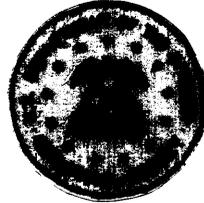


U.S. DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY



ANALYSIS OF TRACE METALS IN BOTTOM SEDIMENTS IN SUPPORT OF
DEEPWATER BIOLOGICAL PROCESSES STUDIES ON
THE U.S. SOUTH ATLANTIC CONTINENTAL SLOPE AND RISE

By

M. H. Bothner¹, E. Y. Campbell², G. P. DiLisio¹,
C. M. Parmenter¹, R. R. Rendigs¹, and J. R. Gillison²

Open-File Report 88-4

Final Report
Prepared in cooperation with the
Minerals Management Service
under Interagency Agreement
14-12-0001-30197

¹Woods Hole, MA
²Reston, VA

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS or MMS.

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ABSTRACT

This study is part of a multidisciplinary program conducted on the continental slope and rise off the North, Middle, and South Atlantic states to characterize the biology, chemistry, and geology of the sea floor in anticipation of exploratory drilling for petroleum resources. The distribution of sediment types and associated trace metals from natural sources will be used to help predict the fate and transport of sediment-reactive contaminants introduced to the water column during future development activities.

Sediment samples collected during three cruises to the continental slope and rise off the South Atlantic states have been analyzed for 12 metals (Al, Ba, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, V, and Zn). The metal concentrations in these silty-clay sediments are the same or lower than those reported for world average shales, indicating an absence of major contamination. There is, as expected, a positive correlation between metals and the concentration of silt and clay.

At most locations, concentrations of lead in the upper 10 cm of sediment are as much as two times higher than concentrations in sediment deeper than 10 cm. The maximum concentration, however, is only 17 ppm, which is less than the 20 ppm value in world average shales. The enrichment is thought to be related to onshore burning of gasoline containing lead additives. Because of our lack of knowledge about the chemical form and bioavailability of lead in these sediments, and because of the lack of similar data in the literature, it is not possible to predict the biological effects of these low level increases in lead.

At stations 11, 12, 13, and 16 the inventories of anthropogenic lead in the upper 30 cm of the sediments are close to the value predicted from the atmospheric flux of lead over the last century. However, at stations 9 and 10, the inventories are 6 to 10 times higher than predicted. The relatively high inventories suggest that processes which enhance scavenging of trace metals from the water column are more active at these two stations than at the other locations in this program. Bioturbation, sediment resuspension and deposition, and chemical precipitation are possible mechanisms. We recommend the analysis of ^{210}Pb and ^{137}Cs to confirm the occurrence of enhanced scavenging processes at these stations.

INTRODUCTION

This study was designed to establish the concentrations of trace metals in sediments prior to petroleum exploration drilling or other resource development activities on the continental slope and rise off the southeastern United States (Figure 1). This study is part of a cooperative, multidisciplinary program that is managed and funded by the U.S. Minerals Management Service. The overall program objectives are to characterize the slope and rise with respect to benthic infaunal and epifaunal communities, trace-metal and hydrocarbon concentrations in sediments and organisms, sediment texture, and water-column hydrography. Separate contracts for major parts of this program have been awarded to Battelle New England Marine Research Laboratory, Woods Hole Oceanographic Institution (WHOI), Lamont-Doherty Geological Observatory, and the U.S. Geological Survey, Branch of Atlantic Marine Geology. Study areas on the continental slope and rise off both the North and Middle Atlantic states are included in the overall program.

Samples for trace-metal analysis were collected only during the second year (phase two) of a two-year sampling program in this study area. Most of the stations were sampled three times in the second year. Cruises were conducted in May, September, and late November 1985.

FIELD SAMPLING AND SAMPLE PREPARATION

Positioning of the ship at each sampling location was based on time delays within the Loran-C navigation network read by a Northstar 6000 receiver (Digital Marine Equipment Corp., Bedford, Mass.). Latitude and longitude values (Appendix Table 1) were calculated using updated additional secondary factor corrections (McCullough and others, 1982, 1983). The accuracy of positioning is more dependent upon wind and current conditions than on the

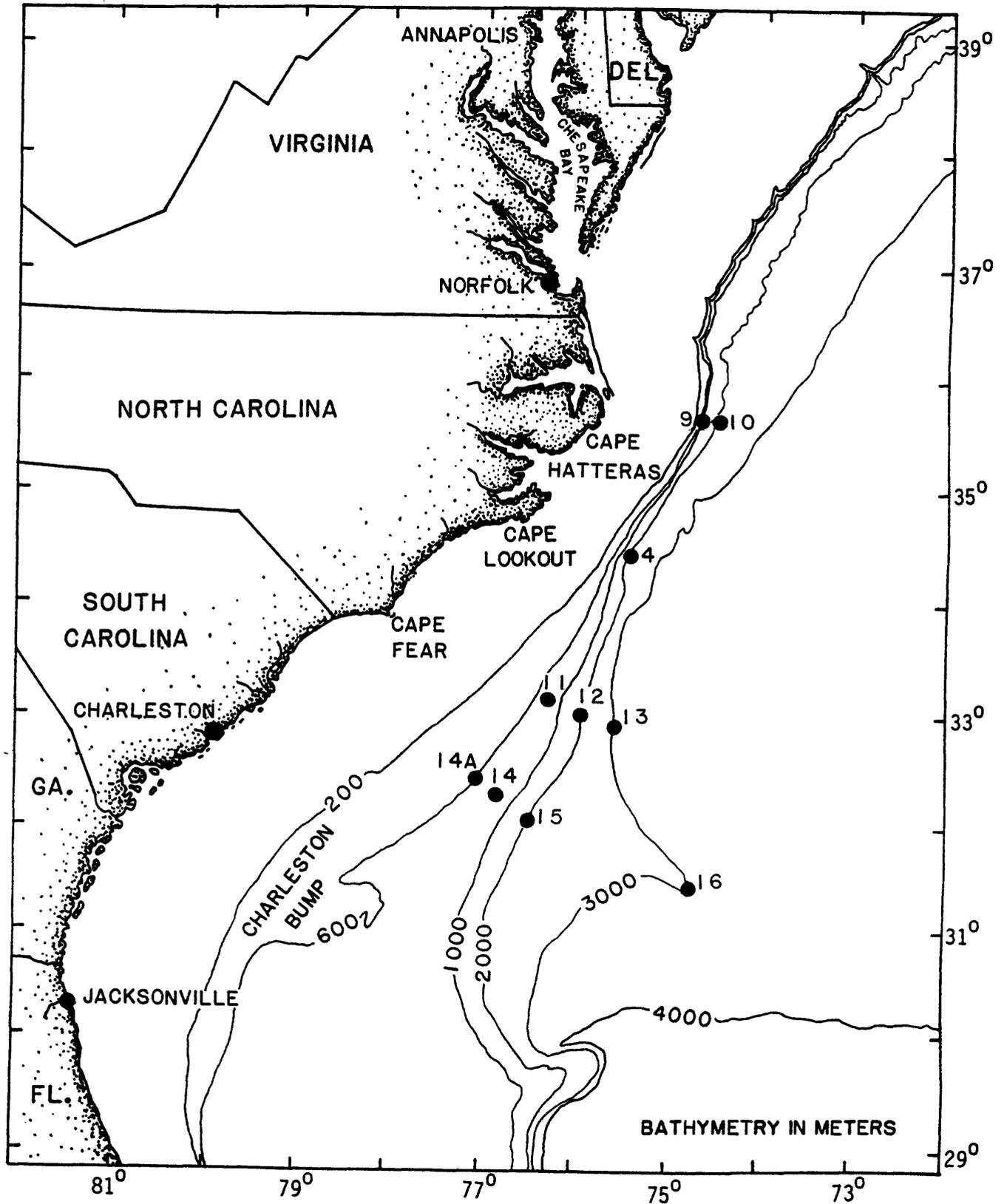


Figure 1. Station locations on the continental slope and rise off the southeastern United States.

navigation system. Replicate samples collected at a given station typically fall within a circle having a diameter of 400 m.

A 0.25-m² box core, manufactured by Ocean Instruments, Inc., San Diego, Calif., was used to collect sediment samples for this study. The sampling box was divided into 25 subcores of 0.01 m² each. Three box cores were collected at each station. Two and occasionally three subcores from each box core were allocated for trace-metal studies. As a precaution against metal contamination, surfaces of the aluminum subcores were precoated with teflon. At sea, an acid-cleaned round plastic tube, 8.2 cm internal diameter was pushed into the center of the sediments collected in the teflon subcores, thereby sampling material not in contact with the coring apparatus. These tubes were capped at both ends and frozen. The length of the core samples averaged 24 cm and typically ranged from 19 to 32 cm.

Surficial sediment was sampled by partially extruding the frozen sediment from the core barrel and cutting off the top 2 cm of the sediment using a plastic utensil. To generate a blend from a single station, the material from the upper 2 cm of each of three replicates was thawed, homogenized by stirring and shaking in a closed container, and then subsampled using a syringe constructed of glass and teflon.

On selected samples, sand and coarser material were removed by washing the wet sample through a 60- μ m nylon sieve using filtered distilled water. The resultant slurry was dried at <70°C in an oven having teflon-coated surfaces and a filtered nitrogen atmosphere.

Cores from selected stations were subsampled in sequential 2-cm depth intervals so that metal concentration profiles could be measured with increasing sediment depth. The frozen cores were extruded into a holding tray, thawed overnight, cut into 2-cm depth intervals using plastic utensils, and oven dried.

All samples prepared for trace-metal analysis were ground using agate grinding tools.

Field numbers (for example, S040111 and S051300) use to identify samples in each data table have the following code: the first three characters define the cruise in the South Atlantic region; the next two characters are the station number; the sixth character is the replicate box core number; and the seventh character is the core number within the box core. The use of "00" for the sixth and seventh characters indicates that the sample is a homogenized mixture of subsamples (sample blend) from each of three replicate box cores. The letter "X" at the end of the field number indicates that the fraction of sediment coarser than 60 micrometers has been removed from the sample. Top and bottom depth of the sample in cm below the sediment surface is listed after the field number.

TRACE-METAL ANALYSES PROCEDURES

Trace-metal analyses were made by the U.S. Geological Survey, Branch of Analytical Laboratories, Reston, Va. Concentrations of the following elements were determined: aluminum (Al), barium (Ba), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), vanadium (V), and zinc (Zn). The various procedures employed in each of the analyses are detailed below and summarized in Table 1.

Preparation of stock solution A

Exactly 0.5 g of ground bulk sediment or 0.2 g of the fine fraction was added to a covered teflon beaker and digested overnight with 5 mL of HClO₄, 5 mL of HNO₃, and 13 mL of HF at approximately 140°C. The covers were removed and the temperature was increased to between 180° and 190°C, first producing

Table 1. Summary of analytical conditions.

Element	Instrument	Instrument conditions	Extraction procedure	Procedure determination limit in sample, $\mu\text{g/g}$	Average blanks, as measured in $\mu\text{g/g}$ in solution
Al	ICP (argon)	308.2 nm FP (Forward power)=1.1 kw Fixed cross flow nebulizer Spectral band width 0.036 nm Observation height 16 mm.	None	50	0.02
Ba	ICP (argon)	455.4 nm FP=1.1 kw Fixed cross flow nebulizer Spectral band width 0.036 nm Observation height 16 mm.	None	20	.01
Cd	Graphite furnace AA.	110°C dry temperature 250°C char temperature 2100°C atom temperature Regular graphite tube Interrupt gas flow W.l.=228.8 nm Slit=0.7 nm.	Butyl acetate and DDTC.	0.02	.0002
Cr	Graphite furnace AA.	110°C dry temperature 900°C char temperature 2700°C atom temperature Pyrolytic tube Normal gas flow (low) W.l.=357.9 nm Slit=0.7 nm.	None	2	.003
Cu	Graphite furnace AA.	110°C dry temperature 850°C char temperature 2700°C atom temperature Regular graphite tube Interrupt gas flow W.l.=324.7 nm Slit=0.7 nm.	Butyl acetate and DDTC.	1	.005
Fe	ICP (argon)	259.9 nm FP=1.1 kw Fixed cross flow nebulizer Spectral band width 0.036 nm Observation height 16 mm.	None	50	.02
Hg	Induction furnace AA.	Wavelength=254 nm Cold vapor AA.	None	.005	.005
Mn	ICP (argon)	257.6 nm FP=1.1 kw Fixed cross flow nebulizer Spectral band width 0.036 nm Observation height 16 mm.	Butyl acetate (removal of iron).	10	.006
Ni	Graphite furnace AA.	110°C dry temperature 900°C char temperature 2700°C atom temperature Pyrolytic tube Normal gas flow (low) W.l.=232.0 nm Slit=0.2 nm.	None	2	.02
Pb	Graphite furnace AA.	110°C dry temperature 500°C char temperature 2700°C atom temperature Regular graphite tube Interrupt gas flow W.l.=283.3 Slit=0.7 nm.	Butyl acetate and DDTC.	1	.02
V	Graphite furnace AA.	110°C dry temperature 1000°C char temperature 2800°C atom temperature Pyrolytic curtained tube Normal gas flow (high) W.l.=318.4 nm Slit=0.7 nm.	None	2	.002
Zn	Flame AA.	Oxidizing; air-acetylene flame W.l.=213.9 Slit=0.7 nm.	Butyl acetate	1	.01

fumes of HClO_4 and then evaporating the solution to dryness. The residue was dissolved and diluted to exactly 25 mL with 8 N HCl. This solution is referred to as stock solution A.

