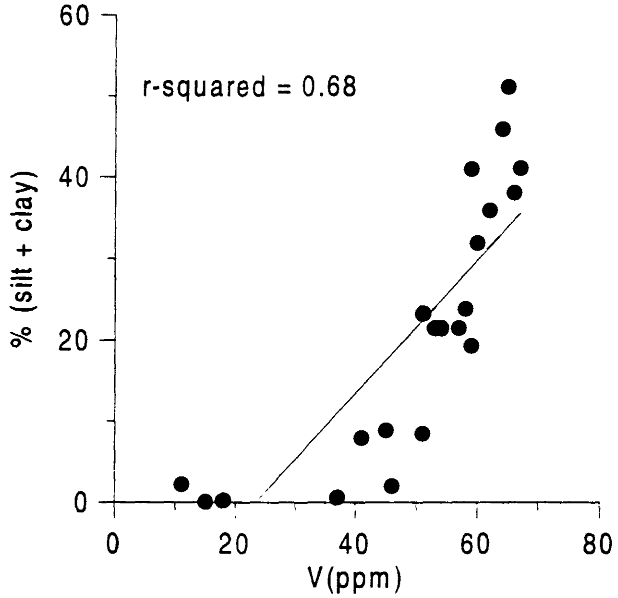
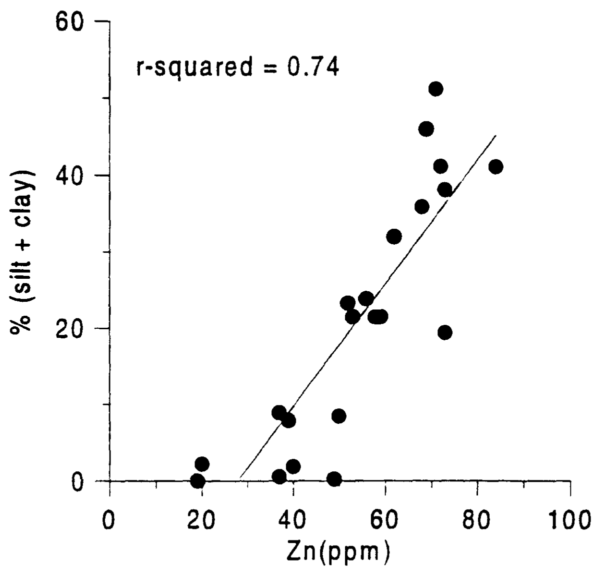


Figure 7. Plots of V and Zn concentrations versus percent fines (silt and clay) in the sediments from eastern Long Island Sound. Textural data from Poppe and others (1992).





the sidescan sonar image (Figure 3). The southwestern part of the study area is primarily characterized by sandy, moderately sorted sediments that have unimodal distributions, contain much less silt and clay (Poppe and others, 1992), and show up as lighter areas in the sidescan sonar mosaic (Figure 3). As expected from the results of earlier studies (Greig and others, 1977; Turekian and others, 1980), these sandier sediments, such as those at stations M-42 and M-44, which contain 99.97% and 97.10% sand respectively, show the lowest concentrations of metals. This correlation between sediment texture and trace metal concentration is related to the higher surface area and adsorptive capacity of the fine fraction, and argues strongly for the performance of sediment grain-size analyses in conjunction with chemical analyses on bulk sediments.

The distributions of trace and major metal concentrations in the sediment samples from Long Island Sound, as in other estuaries Bothner and others, 1993), illustrate the importance of estuarine sediments as trace metal 'sinks' in coastal areas, relative to fluvial and open, inner continental shelf sediments, because of their generally finer-grained nature and proximity to anthropogenic sources.

ACKNOWLEDGMENTS

Sample collection and analysis was funded through a State of Connecticut/U.S. Geological Survey cooperative. We would like to thank M. Doughton (U.S. Geological Survey) for the analytical processing of samples and J. Commeau and M. Buchholtz ten-Brink for reviewing this report.

