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CHESAPEAKE BAY SEDIMENT

TRACE ELEMENTS

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This report contains the results of analyses of surface samples and cores from the main stem of Chesapeake Bay. For the surface samples, both the fine fraction and the unfractionated sediment were analyzed for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb by atomic absorption spectrometry. For the cores, water content, ^{210}Pb, C, N, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Zr were determined at various depths. Alpha spectrometry was used for ^{210}Pb, and DC plasma emission spectrometry was used for all elements except C and N, which were determined by a CHN analyzer. Roughly 10,000 individual analyses are reported, making this the first reasonably comprehensive survey of trace element chemistry in the Bay.

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FOREWORD

The study of toxic chemicals in the Chesapeake Bay was one of three areas of investigation by the U.S. Environmental Protection Agency's Chesapeake Bay Program. Research efforts in the toxic substances program centered on obtaining information about the pathways and fate of these substances by studying the behavior of toxic materials from industrial, agricultural, and atmospheric sources.

This report describes the investigation of trace elements in sediments of Chesapeake Bay, Baltimore Harbor, and the Elizabeth River. It provides the first comprehensive description of the Bay-wide distribution of trace element concentrations in sediments. The analysis of vertically sectioned sediment core samples for trace elements and Pb^{210} dating also provides information on sedimentation rates and how trace element concentrations have changed with time in the Bay.

In addition to reporting trace element concentration values, the investigator has computed enrichment factors for the samples. These values provide additional geochemical information and an indication where perturbation of natural levels of trace elements exist.

Additional work by other investigators studying toxic chemicals as part of the EPA Chesapeake Bay Program may be useful in interpreting the trace element information contained in this report. Of particular geochemical significance is a project report describing the pore water chemistry of the sediment cores listed in this study. Also, reports describing Bay-wide sediment type distribution may be helpful in interpreting the trace element distribution contained in this report.

ABSTRACT

This report contains the results of analyses of surface samples and cores from the main stem of Chesapeake Bay. For the surface samples, both the fine fraction and the unfractionated sediment were analyzed for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb by atomic absorption spectrometry. For the cores, water content, ^{210}Pb, C, N, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn and Zr were determined at various depths. Alpha spectrometry was used for ^{210}Pb, and DC plasma emission spectrometry was used for all elements except C and N, which were determined by a CHN analyzer. Roughly 10,000 individual analyses are reported, making this the first reasonably comprehensive survey of trace element chemistry in the Bay.

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SECTION 1

INTRODUCTION

There have been a number of previous investigations of toxic substances in various parts of Chesapeake Bay. In all cases, however, the analytical work was done as part of isolated projects and methods used were generally not comparable from one project to another. Thus, there has been no possibility of making a regional synthesis that would allow different parts of the Bay to be compared and that would permit past or future changes with time in the Bay's condition to be convincingly documented. The Environmental Protection Agency's Chesapeake Bay Program provided the first opportunity to examine the question of the Bay's contamination on a regional scale in which samples from throughout the Bay were collected and analyzed for a particular class of toxic substances by a single laboratory using consistent, clearly described procedures.

This report is about trace elements in the sediments of Chesapeake Bay. In high concentrations, certain of the trace elements studied are known to be toxic to a large variety of organisms. In low concentrations, however, they may be essential micro-nutrients. Knowledge of the distribution of trace metals is important not only because of their potential impact on the ecosystem, but also because they might serve as tracers for other anthropogenic substances which are themselves much more difficult to detect in the environment.

This study consisted of three components. The concentration of nine elements was determined in 246 surface sediment samples in order to establish the current geographic distribution of these elements, and vertical profiles were determined in 45 cores to investigate the possibility of historical changes. Finally, the ^{210}Pb and ^{226}Ra activity in certain cores was measured in order to determine deposition rates and provide a time scale for any historical changes observed.

All surface samples were collected between April 1977 and June 1981. The sampling stations were located along 25 transects running roughly in an east-west direction and extending from the mouth of Chesapeake Bay to the Susquehanna River as well as channel stations into Baltimore Harbor and the Elizabeth River. A Ponar grab sampler was used and variable-range radar triangulation was the navigation technique. An unfractionated sub-sample and a <63μm sub-sample were measured in most cases. While the unfractionated sediment samples were found to be reasonably reproducible in muddy terraines, the data obtained from sandy environments is limited by the chemical inhomogeneities inherent in sands.

Most of the core samples were obtained during the November 1978, May to June 1979, and May to June 1981 cruises. Samples from two deep cores were also obtained near Fort McHenry in the Baltimore Harbor.

Surface sediments from Chesapeake Bay were extracted with nitric and hydrochloric acids. Analyses of the sample extracts were done by atomic absorption spectroscopy under analysis conditions recommended by the manufacturers. In order to determine a larger group of elements in the core samples, and also in order to have an independent method with which to check the atomic absorption data, another method was developed which involved fusing the samples with lithium metaborate, dissolving the

resulting glass in nitric acid, and using direct current argon plasma emission spectroscopy (DCP) to determine the metal content of the solutions. Deposition rates in the cores were determined by ^{210}Pb assays using the alpha-spectrophotometric measurement of daughter polonium-210.

SECTION 2

CONCLUSIONS

The frequency distributions for all elements in the unfractionated samples were approximately log-normal. Some elements displayed a bimodal distribution. Factor analysis of Bay samples showed that there was only one factor involved in the control of trace elements in the sediments, or, more likely, there were coalescent multiple factors.

Analysis of the data indicates that the elements in the <63 μm fraction decrease seaward, probably reflecting the distance from the Susquehanna River which delivers relatively metal-rich sediment to the Bay. In some places, the metals also decrease eastward across the Bay, suggesting that either seaward transport of Susquehanna-derived sediments is more effective on the western side due to the Coriolis effect or that the western side is enriched due to sediment derived from the Piedmont tributaries. The results for the unfractionated sediments are similar to the <63 μm fraction, but have additional variation due to grain size.

Chromium concentrations tend to decrease down the bay with high concentrations in both the unfractionated and <63 μm fractionated samples occurring in and around Baltimore Harbor and the Elizabeth River.

Manganese ranges from 74 to 6900 ppm in the <63 μm fraction, and also decreases seaward. Elevated levels have been found just north of Baltimore Harbor in the area of the Gunpowder River, as well as in the Harbor itself. Elevated levels are also found in the Elizabeth River.

The distribution of iron shows the typical decrease seaward with elevated levels around Baltimore Harbor and Annapolis in the Bay. The Baltimore enrichment is thought to be due more to local accumulation of fine-grained, iron-rich particles than to industrial activity because the Fe/Al ratio is not particularly anomolous in this region. However, large discharges of iron-rich waste have historically occurred in the Harbor. Slightly elevated levels at the mouth of the Rappahannock River also may be caused by the high clay content in this area.

Cobalt and nickel closely resemble manganese in distribution. In addition to the causes of enrichment already mentioned, the discharge of Back River, which contains both industrial and municipal wastewater from Baltimore, may contribute to the enrichment.

Copper, lead, and zinc also display the typical southward decrease with each showing a strong source from Baltimore Harbor. Copper and zinc show elevated levels just north of the Harbor, and all three are enriched at the mouth of the Rappahannock. These elements are generally enriched in the upper rather than the lower parts of cores, suggesting regional contamination that is presumed to be increasing with time.

Sedimentation rates were also calculated and range from 0.7 to 42.6 mm per year. The highest rates were calculated for Susquehanna River cores and several cores collected near the mouth of the Potomac River. Most of the core samples from the upper and lower portions of the Bay were in the several mm per year accumulation rate range.

The levels of metals in the sediments of Baltimore Harbor and the Elizabeth River area are high compared to the surrounding Bay sediments. However, both areas are composed of fine-grained sediment and part of the

elevated level may be due to this fine fraction. The Elizabeth River area shows consistent anthropogenic enrichment for only Zn, while Baltimore Harbor is enriched in Co, Cr, and Zn with minimal V enrichment.

Baltimore Harbor is working as an effective trap for fine-grained sediment. Most of the deposition is occurring in the inner reaches of the Harbor. The zone of contamination is over three meters in this area. The zone wedges out in a seaward direction and seems to show only very minor signs of appearing in the Bay proper.

SECTION 3

METHODS

ACID EXTRACTION-ATOMIC ABSORPTION PROCEDURE

The acid extraction method for surface sediments from the main Bay is shown in Figure 1. The sediment samples were dried at 105°C for 48 hours and then ground in a mullite ($3Al_2O_3 \cdot 2SiO_2$) mortar. Approximately 5 g (for muds) to 50 g (for sands) were weighed to the nearest 0.01 g on an electronic balance and placed in a 500-mL boiling flask. To the flask, 90 mL of concentrated nitric acid, which acted as an oxidizing agent, and 10 mL of concentrated hydrochloric acid, which complexed iron, were added. A 30-cm Allihn reflux condenser was placed on the flask and the contents were refluxed on a hot plate for four hours, with vigorous boiling to promote mixing.

Upon cooling, the solutions were centrifuged and filtered through Whatman Number 1 filter paper. The remaining sediment was washed two times with 25 mL of water, the wash solution being collected in the beaker. The collected extract (~300 mL) was reduced to approximately 25 mL on a hot plate, transferred to a 50-mL volumetric flask, and brought to volume with 5% nitric acid. The extracts were stored in 125-mL polyethylene bottles.

Throughout all analytical work, de-ionized distilled water was used. The nitric and hydrochloric acids were analytical grade, meeting American Chemical Society specifications. Acid blanks were analyzed to check for contamination and it was found that the levels were usually below the detection limits of conventional flame atomic absorption. The Pyrex glassware and polyethylene bottles were all washed in 12 M sulfuric acid. Bad!

All standard solutions were made from either high purity metals or chloride, chromate, or sulfate salts in a manner similar to that of Dean and Rains (1971). Working standards were prepared by dilution of the stock solutions. The standards of Cr, Co, Ni, Cu, Cd, and Pb were prepared in 5% nitric acid. The standards of Mn, Fe, and Zn were prepared in 1% hydrochloric acid. Analysis for these relatively abundant metals was performed using a 50-fold dilution of the sediment extract in 1% hydrochloric acid. Different extract!

Analyses of the sample extracts were done by atomic absorption spectroscopy (AAS) with several instruments: a Perkin-Elmer 303, an Instrumentation Laboratories 353 or an Instrumentation Laboratories 751. Conditions of analysis were as recommended by the manufacturer except where noted in Table 1. Background correction, using a deuterium lamp, was used for elements with analytical wavelengths of less than 300 nm when the sample extract was analyzed undiluted. A secondary wavelength for Ni was used to obtain better precision. Chromium analyses were done using a lean flame to remove interferences, especially by HNO_3, as noted by Kawa and Henn (1977). Although Cr sensitivity diminishes in a lean flame, the precision and detection limit remained at acceptable levels for analysis of estuarine sediments. Iron analysis was done with the flame perpendicular to the beam. Using this configuration, Butler (1975) reports a working range of 2.8 to 440 ug/mL. In this study, calibration curves for Fe were not enough!

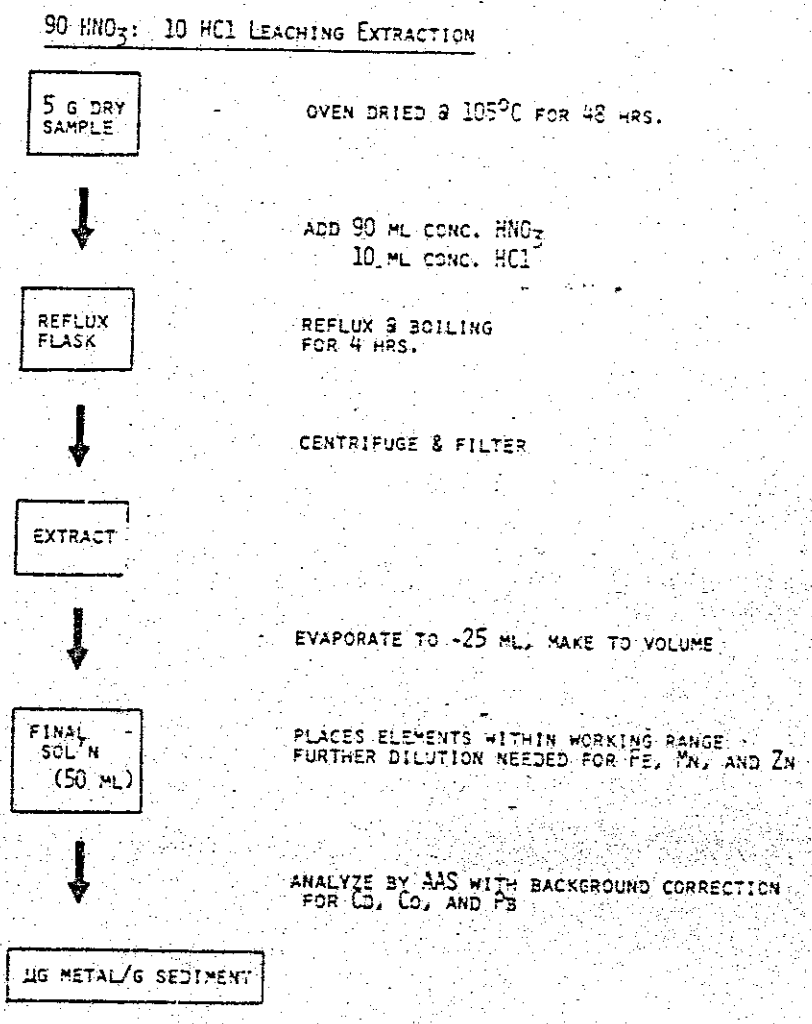


Figure 1. Outline of the $90HNO_3$-10HCl extraction and analysis procedure.

Table 1. Atomic Absorption Spectrometer Conditions*

Metal	Solution Analyzed	Wavelength (nm)	Comments
Cr	Extract	357.9	Lean flame
Mn	Diluted by 50	279.8	–
Fe	Diluted by 50	248.3	Perpendicular flame
Co	Extract	240.7	Background correction used
Ni	Extract	341.5	Greater precision wavelength
Cu	Extract	324.7	–
Zn	Diluted by 50	213.8	Analysis using a single-slot burner
Cd	Extract	228.3	Background correction used
Pb	Extract	217.0	Background correction used

*All settings not described conform to manufacturer instrument settings; all analyses were done with an air - C_2H_2 flame using a Boling burner (except Zn); background corrected elements analyzed on IL, others on PE.

found to be linear up to 200 ug/mL. Background correction was unnecessary for Fe analysis except for extracts of the National Bureau of Standards (NBS) river sediment standard. What!!

PLASMA EMISSION METHOD FOR CORE SAMPLES

In order to determine a larger group of elements in the core samples and in the surface samples from Baltimore Harbor and the Elizabeth River, as well as to have an independent method with which to check the atomic absorption data, another method was developed which involved fusing the samples with lithium metaborate (Suhr and Ingamells, 1966), dissolving the resulting glass in ni ic acid and using direct current argon plasma emission spectroscopy (DCP) to determine the metal content of the solutions. One hundred milligram portions of the dried sediments (see next section) were fused with 0.5 g of lithium metaborate in a graphite crucible at 900°C for approximately 15 minutes. The molten lithium borate glass bead was poured into a 150-mL Teflon FEP beaker containing 100 mL of 4% nitric acid. The beaker was placed on a magnetic stirrer and the contents stirred for approximately 10 minutes. The solution was then transferred to a 125-mL polyethylene bottle. Each sediment was fused in triplicate. Blanks of only lithium metaborate were also fused. Reagent grade nitric acid and de-ionized distilled water were used in the preparations and in cleaning the plastic ware. Working standards were prepared by dilution of the previously described stock solutions using lithium nitrate solution in 4% nitric acid so that the concentration of Li^+ in the samples and the standards match. The solutions were analyzed using a Spectrametrics Spectraspan IV spectrometer equipped with a Spectrajet III plasma source. The conditions were as specified by the manufacturer, and the smallest available slits were used.

~~Cannot cite~~ AAS of partial extracts w/ DCP of total dissolutions

The precision and accuracy of the analytical methods used in this paper have been extensively documented in two theses (Sinex, 1981; Cantillo, 1982) and in two papers (Sinex et al. 1980; Cantillo et al. 1983). These sources should be consulted for further information.

^{210}Pb PROCEDURE

In order to determine deposition rates in the core samples, assays for ^{210}Pb were performed by the following procedure. The refrigerated cores were either hydraulically or mechanically extruded in the laboratory into 2.0 cm intervals and sliced off at the top using a thin plastic sheeting. Since the internal diameter of the core liner was 6.7 cm, each 2.0 cm interval yielded approximately 70 cm^3 of sedimentary material. Precision of the sediment extrusion was assumed to be 1 or 2 mm for any single section. All intervals were trimmed around the circumference to eliminate cross-contamination by material carried from the surficial sediment layers down the inside of the core barrel. Sediments were transferred with plastic spatuals to aluminum weighing dishes and dried to constant weight at 110°C. The weight loss was recorded, which provides a measure of the water content of the sediments. The dried sediment cakes were manually pulverized to a fine powder with mortar and pestle. Radiochemical analyses (i.e. Po-210, Ra-226, Cs-137) were conducted on acid extracts of the dried disaggregated sediments. Since the dried Chesapeake Bay sediments possess

variable salt contents due to their high porosities, all measured concentrations were normalized to salt-free sediment weights calculated on the basis of pore water salinities (Bricker, 1980).

In this study, lead-210 in the Chesapeake Bay sediment samples was determined using the alpha-spectrometric measurement of daughter polonium-210. Secular equilibrium between lead-210 and polonium-210 in the sediments was assumed. In this procedure polonium-210 and lead-210 are taken into solution by oxidizing (wet-ashing) 1 - 4 grams of a dried, ground and accurately weighed sediment aliquot in warm nitric and hydrochloric acids for several hours. The final residual solution is separated from particulates by centrifugation and filtered. After several additions of hydrochloric acid to remove interfering nitrates, the solution is made up in 0.3N hydrochloric acid and spiked with a polonium-209 yield tracer. The two isotopes (^{209}Po and ^{210}Po) are removed from solution by spontaneous electrodeposition at 90°C onto a nickel -200 disc (99.95% pure Ni). The polonium isotopes plated on the nickel disc are counted with a silicon surface barrier detector linked to a pulse height analyzer.

Background activities for the surface barrier detectors were all less than 0.0010 cpm in the polonium-209 energy region and less than 0.0003 cpm in the polonium-210 energy region. Resolution for the 5.33 MeV polonium-210 alpha was about 50 KeV full width at half maximum (FWHM). The efficiency of the detectors for alpha particles is nearly 100%, but geometrical constraints reduce the actual counting efficiency to 25-30%. Of course, the efficiency need not be known because polonium-209 ($t_{1/2}$ = 103 years) was used as a tracer. Polonium-209 was selected as the yield monitor to achieve complete baseline separation between energy peaks (4.88 and 5.30 MeV, respectively). Use of the polonium-208 tracer is less desirable due to its shorter half-life (2.9 years) and the spectral baseline correction necessary to resolve it from polonium-210 due to peak tailing problems (5.11 and 5.33 MeV, respectively).

Alpha activities of the polonium-209 and polonium-210 were determined by comparison of the integrals under their respective peaks. The polonium-209 tracer solution (.004 x 10^{-6}Ci/liter) was standardized by both plating and evaporating a known volume onto the surface of a nickel-200 disc and subsequently counting in a 2π gas proportional courter of 51% efficiency (MECH-TRONICS NUCLEAR #X-319).

SECTION 4

SAMPLING

SURFACE GRAB SAMPLES

Surface sediment samples from the mainstem of Chesapeake Bay were collected along 25 selected traverses oriented principally in the east-west direction across the Bay. The general locations of the traverses are shown in Figure 2 and the exact sample locations are given in Table A-1 (in Appendix A). Time of collection, collection agency, and the method of navigational location (Loran, Raydist, or radar) are also given in Table A-2 (in Appendix A). All main Bay surface samples were collected between April 1977 and May 1979.

Forty-six surface samples were collected later (May and June, 1981) from Baltimore Harbor and the Elizabeth River. Locations of these samples are shown in Figures 3-7.

The surface samples were collected by a Ponar grab sampler and inserted into polyethylene bags. All samples were taken from the middle of the grab to avoid contamination from the walls. Samples were transported back to the laboratory where they were stored at 4°C.

The main Bay surface samples were also fractionated by wet sieving after decantation through a 63 μm nylon screen held in a Plexiglas frame. Distilled water was used in this operation and was carried with the <63 μm material through the analysis so as to retain soluble material.

REPRODUCIBILITY OF SURFACE SAMPLING

In evaluating the precision of monitoring data, it is common to consider only sources of error arising from preparation and analysis of the sample. However, since the final result is expected to indicate something about the environment, it is important to consider the effect of the sampling process itself on overall precision or reproducibility.

In the sampling of sediments, two types of variation can affect reproducibility: navigation error (i.e., failure to reoccupy exactly the same site), and chemical inhomogeneity at the site. These variations were investigated in Chesapeake Bay by the sampling scheme illustrated in the top of Figure 8. Two grab samples were collected at a station, this being repeated at four points on a traverse. Then the vessel circled off, and the traverse was resampled a second time in the reverse direction, again collecting two samples per station. Hence, four samples, collected in pairs, were obtained at each station. Navigation was done by using variable-range radar triangulation.