Two blanks containing all reagents were analyzed along with samples. All reagents were analyzed for contaminants prior to use, as is always necessary. The Canadian reference sediment standard MESS-1 was analyzed in each set of samples. A series of solutions was prepared that approximated the concentration levels expected in the samples; this series was used as the standard in calibrating the inductively coupled plasma (ICP) spectrometer and atomic absorption (AA) spectrophotometer.

Preparation of stock solution B

Stock solution B was made by adding 10 mL of butyl acetate (distilled to remove impurities such as copper) to 15 mL of stock solution A in a 60-mL separatory funnel. This solution was vigorously agitated by an automatic shaker for six minutes to extract iron. The layers were separated, and the extraction step was repeated with an additional 10 mL of butyl acetate. The aqueous layer was evaporated to dryness at 150°C in a 50-mL beaker. The residue was dissolved and diluted to 25 mL with 1 N HCl.

Barium

The measurements for Ba were made by ICP spectrometry with 2 mL of stock solution A diluted to 4 mL with distilled H_2O .

Aluminum, iron, chromium, nickel, and vanadium

Concentrations of Al and Fe were determined by ICP spectrometry by using 1 mL of stock solution A diluted to 10 mL with distilled H_2O . The

measurements for Cr, Ni, and V were made by injecting 20 μ L of diluted (1:10) stock solution A into a graphite-furnace AA spectrophotometer.

Lead, copper, and cadmium

Fifteen mL of 0.5-percent (weight:volume) diethyldithiocarbamic acid diethylammonium salt (DDTC) in chloroform was added to 10 mL of solution B in a 60-mL separatory funnel and mixed for 10 minutes by an automatic shaker. The chloroform layer was drained into a 30-mL beaker and the aqueous layer washed with 10 mL of chloroform. The second chloroform layer was combined with the first, and the total volume of chloroform was evaporated to dryness at 90°C. The organic matter was destroyed by adding 0.1 mL of concentrated HNO₃ and the solution was evaporated to dryness. This residue then was dissolved in 2 mL of warm 1 N HCl. The beaker was rinsed four times with 2-mL portions of distilled H₂O, and the solution was transferred to a small polyethylene container. The measurements for Pb, Cu, and Cd were made by injecting 20 μ L of the final solution into a graphite-furnace AA spectrophotometer.

Manganese and zinc

The measurements for Mn were made by ICP spectrometry with a solution made by diluting 2 mL of stock solution B to 4 mL with H₂O. Zinc was measured by flame AA directly from stock solution B.

Mercury

Mercury concentration was determined on a separate portion of the sample. Two hundred milligrams of sediment were decomposed in a 1-oz teflon screw-top vial using 2 mL of concentrated HNO₃ (J. T. Baker Chemical Co.) and

2 mL of HClO_4 (G. Frederick Smith Chemical Co. (GFS) -- double distilled from Vycor, a pure silica glass). The mixture was heated in a capped vial until the solution reached 200°C . The solution was then heated with the cap off for about 45 minutes, after which the samples were removed from the heat source. Immediately, 1 mL of concentrated HNO_3 was added; the vial was filled with H_2O and capped tightly until used. This sample solution was added to a flask containing 125 mL of H_2O and 4 mL of 10-percent (weight:volume) SnCl_2 in 20-percent HCl . Nitrogen was passed through the solution to remove elemental Hg, which was collected on gold foil located in the center of the coils of an induction furnace. Activation of the furnace released the Hg, which was measured by a cold-vapor AA technique. Blanks, standard rocks, and internal sediment standards were analyzed for each set of samples. A series of solutions was prepared that had the same Hg concentration range expected in the samples.

TEXTURAL ANALYSIS PROCEDURES

Sediment samples selected from different depth horizons within the box cores were analyzed for texture by the standard pipet method (Folk, 1974). The specific procedures were essentially identical to those used by other contractors within this program (Blake and others, 1987). The textural results were calculated according to the method of moments (Krumbein and Pettijohn, 1938) and were reported in whole phi units ($-\log_2 D$) where D is the grain diameter in mm.

ANALYTICAL ACCURACY AND PRECISION

Analytical accuracy was determined by analyzing rock standard MESS-1. All of the metals are within one or, at most, two standard deviations of the

"best value" determined for this sediment standard (Table 2A). A new fine-grained sediment standard (B series, Table 2A) established for the Georges Bank Monitoring Program (Bothner and others, 1986b) was also used during this program.

Analytical precision was determined by periodically analyzing replicate aliquots taken from a single sample (Table 2A) and by occasionally submitting unlabeled duplicates (Blinds, Table 2B). The average coefficient of variation shown in Table 2A is 3.6%. Coefficients of variation greater than 10 percent were occasionally measured for Cd, Hg, Ni, and Pb determinations at concentrations less than five times the detection limit (Table 2A and 2B).

The precision of the textural analyses was determined by including a sediment standard with each batch of samples. The coefficient of variation for the clay fraction was about 5 percent.

During the early phases of this program, we evaluated the metal concentrations in surface sediments that had been in contact with different materials used in the box of the box corer. Mr. George Hampson, WHOI, suggested this experiment and provided the carefully collected samples.

To assess contamination effects from the box core sampler, we compared the metal concentrations in sediments from the center of a teflon-coated subcore (i.e., material that had not been in contact with the sampler) with sediments in direct contact with either the teflon-coated or the uncoated aluminum corer (Table 3). Bulk sediments and the fraction $<60 \mu\text{m}$ were compared. We found that the concentrations of Ba and Cr, the metals most likely to indicate the presence of drilling mud in sediments, were not contaminated by contact with the walls of the box corer. In the bulk sediments, vanadium appeared to be slightly higher in the samples collected from the edge of the teflon-coated subcore compared to the other samples. In

Table 2A. Analysis of sediment standard and replicate sediment samples.

Sediment Standard	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
MESS-1-----	4.99	252	.52	66	24	2.87	-	490	35	29	84	178
	5.61	269	.46	60	24	2.91	-	480	37	26	88	178
	4.72	253	.50	66	24	2.83	.14	483	34	27	88	174
	5.28	259	.44	62	24	2.87	.20	471	36	26	85	174
	5.45	263	.48	60	23	2.89	.14	484	35	27	86	170
	5.50	256	.49	61	23	2.88	.14	476	31	29	75	181
	5.41	260	.47	59	23	2.87	--	479	31	27	75	181
	5.34	261	.55	68	24	2.82	--	503	38	28	78	176
	5.11	259	.41	67	24	2.80	.15	492	37	28	82	176
\bar{x} -----	5.27	259	.48	63.2	23.7	2.86	.154	484	34.9	27.4	82.3	176
σ -----	.28	5	.04	3.5	.5	.04	.026	10	2.5	1.1	5.2	3
CV(%) ¹ -----	5.3	2	8.7	5.5	2.1	1.2	17	2	7.2	4.1	5.3	2
Best value ²	5.8	261	.59	71	25	3.0	-	513	30	34	72	191
σ -----	.2	18	.1	11	4	.2	-	25	3	6	5	17
Sediment Standard	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
B-11 ³	2.99	255	.063	45	5.5	1.60	.015	288	10	16	43	38
(Station 13)	3.22	264	.083	47	5.5	1.62	.015	278	11	13	46	40
	3.20	264	.083	44	6.3	1.61	.013	296	10	14	48	37
B-12	3.43	261	.083	42	5.9	1.64	.015	291	10	15	45	35
(Station 13)	3.36	259	.071	49	6.0	1.58	.015	303	13	15	41	37
\bar{x} -----	3.24	261	.077	45.4	5.84	1.61	.015	291	10.8	14.6	44.6	37.4
σ -----	.17	4	.009	2.7	.34	.02	.001	9	1.3	1.1	2.7	1.8
CV(%) ¹ -----	5.2	1.4	12	6.0	5.9	1.4	6.1	3.2	.1	7.8	6.1	4.9
Sample Replicate	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S410-1-1-12	4.50	300	.055	51	10	2.15	.010 ⁴	281	24	12	62	51
W-232114	4.47	302	.066	50	10	2.16	.010	282	24	12	62	53
	4.55	301	.063	50	10	2.20	.010	278	25	12	60	55
	4.54	306	.055	52	10	2.13	.010	285	25	14	64	53
	4.53	304	.066	51	10	2.16	.010	280	23	13	62	53
\bar{x} -----	4.52	303	.061	50.8	10	2.16	.010	281	24.2	12.6	62	53
σ -----	.03	2	.006	.8	0	.02	0	3	.8	.9	1.4	1.4
CV(%) ¹ -----	.7	.7	9.2	1.6	0	1.2	0	.9	3.5	7.1	2.3	2.7

Table 2A. Analysis of sediment standard and replicate sediment samples-Continued

Sample Replicate	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S412-3-1-10	3.73	236	.075	65	17	2.02	.020	269	23	4.3	66	51
W232135	3.73	238	.075	66	17	2.02	.020	262	26	4.6	68	50
	3.77	238	.058	65	18	2.04	.020	265	26	4.8	68	50
	3.74	240	.075	65	17	2.03	.020	261	26	4.3	66	53
	3.73	244	.071	66	18	2.03	.020	264	26	4.8	66	51
\bar{x} -----	3.74	239	.071	65	17	2.03	.020	264	25	4.6	67	51
σ -----	.02	3	.007	.5	.5	.01	---	3	1	.2	1	1
CV(%) ¹ -----	.5	1.3	10	.8	3.1	.4	---	1.2	5.3	5.5	1.6	24
Sample Replicate	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S414-0-0-02	1.47	104	.11	34	7.6	.73	.02	263	12	4.6	22	25
W231802	1.47	104	.11	33	7.6	.73	.02	270	11	4.2	22	25
	1.48	103	.11	34	7.6	.73	.02	269	11	4.2	22	22
	1.47	104	.091	34	7.5	.73	.02	265	13	4.2	22	23
	1.47	104	.1	34	7.6	.73	.023	266	13	4.8	22	23
\bar{x} -----	1.47	104	.1	33.8	7.58	.73	.021	267	12	4.4	22	23.6
σ -----	0	0	.01	.4	.04	0	.001	3	1	.3	0	1.3
CV(%) ¹ -----	.3	.4	6.7	1.3	.6	0	6.5	1.1	8.3	6.4	0	5.7
Sample Replicate	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S512-0-0-02	3.27	216	.075	55	14	1.68	.05	493	26	4.3	74	45
W233742	3.27	215	.066	56	14	1.67	.05	498	25	4.8	71	45
	3.25	215	.071	55	14	1.70	.06	497	23	4.3	71	45
	3.27	215	.066	57	14	1.68	.05	495	26	4.3	71	45
	3.25	217	.075	55	14	1.66	.05	495	26	4.3	74	45
\bar{x} -----	3.26	216	.071	55.6	14	1.68	.052	496	25.2	4.4	72	45
σ -----	.01	1	.004	.9	-	.01	.004	2	1.3	.2	2	-
CV(%) ¹ -----	.3	.4	6.4	1.6	-	.9	8.6	.4	5.2	5.1	2.3	-
Sample Replicate	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S614-2-1-02	1.53	107	.14	22	7	0.76	.01	240	4.5	4.8	17	25
W234683	1.52	105	.14	22	7.5	0.74	.01	241	3.3	5.3	17	25
	1.51	104	.14	23	7	0.74	.02	243	3.3	4.8	17	23
	1.50	106	.14	22	7	0.74	.02	242	3.3	5.3	17	25
	1.52	105	.15	22	7	0.75	.02	241	3.3	4.8	17	25
\bar{x} -----	1.52	105	.14	22.2	7.1	.75	.02	241	3.6	5	17	24.6
σ -----	.01	1	.004	.4	.2	.01	.01	1	.7	.3	-	.9
CV(%) ¹ -----	.8	1.1	3.1	2	3.1	1.2	34	.5	19	5.5	-	3.6

¹Coefficient of variation

²Values reported by the Marine Analytical Chemistry Standards Program, National Research Council, Canada.

Table 28. - Chemical analysis of blind duplicates.

Field no.	TopDep (cm)	BotDep (cm)	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S041011	2.	4.	W-232110	4.20	307	.066	45.0	7.8	1.90	.02	270.	19.0	9.6	51.0	45.0
S041011	2.	4.	W-232130	4.21	312	.071	43.0	8.6	1.90	.01	280.	16.0	11.0	54.0	48.0
S041521	0.	2.	W-232141	1.57	98	.090	35.0	9.0	1.10	.02	419.	13.0	5.3	24.0	25.0
S041521	0.	2.	W-232150	1.61	99	.083	36.0	9.3	1.15	.02	427.	13.0	5.6	28.0	25.0
S050931	0.	2.	W-233749	4.28	296	.063	46.0	8.3	2.06	.02	307.	26.0	9.8	67.0	51.0
S050931	0.	2.	W-233776	4.29	297	.071	48.0	8.3	2.05	--	305.	23.0	8.6	67.0	51.0
S061431	0.	2.	W-234684	1.42	105	.150	22.0	7.0	.70	.02	218.	3.3	5.3	19.0	27.0
S061431	0.	2.	W-234690	1.44	102	.110	28.0	8.5	.71	.02	218.	6.0	4.3	21.0	23.0

Table 3 - Chemical analyses of replicate samples collected from different areas of a single box core

[Samples A, B, and C from center of a teflon-coated subcore (assumed to be the least contaminated); D, E, and F in contact with the side of teflon-coated subcore; G, H, and I in contact with the side of aluminum subcore. Field no. ending in X means size fraction finer than 60 µm analyzed.]