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Table 1. This table contains the sediment trace and major metal data for silver, aluminum, barium, cadmium, chromium, copper, and iron. The table also contains the standard deviations for the laboratory replicates and field replicates at station M-38. DL = detection limit.

SAMPLE NUMBER	Ag ppm	Al %	Ba ppm	Cd ppm	Cr ppm	Cu ppm	Fe %
M-4	0.25	6.12	342	0.1	58	16	2.54
M-5	0.23	5.86	340	0.11	57	16	2.57
M-7	0.093	5.46	381	0.05	39	7.6	1.98
M-9	0.13	5.67	358	0.083	47	13	2.29
M-10	0.18	5.8	369	0.091	49	15	2.37
M-11	0.15	5.87	345	0.091	48	13	2.40
M-16	0.15	5.74	343	0.074	49	13	2.60
M-18	0.11	5.49	335	0.063	43	8.1	2.15
M-19	0.039	5.84	377	0.05	35	3.1	3.15
M-28	0.15	5.67	336	0.074	48	16	2.29
M-34	0.079	5.12	341	0.072	33	4.2	2.28
M-36	0.039	5.36	376	0.079	35	7.5	2.36
M-38	0.10	5.12	319	0.14	39	7.9	2.29
M-38-2	0.14	5.18	320	0.10	46	8.3	2.25
M-38-3	0.12	5.10	333	0.13	41	8.9	2.25
M-41	0.09	4.96	349	0.091	35	6.8	3.57
M-42	0.025	4.68	404	0.044	9.2	2.0	0.62
M-44	0.022	4.66	445	0.027	7.1	1.2	0.54
M-47	0.093	5.22	377	0.087	34	5.1	2.37
M-51	0.039	4.26	370	0.072	21	2.3	2.25
M-52	0.05	4.20	398	0.075	15	3.9	1.26
MEAN	0.11	5.30	360	0.081	38	8.5	2.21
DL (ppm)	0.02	0.03	1.0	0.002	0.003	0.002	0.03

LABORATORY REPLICATES

M-10	0.15	5.80	369	0.091	49	15	2.37
M-10	0.17	5.75	368	0.083	48	15	2.37
M-10	0.18	5.74	367	0.1	50	15	2.4
M-10	0.14	5.80	374	0.1	49	15	2.4
M-10	0.15	5.80	366	0.088	48	15	2.36

STANDARD DEVIATION OF LABORATORY REPLICATES

9.30%	0.47%	0.76%	7.29%	1.53%	0%	0.70%

STANDARD DEVIATION OF FIELD REPLICATES

1.36%	0.66%	1.97%	13.82%	7.01%	4.91%	0.83%

Table 2. This table contains the trace and major metal data for manganese, sodium, nickle, lead, vanadium, zinc, and mercury. This table also contains the standard deviations for the laboratory replicates and field replicates at station M-38. DL = detection limit.

SAMPLE NUMBER	Mn ppm	Na %	Ni ppm	Pb ppm	V ppm	Zn ppm	Hg ppm
M-4	539	2.66	17	25	65	71	0.040
M-5	654	2.66	18	26	67	72	0.040
M-7	600	2.28	12	21	51	52	0.030
M-9	642	2.34	14	22	60	62	0.020
M-10	652	2.39	17	25	66	73	0.070
M-11	640	2.42	15	22	62	68	0.030
M-16	826	2.32	15	22	64	69	0.040
M-18	677	2.35	13	20	58	56	0.060
M-19	1360	1.79	6.7	17	46	40	0.030
M-28	773	2.44	15	25	59	84	0.040
M-34	936	1.96	8	18	41	39	0.050
M-36	931	1.84	8.5	19	45	37	0.030
M-38	694	2.25	11	20	53	53	0.053
M-38-2	637	2.40	12	20	54	58	0.400
M-38-3	636	2.11	13	20	57	59	0.030
M-41	619	1.96	12	24	59	73	0.023
M-42	320	2.27	4.2	18	15	19	0.010
M-44	205	2.02	3.4	19	11	20	<0.002
M-47	772	2.10	10	19	51	50	0.040
M-51	905	1.65	5.9	18	37	37	0.020
M-52	523	1.81	6.7	21	18	49	0.020
MEAN	692	2.19	11	21	49	54	0.051
DL (ppm)	0.05	0.1	0.02	0.02	0.02	0.12	0.002
LABORATORY REPLICATES							
M-10	562	2.39	17	25	66	73	0.070
M-10	556	2.40	17	25	66	72	0.066
M-10	557	2.36	17	25	66	74	0.065
M-10	564	2.39	17	24	66	73	0.073
M-10	565	2.40	18	25	65	73	0.070
STANDARD DEVIATIONS FOR LABORATORY REPLICATES							
M-10	0.65%	0.61%	2.33%	1.61%	0.61%	0.87%	4.25%
STANDARD DEVIATIONS FOR FIELD REPLICATES							
M-38	4.13%	5.26%	6.80%	0%	3.11%	4.63%	27.71%