The results for copper, obtained by analyzing these samples by the acid extraction procedure, are illustrated in Figure 8. These results are representative of those for the other metals, which are given in Tables 2 and 3. Considering first the mud-type samples (Stations 1 and 2), it can be seen by scanning horizontally across Figure 8 that variation is small between all four samples at a given station. For the unfractionated samples (open bars in Figure 8), there is some difference between pairs (A-B vs. C-D), possibly reflecting navigational error, but this is not much

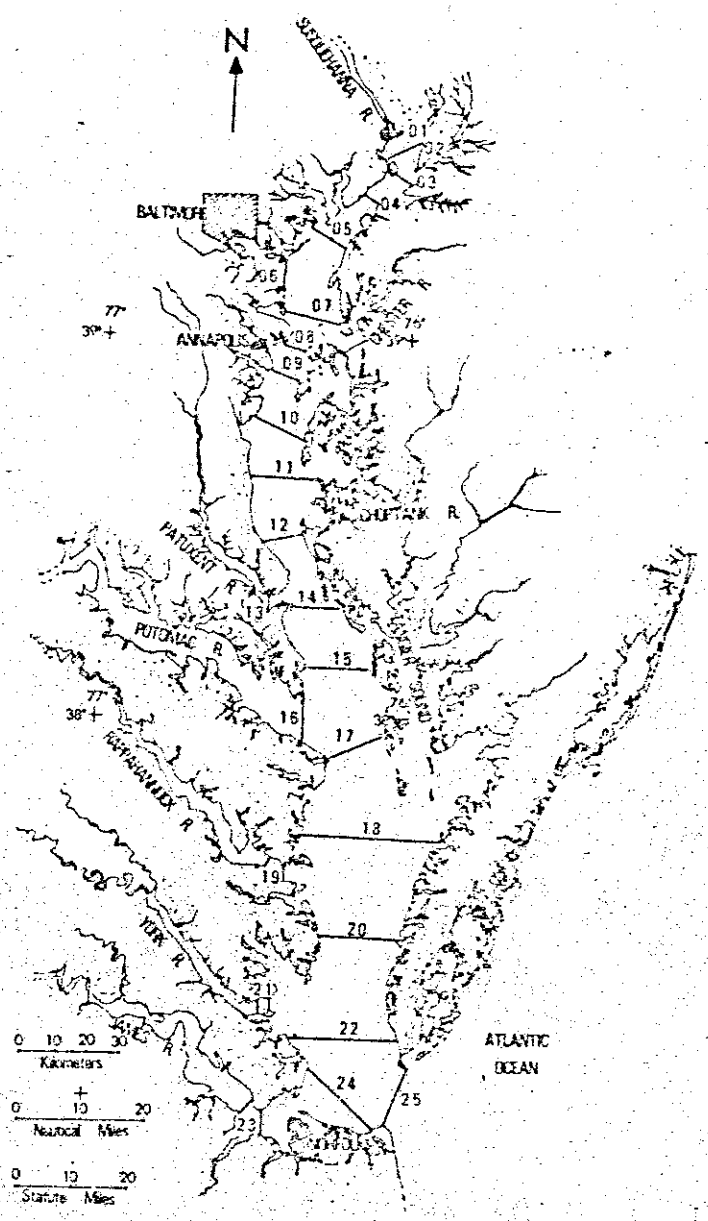


Figure 2. Traverse locations for grab samples.

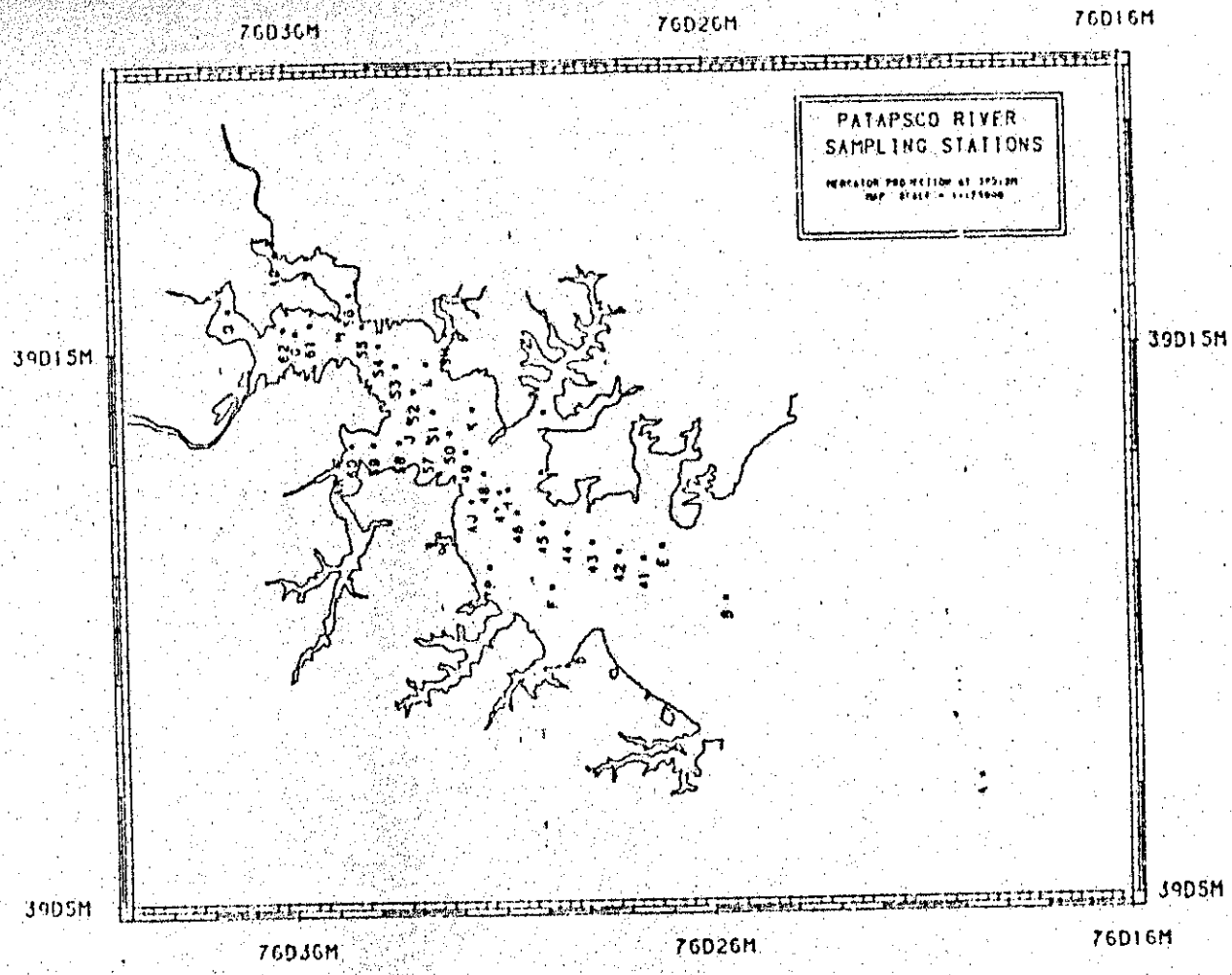


Figure 3. Patapsco River Sampling Locations

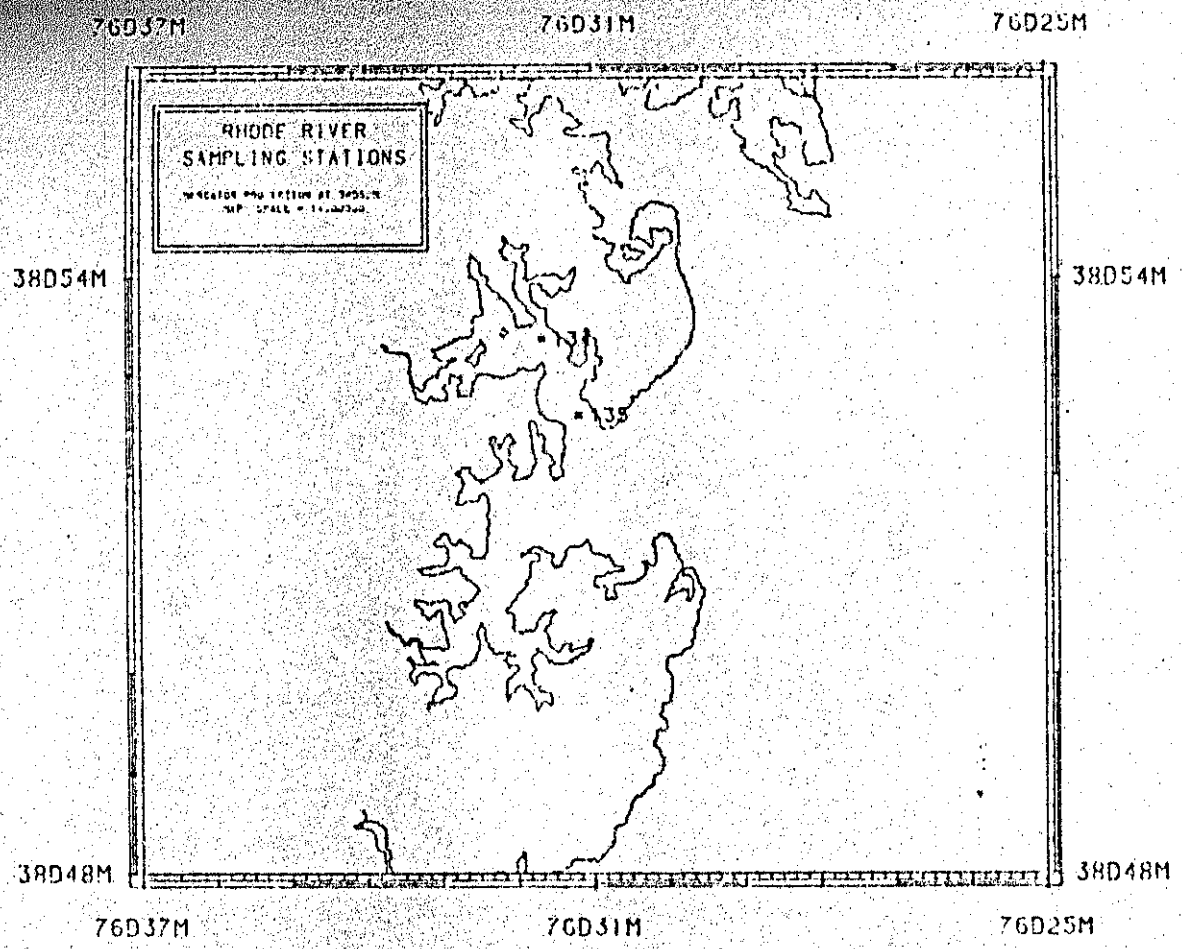


Figure 4. Rhode River Sampling Locations

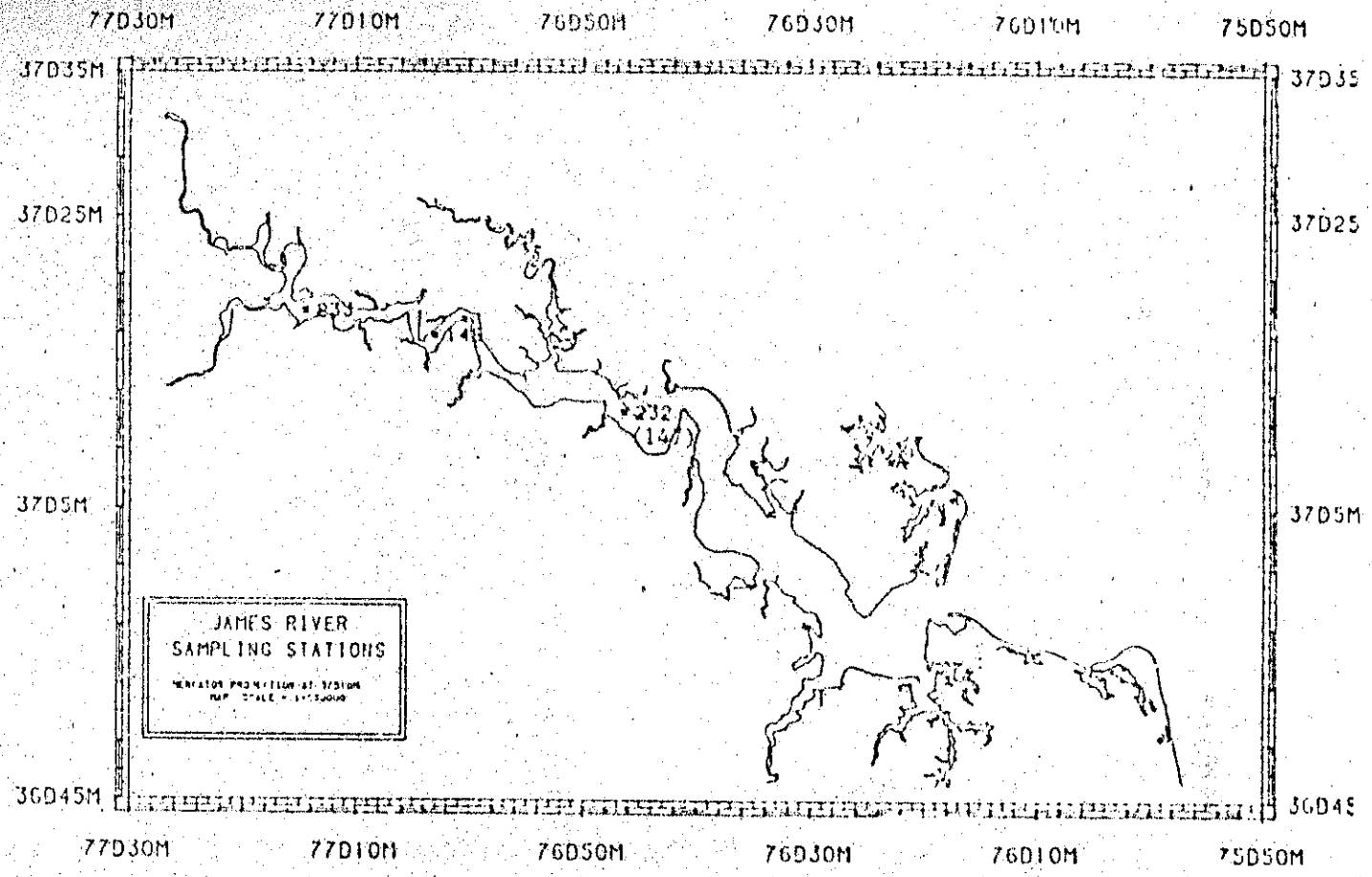


Figure 5. James River Sampling Locations

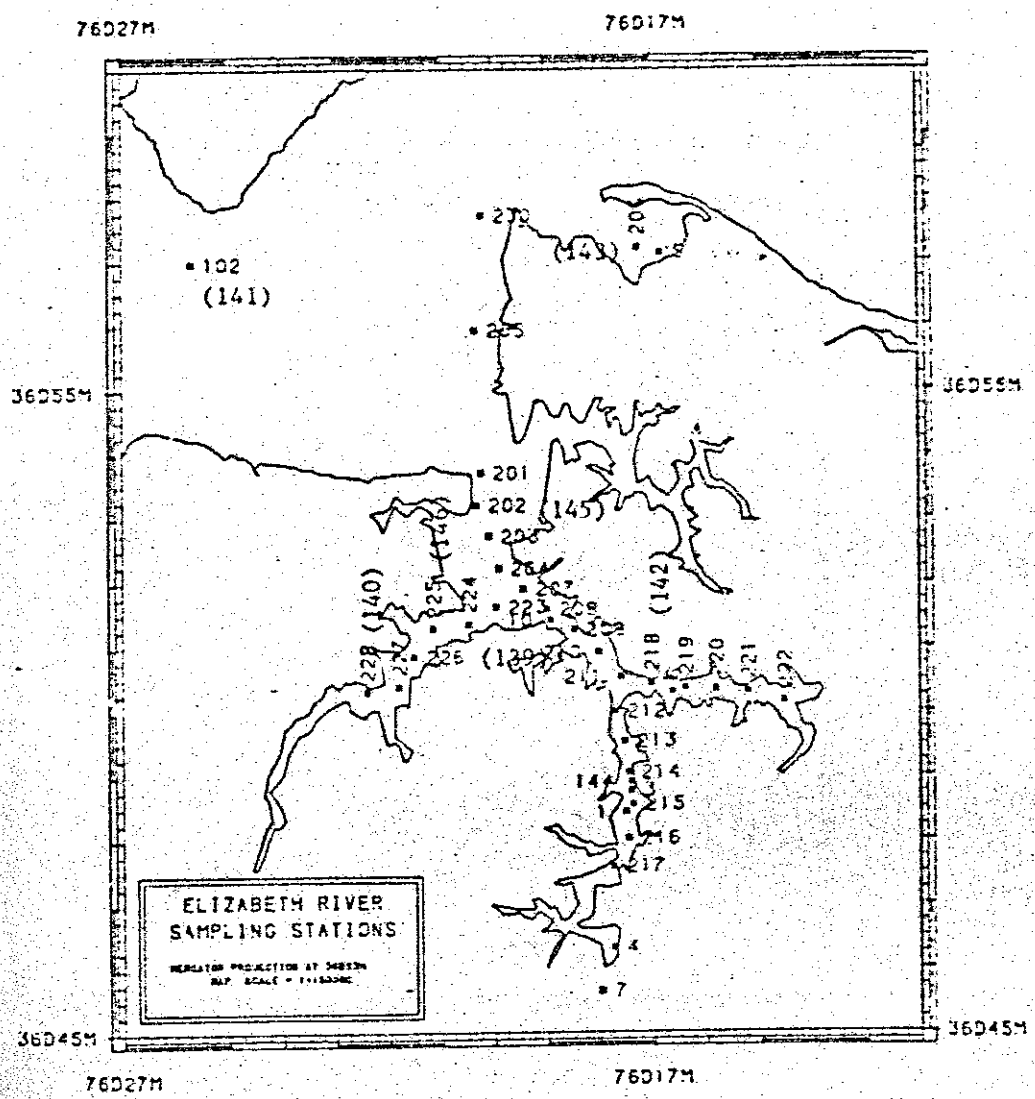


Figure 6. Elizabeth River Sampling Locations

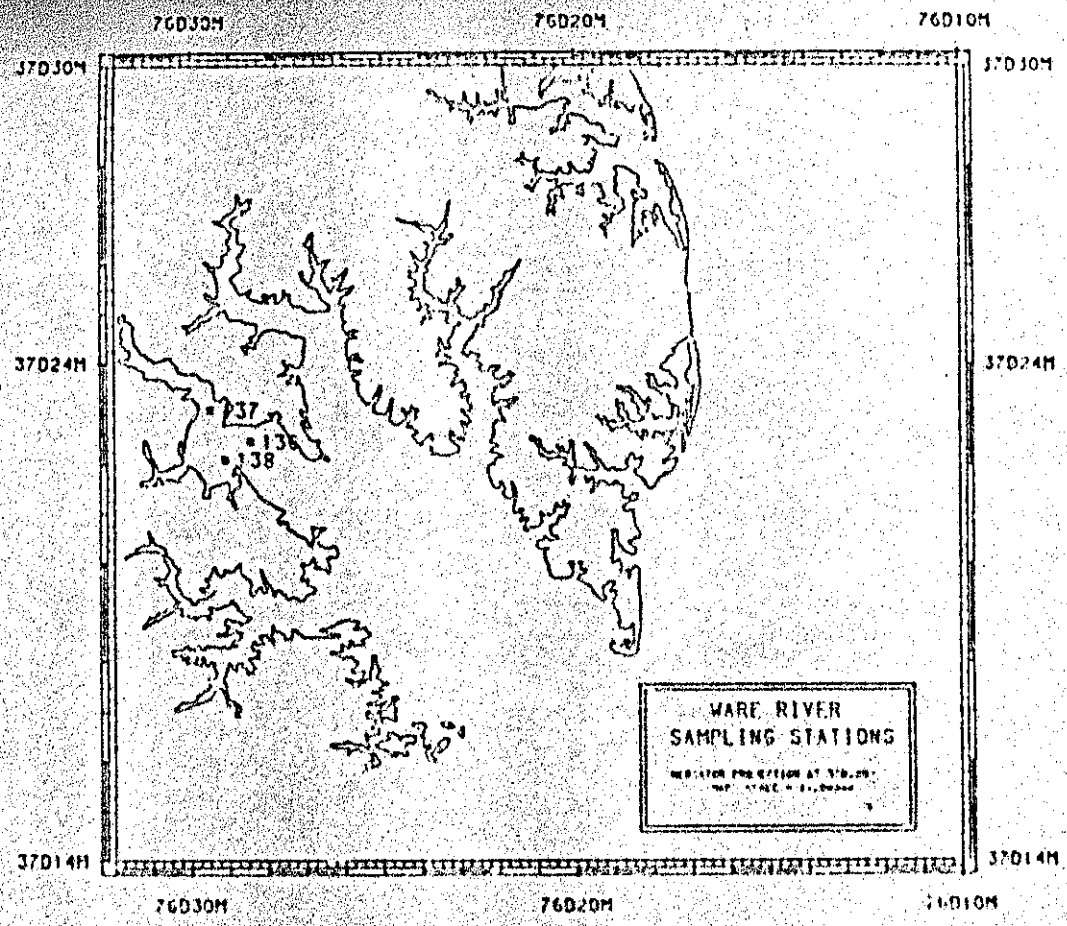


Figure 7. Ware River Sampling Locations

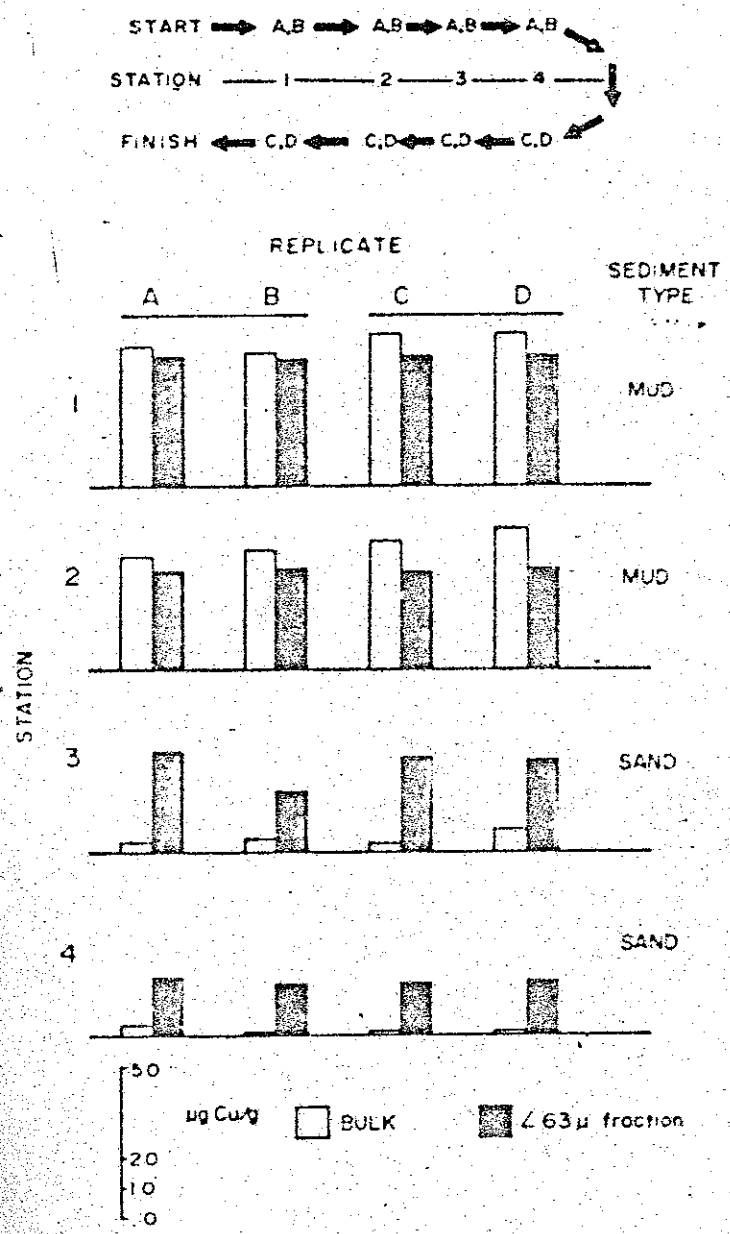


Figure 8. Variability in copper concentrations in the sampling replication experiment (see text for explanation).