Field no.	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S02021A	W-226341	1.8	120	0.068	26	8.4	1.1	0.02	120	11	5	12	30
S02021B	W-226342	1.8	130	.140	26	8.6	1.0	.02	120	11	5	17	32
S02021C	W-226343	1.9	130	.180	28	12	1.1	--	120	13	6	16	32
\bar{x}		1.83	127	.13	26.7	9.7	1.07	.02	120	11.7	5.3	15	31
σ		.06	5.8	.06	1.2	2.0	.06	0	0	1.2	.6	2.6	1.2
CV(%)		3.2	4.6	44	4.3	21	5.4	0	0	9.9	10.8	17.6	3.7
S02021D	W-226344	1.9	130	.150	26	10	1.1	.02	130	12	7	20	33
S02021E	W-226345	1.9	130	.130	26	8.6	1.1	.02	130	11	5	21	32
S02021F	W-226346	1.9	130	.088	29	7.8	1.1	.02	150	12	6	23	32
\bar{x}		1.9	130	.12	27.0	8.8	1.1	.02	137	11.7	6.0	21	32
σ		0	0	.03	1.7	1.1	0	0	12	.6	1.0	1.5	.6
CV(%)		0	0	26	6.4	13	0	0	8.4	4.9	16.7	7.2	1.8
S02021G	W-226347	1.8	120	.083	26	10	1.1	.02	160	11	6	10	30
S02021H	W-226348	1.8	130	.110	25	7.5	1.0	.02	130	11	5	12	30
S02021I	W-226349	1.8	130	.130	26	8.0	1.0	.02	120	11	4	10	30
\bar{x}		1.80	127	.11	25.7	8.5	1.03	.02	137	11	5.0	11	30
σ		0	5.8	.02	.6	1.3	.06	0	21	0	1.0	1.2	0
CV(%)		0	4.6	22	2.2	16	5.6	0	15	0	20	10.8	0
S02021AX	W-226350	2.8	160	.085	35	13	1.28	.04	149.5	20	8	36	48.0
S02021BX	W-226351	2.8	158	.105	35	14	1.26	.04	147.5	20	7	33	44.2
S02021CX	W-226352	2.7	158	.148	35	14	1.27	--	147.7	20	6	33	44.3
\bar{x}		2.79	159	.11	35	14	1.27	.04	149	20	7.0	34	45.3
σ		.05	1.2	.03	0	.6	.01	0	1.2	0	1.0	1.7	2.3
CV(%)		1.8	0.7	28	0	4.2	.8	0	.8	0	14.3	5.1	5.1
S02021DX	W-226353	2.8	161	.098	35	9.8	1.29	.05	150.3	19	11	33	48.3
S02021GX	W-226354	2.8	160	.097	35	13	1.28	.04	192.5	20	10	37	48.1
\bar{x}		2.78	160	.10	35	11	1.28	.04	172	19.5	10.5	35	48.2
σ		.01	.7	0	0	2.3	.01	.01	30	.7	.7	2.8	.1
CV(%)		.2	.4	.7	0	20	.6	16	18	3.6	6.7	8.1	.2

¹Coefficient of variation.

the fine fraction, the lead values from the edges of the subcores are about 40 percent higher than in the sediment not in contact with the box-core material.

The material that was in contact with the walls of the subcore probably represent the worst case of contamination from the material used to construct the box-core sample chamber. The sediment that is routinely removed from the subcore for trace-metal analysis, however, excludes the material in contact with the wall of the subcore. We therefore conclude that contamination from the walls of the box core is insignificant. Although this test does not rule out the possibility that metal contamination could occur from flakes of material falling onto the sediment surface from the coring apparatus above the sample box, such contamination would be random and severe and should be obvious from the chemical analyses. Within this program we have observed less than five spurious values that might be explained by contamination from field or laboratory operations.

RESULTS AND DISCUSSION

Within-station variability

We determined the variability of metal concentrations both within a single box core and between replicate box cores for two stations (Table 4A,B). Using the average coefficient of variation as an index, the within-box core and within-station variability is similar: about 10 percent at station 4 and 7 percent at station 9. The average within-station variability at other stations (Table 4C) is 7.5 percent. The values are larger than the 4% average precision shown in Table 2, but are much smaller than the variability between stations.

The values for within-box core and within-station variability are similar to those found in the Mid-Atlantic study (Bothner and others, 1987a) but

Table 4A. - Comparison of within - station variability to within box core variability at Station 4, Cruise 4.

Field no.	Top (cm)	Btm (cm)	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S040411	0	2	W-231805	3.98	271	.100	56	14	1.97	0.02	493	30	8.8	54	55
S040421	0	2	W-231806	3.84	267	.066	56	14	1.91	0.02	414	29	7.5	62	50
S040431	0	2	W-231807	3.93	265	.063	54	14	1.95	0.02	424	29	7.5	60	53
\bar{x}			3.92	268	.076	55.3	14	1.94	0.02	444	29.3	7.9	58.7	52.7	
σ			.07	3	.020	1.2	0	.03	0	.43	.6	.8	4.2	2.5	
CV(%)			1.8	1.1	2.1	0	0	1.2	0	9.7	2	9.5	7.1	4.8	
S040411	0	2	W-231805	3.98	271	.100	56	14	1.97	.02	493	30	8.8	54	55
S040412	0	2	W-231808	3.97	271	.038	57	14	1.98	.03	499	29	6.1	62	48
S041413	0	2	W-231809	3.90	260	.042	57	12	1.98	.03	411	29	6.1	54	50
\bar{x}			3.95	267	.060	56.7	13.3	1.98	.03	468	29.3	7.0	56.7	51	
σ			.04	6.4	.035	.6	1.2	.01	.01	.49	.6	1.6	4.6	3.6	
CV(%)			1.1	2.4	1	8.7	.3	.22	22	10	2	22	8.2	7.1	

Table 4B - Comparison of within-station variability to within box core variability at Station 9, Cruise 5.

Field no.	Top (cm)	Btm (cm)	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S050911	0	2	W-233747	4.02	295	.058	46	7.3	1.98	0.03	303	23	8	71	45
S050921	0	2	W-233748	3.92	289	.058	41	7.6	1.91	0.03	300	20	8.6	67	45
S050931	0	2	W-233749	4.28	296	.063	46	8.3	2.06	0.02	307	26	9.8	67	51
\bar{x}			4.07	293	.060	44.3	7.7	1.98	0.03	303	23	8.8	68.3	47	
σ			.19	4	.003	2.9	0.5	.08	0.01	4	3	0.9	2.3	3.5	
CV(%)			4.6	1.3	4.8	6.5	6.6	3.8	22	1.1	1.3	10	3.4	7.4	
S050921	0	2	W-233748	3.92	289	.058	41	7.6	1.91	.03	300	20	8.6	67	45
S050922	0	2	W-233750	4.19	303	.066	46	7.5	2.01	.03	303	23	8	63	50
S050923	0	2	W-233751	3.94	290	.075	44	6.6	1.87	.02	313	20	8	55	45
\bar{x}			4.02	294	.066	43.7	7.2	1.93	.03	305	21.0	8.2	61.7	46.7	
σ			.15	7.8	.008	2.5	.6	.07	.01	7	1.7	.3	6.1	2.9	
CV(%)			3.7	1.9	1.3	5.8	7.6	3.7	22	2.3	8.2	4.2	9.9	6.2	

Table 4C - Within-station variability for Cruise 4, Stations 9 and 11; Cruise 5, Station 15, Cruise 6, Stations 14 and 16

Field no.	Top Btm (cm)	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)	
S040911	0	2	W-231810	3.97	300	.042	46	8.3	1.85	.02	340	21	8.3	47	45
S040921	0	2	W-231811	4.19	293	.050	51	9.3	2.02	.02	329	26	9.6	56	53
S040931	0	2	W-23812	4.10	302	.042	49	9.6	1.95	.02	333	24	9.1	64	48
\bar{x}			4.09	298	.045	48.7	9.1	1.94	.02	334	23.7	9.0	55.7	48.7	
σ			.11	4.7	.005	2.5	.7	.08	0	6	2.5	.7	8.5	4	
CV(%)			.03	1.6	1.0	5.2	7.5	4.4	0	1.7	11	7.3	15	8.3	
S041111	0	2	W-232119	1.75	118	.083	36	8	.91	.02	248	9	3.8	26	20
S041121	0	2	W-232120	1.73	115	.100	38	7.5	.95	.02	228	10	3	28	23
S041131	0	2	W-232121	1.58	108	.075	35	7.5	.88	.02	217	8	3.8	23	18
\bar{x}			1.69	114	.086	36.3	7.7	.91	.02	231	9	3.5	25.7	20.3	
σ			.09	5	.013	1.5	.3	.04	0	16	1	.5	2.5	2.5	
CV(%)			5.5	4.5	15	4.2	3.8	3.8	0	6.8	11	13	9.8	12	
S051511	0	2	W-233752	1.63	103	.091	31	9.6	1.08	.02	392	15.0	5.1	30	32
S051521	0	2	W-233753	1.69	104	.075	34	8.3	1.13	.02	383	16.0	4.8	28	28
S051531	0	2	W-233754	1.57	95	.083	29	7.6	1.10	.02	425	16.0	5.3	30	32
\bar{x}			1.63	101	.083	31.3	8.5	1.10	.02	400	15.7	5.1	29.3	30.7	
σ			.06	5	.008	2.5	1	.02	0	22	.6	.2	1.2	2.3	
CV(%)			3.7	5	9.6	8	12	2.3	0	5.5	3.7	5	3.9	7.5	
S061411	0	2	W-234682	1.53	101	.12	23	7.5	.74	.02	263	4.5	4.3	21	25
S061421	0	2	W-234683	1.52	105	.14	22	7.1	.75	.02	241	3.5	5.0	17	25
S061431	0	2	W-234684	1.42	105	.15	22	7	.70	.02	218	3.3	5.3	19	27
\bar{x}			1.49	104	.14	.3	7.2	.73	.02	241	3.8	4.9	19	25.7	
σ			.06	2	.015	.6	.3	.03	0	22	.6	.5	2	1.2	
CV(%)			4.1	2.2	11	2.6	3.7	3.6	0	9.3	17	10	10	4.5	
S061611	0	2	W-234685	4.16	233	.11	49	19	2.23	.02	1011	27.0	5.3	58	55
S061621	0	2	W-234686	4.10	228	.046	54	18	2.23	.01	1526	27.0	5.5	60	56
S061631	0	2	W-234687	4.31	249	.063	56	20	2.30	.02	1099	31.0	4.8	60	56
\bar{x}			4.19	237	.073	53	19	2.25	.02	1212	28.3	5.2	59.3	55.7	
σ			.11	11	.033	3.6	1	.04	.01	275	2.3	.4	1.2	.6	
CV(%)			2.6	4.6	4.5	6.8	5.3	1.8	35	23	8.2	6.9	1.9	1	

1 Coefficient of variation

smaller than those measured in the North Atlantic study area (Bothner and others, 1987b) where wider within-station variability in texture has also been noted.

Distribution of metals in surface sediments

The concentration of metals and textural parameters for each station occupied during Cruise 4 (Fig. 2A, B, C and D and Table 5) have been plotted in the order of decreasing latitude, which preserves the order of stations within each transect across the slope. Textural data and organic carbon values were provided by the WHOI and Battelle contractors for this program.

The concentrations of metals in these sediments are the same or lower than those measured in average shales from various locations around the world (Krauskopf, 1967). This similarity suggests that these sediments are not enriched in trace metals by natural diagenetic processes or by industrial activity. Within this study area, most metal concentrations vary by a factor of 3; Ba, Cu, Al, Mn, and Zn vary by a factor of 4 to 6.

The variation in concentration of metals and clay is similar from station to station. The close correlation among these variables can be explained by the varying proportion of clay-sized material in the sediment. Because of its higher surface area and adsorption capacity, the clay-sized fraction is expected to contain higher concentrations of sediment-reactive trace metals than do the coarser sediment fractions. For example, at station 16 the highest concentrations of clays and most metals were measured. Compared to stations 4, 12 and 16, station 11 has relatively low concentrations of metals and clay (Figure 2). As expected, the sediment fraction finer than 60 μm (Table 6) typically has higher metal concentrations than the bulk sample (Table 5).