APPENDIX A

This table contains the navigation and bathymetry for those sediment samples from the sidescan mosaic off New London, Connecticut with associated trace and major metal chemical data.

SAMPLE NUMBER	LATITUDE	LONGITUDE	WATER DEPTH
M-4	41.304642	-72.049247	10
M-5	41.298337	-72.049120	11
M-7	41.291522	-72.047507	12
M-9	41.285537	-72.057657	14
M-10	41.286062	-72.053680	13
M-11	41.285907	-72.060353	14
M-16	41.292040	-72.067807	14
M-18	41.293420	-72.080773	12
M-19	41.287852	-72.094513	14
M-28	41.278745	-72.078787	16
M-34	41.271073	-72.094728	24
M-36	41.273268	-72.088760	24
M-38	41.274062	-72.097043	24
M-41	41.282203	-72.096760	17
M-42	41.285983	-72.104595	12
M-44	41.281850	-72.118217	15
M-47	41.274613	-72.117040	23
M-51	41.267955	-72.124942	29
M-52	41.269290	-72.122967	23

APPENDIX B

This table contains the sample weight analyzed, percent gravel (>2.0 mm), percent sand (2.0 mm>x>0.062 mm), percent silt (0.063 mm>x>0.004 mm), percent clay (<0.004 mm), and the verbal-equivalent sediment classification (Shepard, 1954) for those sediment samples with associated trace and major metal chemical analyses. Textural data from Poppe and others (1992).

SAMPLE NUMBER	WEIGHT (GRAMS)	PERCENT GRAVEL	PERCENT SAND	PERCENT SILT	PERCENT CLAY	SEDIMENT CLASS
M-4	30.1812	0.00	48.88	26.28	24.84	SAND-SILT-CLAY
M-5	39.3628	0.00	58.91	30.41	10.68	SILTY SAND
M-7	52.6727	0.00	76.71	11.21	12.08	SAND
M-9	56.2613	0.00	68.05	16.11	15.84	SILTY SAND
M-10	42.7473	0.00	61.91	25.36	12.72	SILTY SAND
M-11	47.3572	0.00	64.08	18.76	17.16	SILTY SAND
M-16	36.8060	0.00	54.11	28.97	16.93	SILTY SAND
M-18	56.0319	0.00	76.09	19.67	4.24	SAND
M-19	55.8246	32.31	65.74	1.14	0.81	GRAVELLY SAND
M-28	49.4311	4.87	54.11	34.18	6.84	SILTY SAND
M-34	56.1791	8.75	83.32	4.72	3.21	SAND
M-36	49.1520	1.70	89.41	5.92	2.98	SAND
M-38	56.2137	0.53	77.97	13.28	8.23	SAND
M-41	54.1726	0.47	80.16	13.08	6.29	SAND
M-42	53.6342	0.00	99.97	0.01	0.02	SAND
M-44	27.8677	0.70	97.10	1.06	1.14	SAND
M-47	50.1899	1.77	89.77	5.91	2.56	SAND
M-51	55.2916	0.00	99.44	0.13	0.43	SAND
M-52	49.0090	1.86	97.93	0.05	0.17	SAND