Table 2. Reproducibility of Sampling; Results for Unfractionated Samples (ug/g except where %)

Station	Replicate	Cr	Mn	Fe(%)	Co	Ni	Cu	Zn	Cd	Pb
1	A	54	650	4.0	20	47	46	280	1.1	43
	B	59	690	4.0	22	50	44	320	1.1	41
	C	58	690	4.0	21	46	50	320	1.1	43
	D	57	650	3.9	19	43	50	270	1.1	41
2	A	53	570	4.0	18	45	37	230	0.74	33
	B	57	550	4.0	17	48	39	230	0.75	31
	C	57	540	4.0	18	49	42	230	0.59	34
	D	54	580	4.0	18	43	46	210	0.60	36
3	A	11	70	1.1	4.2	8.2	3.2	30	Tr[1]	3.4
	B	14	110	1.5	5.0	11	4.2	32	Tr	3.6
	C	11	79	1.3	4.5	8.5	3.3	41	0.03	3.5
	D	16	140	1.6	5.7	13	7.5	66	0.11	7.0
4	A	4.6	57	0.37	1.5	3.8	2.9	15	0.03	2.9
	B	1.1	14	0.08	0.5	0.7	0.7	4.5	ND[2]	1.1
	C	1.4	10	0.09	0.6	1.4	0.8	5.0	ND	1.2
	D	1.7	18	0.12	0.7	1.3	1.0	4.2	Tr	1.2

[1] Trace.
[2] None detected.

Table 3. Reproducibility of Sampling; Results for Fractionated (63 um) Samples (ug/g) except where %

Station	Replicate	Cr	Mn	Fe(%)	Co	Ni	Cu	Zn	Cd	Pb
1	AF	51	640	3.9	18	43	43	250	1.0	40
	BF	53	700	3.8	18	160[1]	42	1200[1]	0.90	54
	CF	50	670	3.8	17	46	43	260	0.87	39
	DF	54	590	3.7	18	47	43	240	0.76	37
2	AF	48	490	3.6	15	39	32	190	0.44	28
	BF	57	--[2]	--	--	39	33	--	--	--
	CF	58	--	--	--	38	32	--	--	--
	DF	62	--	--	--	37	33	--	--	--
3	AF	46	290	3.8	13	35	33	170	0.47	27
	BF	60	--	--	--	32	20	--	--	--
	CF	64	--	--	--	38	31	--	--	--
	DF	58	--	--	--	37	30	--	--	--
4	AF	27	260	2.2	8.6	24	19	95	0.14	14
	BF	33	--	--	--	23	17	--	--	--
	CF	36	--	--	--	23	17	--	--	--
	DF	35	--	--	--	23	18	--	--	--

[1] Contamination with Zn-Ni phase.
[2] Not analyzed.

larger than analytical error. The unfractionated samples are slightly more Cu-rich than the <63 μm fraction in the case of muds, probably because of metal-rich grain coatings on the sand fraction. In contrast, for the sand-type samples (Stations 3 and 4), the variation in unfractionated samples is somewhat larger on a relative basis. Because large quantities (~50 g) were extracted to avoid loss of precision at low levels, these variations cannot be dismissed on account of analytical error. Variation by as much as a factor of three occurs in the unfractionated sand samples. However, the variation in these samples is as large between samples collected during the same occupation of a station (i.e., compare 3C with 3D) as it is between the samples collected during first and second occupation of the station (3C,D vs. 3A,B). Thus, navigational error is clearly not the source of this variation. It is probably caused by small-scale changes in the proportions of heavy minerals, sand, and clay because of local hydrodynamic sorting such as might be associated with formation of ripples on the bottom. The concentration of trace metals per unit mass of sediment is known to be much larger for fine-grained material (de Groot, 1976). When the grain-size variable is removed by analyzing only the <63 μm fraction, the reproducibility at a given station is much better (see solid bars in Figure 8).

Thus, reproducibility tends to be poorer than expected on the basis of instrumental uncertainty in the case of coarse-grained sediments. This was observed most clearly in comparing different samples collected at the same site (Figure 8). However, the effect was also noted in pairs of analyses of material from the same samples. For sand-type samples, these pairs of analyses were discordant by more than 30% in some cases, whereas they were much less discordant for mud-type sediments. It would appear from these results, that the quality of monitoring data obtained from sandy environments is limited not by analytical uncertainty, but by the chemical inhomogeneities inherent in sands. If sediment analyses are to be used to monitor environmental quality in sandy terranes, it would seem advisable to place emphasis on changes in the composition of the fine-fraction rather than on changes in bulk composition. The unfractionated sediment samples are reasonably reproducible in muddy terranes.

CORE SAMPLES

Seventeen 6.7 cm diameter gravity cores were collected at stations in the main stem of Chesapeake Bay (Table 4, Figure 9). The bulk of the samples were obtained during the November, 1978 and May-June, 1979 cruises of the R/V Retriever. When possible, the core catcher was eliminated from the gravity corer to minimize perturbation of the sedimentary layers. Core samples were refrigerated upright at 4°C in their cellulose acetate butyrate core liners prior to analysis. In May and June, 1981, an additional 28 gravity cores were collected from Baltimore Harbor (Figure 3, letter designations) and the Elizabeth River (Figure 5). In addition, two deep cores near Fort McHenry, in Baltimore Harbor, were obtained from the Maryland Highway Administration.

Table 4. Chesapeake Bay Sample Locations

Station	Sampling Date	Latitude	Longitude	Core Length (cm)
52	6/6/79	39°29'15"N	75°56'30"W	88
4	11/1/78	39°19' N	76°14' W	96
6	6/3/79	39°09' N	76°23' W	76
55	7/2/79	38°48'30"N	76°23'30"W	104
14	6/30/79	38°39' N	76°25'30"W	96
18	11/6/78	38°19' N	76°20' W	86
60	6/9/79	38°11'30"N	76°19'30"W	84
62	6/28/79	38°10'30"N	76°14' W	104
63	6/27/79	38°11'30"N	76°07'45"W	82
64	6/26/79	38°12'30"N	75°57'50"W	90
24	11/3/78	38°00' N	76°13' W	126
83	6/21/79	37°41'30"N	76°14'30"W	77
85	6/23/79	37°41'15"N	76°04'30"W	96
86	6/21/79	37°43'15"N	75°55'15"W	102
102	9/19/78	37°24' N	76°04' W	52
99	6/20/79	37°00'30"N	76°14'15"W	34
4 (Susquehanna) River	5/25/79			

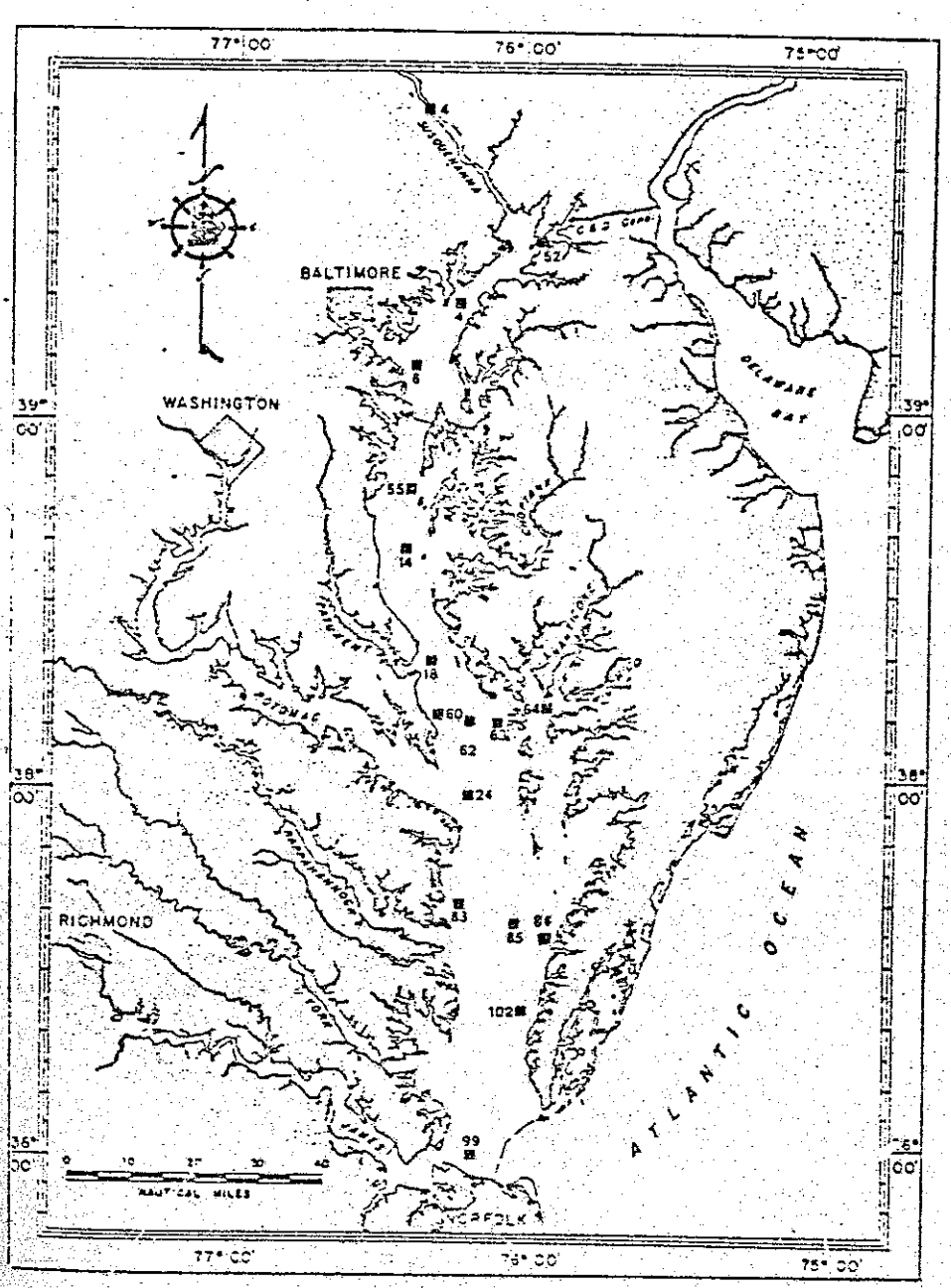


Figure 9. Locations of cores.

SECTION 5

COMPOSITION OF SURFACE SEDIMENTS

MAIN BAY -- STATISTICAL DESCRIPTION

Data on the main Bay surface samples are presented in Appendix A. The frequency distributions for all the elements in the main Bay unfractionated samples were approximately log-normal. This is not unusual, especially since the lower end of the distribution is controlled by the detection limit for each element. This is a common distribution for geochemical data (Koch & Link, 1970). Figure 10 illustrates the type of plots obtained from the data. The Cr distribution (Figure 10A) along with those of Fe, Ni, and Cu are slightly bimodal. The Zn plot (Figure 10B) along with Mn, Co, and Pb show a decrease in frequency as metal levels increase.

The <63 μm fractionated samples show distributions that were for the most part skewed to the right. A representative example is illustrated using the Ni data in Figure 11A; Mn, Co, Zn, and Pb have similar distributions. The Cu distribution shown in Figure 11B has a bimodal character. The exceptions to the skewed distributions above are Cr and Fe. The Cr distribution (Figure 12A) looks fairly normally distributed; however, a cumulative frequency plot showed it to be slightly skewed to the left. The Fe (Figure 12B) shows a platykurtic distribution while a cumulative frequency plot showed it to be closest to normally distributed. When all the <63 μm fractionated sample data were logarithmically transformed, Mn, Co, and Pb appeared to be bimodally distributed and Cu and Zn possibly also were bimodal. This is illustrated in Figure 13.

The standard product-moment correlation coefficients were calculated for the unfractionated and <63 μm data sets for all metals except Cd. Approximately half of the samples in the main Bay gave trace or undetectable Cd levels; hence the Cd data were removed before statistical treatment. The correlation coefficient matrix is shown in Table 5. The results for the unfractionated samples are shown below and to the left of the diagonal while the <63 μm fractionated samples are above and to the right. All the values are significant at the 1% level, given the number of samples indicated on the table.

A number of important observations can be made from Table 5. For example, the correlation coefficients for the unfractionated samples are larger than the <63 μm fractionated samples. This increase could be caused by the wider range covered by the unfractionated samples, since many sand samples are included in this set. A related way of causing a wider range would be by removing a metal-rich component during the laboratory size fractionation process. Coatings of hydrous Fe-Mn oxides on sand (>63 μm material) may be a significant component in muds. The highest correlation typically occurs between Mn and Co, Ni, and Cu. Hydrous manganese oxides have been shown to adsorb strongly Ni, Cu, and especially Co (Murray, 1975ab; Hem, 1978). Grain coatings of hydrous manganese oxides may be an important control on metals in the sediments, especially since coatings are abundant on sand grains in Bay sediments. Other high correlations are also evident, like Cu-Zn and Cu-Pb which may reflect

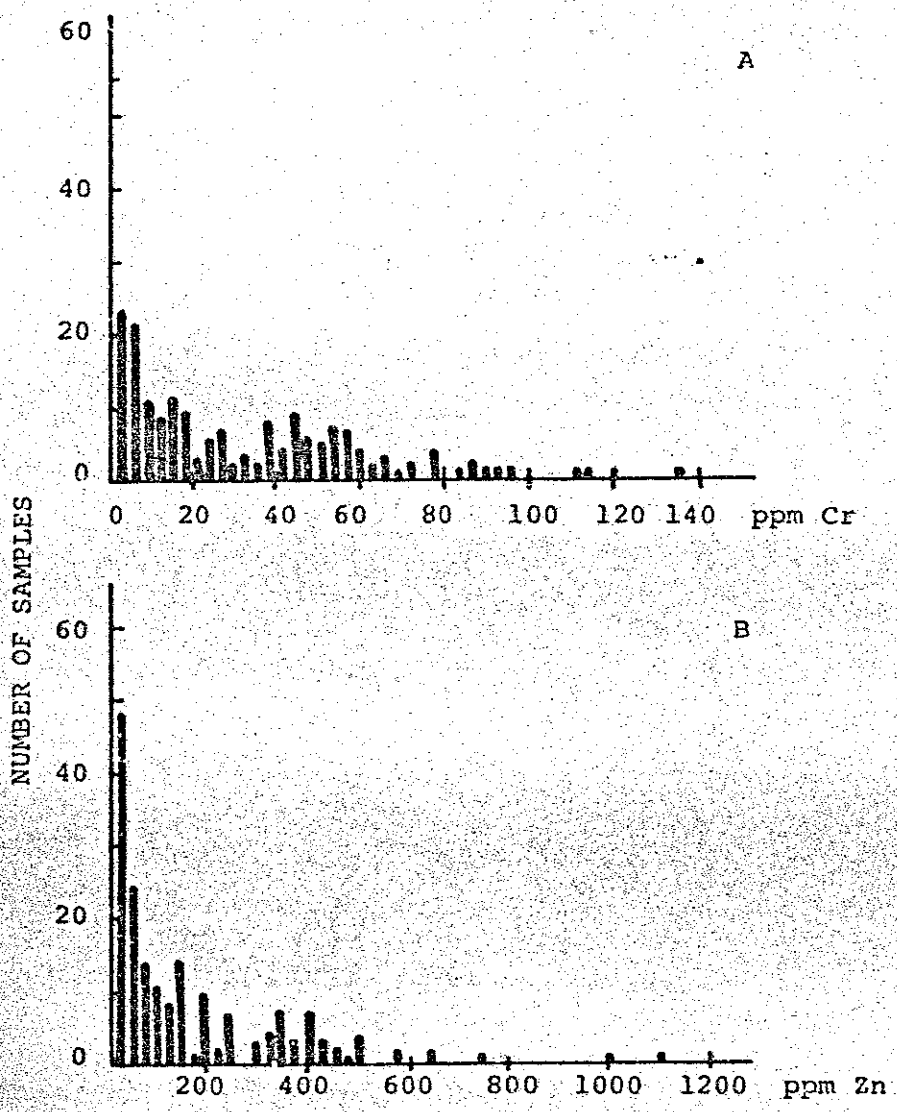


Figure 10. Frequency distribution of Cr (A) and Zn (B) in the unfractionated sediment samples from the main Bay.

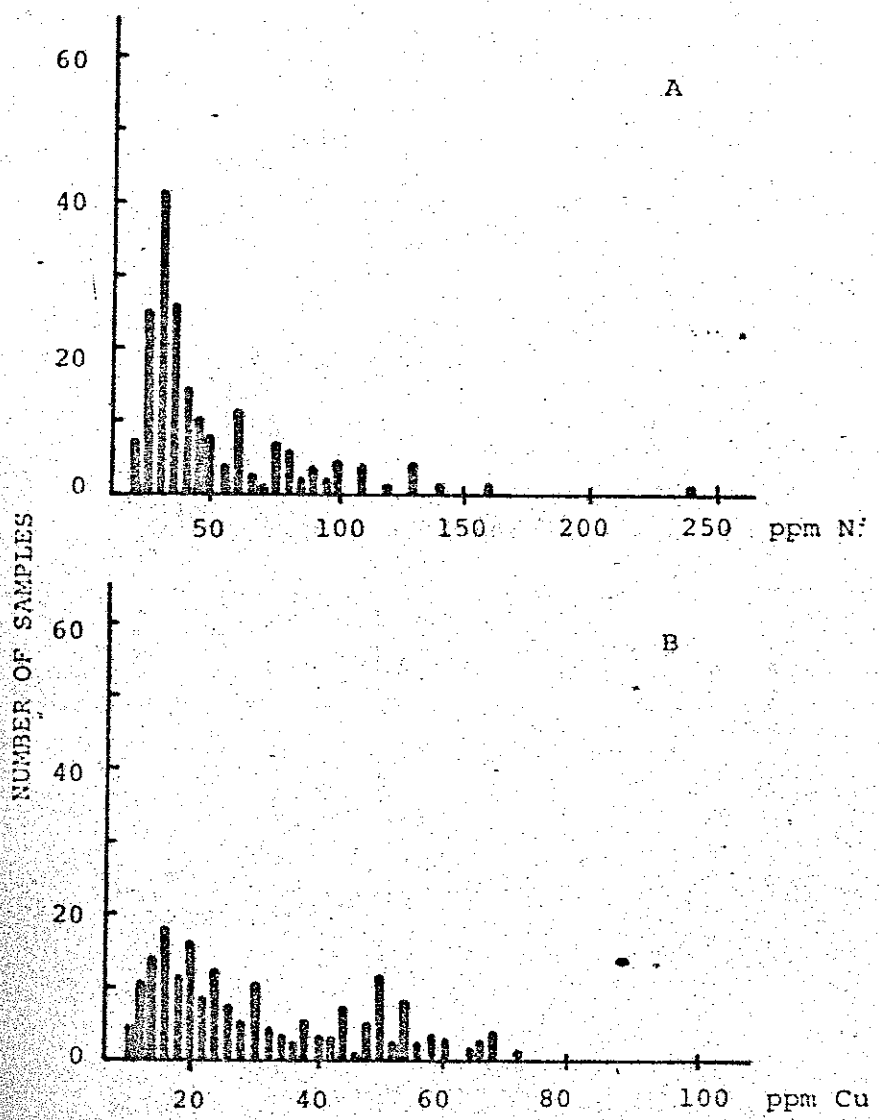


Figure 11. Frequency distribution of Ni (A) and Cu (B) in the <63 micron fractionated sediment samples from the main Bay.