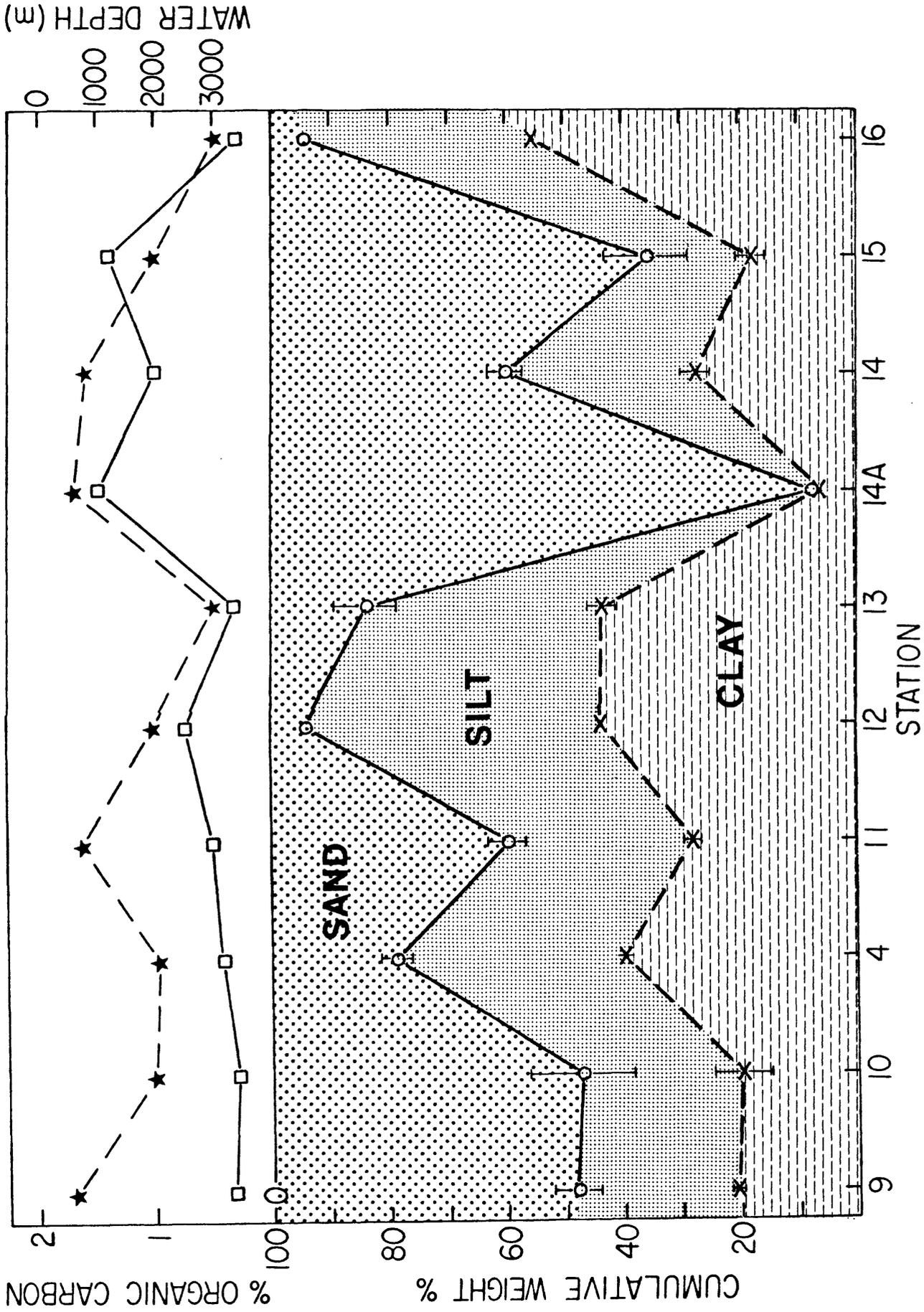


Figure 2A. Average concentration of organic carbon (\square in percent) and water depth (\star in meters) at stations from Cruise 4 (14A Cruise 5) listed from north to south.

2B. Average concentration of clay (---), silt, (---), and sand (---) in cumulative weight percent at stations from Cruise 4 (14A Cruise 5) listed from north to south. Error bars represent standard deviation among three replicates. When not shown, error is within the area of the point.

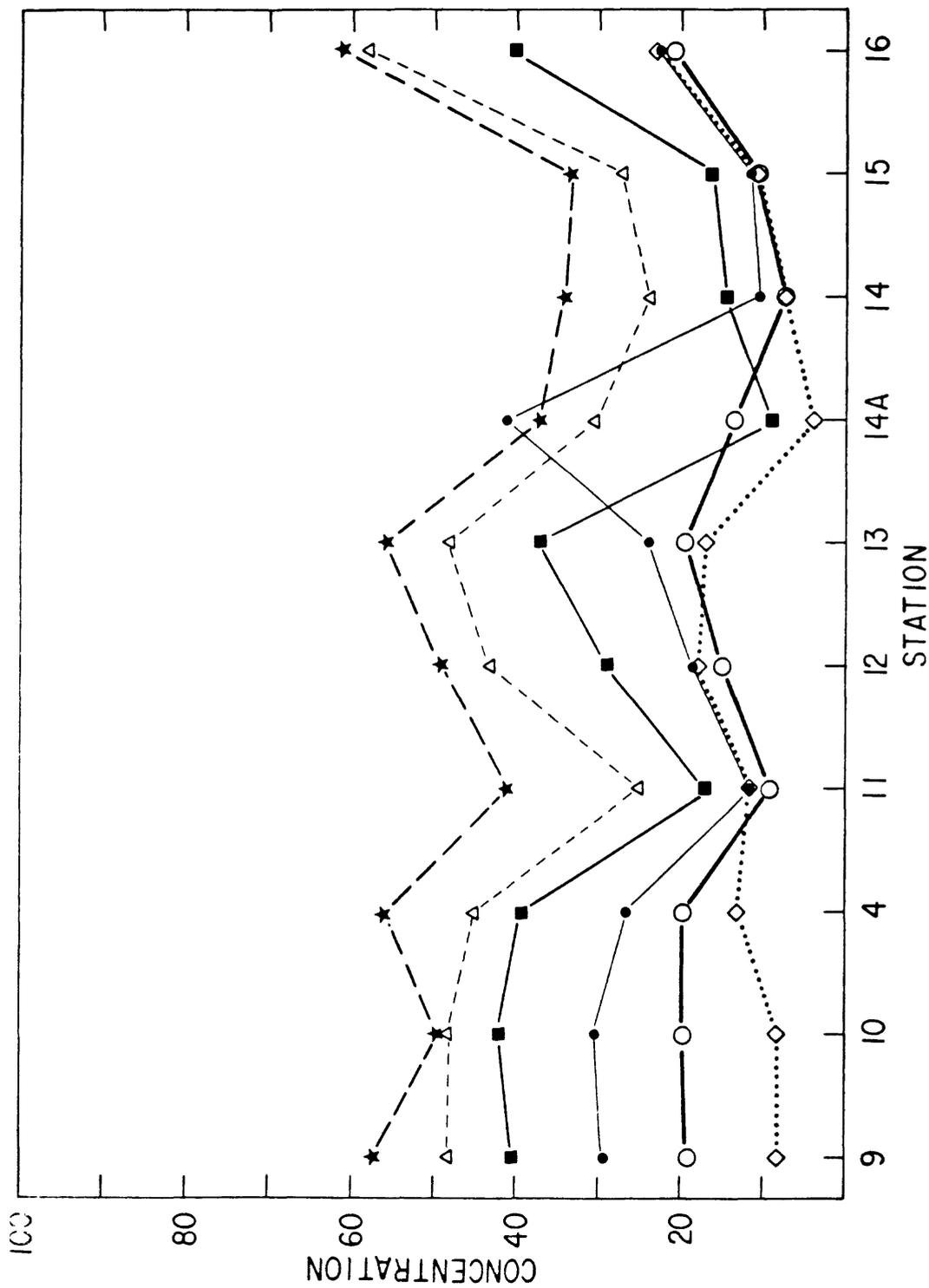


Figure 2C. Concentrations of metals in station blends from Cruise 4 (station 14A individual replicate, Cruise 5) South Atlantic. Stations listed from north to south, preserving transects. (Al, ■ % x 10; Ba, ● ppm x 10⁻¹; Cr, ★ ppm; Cu, ◇ ppm; Fe, ○ % x 10; Zn, △ ppm).

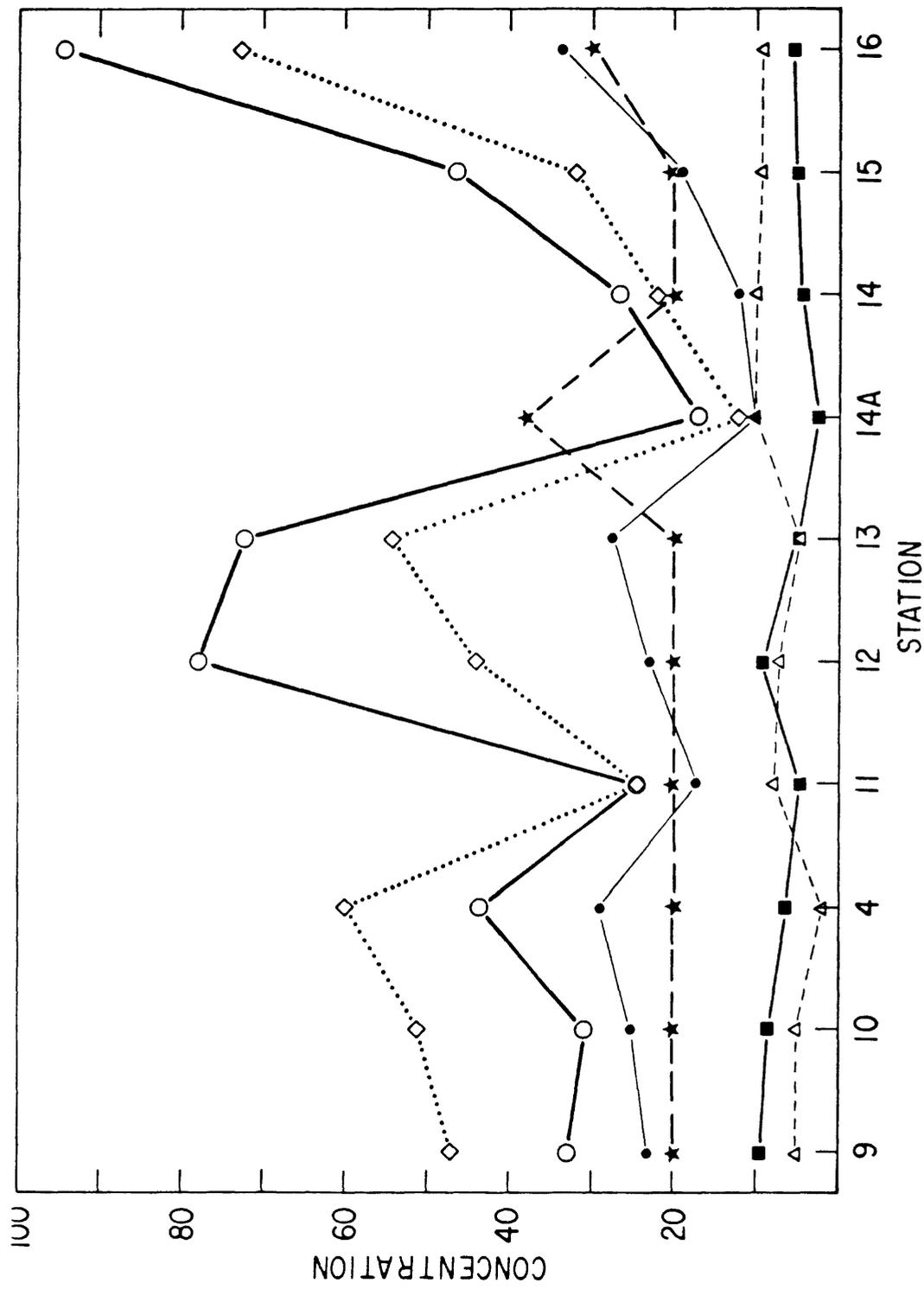


Figure 2D. Concentration of metals in station blends from Cruise 4 (station 14A individual replicate, Cruise 5), South Atlantic. Stations listed from north to south, preserving transects.
 (Cd, Δ ppm $\times 10^2$; Hg \star ppm $\times 10^3$; Mn, \circ ppm $\times 10^{-1}$; Ni, \bullet ppm, Pb, \blacksquare ppm, V \diamond ppm $\times 1/2$).

Table 5. - Chemical analysis of station blends.

Field no.	Top (cm)	Btm (cm)	Lab no.	Al (Z)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (Z)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S040400	0	2	W-231796	3.92	264	020L	56.0	13.0	1.96	.02	439	29.0	6.3	60.0	45.0
S040900	0	2	W-231797	4.05	295	.050	57.0	8.3	1.94	.02	329	23.0	9.6	47.0	48.0
S041000	0	2	W-231798	4.19	302	.050	49.0	8.3	1.96	.02	307	25.0	8.3	51.0	48.0
S041100	0	2	W-231799	1.69	115	.075	41.0	12.0	.92	.02	247	17.0	4.2	24.0	25.0
S041200	0	2	W-231800	2.88	185	.071	49.0	18.0	1.48	.02	777	23.0	9.1	44.0	43.0
S041300	0	2	W-231801	3.70	239	.042	56.0	17.0	1.94	.02	723	27.0	4.8	54.0	48.0
S041400	0	2	W-231802	1.47	104	.100	34.0	7.6	.73	.02	267	12.0	4.4	22.0	24.0
S041500	0	2	W-231803	1.61	107	.091	33.0	11.0	1.09	.02	464	19.0	4.8	32.0	27.0
S041600	0	2	W-231804	4.01	234	.091	61.0	23.0	2.12	.03	947	34.0	5.8	73.0	58.0
S050400	0	2	W-233739	3.74	254	.075	54.0	13.0	1.87	.05	362	22.0	6.6	87.0	50.0
S050900	0	2	W-233740	4.00	290	.063	46.0	8.3	1.97	.04	300	21.0	9.3	89.0	48.0
S051100	0	2	W-233741	1.68	115	.120	37.0	7.5	.94	.03	186	11.0	3.5	36.0	30.0
S051200	0	2	W-233742	3.26	216	.071	56.0	14.0	1.68	.05	496	25.0	4.4	72.0	45.0
S051300	0	2	W-233743	3.65	238	.058	55.0	14.0	1.90	.04	658	29.0	3.8	83.0	50.0
S051400	0	2	W-233744	1.49	108	.120	29.0	9.1	.71	.04	203	10.0	4.8	23.0	27.0
S051500	0	2	W-233745	1.56	103	.110	32.0	8.3	1.08	.03	413	16.0	5.1	35.0	30.0
S051600	0	2	W-233746	4.08	234	.075	62.0	24.0	2.19	.05	1117	38.0	6.0	99.0	61.0
S060400	0	2	W-234674	4.05	266	.058	46.0	14.0	2.02	.02	406	25.0	8.5	68.0	48.0
S061000	0	2	W-234675	4.66	311	.066	43.0	11.0	2.31	.02	335	22.0	11.0	60.0	51.0
S061100	0	2	W-234676	1.76	117	.110	26.0	9.3	.96	.01	270	7.0	4.5	20.0	27.0
S061200	0	2	W-234677	3.75	249	.083	51.0	16.0	1.92	.02	498	25.0	6.5	68.0	46.0
S061300	0	2	W-234678	3.30	215	.088	41.0	16.0	1.76	.01	627	17.0	5.0	66.0	42.0
S061400	0	2	W-234679	1.49	104	.130	25.0	8.1	.75	.02	246	4.5	5.3	24.0	25.0
S061500	0	2	W-234680	2.71	187	.066	38.0	12.0	1.56	.01	440	17.0	5.3	46.0	37.0
S061600	0	2	W-234681	4.30	241	.091	51.0	22.0	2.32	.02	249	30.0	5.5	68.0	56.0

Table 6. - Chemical analyses of the fine fraction from station blends

Field no.	Top (cm)	Btm (cm)	Lab no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S041100X	0	2	W-231813	2.10	135	.075	45.0	8.3	.94	.04	305	21.0	4.6	32.0	30.0
S041200X	0	2	W-231814	3.28	212	.071	54.0	16.0	1.68	.05	870	27.0	8.3	58.0	48.0
S050400X	0	2	W-233737	2.33	147	.042	40.0	12.0	1.21	.05	416	18.0	3.3	50.0	33.0
S051500X	0	2		4.05	259	.110	66.0	13.0	2.13	.06	414	32.0	7.0	103.0	60.0
S061400X	0	2	W-234688	2.00	128	.100	36.0	9.3	.87	.02	287	10.0	4.8	32.0	28.0
S061600X	0	2	W-234689	4.55	249	.076	62.0	20.0	2.44	.02	1158	38.0	4.8	82.0	60.0

Trace-metal variations with depth in bulk sediments

Samples from seven stations, all from Cruise 4 (the first cruise in phase 2), have been subsampled as a function of sediment depth to determine the depth profiles of metals. The metal concentrations are listed in Table 7 and the Mn and Pb concentrations are plotted in Figures 3-8. We have also plotted the ratios of Mn and Pb to Al, a calculation which partially corrects for variability in texture, carbonate, and interstitial salt.