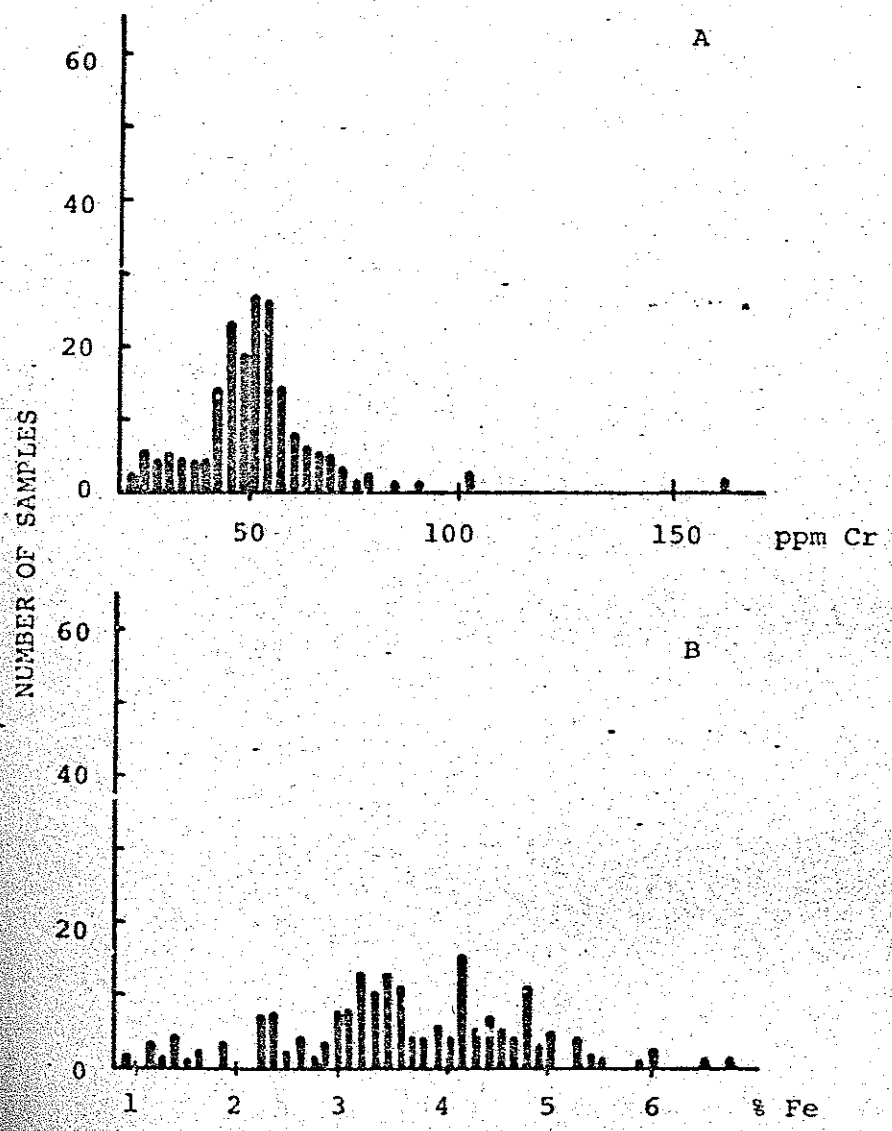


Figure 12. Frequency distribution of Cr (A) and Fe (B) in the <63 micron fractionated sediment samples from the main Bay.

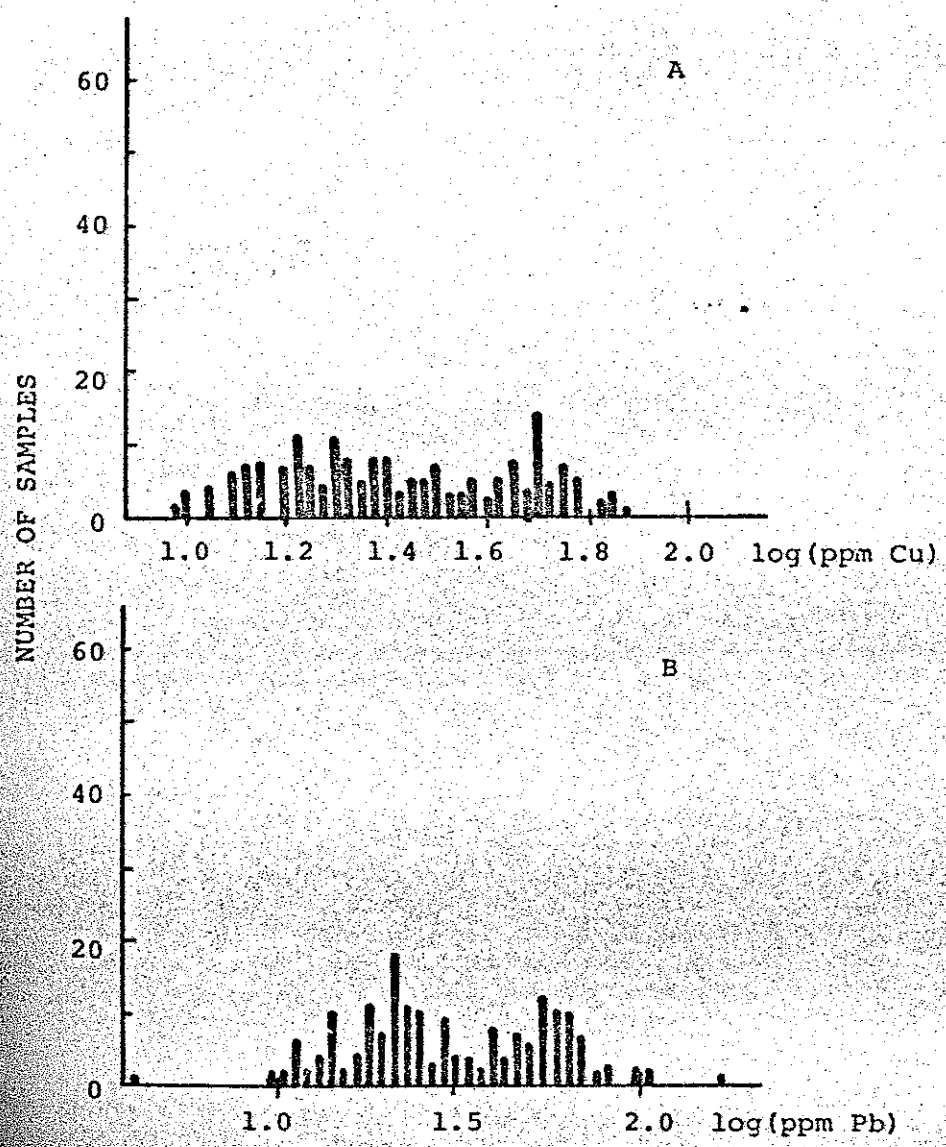


Figure 13. Frequency distribution of Cu (A) and Pb (B) in the <63 micron fractionated samples using the logarithmically transformed data. Only data from the main Bay have been included.

Table 5. Correlation Coefficient for Main Bay Surface Samples.
(All values are significant at the 1% level.)

	Cr	Mn	Fe	Co	Ni	Cu	Zn	Pb
Cr		0.29	0.76	0.39	0.29	0.61	0.30	0.70
Mn	0.72		0.59	0.87	0.80	0.69	0.38	0.57
Fe	0.96	0.71		0.73	0.62	0.79	0.35	0.78
Co	0.79	0.92	0.79		0.90	0.87	0.47	0.76
Ni	0.82	0.90	0.82	0.97		0.80	0.67	0.69
Cu	0.83	0.75	0.86	0.91	0.90		0.50	0.91
Zn	0.86	0.74	0.86	0.85	0.85	0.88		0.52
Pb	0.85	0.66	0.84	0.81	0.79	0.88	0.93	

<63 μm fractionated samples (n = 185)
unfractionated samples (n = 177)

associations in organic matter (Hallberg, 1979) or Fe with most other metals which may indicate the presence of these metals in iron oxyhydroxide grain coatings (Hem, 1977).

In an effort to try to explore these associations, factor analysis was run on both the unfractionated and <63 μm fractionated sample data. Factor analysis assumes that each of the variables can be linearly related to some number of underlying factors. Variables may be partly or completely dependent on one another (Koch & Link, 1971). Factor analysis was performed on both the data sets using the BMD 03M program (1976 version). The results of the factor analysis showed that either there was only one factor involved in the control of trace elements in the sediments or, most likely, there were coalescent multiple factors. This was true for both unfractionated and <63 μm fractionated sample data from the main Bay - all factor loading went to one factor for each data set. The cumulative proportion of the total variance attributable to one factor was greater than 70% (H.G. Siegrist, Jr., per. comm.). A logarithmic transformation of the data was also subjected to factor analysis and again only one factor controlled the loading.

ELEMENTAL DISTRIBUTION PATTERNS

The distribution of each element in the main Bay has been displayed by a map produced by a computer graphics package called SYMAP (Dougenik & Sheehan, 1976). All of the unfractionated sample data are presented as contour maps, based on interpolation between data, while the 63 um fractionated sample data are presented as smoothed, 5th order trend surfaces and their accompanying residual maps. Once again the Cd data have been excluded due to limited data coverage. The data from Baltimore Harbor and the Elizabeth River were excluded from this analysis because the high density of anomalous metal concentrations in these areas would distort the main Bay trends.

A trend surface is a smooth surface that is fitted to the data points. The surface is described by a mathematical equation and increasing the order of the equation increases the complexity of the surface. To select the trend surface of best fit, the following were considered. The residual (and hence the residual map), or the difference between the trend surface and the data points, was kept to a minimum. The variation (expressed as a percentage) explained by the surface and the correlation coefficient between the data points and points on the surface both increase as the order of the surface increases. However, as the order increases the surface becomes more contorted. Hence, the highest percentage variation explained and correlation coefficients were obtained while keeping the residual to a minimum and the surface reasonable (not too contorted, producing negative areas). All of the data were tested with third to sixth order trend surfaces. Lower order surfaces showed poor fit.

Sixth order and hence higher order surfaces were rejected because artifactual maxima and minima appeared in the case of some metals at various positions within the Bay. Use of 5th order trend surfaces largely removed this problem in most cases. An exception is Mn (see Figure 15; near the mouth of the Bay a negative area appears). Fifth order was chosen because the surfaces were generally reasonable, residuals were fairly low,

percentage variation explained by the surfaces were 69% or greater, and all correlation coefficients were 0.83 or greater. This is summarized for the <63 μm fractionated samples in Table 6. The trend surface for Zn was not presented because the variation explained by the surface was poor; instead, a contour map was generated.

The equations for the 5th order trend surfaces are presented in Table 7. They are intended for interpolation and smoothing, in order to discern regional trends in the main stem of the Bay. The 5th order equations produce artifacts if extrapolated only a short distance outside the region where they are controlled by data. The equations are written in terms of SYMAP coordinates. SYMAP uses a coordinate system in which the northwest corner is the origin and the X direction increases to the east and the Y direction increases to the south. The equations to convert latitude and longitude in decimal form as degrees to SYMAP coordinates are given in Table 7. The SYMAP coordinates may then be substituted in the 5th order polynomial and the concentration of the metal (Z) determined using the appropriate coefficients from Table 7.

The contour intervals on both the trend surface and contour maps were chosen by considering the frequency distributions mentioned earlier. The middle interval encompassed a range of one standard deviation centered on the mean. The two lower and two higher intervals were then assigned additional standard deviation-wide bands below and above the middle interval. The lowermost or uppermost intervals were occasionally expanded to include outlying data. In most instances, the intervals were shifted slightly to distribute the data somewhat more evenly within the intervals. The above method for determining the intervals causes the unusual interval size and cut points, but makes graphical comparison of the data for different metals easier. The residual map intervals were determined by setting the middle interval to residuals of less than 10% (the difference between the interpolated surface and the trend surface). The other intervals were also 10%-wide bands above and below the middle, covering residuals up to above 25% difference.

All orders of trend surfaces tested (third to sixth order) revealed that the elements in the <63 μm fraction decrease seaward, probably reflecting the distance from the major source (Susquehanna River). The metals also decrease eastward across the Bay, suggesting that seaward transport is more effective on the western side caused by the Coriolis effect. An alternate cause of this western side enrichment could be anthropogenic input from Baltimore Harbor or erosion of the Piedmont which adjoins the Bay in this upper region. Obviously enriched material could be introduced on the western side and be affected by seaward transport.

The results for the unfractionated sediments are similar to the <63 μm fraction, but have additional variation due to grain-size. The effect of grain-size can be seen when the unfractionated and <63 μm fractionated data for the Susquehanna flats are compared to each other. Metal concentrations in the <63 μm fraction are substantially larger on the flats while the unfractionated samples are depleted because of the large sand component in this high energy environment. The <63 μm fraction on the flats has a composition close to that of the Susquehanna River suspended matter (Carpenter et al., 1975).

In the following paragraphs, the trends for each element or groups of elements will be considered in both the unfractionated and <63 μm

Table 6. Statistics Used to Judge Best Fit for Fifth Order Trend Surfaces (<63 μm fractionated data)

	Cr	Mn	Fe	Co	Ni	Cu	Zn[1]	Pb
percentage variation explained by surface	69	70	72	87	76	88	29	79
correlation coefficient[2]	0.83	0.84	0.85	0.94	0.87	0.94	0.54	0.89

[1] Zn trend surface map not produced.
[2] All values are significant at 1% level (n=185).

Table 7. Trend Surface Equations

Conversion of Long. and Lat. data to SYMAP coordinates:

$$X_{SYMAP} = (76.75-LONG.)*11.30672$$

$$Y_{SYMAP} = (LAT.-36.75)*2.71166$$

with Long. & Lat. values in decimal form as degrees.

General Form of 5th order equation:

Metal value calculates as Z in units of ug/g except % Fe.

$$Z = A_0 + A_1X + A_2Y + A_3X^2 + A_4XY + A_5Y^2 + A_6X^3 + A_7X^2Y + A_8XY^2 + A_9Y^3 + A_{10}X^4 + A_{11}X^3Y + A_{12}X^2Y^2 + A_{13}XY^3 + A_{14}Y^4 + A_{15}X^5 + A_{16}X^4Y + A_{17}X^3Y^2 + A_{18}X^2Y^3 + A_{19}XY^4 + A_{20}Y^5$$

Continued

Table 7. Cont'd. Coefficients of 5th Order Equation

	A_0	A_1	A_2	A_3	A_4	A_5
Cr	$0.12\times10^{+4}$	$-0.48\times10^{+3}$	$-0.95\times10^{+2}$	$0.45\times10^{+2}$	$0.52\times10^{+2}$	0.13×10^{0}
Mn	-0.34×10^{5}	0.12×10^{5}	0.57×10^{4}	0.18×10^{3}	-0.20×10^{4}	-0.31×10^{3}
Fe	-0.99×10^{1}	0.86×10^{1}	0.35×10^{1}	-0.33×10^{1}	-0.20×10^{0}	-0.40×10^{0}
Co	-0.14×10^{3}	-0.37×10^{2}	0.62×10^{2}	0.63×10^{2}	-0.26×10^{2}	-0.3×10^{1}
Ni	-0.28×10^{2}	-0.21×10^{3}	0.92×10^{2}	0.20×10^{3}	-0.61×10^{2}	-0.23×10^{1}
Cu	0.74×10^{3}	-0.26×10^{3}	-0.74×10^{2}	0.26×10^{2}	0.26×10^{2}	0.23×10^{1}
Pb	0.17×10^{4}	-0.84×10^{3}	-0.13×10^{3}	0.20×10^{3}	0.37×10^{2}	0.45×10^{1}

	A_6	A_7	A_8	A_9	A_{10}
Cr	0.31×10^{1}	-0.73×10^{1}	-0.12×10^{1}	0.14×10^{0}	-0.57×10^{0}
Mn	-0.61×10^{3}	0.37×10^{3}	0.38×10^{2}	0.11×10^{2}	0.97×10^{2}
Fe	0.66×10^{0}	-0.79×10^{-1}	0.35×10^{-1}	0.17×10^{-1}	-0.61×10^{-1}
Co	-0.18×10^{2}	0.52×10^{1}	0.37×10^{0}	0.13×10^{0}	0.20×10^{1}
Ni	-0.52×10^{2}	0.13×10^{2}	0.72×10^{0}	0.95×10^{-1}	0.55×10^{1}
Cu	0.60×10^{0}	-0.16×10^{1}	-0.13×10^{1}	0.40×10^{-1}	0.36×10^{-1}
Pb	-0.32×10^{-2}	-0.32×10^{0}	-0.21×10^{1}	0.41×10^{-1}	0.31×10^{1}

Table 7. Cont'd. Coefficients of 5th Order Equation

	A_{11}	A_{12}	A_{13}	A_{14}	A_{15}
Cr	0.33×10^{0}	0.16×10^{0}	0.55×10^{-2}	-0.36×10^{-2}	0.17×10^{-1}
Mn	-0.41×10^{2}	-0.28×10^{0}	-0.91×10^{0}	-0.20×10^{0}	-0.47×10^{1}
Fe	0.88×10^{-2}	0.18×10^{-3}	-0.10×10^{-2}	-0.35×10^{-3}	0.20×10^{-2}
Co	-0.54×10^{0}	-0.18×10^{-1}	-0.63×10^{-2}	-0.26×10^{-2}	-0.83×10^{-1}
Ni	-0.12×10^{1}	-0.11×10^{0}	-0.26×10^{-2}	-0.26×10^{-2}	-0.21×10^{0}
Cu	-0.12×10^{0}	0.11×10^{0}	0.19×10^{-1}	-0.25×10^{-2}	-0.48×10^{-2}
Pb	-0.46×10^{0}	0.16×10^{0}	0.30×10^{-1}	-0.36×10^{-2}	-0.12×10^{0}

	A_{16}	A_{17}	A_{18}	A_{19}	A_{20}
Cr	-0.49×10^{-2}	-0.32×10^{-2}	-0.13×10^{-2}	0.94×10^{-4}	0.27×10^{-4}
Mn	0.17×10^{1}	0.23×10^{-1}	-0.70×10^{-2}	0.92×10^{-2}	0.14×10^{-2}
Fe	-0.20×10^{-3}	-0.75×10^{-4}	0.22×10^{-4}	0.66×10^{-5}	0.28×10^{-5}
Co	0.19×10^{-1}	0.19×10^{-2}	-0.25×10^{-3}	0.82×10^{-4}	0.19×10^{-4}
Ni	0.36×10^{-1}	0.64×10^{-2}	-0.19×10^{-3}	0.47×10^{-4}	0.24×10^{-4}
Cu	0.65×10^{-2}	-0.14×10^{-3}	-0.14×10^{-2}	-0.30×10^{-4}	0.25×10^{-4}
Pb	0.25×10^{-1}	-0.16×10^{-2}	-0.17×10^{-2}	-0.10×10^{-3}	0.40×10^{-4}

fractionated samples. Chromium. The distribution of Cr shows a general decrease down the Bay. High concentrations in both the unfractionated and <63 um fractionated samples occur around Baltimore Harbor (Figure 14).

One distinctive feature of Cr in the .63 um fraction is the plume which occurs at the mouth of the Bay and extends up the eastern side of the Bay (Figure 14). The distribution of this plume follows a pattern that might be expected if the Cr-bearing particles were being carried into the Bay by bottom currents. How careful inspection of the data in Appendix A suggests that this anomaly may be largely a fitting artifact and that in any case the feature in not as prominent as suggest by Figure 14.

Manganese. Manganese also decreases seaward (Figure 15). Unfractionated samples show elevated levels just north of Baltimore Harbor in the area of the Gunpowder River (Figure 15a). The Mn data have a range from 74 to 6900 ug/g in the <63 μm fraction. This large range causes some problems when setting the contour intervals because the data are skewed such that the lower end of the distribution contains most of the samples. This grouping causes little structure to show up on the map. Because of the large variation in data, the residuals were set by percentage differences for the northern Bay data, which gives an indication of good fit, but overestimates in the southern Bay. This is not a problem with the other metals due to their smaller range in variation.

Iron. The distribution of Fe shows a general decrease down the Bay, with the unfractionated samples showing elevated levels around Baltimore Harbor and around Annapolis (Figure 16). Although there have been large discharges of iron rich wastes to Baltimore Harbor in the past (Carpenter, et al, 1961), the iron anomally near the Harbor mouth is probably not an anthropogenic feature. Later, it will be shown that the Fe/Al ratio is not anomalous in this region, so the high Fe values must simply reflect a high concentration of fine-grained sediment. The elevated levels are produced by only three samples, so the area with the elevated levels may be somewhat exaggerated on the map (Figure 16a).

The effect found around the Annapolis area needs to be considered here. The extent of the elevated levels near the Annapolis area is real but small and will have little effect on the overall iron input to the Bay. The samples yielding elevated concentrations around Annapolis are near-shore mud samples. Besides having elevated Fe levels, the levels of Cr (Figure 14) and Zn (Figure 20a) are also elevated. Municipal wastewater, especially the particulate matter, is highly enriched in Cr, Fe, and Zn (Galloway, 1979). An alternate source of this enriched material could be dredge spoil from Baltimore Harbor which was disposed off of Kent Island. The Harbor sediment is enriched in Cr, Fe, Zn, and other metals. However the spoil material which was disposed off the northern part of Kent Island would have to be transported to the shallow near-shore environment off Annapolis. Other possible sources also exist. The area off Annapolis is an anchorage for marine vessels awaiting dock space in Baltimore Harbor. The trace element anomaly near Annapolis could be caused by material from the ships, either waste or cargo. But again the material would have to be transported into shallow water.

A distinctive feature of the Fe data in the unfractionated and especially in the <63 μm fraction (Figure 16b) is the Rappahannock ripple, found in the vicinity to the north and south of the Rappahannock River.

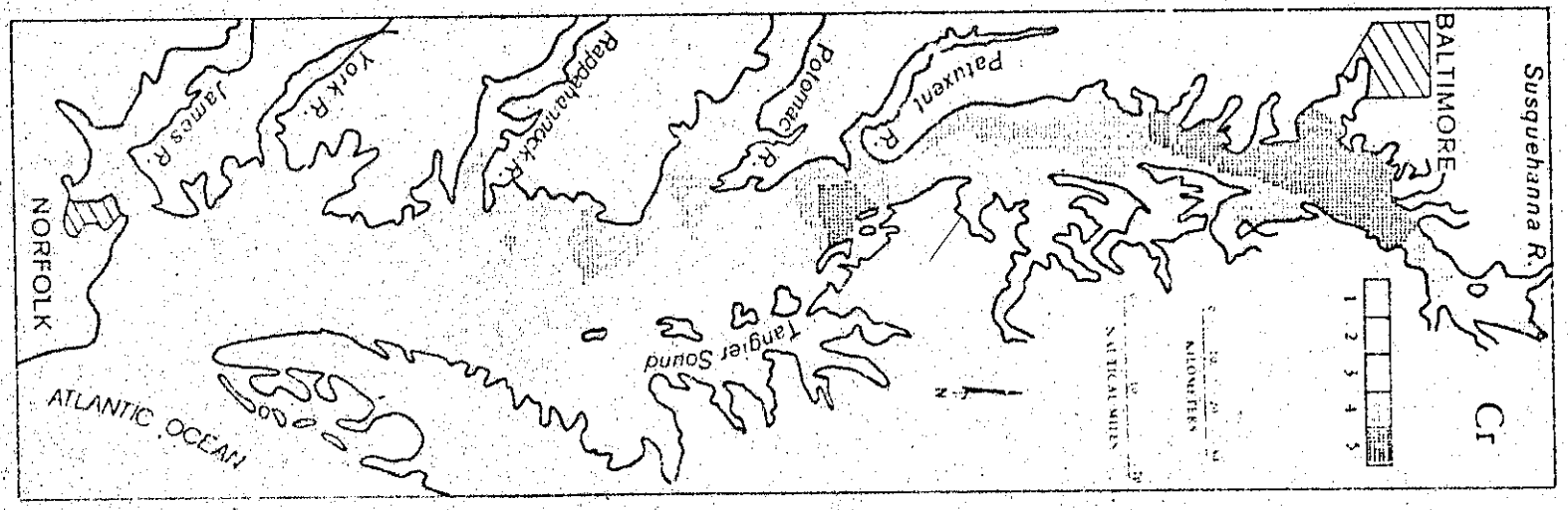


Figure 14a. Distribution of Cr(μg/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 7.9)	Value range applying to each level ("maximum" included in highest level only)
2 (7.9 - 23.8)	
3 (23.8 - 39.7)	
4 (39.7 - 55.6)	
5 (55.6 - 135)	

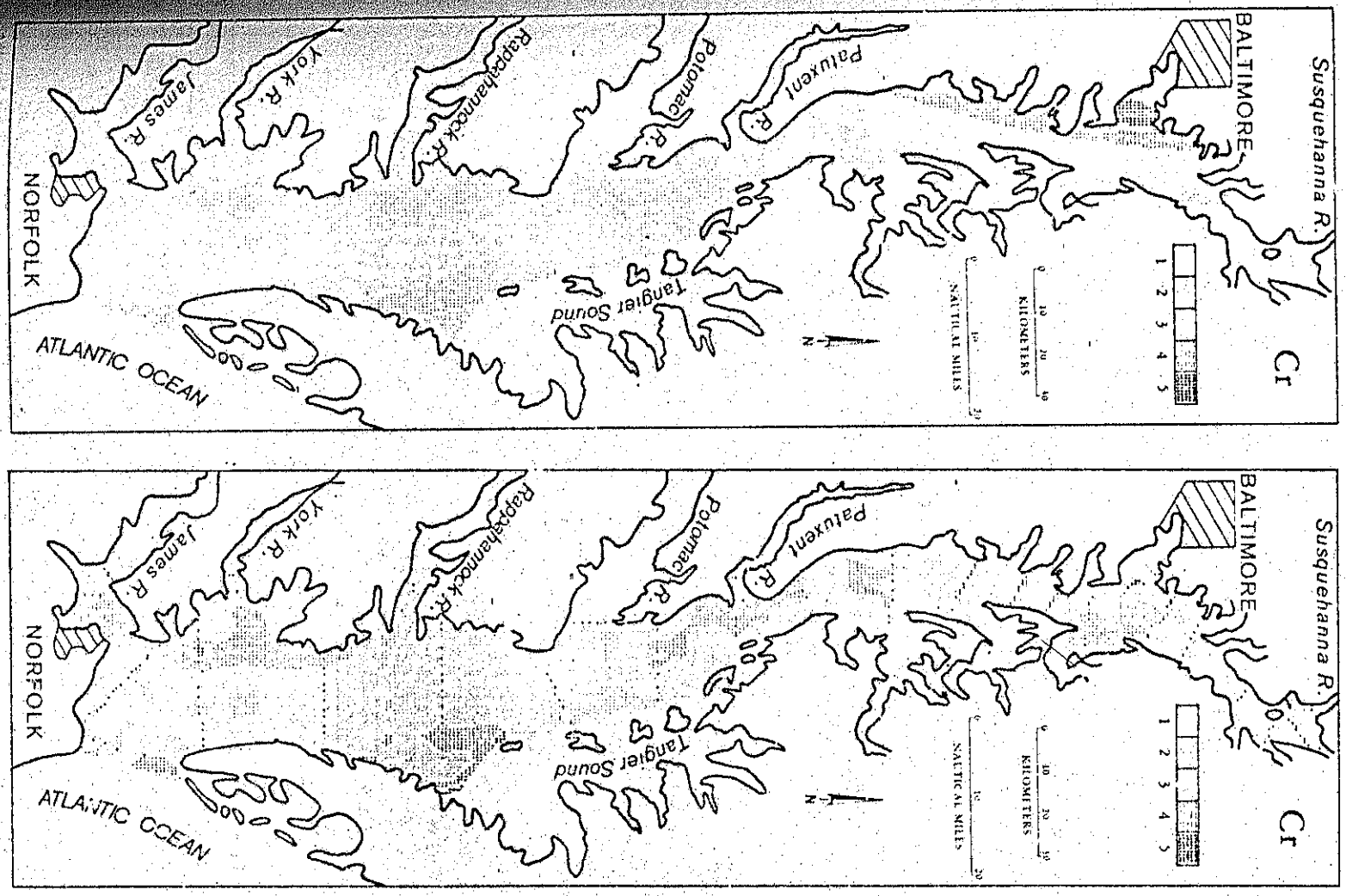


Figure 14b. Distribution of Cr(ug/g) in <63 µm fraction.

Key to Legend on Map

Left - Trend Surface	Right - Residual
1 (20.0 - 30.9)	1 (-25 to -15)
2 (30.9 - 47.6)	2 (-15 to -5)
3 (47.6 - 69.8)	3 (-5 to 5)
4 (69.8 - 97.8)	4 (5 to 15)
5 (97.8 - 160)	5 (15 to 25)

Best Fit of Trend Surface is when residual is at minimum (3)

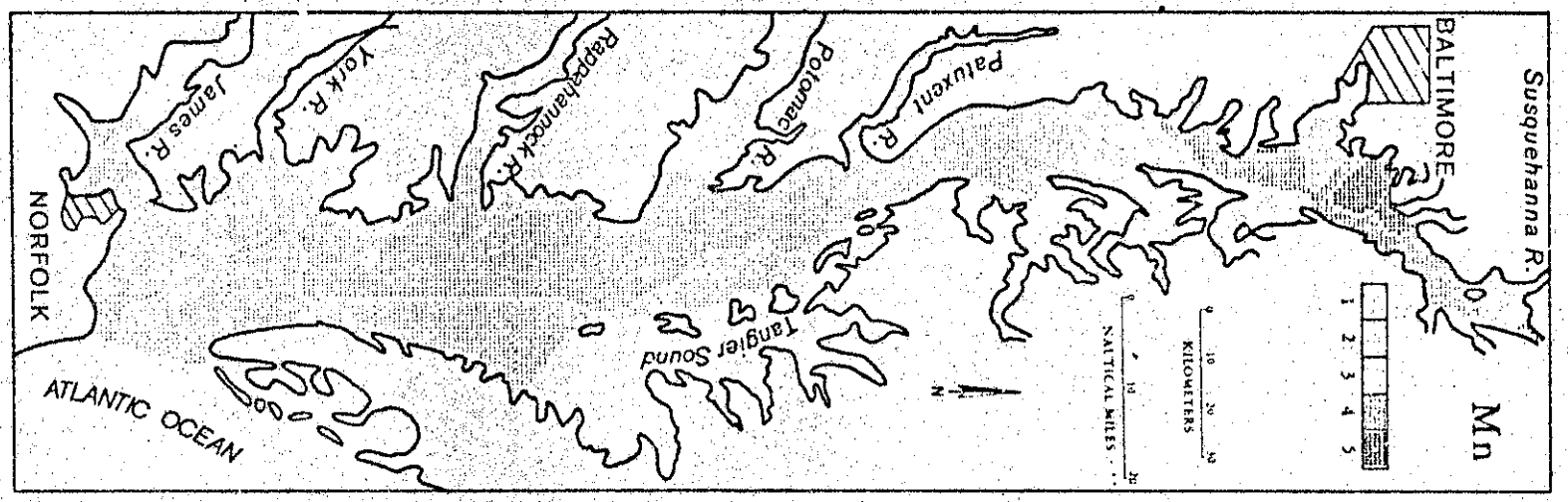
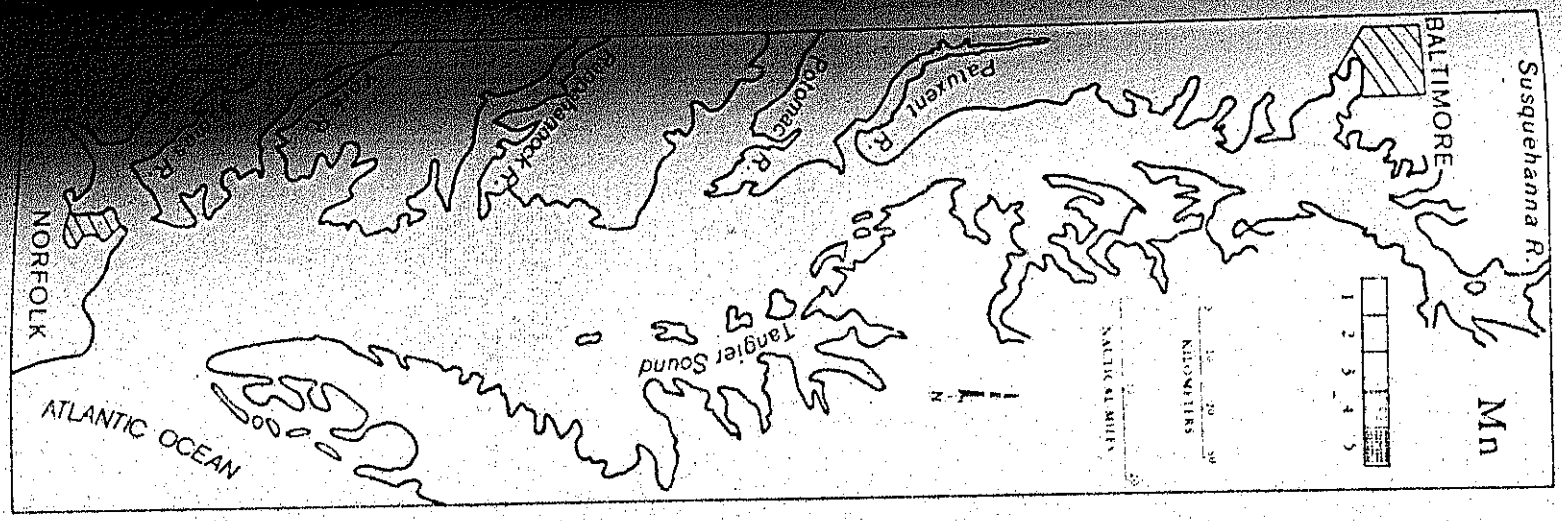


Figure 15a. Distribution of Mn(μg/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 117)
2 (117 - 703)
3 (703 - 1523)
4 (1523 - 2696)
5 (2696 - 5040)



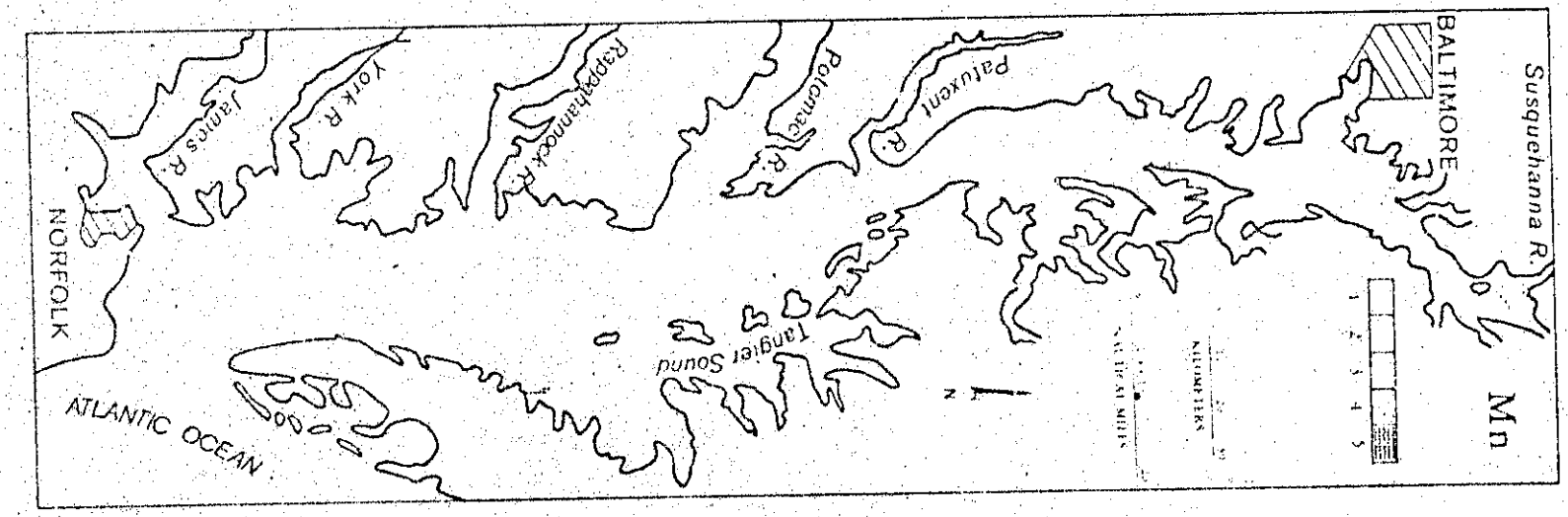


Figure 15b. Distribution of Mn(μg/g) in <63 μm fraction.

Key to Legend on Map

Left - Trend Surface	Right - Residual
1 (74.0 - 219)	1 (-2000 to -1200)
2 (219 - 655)	2 (-1200 to -400)
3 (655 - 1623)	3 (-400 to 400)
4 (1623 - 3560)	4 (400 to 1200)
5 (3560 - 6900)	5 (1200 - 2000)

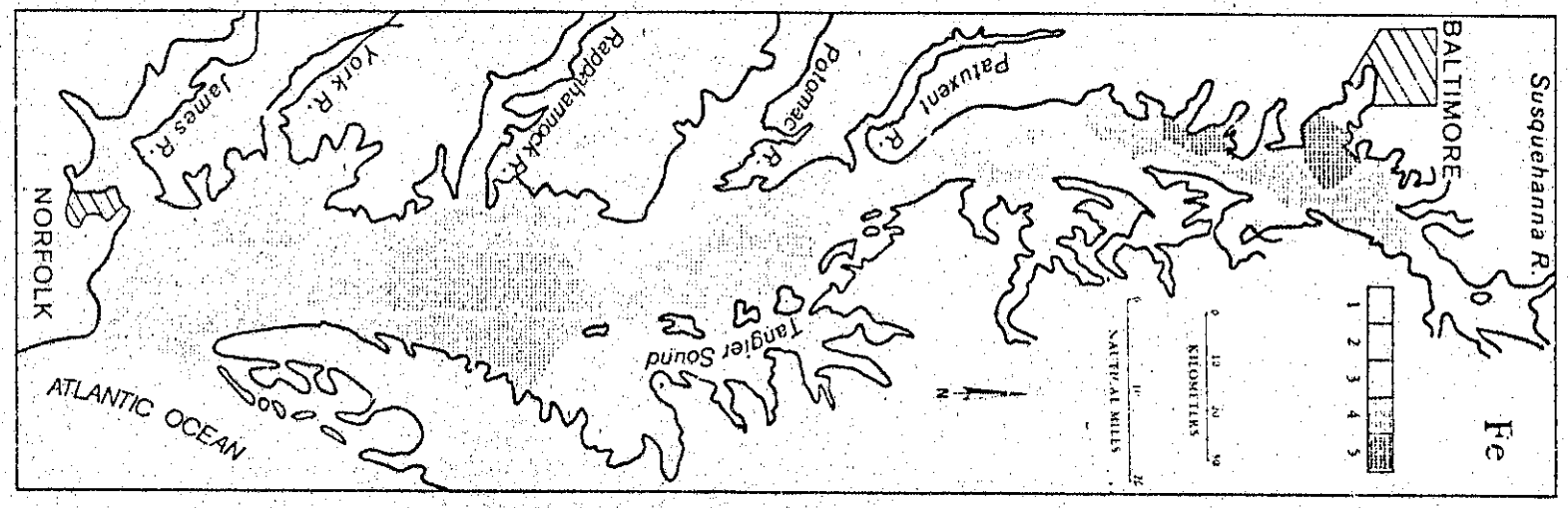
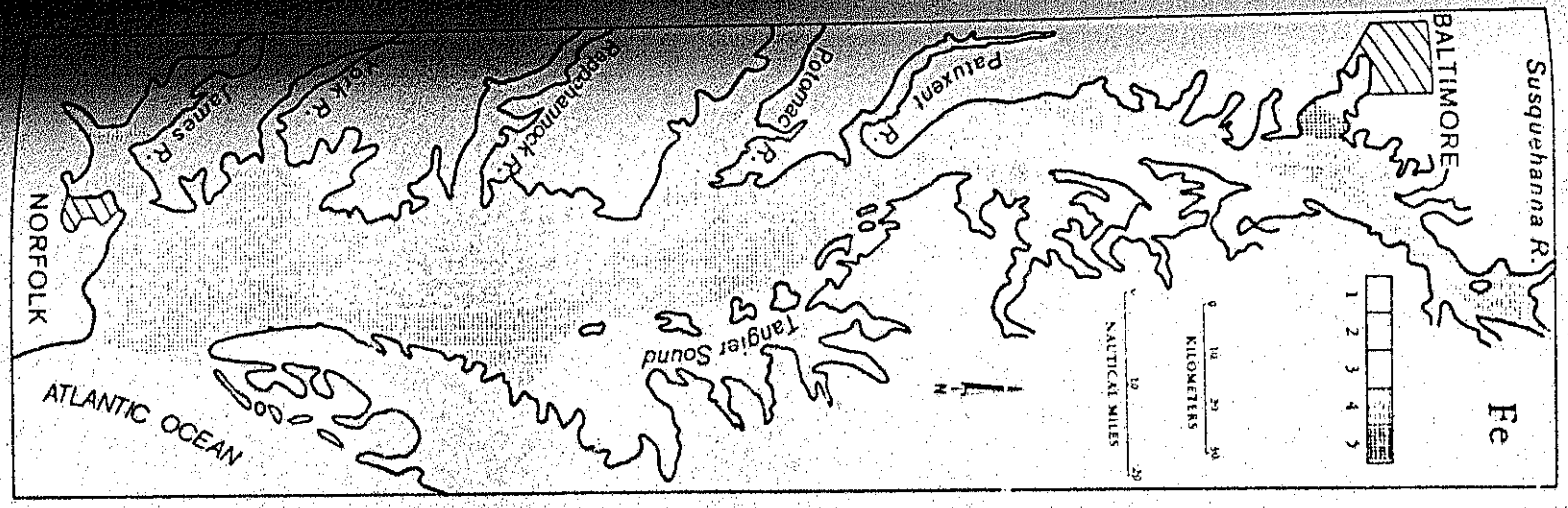


Figure 16a. Distribution of Fe(%) in unfractionated sediment.