The concentrations of Mn are typically highest near the sediment surface, and decrease with depth in the core (Figures 3, 4, and 5). This profile of Mn is common in sediments that undergo a transition from oxidizing conditions near the water/sediment interface to reducing conditions in deeper sediments. This profile (best example in Figure 4) results when MnO_2 dissolves under reducing conditions, diffuses upward, and precipitates in the oxidizing environment near the surface (Lynn and Bonati, 1965).

The profiles of Pb and Pb/Al with depth also show elevated values at or near the sediment surface, particularly at stations 9, 10, 11, and 15 (Figures 6, 7, and 8). Profiles of this type are common in areas of fine sediment on the continental shelf and slope (Bothner and others, 1981; Bothner and others, 1987a, b). At these stations, the maximum concentrations of Pb in the upper part of the cores are as much as a factor of two higher than concentrations measured in sediments deeper than 10 cm. However, the highest concentration measured in surface sediments from this area is only 17 ppm, which is less than the value in world average shales (20 ppm; Krauskopf, 1967). For additional perspective, the average concentration of Pb in bulk surface sediments of Boston Harbor is 145 ppm (M.H. Bothner, unpublished data, 1985).

Table 7. - Chemical analysis of core samples subsectioned in 2-cm intervals.

Field no.	Top (cm)	Btm (cm)	Lab. no.	Al (%)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Cu (ppm)	Fe (%)	Hg (ppm)	Mn (ppm)	Ni (ppm)	Pb (ppm)	V (ppm)	Zn (ppm)
S040931	0	2	W-232100	4.16	298	.066	45.0	8.8	2.01	.02	320	16.0	10.0	54.0	46.0
S040931	2	4	W-232101	4.45	300	.075	48.0	11.0	2.21	.02	312	22.0	13.0	60.0	76.0
S040931	4	6	W-232102	4.77	301	.083	51.0	10.0	2.40	.02	324	24.0	16.0	66.0	58.0
S040931	6	8	W-232103	4.82	303	.110	53.0	11.0	2.37	.03	309	25.0	15.0	68.0	60.0
S040931	8	10	W-232104	4.85	303	.100	54.0	11.0	2.40	.03	319	27.0	16.0	62.0	68.0
S040931	10	12	W-232105	4.79	310	.100	53.0	10.0	2.36	.03	318	26.0	17.0	64.0	66.0
S040931	16	18	W-232106	4.68	310	.091	51.0	9.8	2.25	.01	311	24.0	14.0	56.0	56.0
S040931	22	24	W-232107	4.63	307	.100	50.0	12.0	2.25	.03	300	24.0	14.0	58.0	63.0
S040931	26	28	W-232108	4.66	306	.075	52.0	9.6	2.25	.03	306	22.0	13.0	56.0	60.0
S041011	0	2	W-232109	4.54	291	.075	50.0	11.0	2.28	.02	306	24.0	10.0	56.0	58.0
S041011	2	4	W-232110	4.20	307	.066	45.0	7.8	1.90	.02	270	19.0	9.6	51.0	45.0
S041011	4	6	W-232111	4.51	315	.050	48.0	8.3	2.12	.02	293	21.0	10.0	58.0	48.0
S041011	6	8	W-232112	4.54	306	.055	51.0	9.6	2.12	.02	291	22.0	10.0	64.0	63.0
S041011	8	10	W-232113	4.42	319	.050	49.0	9.6	2.07	.02	278	22.0	12.0	62.0	51.0
S041011	10	12	W-232114	4.52	303	.061	51.0	10.0	2.16	.03	281	24.0	13.0	62.0	53.0
S041011	16	18	W-232115	5.00	319	.066	56.0	11.0	2.36	.02	302	25.0	12.0	71.0	55.0
S041011	22	24	W-232116	5.00	314	.075	55.0	12.0	2.42	.01	295	27.0	8.3	75.0	48.0
S041011	28	30	W-232117	5.44	334	.055	60.0	13.0	2.78	.01	324	32.0	8.8	84.0	63.0
S041011	32	34	W-232118	5.41	329	.071	60.0	13.0	2.71	.01	314	31.0	7.6	79.0	60.0
S041100	0	2	W-231799	1.69	115	.075	41.0	12.0	.92	.02	247	17.0	4.2	24.0	25.0
S041111	2	4	W-232122	1.73	113	.071	39.0	8.6	1.00	.02	149	9.0	3.0	28.0	27.0
S041111	4	6	W-232123	1.68	114	.120	37.0	8.0	.91	.02	79	9.0	2.7	28.0	18.0
S041111	6	8	W-232124	1.78	116	.160	37.0	7.5	.93	.01	78	10.0	2.5	32.0	22.0
S041111	8	10	W-232125	1.79	119	.140	38.0	7.0	.93	.01	81	9.0	2.2	30.0	25.0
S041111	10	12	W-232126	1.83	121	.150	37.0	7.1	.93	.01	81	11.0	1.7	32.0	25.0
S041111	16	18	W-232127	1.77	116	.220	39.0	7.0	.96	.01	82	10.0	1.7	34.0	23.0
S041111	22	24	W-232128	2.00	122	.260	40.0	8.0	1.11	.01	85	11.0	1.7	34.0	28.0
S041111	24	26	W-232129	2.07	127	.310	40.0	7.5	1.15	.01	90	13.0	2.2	36.0	28.0
S041231	0	2	W-232131	3.14	195	.083	54.0	16.0	1.64	.03	463	19.0	7.8	52.0	71.0
S041231	2	4	W-232132	3.55	224	.091	60.0	17.0	1.91	.03	1822	27.0	6.8	61.0	50.0
S041231	4	6	W-232133	3.67	320	.066	64.0	18.0	2.08	.03	942	26.0	5.8	68.0	50.0
S041231	6	8	W-232134	3.78	236	.075	64.0	17.0	1.97	.02	312	26.0	4.8	61.0	50.0
S041231	8	10	W-232135	3.74	239	.071	65.0	17.0	2.03	.02	264	25.0	4.6	67.0	51.0
S041231	10	12	W-232136	3.78	238	.066	66.0	18.0	2.04	.02	243	26.0	4.2	70.0	48.0
S041231	16	18	W-232137	3.76	240	.100	73.0	17.0	1.92	.02	233	30.0	3.7	70.0	50.0
S041231	22	24	W-232138	3.62	232	.100	62.0	17.0	1.86	.02	228	23.0	3.8	68.0	50.0
S041231	28	30	W-232139	3.55	228	.110	62.0	17.0	1.80	.02	226	25.0	5.8	70.0	46.0
S041300	0	2	W-231801	3.70	239	.042	56.0	17.0	1.94	.02	723	27.0	4.8	54.0	48.0
S041321	2	4	W-231815	4.07	264	.033	59.0	17.0	2.08	.02	746	33.0	4.2	62.0	51.0
S041321	4	6	W-231816	4.09	264	.020L	60.0	17.0	2.10	.02	954	40.0	4.8	69.0	51.0
S041321	6	8	W-231817	4.03	269	.042	62.0	19.0	2.10	.02	1554	38.0	4.2	66.0	51.0
S041321	8	10	W-231818	4.01	267	.033	64.0	18.0	2.24	.02	527	31.0	4.0	66.0	51.0
S041321	12	14	W-231819	4.06	258	.075	65.0	19.0	2.09	.02	212	29.0	3.8	71.0	51.0
S041321	16	18	W-231820	4.03	258	.180	65.0	24.0	2.05	.02	217	30.0	3.8	84.0	53.0
S041521	0	2	W-232141	1.57	98	.090	35.0	9.0	1.10	.02	419	13.0	5.3	24.0	25.0
S041521	2	4	W-232142	1.73	109	.075	39.0	10.0	1.15	.02	389	13.0	4.3	29.0	27.0
S041521	4	6	W-232143	1.85	116	.063	40.0	9.8	1.16	.02	388	13.0	2.8	29.0	27.0
S041521	6	8	W-232144	1.92	121	.058	40.0	13.0	1.21	.02	414	15.0	3.3	33.0	27.0
S041521	8	10	W-232145	1.93	118	.066	41.0	13.0	1.22	.01	391	15.0	2.8	38.0	28.0
S041521	10	12	W-232146	1.97	116	.058	43.0	11.0	1.33	.01	356	15.0	3.8	38.0	28.0
S041521	16	18	W-232147	2.70	150	.042	50.0	14.0	1.62	.01	311	18.0	3.8	42.0	40.0
S041521	22	24	W-232148	3.76	172	.058	85.0	18.0	2.05	.01	462	30.0	4.8	72.0	46.0
S041600	0	2	W-231804	4.01	234	.091	61.0	23.0	2.12	.03	947	34.0	5.8	73.0	58.0
S041621	2	4	W-231821	4.56	260	.042	67.0	25.0	2.42	.02	1171	44.0	5.3	74.0	61.0
S041621	4	6	W-231822	4.59	275	.033	69.0	27.0	2.44	.03	1233	44.0	5.8	78.0	61.0
S041621	6	8	W-231823	4.56	272	.042	69.0	27.0	2.42	.03	1456	56.0	5.8	80.0	61.0
S041621	8	10	W-231824	4.65	282	.063	70.0	34.0	2.46	.02	1644	46.0	5.0	82.0	61.0
S041621	10	12	W-231825	4.68	283	.050	67.0	43.0	2.48	.02	2756	52.0	5.8	74.0	63.0
S041621	14	16	W-231826	4.53	281	.091	67.0	28.0	2.52	.02	2216	38.0	5.3	73.0	60.0
S041621	18	20	W-231827	4.42	281	.151	67.0	28.0	2.33	.02	637	39.0	5.0	76.0	61.0

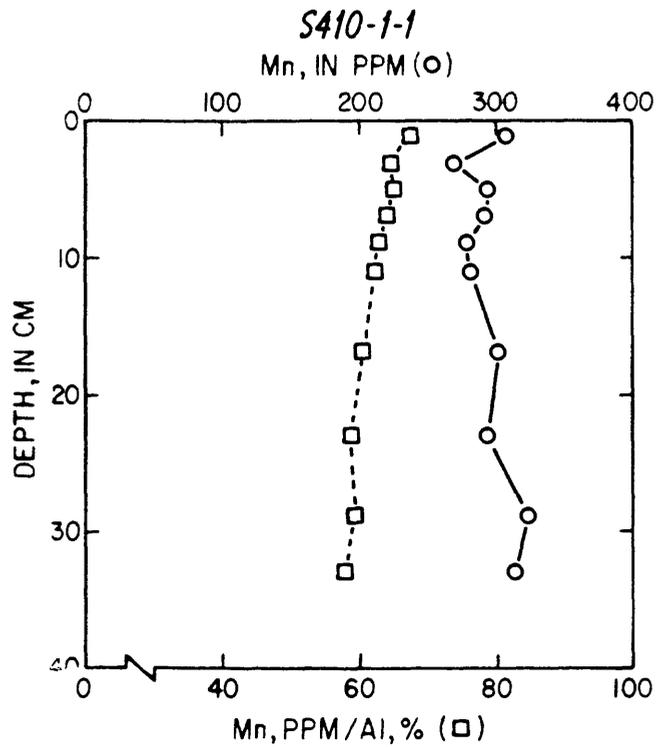
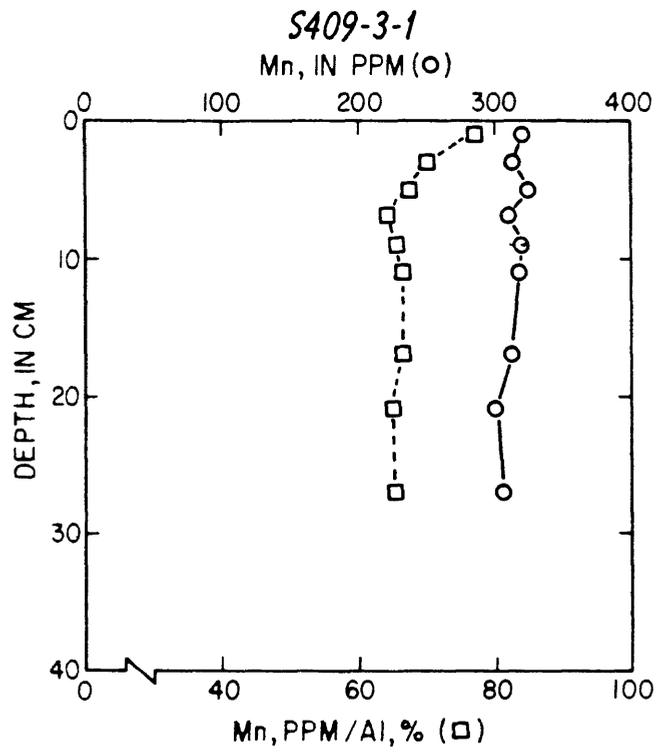


Figure 3. Distribution of Mn and the Mn to Al ratio with sediment depth at Stations 9 and 10, Cruise 4.

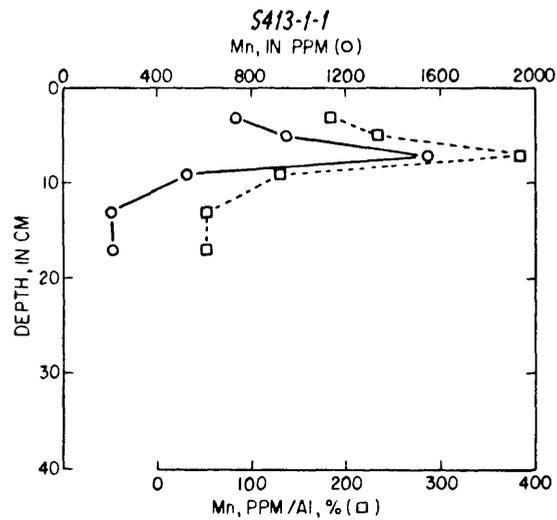
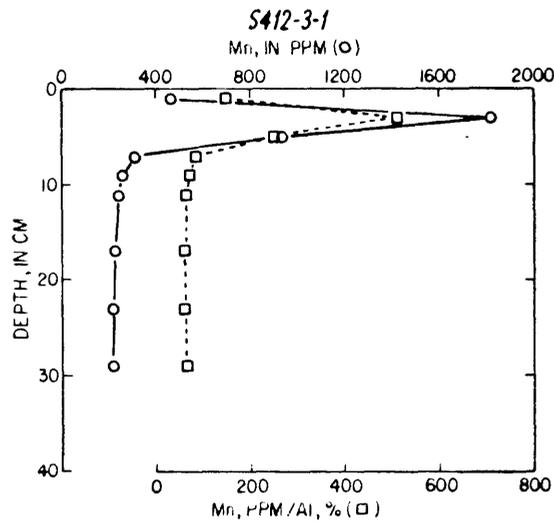
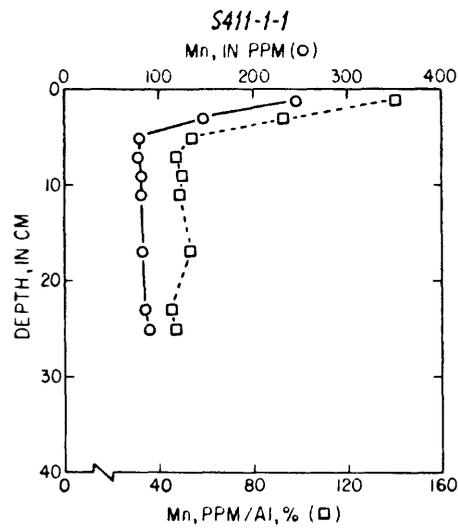


Figure 4. Distribution of Mn and the Mn to Al ratio with sediment depth at Stations 11, 12, and 13, Cruise 4.

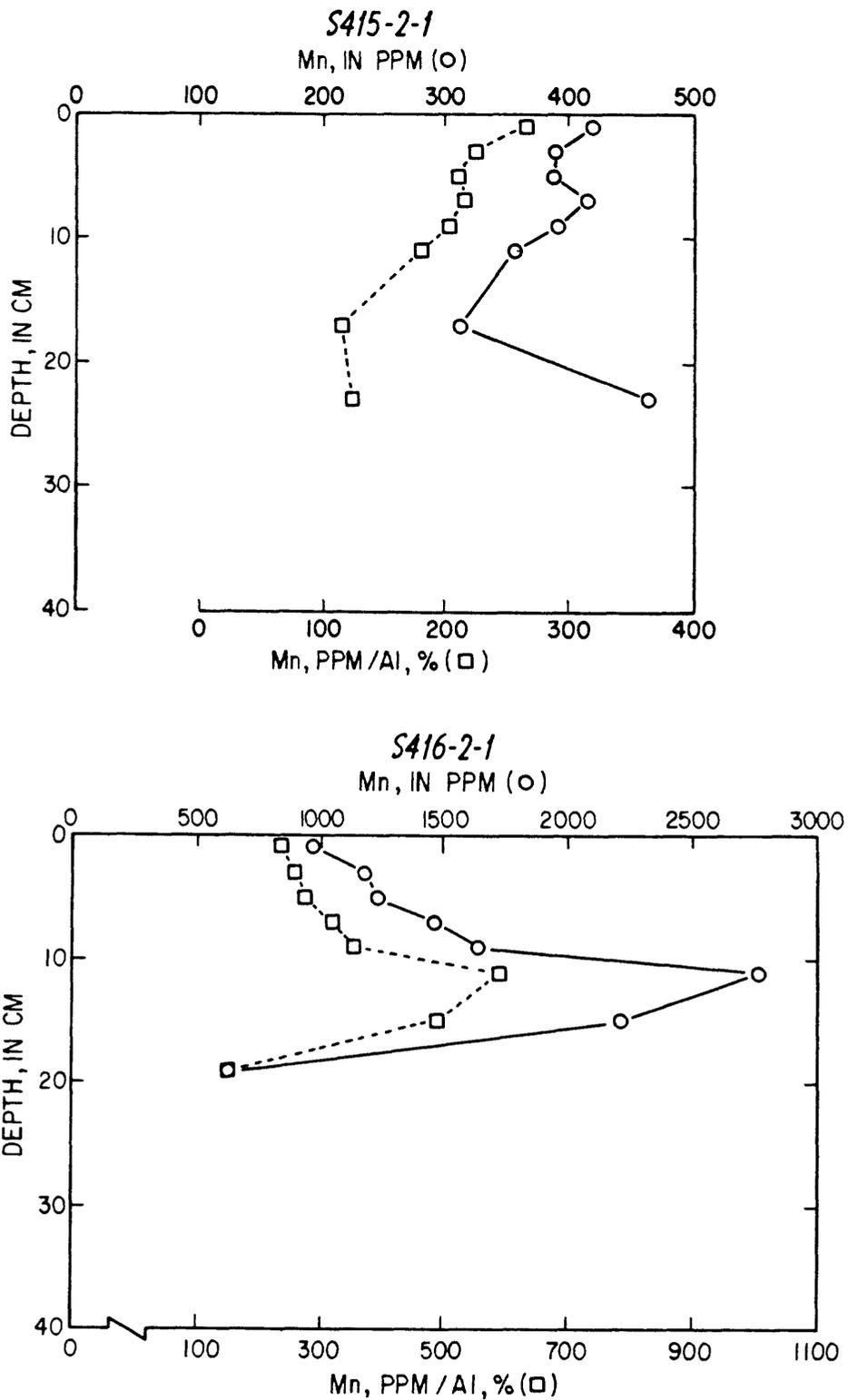


Figure 5. Distribution of Mn and the Mn to Al ratio with sediment depth at Stations 15 and 16, Cruise 4.

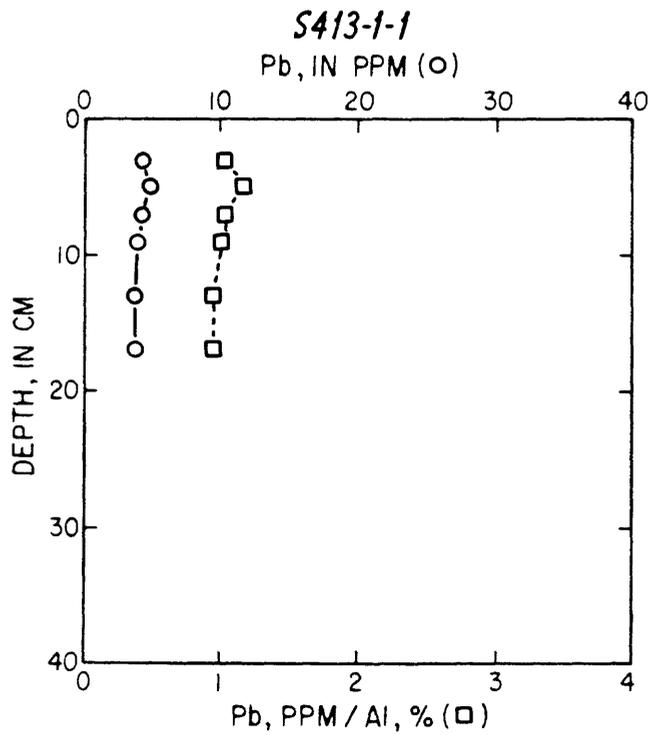
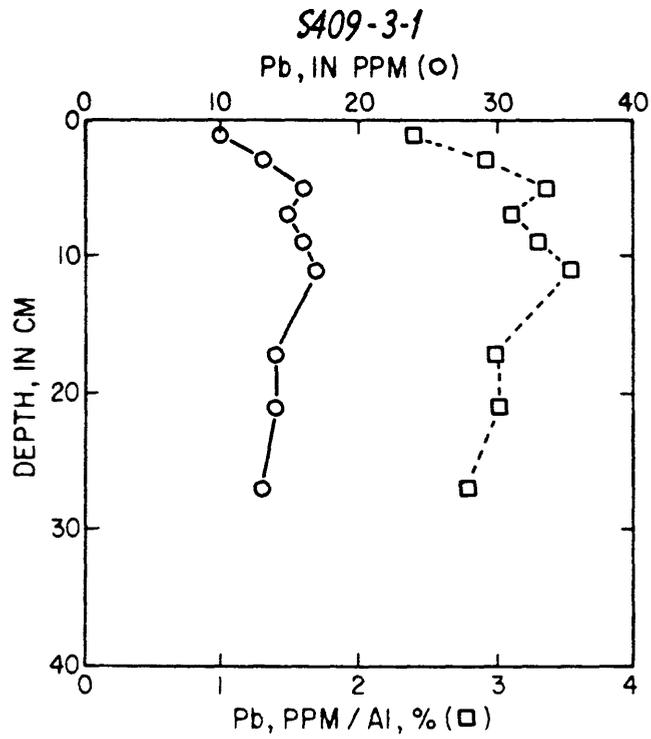
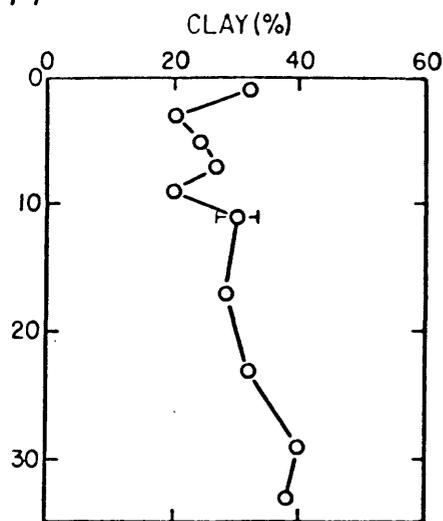
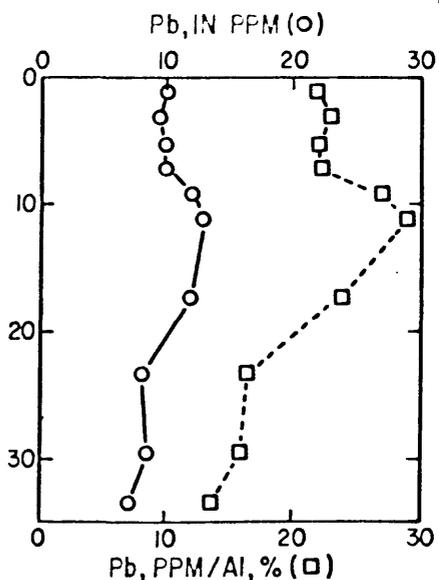
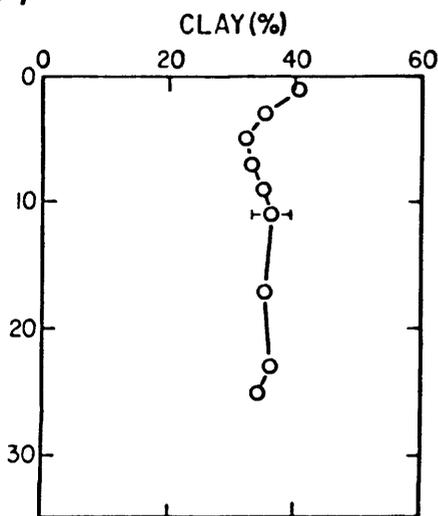
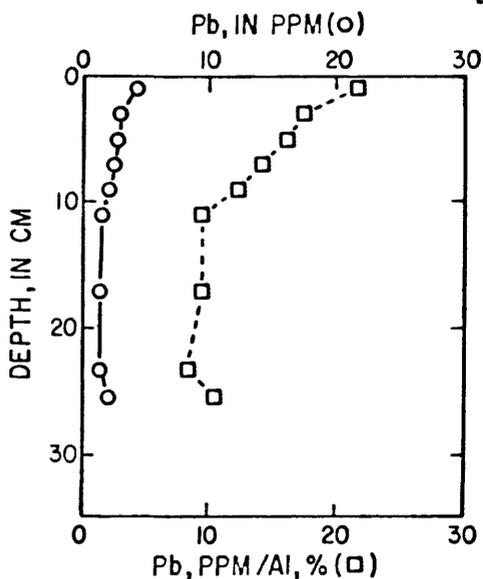


Figure 6. Distribution of Pb and the Pb to Al ratio with sediment depth at Stations 9 and 13, Cruise 4.