Key to Legend on Map

1 (0 - 0.87)
2 (0.87 - 2.61)
3 (2.61 - 4.35)
4 (4.35 - 6.09)
5 (6.09 - 8.70)



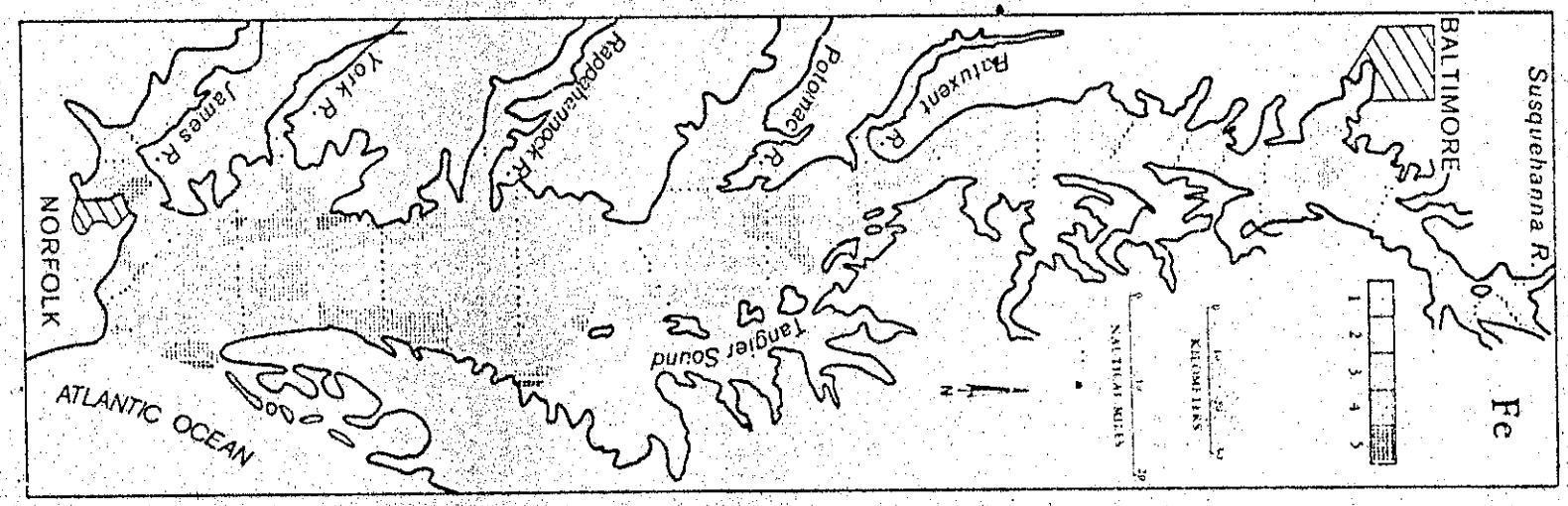


Figure 16b. Distribution of Fe(%) in <63 µm fraction.

Key to Legend on Map

Left - Trend Surface	Right - Residual
1 (0.87 - 2.04)	1 (-2.0 to -1.2)
2 (2.04 - 3.20)	2 (-1.2 to -0.40)
3 (3.20 - 4.37)	3 (-0.40 to 0.40)
4 (4.37 - 5.53)	4 (0.40 to 1.2)
5 (5.53 - 6.70)	5 (1.2 to 2.0)

The lower Bay, below the mouth of the Potomac Riuver, is composed of mainly sand/silt sediments, with only minor clay. The area of the Rappahannock ripple is a channel composed of clay-rich mud (Shideler, 1975). The high clay content causes the elevated iron levels even in the .63 um fraction. This fraction contains both silt and clay and, within the ripple, clay is very abundant. The other elements, especially in the unfractionated samples, also show an increase in this area.

Cobalt and Nickel. The patterns for Co (Figure 17) and Ni (Figure 18) closely resemble Mn (Figure 15). This is not surprising considering the high correlation mentioned earlier for Mn, Co, and Ni. Cobalt and nickel both show elevated levels around the Gunpowder River, north of Baltimore Harbor, in the unfractionated sediment samples. An explanation of this might be that this area is composed of more fine sediment than to the north or south. However, Ryan's (1953) sedimentological map does not support this idea. This whole area of the Bay is about the same sedimentologically.

There are a number of possible sources of material to this area besides the ones mentioned earlier. There may be some input of enriched material from the Gunpowder River, especially since this river drains mainly from the Piedmont. Another source might be the Back River just to the south of the area. This river receives both industrial and municipal wastewater from the city of Baltimore. The discharge of this river probably flows northward due to the obstruction by Hart and Miller Islands. Helz et al. (1975) have suggested the remobilization of Mn from the Back River sediment. No data on redox chemistry for this area exist to check for diagenetic input of the Mn from depth. Supposedly this is not an area of dredge spoil disposal from Baltimore Harbor.

Copper, Zinc, and Lead. These three elements show the typical decrease southward, but each also show a strong source from Baltimore Harbor (Figures 19, 20, and 21) both in the unfractionated and .63 um fractionated samples. Cu and Zn also show elevated levels just north of the Harbor. Each metal also shows the Rappahannock ripple in the unfractionated samples (Figures 19a, 20a, and 21a).

COMPARISON WITH OTHER ESTUARIES

Crustal enrichment factors were calculated in a manner similar to the method outlined by Zoller et al. (1974) using continental crust data from Taylor (1964). The enrichment factor used is given as:

$$EF = \frac{(X/Fe)_{sediment}}{(X/Fe)_{crust}}$$

Where X/Fe is the ratio of the concentrations of element X to Fe in the sediment and in the crust. Iron was chosen as the element for normalization because anthropogenic sources are small compared to natural sources. The element for normalization should be one supplied only by natural crustal weathering. Zoller et al. (1974) used aluminum for normalization, and we will also use this element in preference to iron later in this report. However Al analyses for the main Bay surface sediments are not available. An enrichment factor of one implies no enrichment over the crustal values.

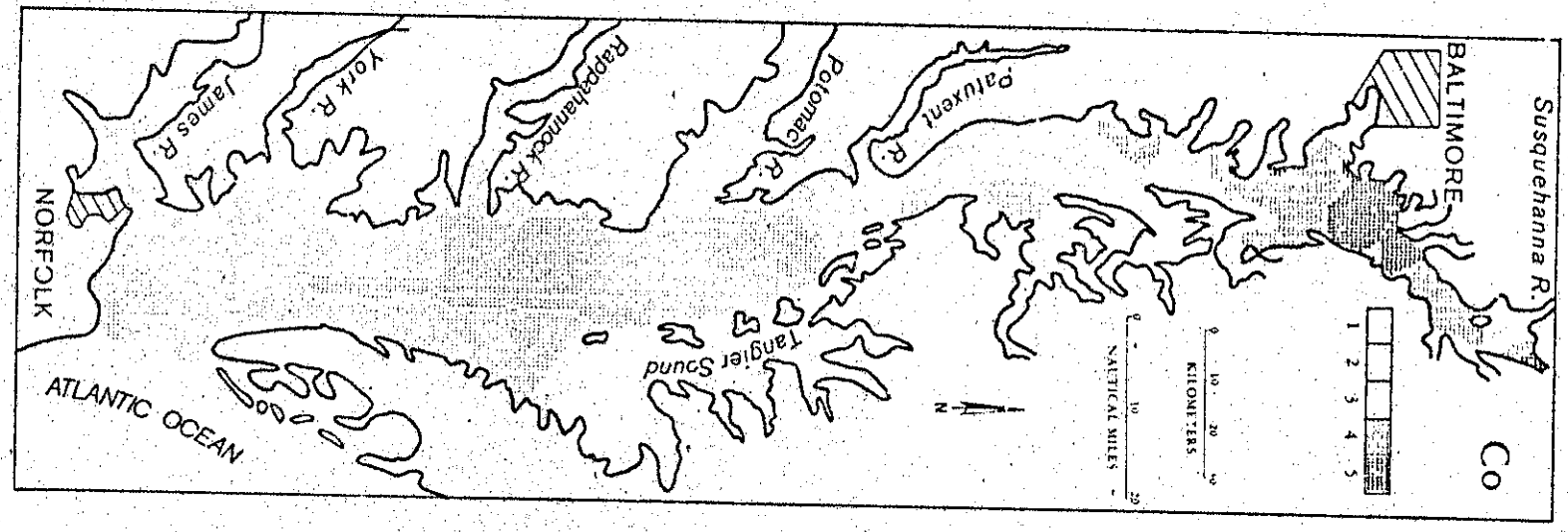
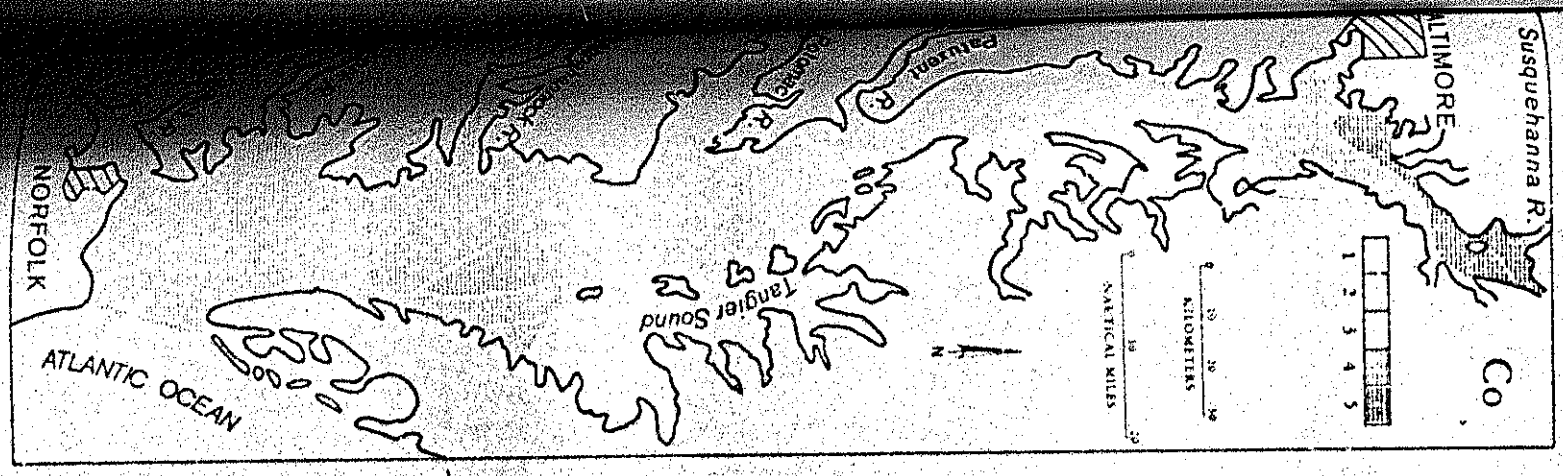


Figure 17a. Distribution of Co(μg/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 3.2)
2 (3.2 - 11.2)
3 (11.2 - 27.1)
4 (27.1 - 43.1)
5 (43.1 - 75.0)



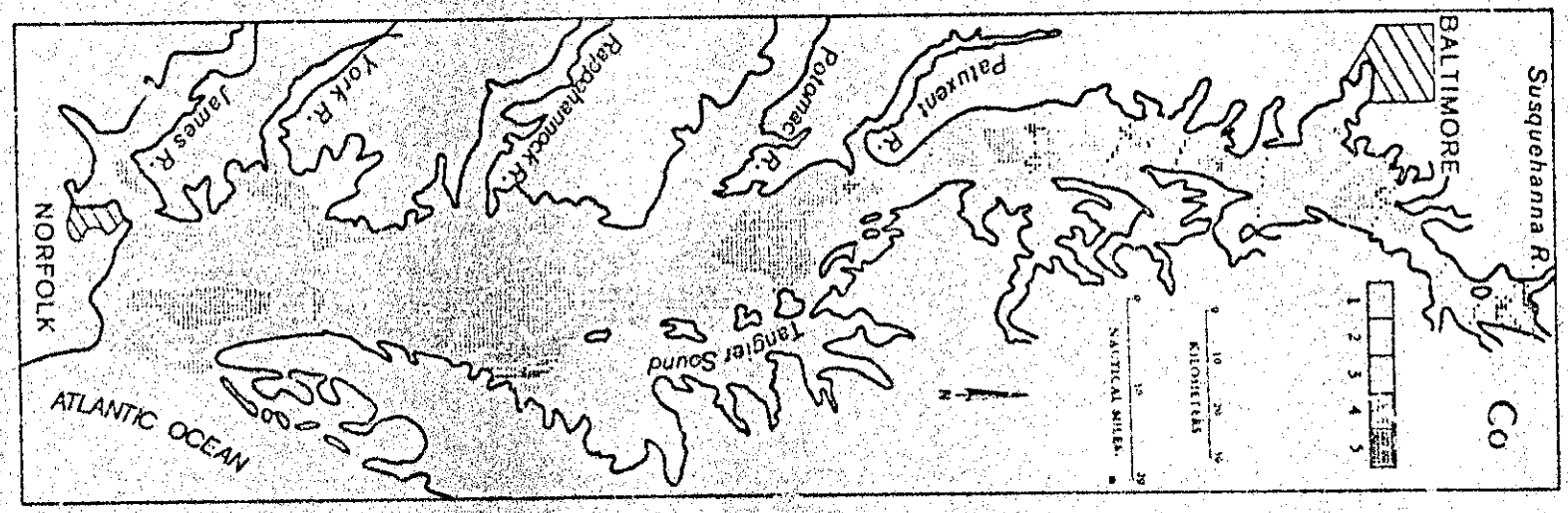


Figure 1b. Distribution of Co(µg/g) in <63 µm fraction.

Key to Legend on Map

Left - Trend surface	Right - Residual
1 (0 - 10.0)	1 (-14.0 to -6.0)
2 (10.0 - 20.0)	2 (-6.0 to -2.0)
3 (20.0 - 30.0)	3 (-2.0 to 2.0)
4 (30.0 - 40.0)	4 (2.0 to 6.0)
5 (40.0 - 80.0)	5 (6.0 to 14.0)

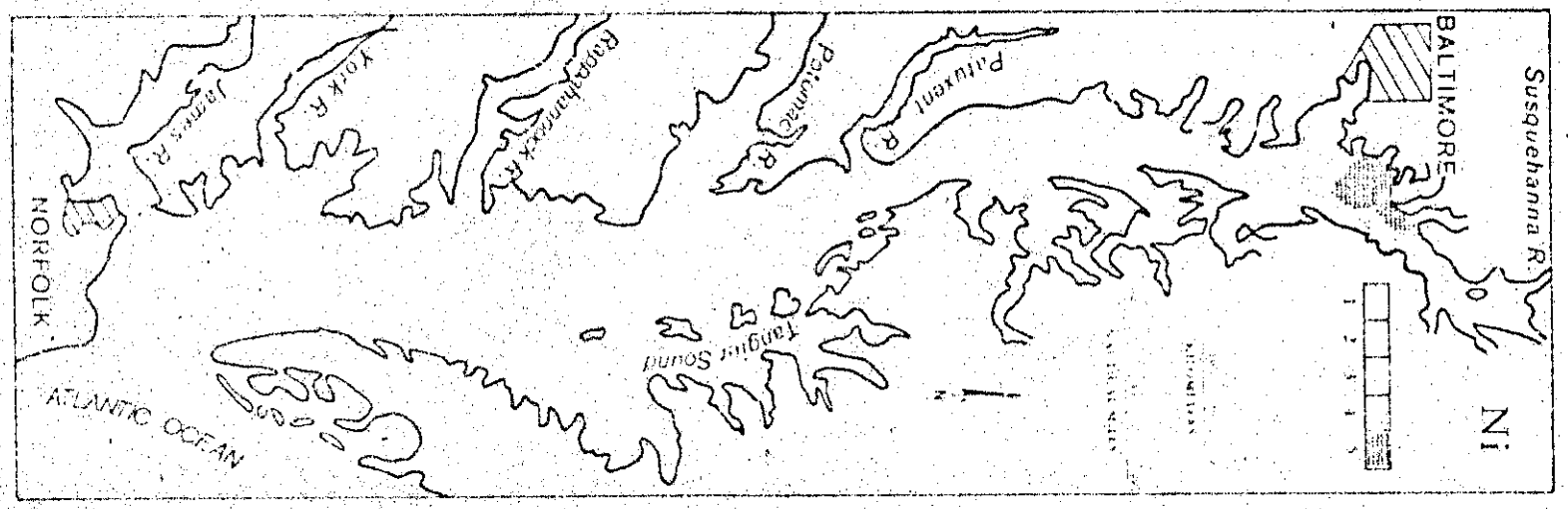
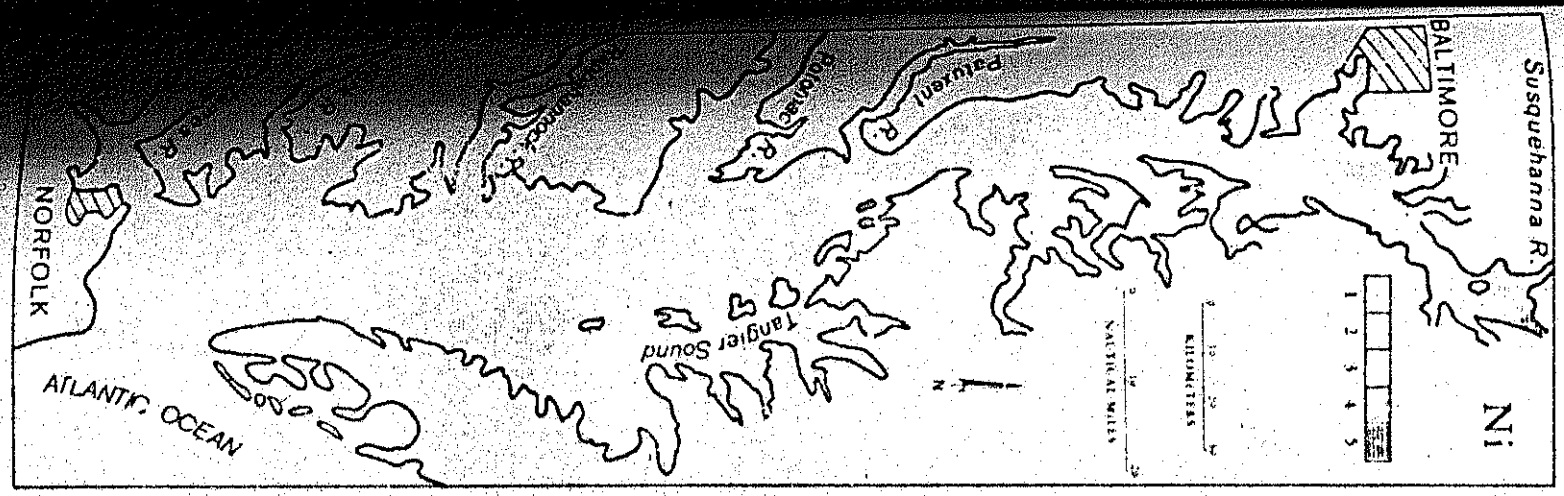


Figure 18a. Distribution of Ni(ug/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 6.6)
2 (6.6 - 32.8)
3 (32.8 - 59.1)
4 (59.1 - 85.4)
5 (85.4 - 151)



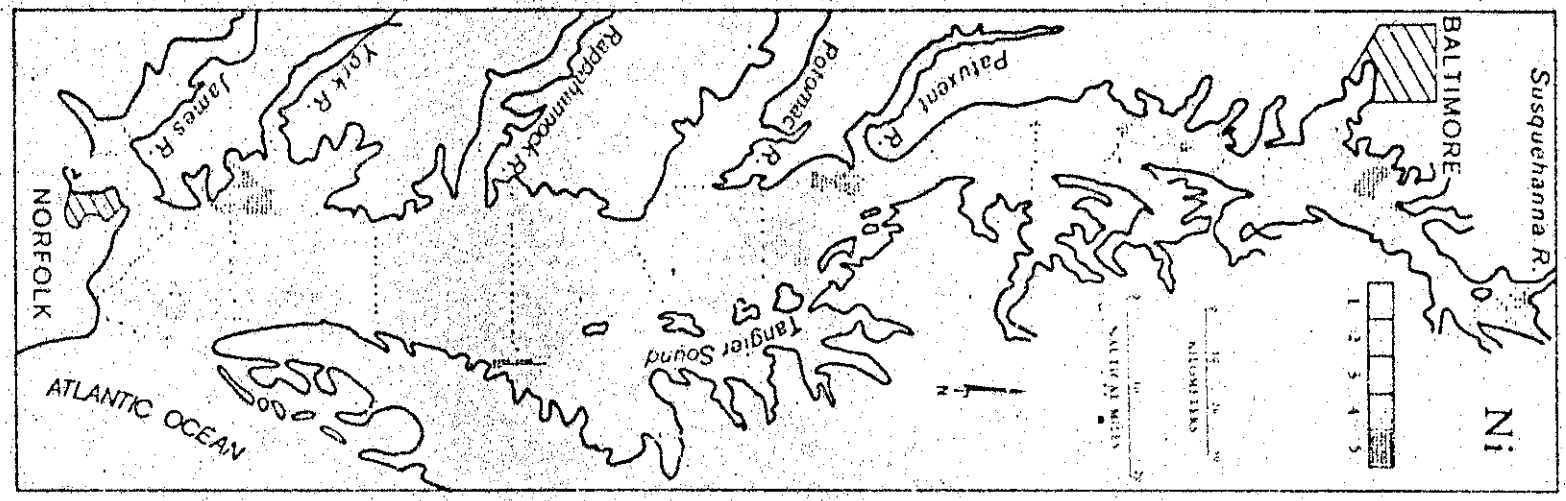


Figure 18b. Distribution of Ni(μg/g) in <63 um fraction.