S410-1-1



S411-1-1



S412-3-1

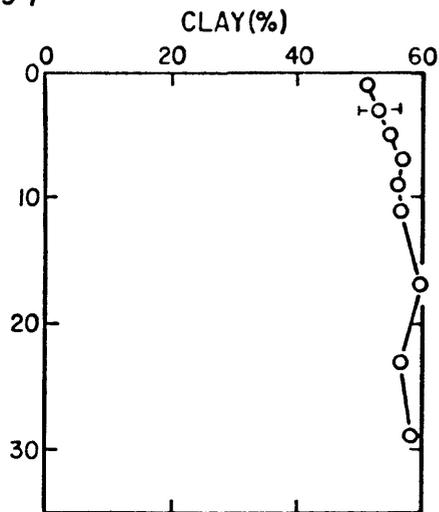
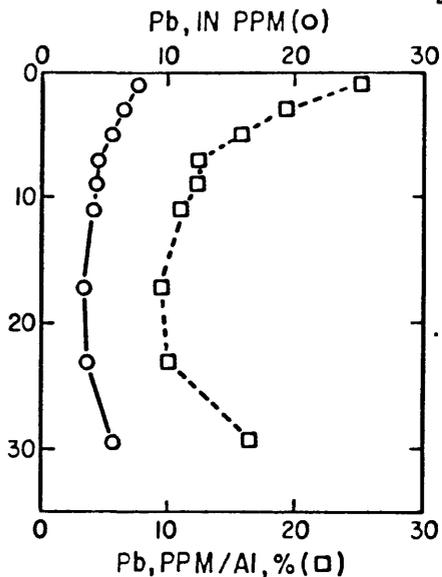


Figure 7. Distribution of Pb and Pb to Al ratio with sediment depth and the distribution of clay with sediment depth at stations 10, 11, and 12, Cruise 4.

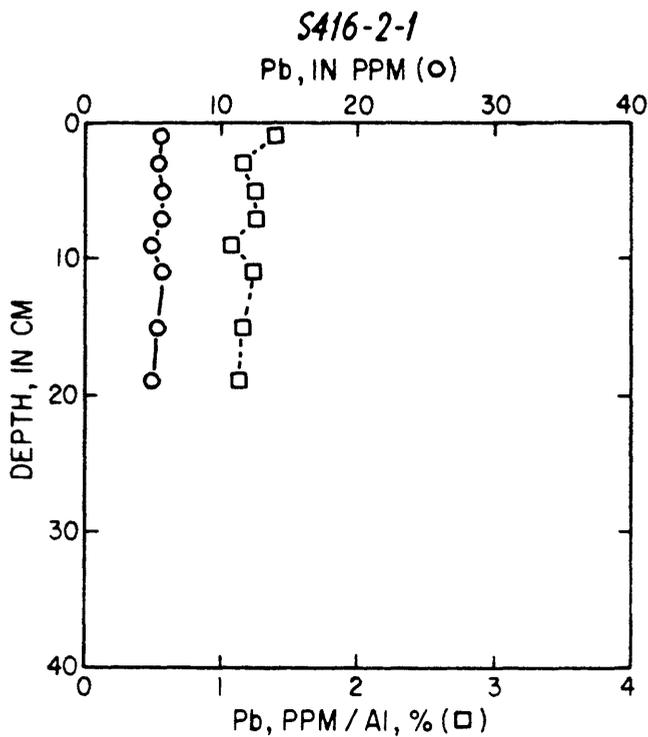
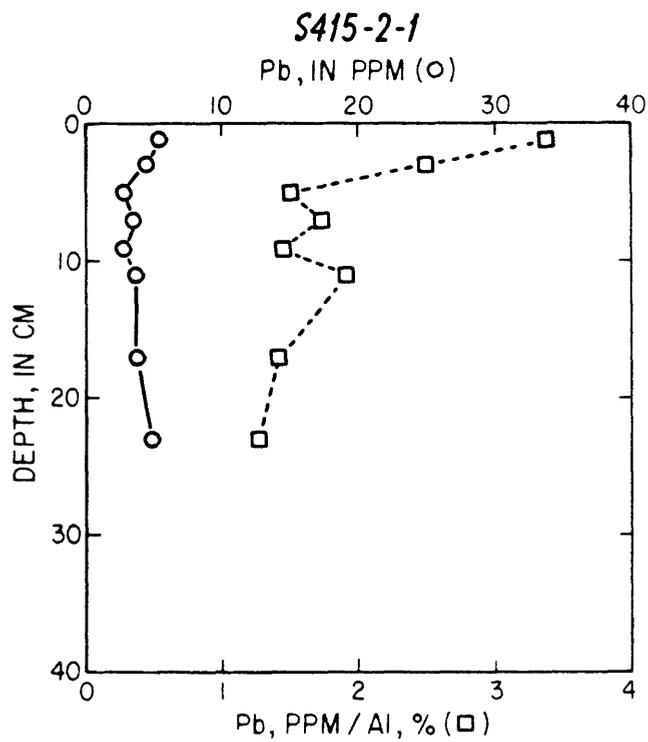


Figure 8. Distribution of Pb and the Pb to Al ratio with sediment depth at Stations 15 and 16, Cruise 4.

The elevated Pb concentrations in surficial sediments in this study area are thought to be related to the atmospheric flux of Pb to the sea surface, largely derived from the burning of Pb alkyls in gasoline in coastal metropolitan areas. Such use of Pb alkyls began in 1924 and, since 1940, has increased each year until the recent switch to unleaded gasoline. The occurrence of elevated Pb concentrations typically extending more than 10 cm below the sediment surface (see station 10) is probably related to biological or physical mixing of the sediments. Without mixing, the Pb deposited since 1924 would be confined in the upper 2 cm of sediment if one assumes that the accumulation rate of 0.022 cm/yr, measured on the Middle Atlantic slope by Doyle and others (1979), applies to this study area. The enrichments of Pb, seen more dramatically in the Pb/Al profile, do not appear to be related to the clay content of these sediments (Figure 7).

The impact of this increase in Pb is unknown. Important questions are: How is the Pb bound in the sediments? What is the bioavailability of this Pb? What is the response of organisms at different life stages to long-term, low-level Pb contamination? Although a few studies show a relationship between the Pb concentrations in the tissue of deposit feeding organisms and Pb concentrations in acid-leached sediment (Luoma and Bryan, 1978; Tessier and others, 1984), no guidelines for "safe" levels of Pb in sediments have been established. Studies addressing this complex issue are presently funded by the Environmental Protection Agency.

Lead inventories

An inventory of the lead added to these sediments as a result of man's industrial use of lead can be estimated from the profiles of lead with sediment depth. For this calculation, we assumed that the enhanced

concentrations of lead in the near-surface sediments are from anthropogenic sources. This assumption seems justified because of the evidence against lead enrichment resulting from post-depositional mobility (Bruland and others, 1974). We also assumed that the background concentration of lead in a particular core was represented by the concentration in the lowest 5 to 10 cm and remained constant throughout the core. This background value was subtracted from the total value for each interval analyzed. Values for intervals not analyzed were interpolated and values for all intervals were summed to determine the net anthropogenic contribution. Correcting for porosity (using water content) and assuming a constant grain density of 2.7 g/cc, the inventory of added lead in $\mu\text{g}/\text{cm}^2$ was calculated (Figure 9).

The atmospheric flux of lead to the Atlantic Ocean in the vicinity of Bermuda is estimated to have been about $1 \text{ mg}/\text{m}^2/\text{yr}$ during the early 1980's (Church and others, 1984; Jickells and others, 1984a, b). Mr. G.T. Shen, Massachusetts Institute of Technology (M.I.T.) has kindly provided data showing the variations in the Pb to Ca ratio in annual growth bands of a coral head (D. Strigosa) over the last 100 years. Assuming that the record of lead incorporated into coral correlates with the atmospheric flux of lead to the ocean, it is possible to estimate and sum the total deposition of anthropogenic lead on an area basis. The value obtained is $6.2 \mu\text{g}/\text{cm}^2$.

The estimated inventories at stations 11, 12, 13, and 16 are close (within a factor of 2) to the total atmospheric deposition (Figure 9). The inventories at stations 9 and 10, at the northern edge of the study area, are higher than predicted from the atmospheric flux by a factor of 5 and 10, respectively.

Profiles of ^{210}Pb and ^{137}Cs and other bomb-produced radionuclides would be extremely useful for interpreting these different inventories of lead.

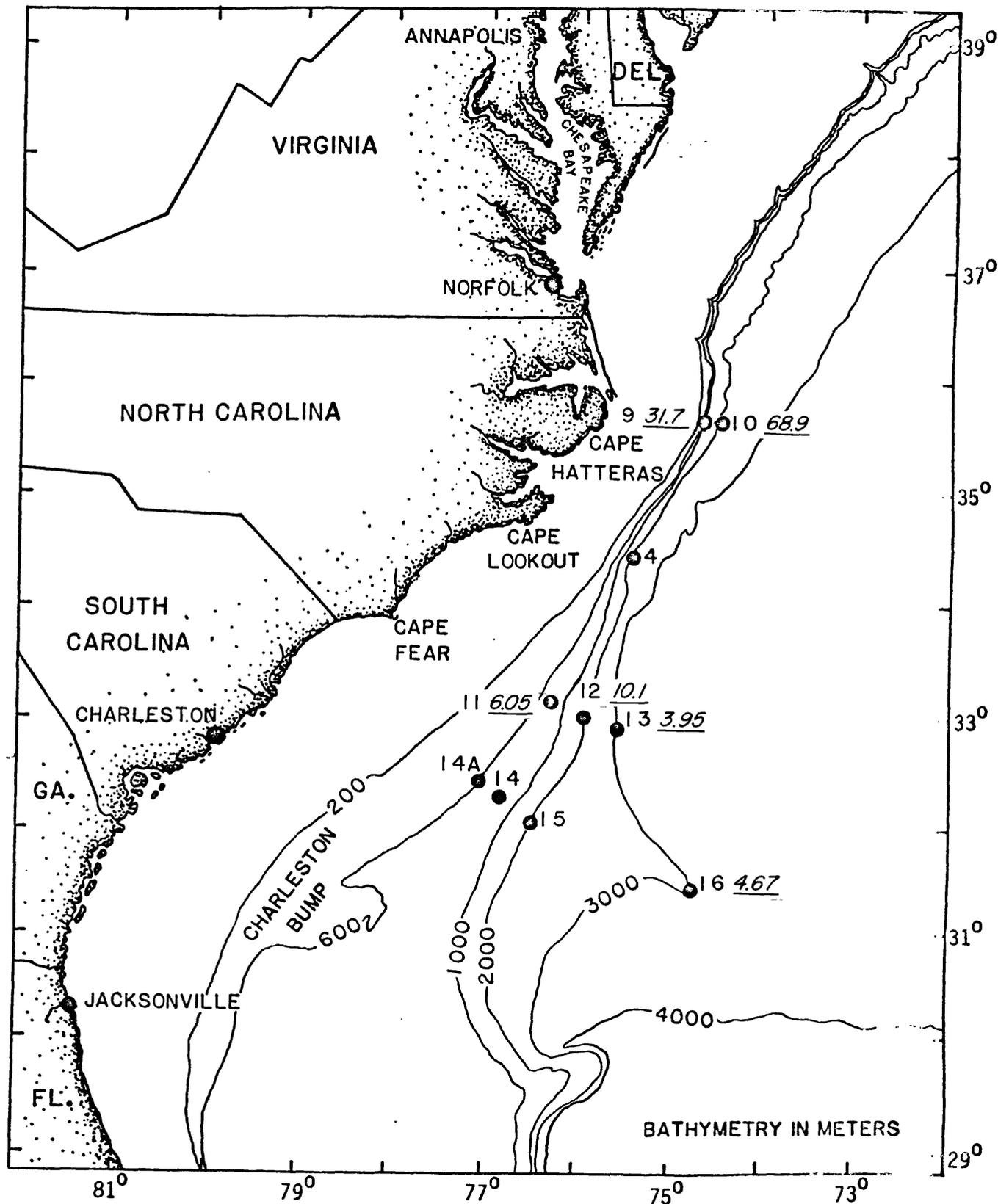


Figure 9. Underlined values represent the inventory of anthropogenic lead (total-background) in $\mu\text{g}/\text{cm}^2$.

Based on these preliminary estimates, we conclude that at the four stations south of 34° N. latitude, lead has been deposited on the sea floor in amounts nearly equivalent to the lead flux added to the sea surface. At the two locations north of 34° N. latitude, more lead is being deposited than is being added to an equivalent area of the sea surface. The concentration of lead is probably related to a process or a combination of processes which enhance the scavenging of lead from the water column. These processes could include bioturbation, sediment irrigation by organisms, sediment resuspension and deposition, and chemical precipitation.

The suggestion that scavenging processes are enhanced in this area of the continental slope is also supported by the anomalously high concentrations of hydrocarbons measured at stations 9 and 10 (Blake and others, 1987, Chapter 6). The possibility that the scavenging might be partially a result of biological processes is supported by the observation in photographic transects of anomalously high densities of worm tubes (Blake and others, 1987, Chapter 5).