Key to Legend on Map

Left - Trend Surface	Right - Residual
1 (0 - 30.0)	1 (-20 to -10)
2 (30.0 - 60.0)	2 (-10 to -5.0)
3 (60.0 - 90.0)	3 (-5.0 to 5.0)
4 (90.0 - 120)	4 (5.0 to 10)
5 (120 - 240)	5 (10 to 20)

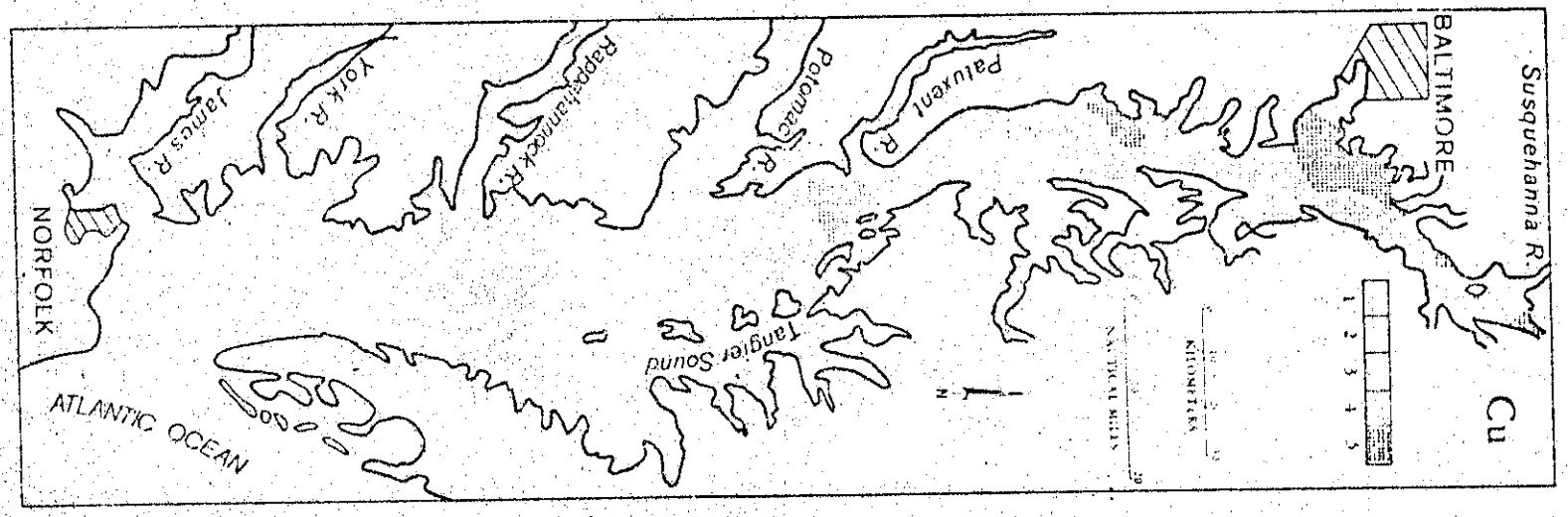


Figure 19a. Distribution of Cu(μg/g) in unfractionated sediment.

Key to Legend on Map

1 (0-5.0)
2 (5.0 - 15.0)
3 (15.0 - 35.0)
4 (35.0 - 55.0)
5 (55.0 - 100)

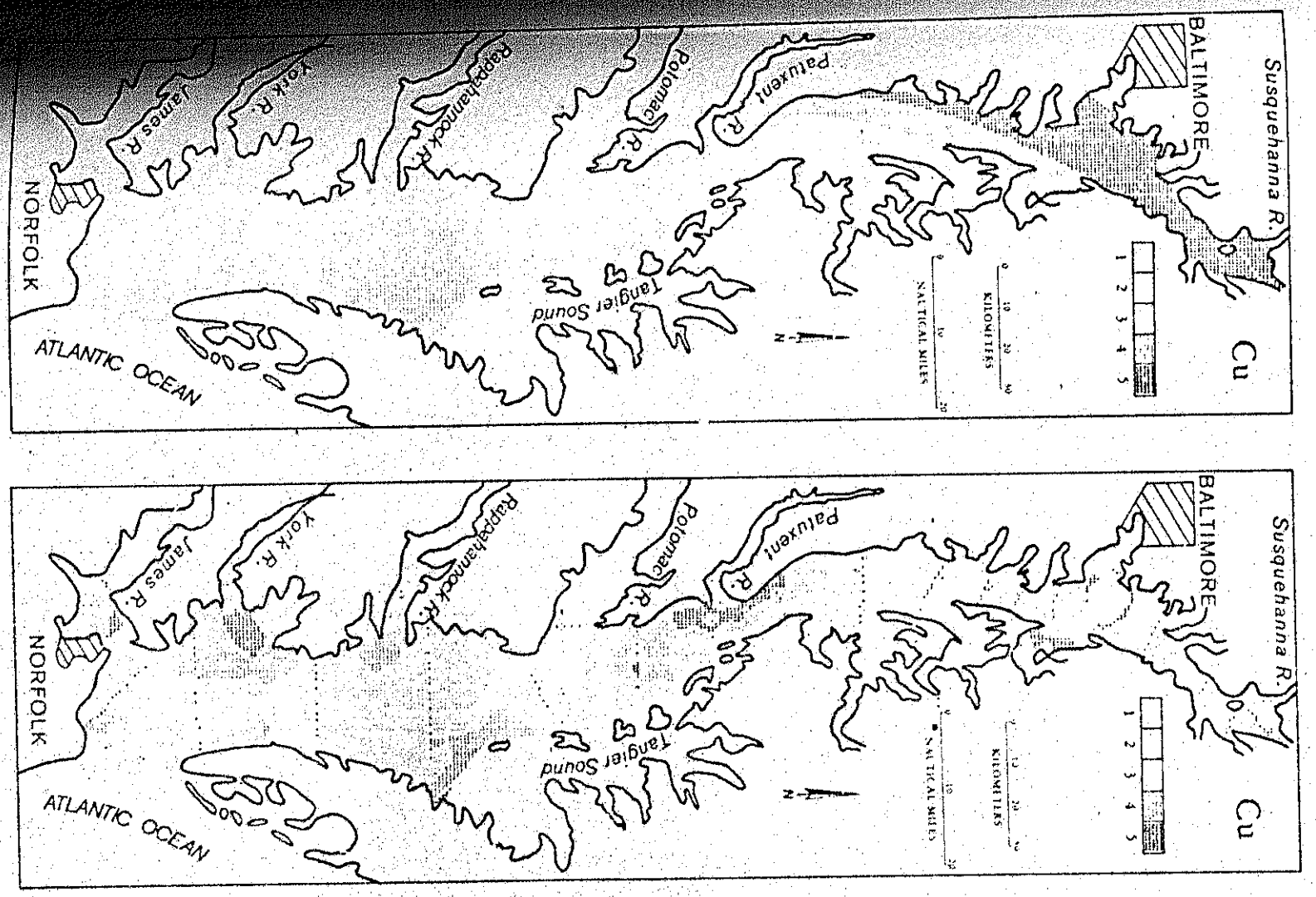


Figure 19b. Distribution of Cu(μg/g) in <63 μm fraction.

Left - Trend Surface	Right - Residual
1 (0 - 11.1)	1 (-12 to -6.0)
2 (11.1 - 22.2)	2 (-6.0 to -2.0)
3 (22.2 - 33.3)	3 (-2.0 to 2.0)
4 (33.3 - 44.4)	4 (2.0 to 6.0)
5 (44.4 - 100)	5 (6.0 to 12)

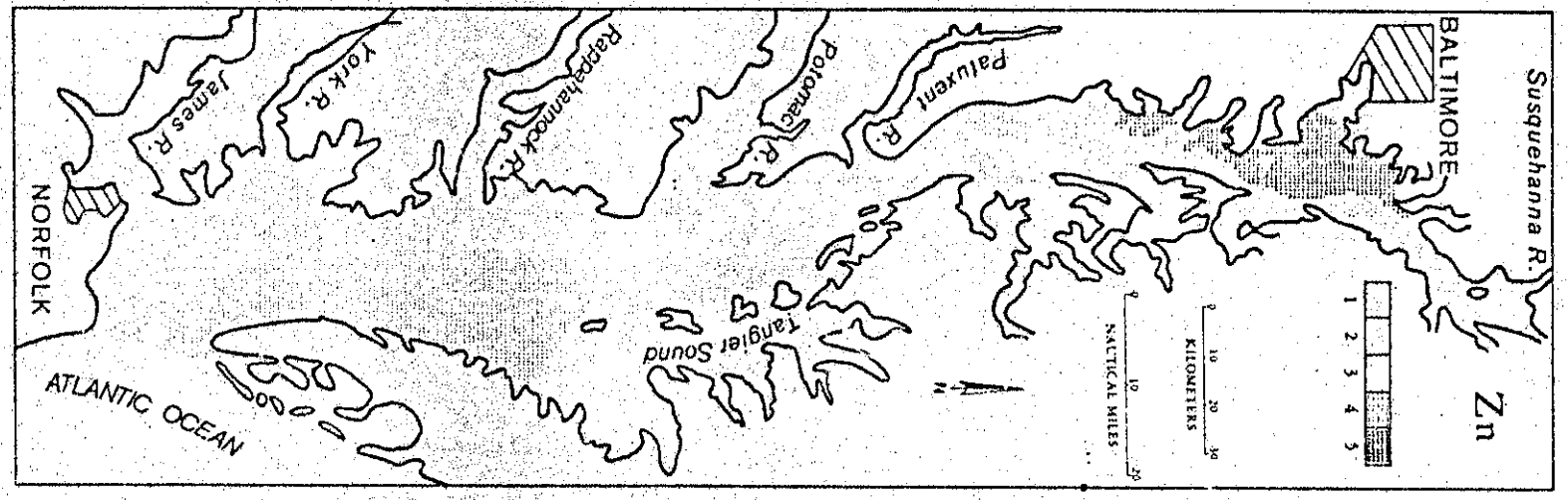


Figure 20a. Distribution of Zn (ug/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 50.0)
2 (50.0 - 100)
3 (100 - 200)
4 (200 - 400)
5 (400 - 1100)

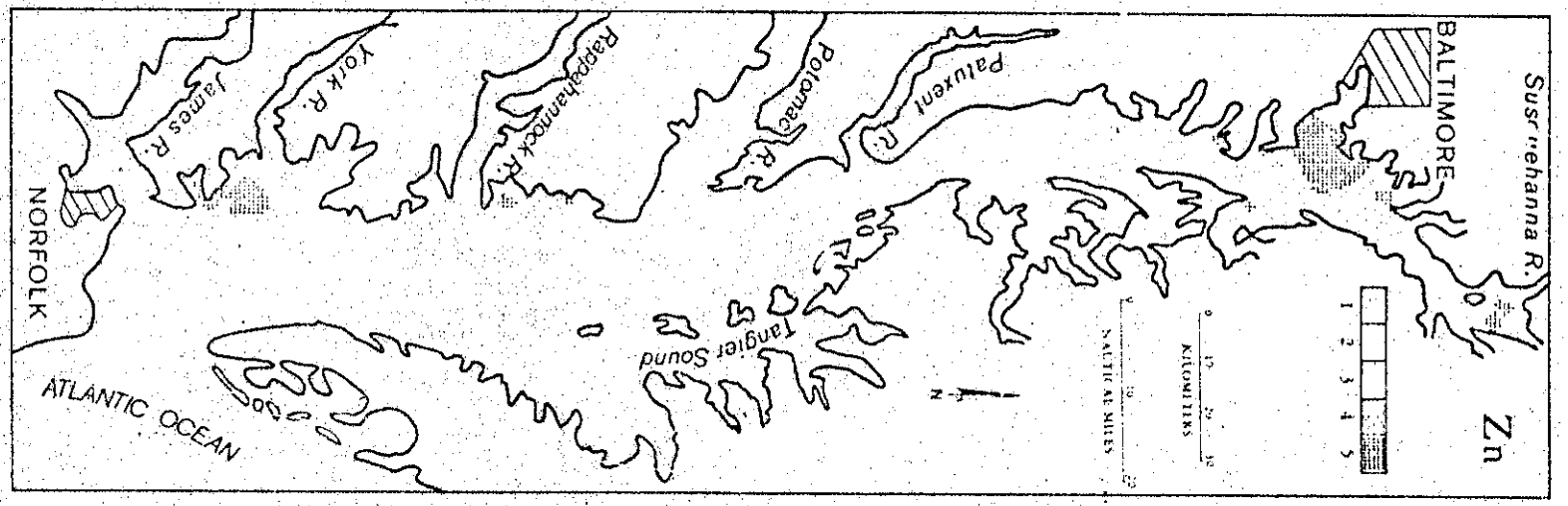


Figure 20b. Distribution of Zn(μg/g) in <63 μm fraction.

Key to Legend on Map

1 (39.0 - 103)
2 (103 - 230)
3 (230 - 358)
4 (358 - 486)
5 (486 - 2400)

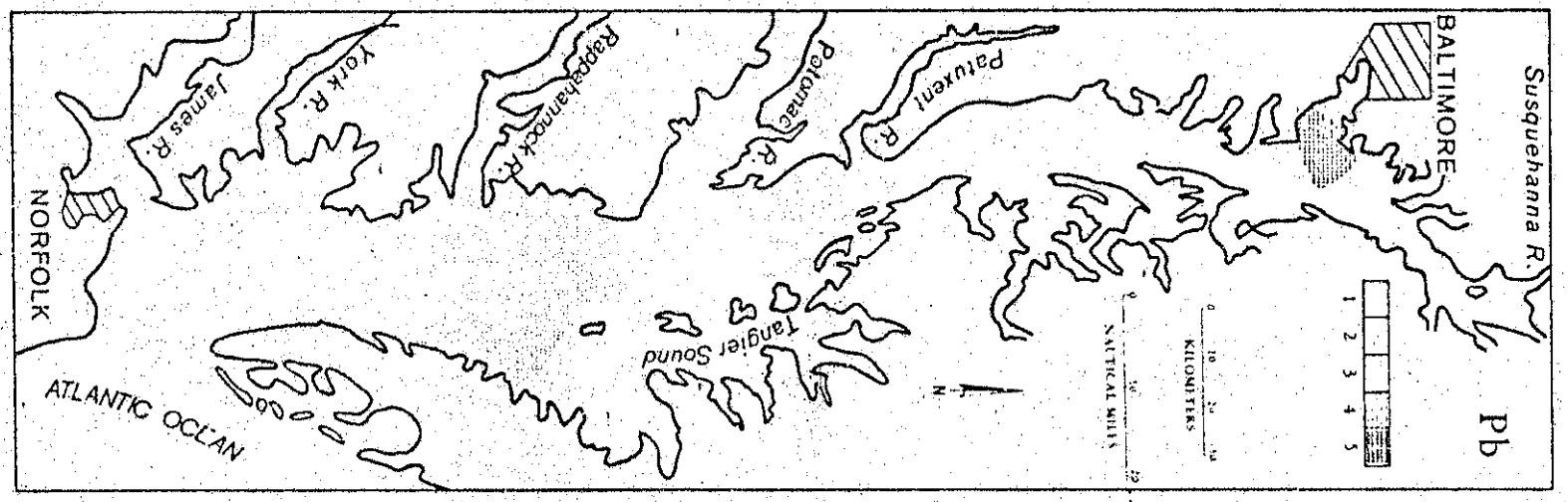
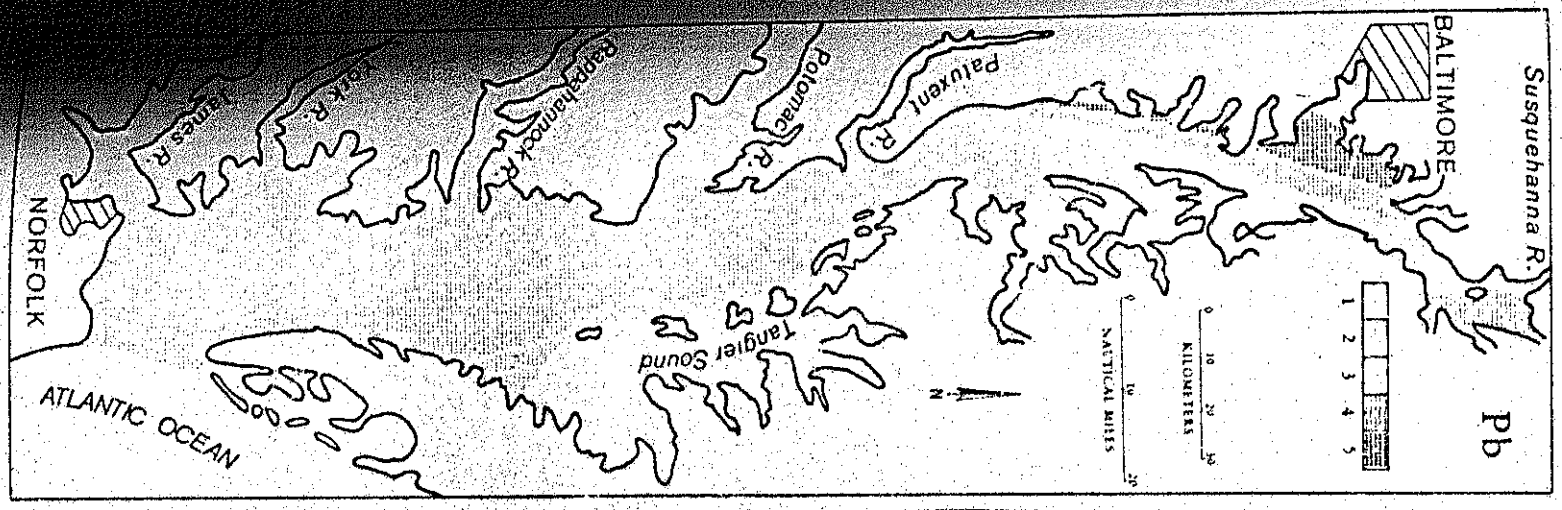


Figure 21a. Distribution of Pb(μg/g) in unfractionated sediment.

Key to Legend on Map

1 (0 - 10.0)
2 (10.0 - 33.2)
3 (33.2 - 74.6)
4 (74.6 - 116)
5 (116 - 752)



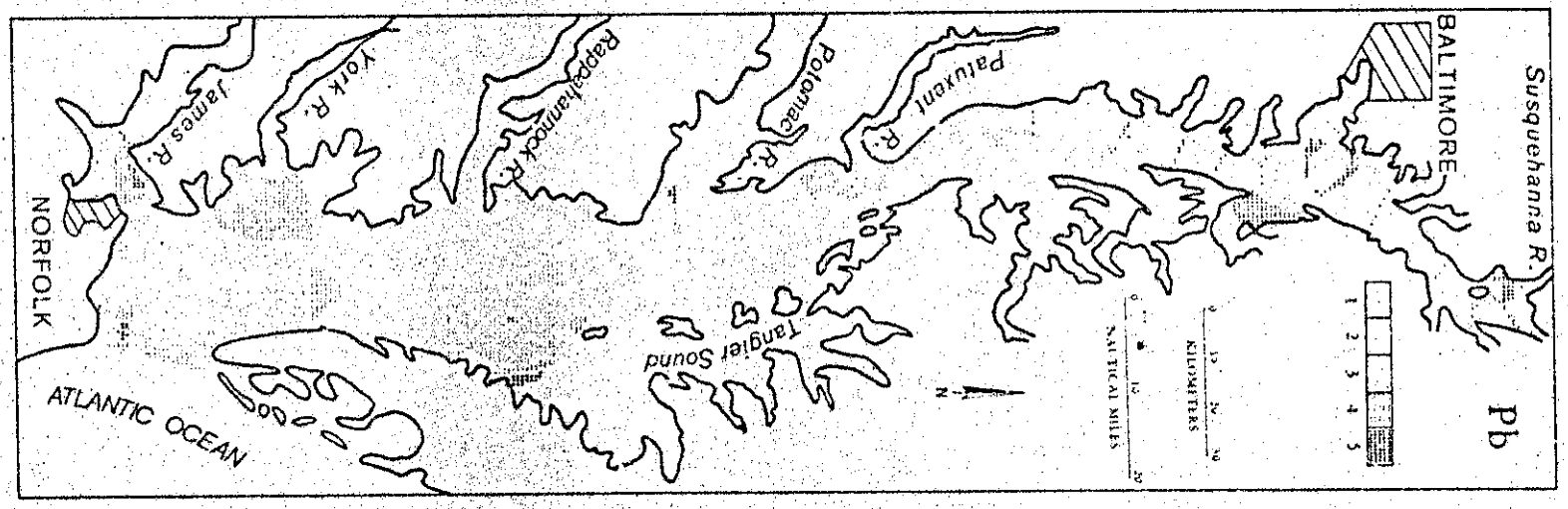


Figure 21 b. Distribution of Pb(ug/g) in <63 µm fraction.

Key to Legend on Map

Left - Trend Surface	Right - Residual
1 (3.0 - 17.2)	1 (-35 to -15)
2 (17.2 - 37.6)	2 (-15 to -5.0)
3 (37.6 - 57.9)	3 (-5.0 to 5.0)
4 (57.9 - 78.3)	4 (5.0 to 15)
5 (78.3 - 180)	5 (15 to 35)

Enrichment factors for several of the elements in the unfractionated samples from the mid-point of each traverse down the Bay are shown in Figure 22. The Mn and Cu values drop to unity fairly fast in the upper Bay as do Co and Ni which are not shown. The Cr values, also not shown, stay close to unity throughout the entire bay. The limited values for Cd, closely resemble Zn.

A number of causes exist that could explain the enrichment of Zn, Cd, and Pb. Based on the data of Muhlbaier (1978), atmospheric deposition of anthropogenically derived contaminants is probably significant for these three elements. Another possible cause of the enrichment of Zn, Cd, and Pb could be unrepresentative crustal abundance data. The Susquehanna drainage basin and Chesapeake Bay may be anomalous compared to the average continental crust. Note that the high levels of enrichment do not appear to be associated spacially with the mouth of Baltimore harbor at 250 km. Thus those enrichments are not ascribable to contaminants emanating from the Harbor, unless it is assumed that the contaminants have become widely distributed over a hundred km or so of the upper bay.

It is of interest to see if other east coast estuaries display similar enrichments of Zn, Cd, and Pb or any of the other elements. Enrichment factors for the various elements for a number of east coast and Gulf coast estuaries are shown in Table 8. It can be seen that in general Zn, Cd, and Pb are enriched in all areas listed.

The enrichment factors (Table 8) show the Delaware bay to be somewhat enriched in the various elements. Since the Delaware is another large estuary just to the north of the Chesapeake Bay, further comparison between the two is warranted. The Delaware River, which is the main fluvial source to the Delaware Bay, has a drainage basin geologically similar to that of the Susquehanna River. However, extractable metal levels in the .63 um sediment fraction of the Delaware Bay are higher for Cr, Ni, Cd, and Pb (Bopp and Biggs, 1973) than in the Chesapeake Bay, hence the larger enrichment factors (Table 18). The difference between the Delaware and Chesapeake Bays is probably caused by industrial sources which are spread along the flanks of the Delaware, but concentrated in the subestuaries in Chesapeake Bay, i.e., in Baltimore Harbor on the Patapsco River and the Norfolk area in the James River.