Sediment texture

Two of the three cores analyzed for texture show a nearly uniform distribution of sand, silt, and clay with depth of sediment (Figure 10, Table 8). On the basis of the grain-size distribution, the sediments at stations 10 and 11 are sandy-silty-clays and sediments from station 12 are silty-clay.

The concentration of sand is fairly constant throughout the cores from stations 11 and 12 (Figure 10) and average about 25 percent and 2 percent respectively. The sand component is predominantly foraminifera tests with minor amounts (less than 10%) of sponge spicules and shell hash, and trace amounts (<1%) of the authigenic mineral glauconite.

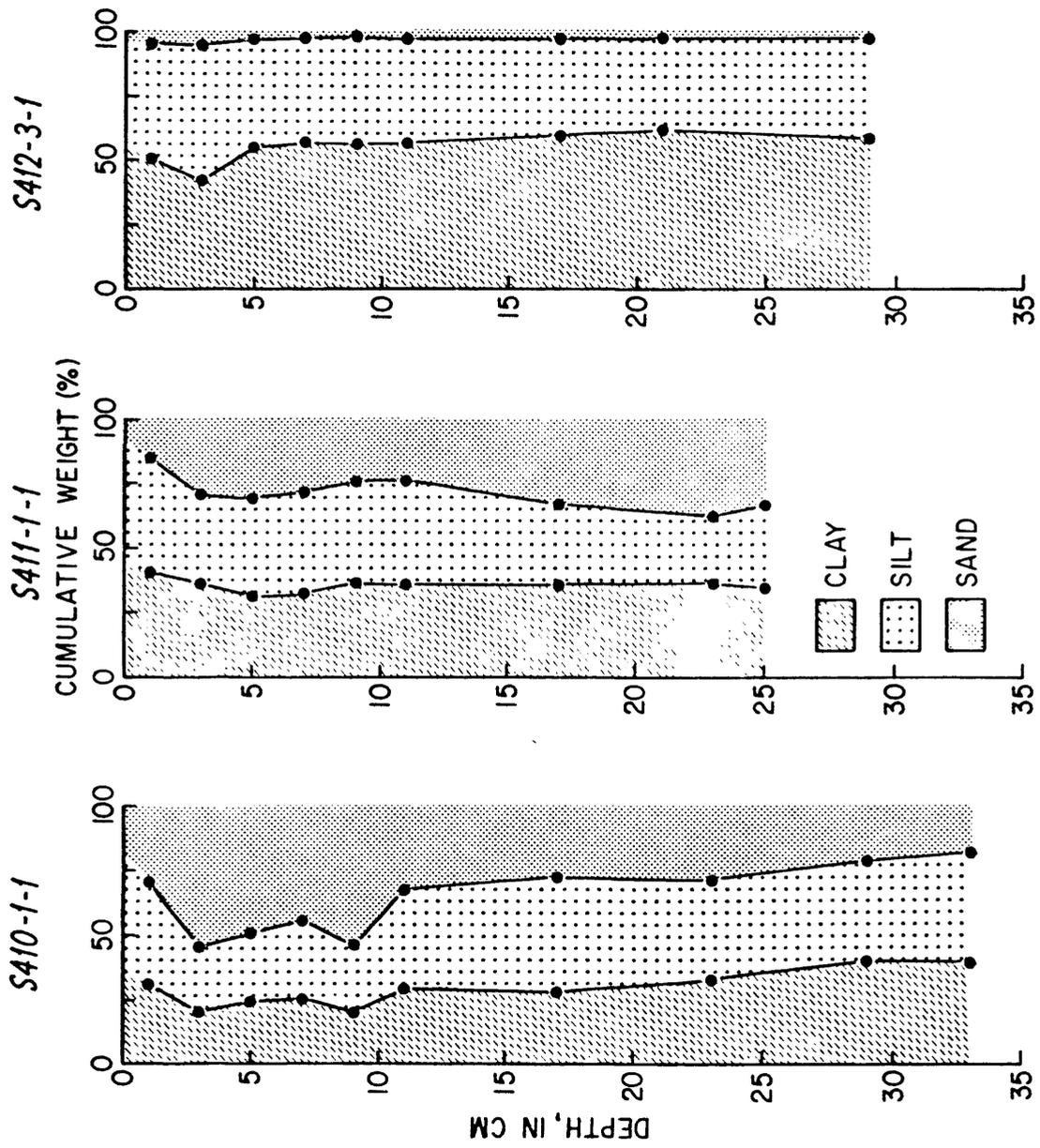


Figure 10. Grain-size analyses of sediment cores collected from the fourth cruise in the South Atlantic study area.

At station 10, the sand content above 10 cm is about 50 percent, and about 25 percent in deeper sections of the core (Figure 10). Unlike the other two cores, the sand fraction at station 10 consists of 90 percent quartz. Shell hash, foraminifera tests, glauconite and other minerals make up the remaining 10 percent. At the 32- to 34-cm interval, glauconite represented 25 percent of the sand fraction.

SUMMARY OF IMPORTANT FINDINGS

1. There are generally higher concentrations of Pb in the surface sediments (higher by as much as a factor of 2) than in sediments deeper in the cores. The maximum concentration of Pb in bulk surface sediments from this study area is 17 ppm, lower than the 20-ppm concentration in average world shales. Similar Pb profiles have been previously described in sediments from other locations off the U.S. East Coast (Bothner and others, 1981; Bothner and others, 1987a, b). The enrichment is thought to be related to the burning of gasoline containing Pb additives and its subsequent atmospheric transport to offshore marine areas.

The question of what biological effects might result from the measured Pb enhancement cannot be answered with the data at hand. The biological effects are related to the bioavailability of Pb, its chemical form, and the long-term effects of specific chemical forms on various life stages of the resident organisms.

2. Using estimates obtained from the literature for the annual flux of lead to the Atlantic Ocean in the vicinity of Bermuda and the record of lead deposition in annual bands of coral over the last century (kindly

provided by G. T. Shen, M.I.T.), we have estimated that the deposition of lead in this area totals $6.2 \mu\text{g}/\text{cm}^2$ in the last century. The inventory of lead in four sediment cores south of 34° N. latitude is close to the value estimated from atmospheric deposition. Stations 9 and 10 at the northern limit of the study area have lead inventories 5 to 10 times higher than the total atmospheric deposition. This implies increased scavenging of lead from the water column at these locations.

3. The concentrations of metals at the slope stations of this program are the same or lower than published values for average world shales. This suggests that the sediments in those areas are not enriched in trace metals by natural processes or by industrial contamination.

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Appendix table 1. Navigation data for stations analyzed for chemistry. Values corrected for additional secondary factors (asf), (McCullough and others, 1983).

[Time delay X (26000, Nantucket, Mass.), Z (59000, Dana, Indiana) and Y (40000, Carolina Beach, N.C.) are Loran-C time delay values for the 9960 Loran-C chain].

Field Number	Station	Collection date (Yr Mo Dy)	Water depth (m)	Time delay (m seconds)	Time delay (m seconds)	Latitude (degrees) (and minutes)	Longitude (degrees) (and minutes)
<u>Core profiles</u>							
S040931	09	1985 5 24	623	26780.10	40558.70	35 28.3524	-74 47.4606
S041100	11	1985 5 22	800	59264.80	44869.50	33 04.9110	-76 24.9192
S041011	10	1985 5 24	2003	26756.10	40561.90	35 26.3400	-74 41.3667
S041231	12	1985 5 22	2000	59272.20	44807.00	33 00.1850	-76 07.1412
S041321	13	1985 5 21	3013	59278.50	44748.90	32 55.8377	-75 49.4682
S041521	15	1985 5 16	1991	59608.00	44688.50	32 12.0042	-76 42.0675
S041621	16	1985 5 15	3003	59611.30	44339.70	31 35.0494	-75 09.9084
<u>Station replicates</u>							
S040411	04	1985 5 23	2093	26890.40	39741.60	34 11.3684	-75 38.4776
S040412	04	1985 5 23	2093	26890.40	39741.60	34 11.3684	-75 38.4776
S040413	04	1985 5 23	2093	26890.40	39741.60	34 11.3684	-75 38.4776
S040421	04	1985 5 23	2051	26890.90	39740.90	34 11.3722	-75 38.3653
S040431	04	1985 5 23	2015	26891.20	39741.10	34 11.4549	-75 38.7085
S040911	09	1985 5 24	640	26779.90	40560.10	35 28.4778	-74 47.3793
S040921	09	1985 5 24	603	26780.40	40559.70	35 28.4847	-74 47.5134
S040931	09	1985 5 24	624	26780.10	40558.70	35 28.3524	-74 47.4606
S041111	11	1985 5 22	800	59265.00	44869.60	33 04.8523	-76 25.0112
S041121	11	1985 5 22	802	59264.50	44869.40	33 04.9143	-76 24.8353
S041131	11	1985 5 22	799	59264.90	44869.60	33 04.8670	-76 24.9882
S050911	09	1985 9 25	629	26780.00	40560.00	35 28.4772	-74 47.4065
S050921	09	1985 9 25	629	26780.10	40560.00	35 28.0793	-74 46.4341
S050922	09	1985 9 25	629	26780.10	40560.00	35 28.0793	-74 46.4341
S050923	09	1985 9 25	629	26780.10	40560.00	35 28.0793	-74 46.4341
S050931	09	1985 9 25	651	26780.40	40558.20	35 27.9216	-74 46.5492
S051511	15	1985 9 18	1988	59608.50	44688.40	32 11.9494	-76 42.1264
S051521	15	1985 9 18	1991	59608.50	44688.40	32 11.9494	-76 42.1264
S051531	15	1985 9 18	1991	59608.40	44688.30	32 11.9487	-76 42.0879
S061411	14	1985 11 18	799	59587.60	44791.00	32 23.6710	-77 01.0406
S061421	14	1985 11 18	799	59587.90	44790.70	32 23.6165	-77 01.0205
S061431	14	1985 11 18	799	59587.60	44790.70	32 23.6424	-77 00.9781
S061611	16	1985 11 20	3029	59611.00	44339.90	31 35.1050	-75 09.8859
S061621	16	1985 11 20	3012	59611.00	44339.80	31 35.0932	-75 09.8536
S061631	16	1985 11 20	3012	59610.60	44340.00	31 35.1594	-75 09.8020

Appendix table 1. continued

Field Number	Station	Collection date (Yr Mo Dy)	Water depth (m)	Time delay (m seconds)	Time delay (m seconds)	Latitude (degrees) (and minutes)	Longitude (degrees) (and minutes)
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Station blends - average position of three box core replicates

S040400	04	1985 5 23	2053	26890.80	39741.20	34 11.3922	-75 38.5982
S040900	09	1985 5 24	633	26780.10	40559.50	35 28.4351	-74 47.4428
S041000	10	1985 5 24	1992	26756.20	40562.60	35 26.4237	-74 41.3769
S041100	11	1985 5 22	800	59264.80	44869.50	33 04.8759	-76 24.9348
S041200	12	1985 5 22	2002	59271.80	44807.20	33 00.2596	-76 07.1008
S041300	13	1985 5 21	2018	59280.50	44746.80	32 55.3811	-75 49.3371
S041400	14	1985 5 20	803	59588.00	44790.70	32 23.6079	-77 01.0346
S041500	15	1985 5 16	1996	59611.40	44687.10	32 11.5615	-76 42.3076
S041600	16	1985 5 23	3006	59611.10	44339.90	31 35.0943	-75 09.9149
S050400	04	1985 9 24	2028	26891.10	39741.10	34 11.4359	-75 38.6818
S051100	11	1985 9 23	830	59281.20	44746.70	32 55.2583	-75 49.5099
S051200	12	1985 9 22	2004	59271.20	44807.60	33 00.3772	-76 07.0725
S051300	13	1985 9 21	3010	59281.20	44746.70	32 55.2583	-75 49.5099
S051400	14	1985 9 20	798	59588.40	44790.80	32 23.5829	-77 01.1118
S051500	15	1985 9 18	1990	59608.50	44688.40	32 11.9494	-76 42.1264
S051600	16	1985 9 15	3006	59611.10	44339.90	31 35.0943	-75 09.9149
S060400	04	1985 9 24	2053	26890.90	39740.80	34 11.3592	-75 38.6387
S061000	10	1985 11 25	2000	26756.20	40562.00	35 26.3604	-74 41.3897
S061100	11	1985 11 22	805	59264.70	44869.70	33 04.9021	-76 24.9726
S061200	12	1985 11 21	1996	59270.80	44808.20	33 00.4745	-76 07.1618
S061300	13	1985 11 20	3002	59281.40	44747.50	32 55.2715	-75 49.8441
S061400	14	1985 11 18	1632	59587.70	44790.80	32 23.6433	-77 01.0131
S061500	15	1985 11 19	1632	59608.40	44688.20	32 11.9389	-76 42.0657
S061600	16	1985 11 20	3017	59610.90	44339.90	31 35.1157	-75 09.8568

Fine fraction

S041100X	11	1985 5 22	800	59264.80	44869.50	33 04.8759	-76 24.9348
S041200X	12	1985 5 22	2002	59271.80	44807.20	33 00.2596	-76 07.1008
S050400X	04	1985 9 24	2028	26891.10	39741.10	34 11.4359	-75 38.6818
S051500X	15	1985 9 18	1990	59608.50	44688.40	32 11.9494	-76 42.1264
S061400X	14	1985 11 20	1632	59587.70	44790.80	32 23.6433	-77 01.0131
S061600X	16	1985 11 20	3017	59610.90	44339.90	31 35.1157	-75 09.8568