Goldberg and his colleagues have studied several other east coast estuaries, allowing comparison of depositional fluxes for Cu, Zn, and Pb, based on Pb-210 sedimentation rates to be made. The fluxes in Chesapeake Bay (Goldberg et al., 1978) are comparable to those in the Savannah River estuary (Goldberg et al., 1979, calculated assuming a sediment porosity of 75 percent) and lower than those in Narragansett Bay (Goldberg et al., 1977). However, Santschi (1981) has argued that the fluxes obtained by Goldberg et al. in Narragansett Bay are too high. If Santschi's values are used. The the Chesapeake Bay and Narragansett bay have comparable fluxes.

On a broader, regional scale, what are some factors that must be considered when making a comparison between east coast estuaries? One would like to be able to evaluate anthropogenic effects after considering differences due to variation in the geological environment of the drainage basin. The northern estuaries predominantly drain areas of crystalline igneous and metamorphic rocks, while as one proceeds further south, coastal plain unconsolidated sediments constitute more of the drainage basin.

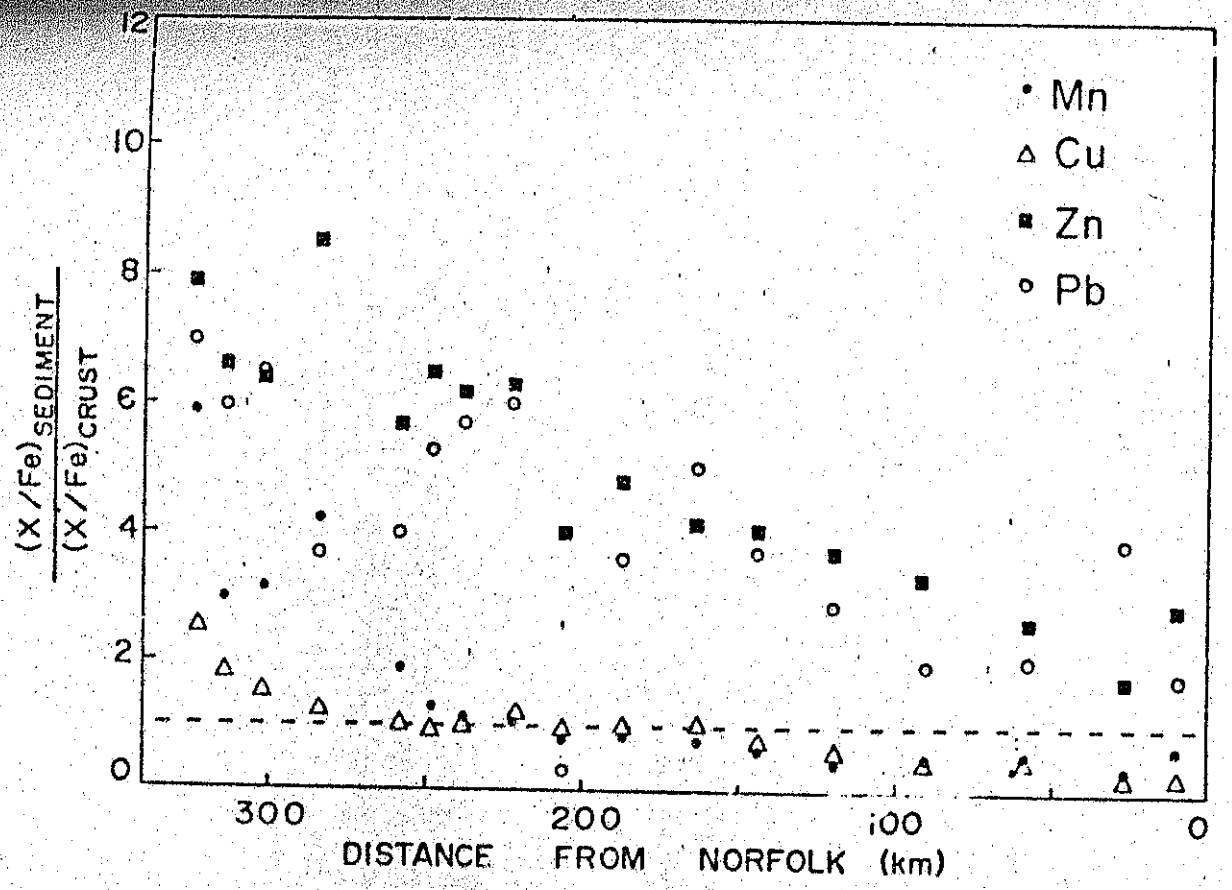


Figure 22. Typical enrichment factors for Mn, Cu, Zn, and Pb calculated from mid-point traverse samples (unfractionated sediment).

Table 8. Comparison of Average Enrichment Factors[1] in Various East and Gulf Coast Estuaries (North to South)

	Cr	Mn	Co	Ni	Cu	Zn	Cd	Pb	n[2]
Narragansett Bay (Goldberg et al. 1977)	3	1	1	1	6	6	6	17	(1)
Hudson Estuary (Williams et al. 1978)	-	2	-	-	2	4	-	9	(37)
Delaware Bay (Hopp & Biggs, 1973)	3	-	-	13	2	10	17	16	(124)
Chesapeake Bay (this study)	1	2	1	1	1	5	5	5	(177)
Baltimore Harbor (Villa & Johnson, 1974)	7	1	-	1	10	20	50	41	(194)
Savannah River (Goldberg et al. 1979)	1	1	1	1	1	1	-	3	(5)
Mobile Bay (Shannon et al. 1977)	-	1	-	-	1	4	-	-	(8)
Mississippi Delta ([illegible]y & Presley, 1976)	-	1	-	1	1	3	4	3	(72)
[illegible]ton Bay ([illegible] & Slowey, 1976)	4	3	-	2	2	6	-	15	(44)
[illegible]tonio Bay ([illegible] & Presley, 1976)	-	1	-	1	1	3	5	4	(51)

[1] $(X/Fe)_{Sed}/(X/Fe)_{Crust}$; crustal data from Taylor (1964).
[2] [illegible] of samples.

Erosion and subsequent transport should be greater in the coastal plain province. The crystalline rocks west of the fall line in the southern part are highly weathered and include saprolite in parts of North and South Carolina and further south. Meade and Trimble (1974) report suspended sediment data from circa 1910 which show that amounts of suspended sediment increased in a southerly direction. However, the suspended sediment discharge in most southern rivers has decreased between 1910 and 1970 due to the construction of reservoirs (Meade and Trimble, 1974). For the Susquehanna River and rivers to the north, suspended sediment discharge has increased between 1910 and 1970 by a small amount due to changes in land use, despite the fact that a number of reservoirs have been constructed on the Susquehanna river.

Besides the geology of the drainage basin, continental shelf input (Meade, 1969, 1972a) is another important source of sediment, especially in small estuaries. Hathaway (1972) found two major clay mineral facies along the Atlantic continental margin and in the associated estuaries. The Chesapeake Bay and estuaries to the north are characterized by illite and chlorite as a result of reworking and redeposition of material contributed during the Pleistocene (Hathaway 1972). The Chesapeake Bay is the southern-most estuary that is fed by rivers that drained glaciated areas. Estuarine sediments to the south of the Bay are characterized by kaolinite and montmorillonite.

One last factor must be considered when making a comparison of trace metals in various east coast estuaries. This is the method of sample preparation. Different acid extractions have different leaching efficiencies, and total digestions with HF or fusions produce higher results than extractions due to dissolution of heavy minerals. Thus it should be clear that all estuaries are not equal with respect to geological environment, metal analyses are not always comparable, and man has a varying influence on contaminating the coastal environment. This makes overall comparisons tenuous especially when one is trying to evaluate anthropogenic effects.

BALTIMORE HARBOR AND ELIZABETH RIVER SEDIMENTS

The data for both core and surface samples for Baltimore Harbor and the Elizabeth River are shown in Appendix B. Five samples from each core were analyzed, these were selected from the top, bottom, and at three equally spaced intermediates. The surface samples in the Harbor are from the channel that runs the length of the Harbor.

A number of general observations can be made from the data. The Al content in both regions is high compared to the main Bay in each area, but is especially high in Baltimore Harbor. For the Hampton Roads area this is not surprising since the southern Bay proper has mainly sand-silt sized sediments. For Baltimore Harbor the Al content in surface sediments increases into the Harbor, ranging from approximately six percent to eight percent Al (Figure 23). The trace element levels in Baltimore Harbor are higher than in the Hampton Roads area. The average concentrations of V, Cr, Mn, Co, Ni, and Zn are usually a factor of two higher in Baltimore Harbor (Table 9). Also shown in Table 9 are results from other investigators for comparison. The large differences can be attributed in a

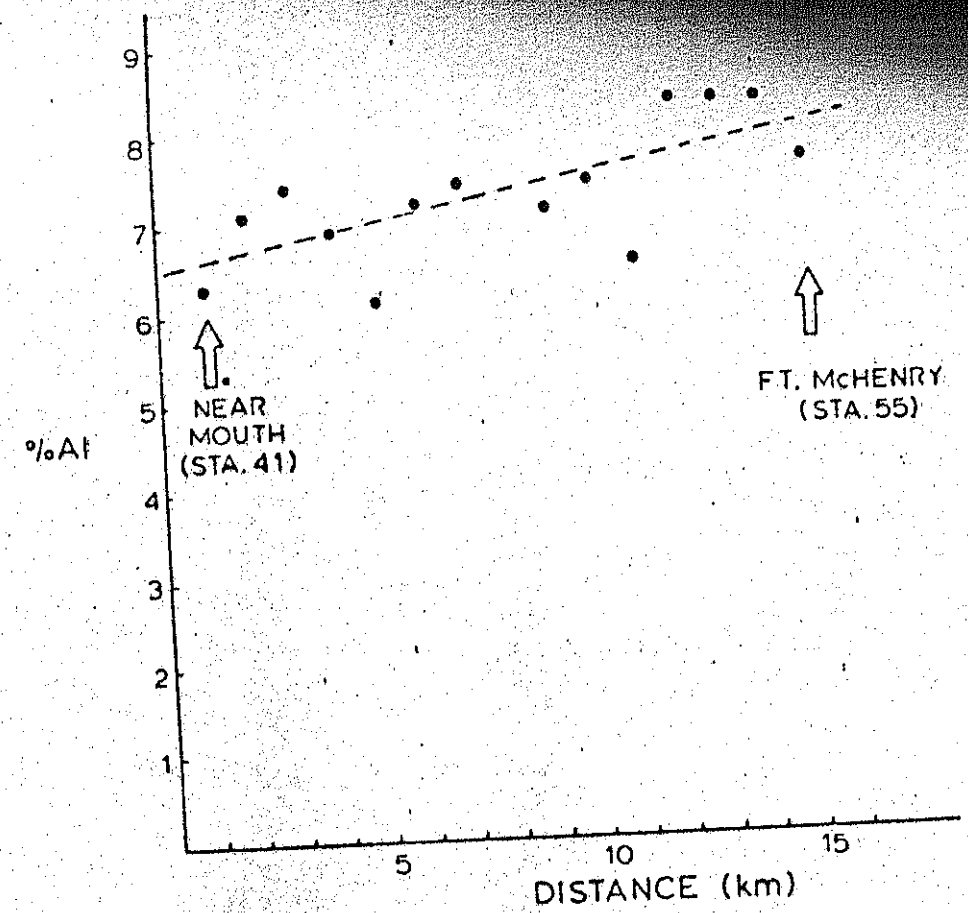


Figure 23. Al concentration vs. distance into Baltimore Harbor for surface channel samples

Table 9. Average Concentration of Elements in Sediments of Baltimore Harbor and Hampton Roads Area (ug/g except where %)

Baltimore Harbor			Hampton Roads	
this study	Villa & Johnson [a]	Tsai & others [b]	this study	Johnson & Villa [a]
7.6%	-	-	6.3%	-
25%	-	-	28%	-
0.39%	-	-	0.43%	-
180	-	-	110	-
350	492	1100	77	44
750	739	631	380	-
5.0%	-	-	3.8%	-
32	-	-	5	-
71	36	85	36	-
450	888	1400	240	379
75	200	9	65	96

[a] Total samples analyzed by acid extraction
[b] Total composites of core samples analyzed by acid extraction
[c] Number of samples

large part to differences in sample distributions. Sampling in this study was limited to the main Harbor while the others sampled in the more contaminated back creeks.

Preliminary statistical considerations for the Hampton Roads area show a number of significant correlations betweeen metals which agree with those determined in the main Bay. One strong association found in both areas is Al with Ti, V, Cr, Fe, and Ni. Factor analysis also shows this association, which is interpreted as being due to fine-grained clays. This factor is the major controlling one both in the Bay and in the Hampton Roads area. The results for Baltimore Harbor are somewhat different. Factor analysis shows Fe (presumably on grain coatings) to have major control; clays (represented by Al) are second. Strong correlations with Al are not apparent although a correlation bewtween Al, Mn, and Co does exist. A strong correlation between Cr - Zn occurs and is probably due to anthropogenic input.

The samples in Baltimore Harbor have an Al content that exceeds eight percent in the inner reaches of the Harbor, while the Al content in the Bay will be shown to rarely exceed 7.5 percent. A possible reason for this higher Al content is that the Harbor may be a trap for fine-grained sediments. It is unlikely that Al is an anthropogenic contaminant, since anthropogenic addition of Al would require massive amounts.

The trend of increasing Al with distance into the Harbor (Figure 23) is consistent with data from physical sedimentology. Palmer (1975) found the upper third of the Harbor to have 60 percent clay. He also found 5 percent glauconite and 5 percent muscovite in the same area. The glauconite is present as silt-sized particles. The higher clay content and to a lesser extent the presence of glauconite are probably responsible for the high Al content. More recent unpublished sedimentological data from the Maryland Geological Survey also support the fine-grained nature of the Harbor. This is in agreement with the conclusions of Gottschalk (1944) and Carland (1952) that deposition of silt and clay in the Harbor is unusually high. Obviously this high deposition is the main reason for dredging operations.

Baltimore Harbor has a unique three-layered circulation system in which water flows in at the surface and bottom and out at mid-depth (Carpenter et al., 1961). The Patapsco River and other small streams entering the Harbor have only a small input compared to the input from the Bay. The Harbor has a flushing rate of 10 percent/day or the water is turned-over once in about 10 days. This is relatively fast and allows for the transport of suspended material from the Bay to be carried in and deposited, especially in the upper reaches of the Harbor. Harris et al. (1979) report metal ratios (Pb/Fe, Cu/Fe, Sn/Fe) for northern Bay sediments to be similar to those found in the Harbor. They suggest that the Harbor is a source to the Bay. However the Bay is probably also a sediment source for the Harbor.

Because of the high Al content (fine-grained sediment) it would not be entirely fair to judge the contamination of Baltimore Harbor from absolute concentrations of metals. Therefore enrichment factors have been computed. Since Al measurements were made on these samples; and since there is reason to believe that Fe concentrations have been influenced by human activities (Carpenter, et al., 1981), the enrichment factors have been computed with an Al base:

$$EF = \frac{(X/Al)_{sediment}}{(X/Al)_{average\ shale}}$$

where X/Al is the ratio of the concentrations of element X to Al. Turekian and Wedepohl's (1961) average shale data are used here because both Baltimore Harbor and the Hampton Roads area are composed of argillaceous sediments such as those from which shales evolve. The enrichment factors are presented in appendix B.

In Baltimore Harbor, there is a large amount of enrichment of Cr, Co, and Zn usually found down the length of the cores. The other elements (Ti, Mn, Fe, Ni) show minimal enrichment. Vanadium does show some enrichment in certain areas. The enrichment can be seen in the surface samples from the Harbor mouth to the inner Harbor near Fort McHenry (Figure 24). Three different patterns emerge - (1) V shows no enrichment, core samples closer to shore however do show some enrichment, (2) Cr shows increasing enrichment up the Harbor, and (3) Zn shows enrichment throughout the Harbor. In the Hampton Roads area, there is no consistent anthropogenic effect on Cr or V but Zn is highly enriched.

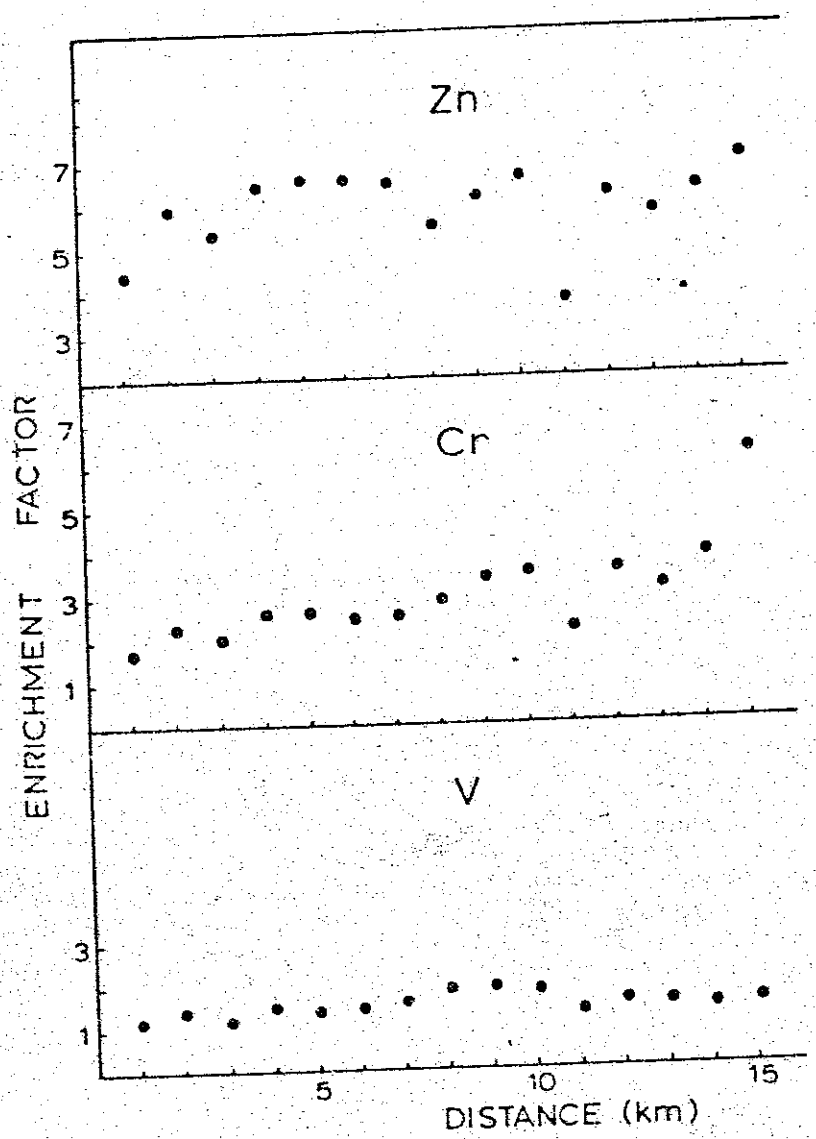


Figure 24. Enrichment factor for V, Cr, and Zn in Baltimore Harbor surface channel samples

SECTION 6

GEOCHRONOLOGY OF THE CORES

The lead-210 data obtained for the Chesapeake Bay gravity cores are tabulated in Appendix C. In Figure 25 the total lead-210 vs. depth is plotted for one core; the vertical bars represent the depth interval sampled (2.0 cm) and the horizontal bars represent $\pm 1\sigma$ uncertainties in the lead-210 activities. The method of calculating the excess (unsupported) lead-210 activities and their statistical uncertainties from the counting data was as follows:

$$^{210}Pb\ (dpm/gram) = \frac{a \times c}{b \times d} - {}^{226}Ra$$

where a = background corrected ^{210}Po counts
b = background corrected ^{209}Po counts
c = activity of ^{209}Po yield tracer
d = weight of sediment sample which underwent acid leaching

The uncertainties in each factor contribute to the total analytical uncertainty in the following manner:

$$\mu^2 = (\mu_a/a)^2 + (\mu_b/b)^2 + (\mu_c/c)^2 + (\mu_d/d)^2$$

where μ represents the 68 percent confidence interval. IN this equation, μ is expressed as a fraction of the lead-210 activity. To evaluate this equation one percent uncertainties were assumed for parameters c and d. As is standard in calculating uncertainties in counting data μ_a and μ_b were taken as the square roots of parameters a and b, respectively. For a typical case of 1000 polonium-210 counts and 2000 polonium-209 counts, μ will be 4.2 percent. This was the error associated with the total lead-210 data in Appendix C. To compute the total uncertainty in excess (unsupported) lead-210, an error must be assigned to the radium-226 activity. Radium-226 was determined on acid leached sediments from the tops and bottoms of each sediment core. The uncertainty in a single measurement of radium-226 was assumed to be $\pm$ seven percent, even though counting statistics were usually better than $\pm$ three percent. The larger uncertainty includes fluctuations in the efficiency of the radon-222 counting and extraction systems and inhomogeneities in the sediment samples digested. The total uncertainty in the excess lead-210 activity can be expressed as:

$$\sigma^2 = (\mu \times {}^{210}Pb)^2 + \left(\frac{0.07}{\sqrt{n}} \times {}^{226}Ra\right)^2$$

where n is the number of times that the radium-226 sample was analyzed.

Sedimentation rates for the sediment cores were computed on the basis of the unsupported lead-210 values. These concentrations were derived by subtracting the average radium-226 concentration from the total lead-210 activity. Only the unsupported or excess component is useful for sediment

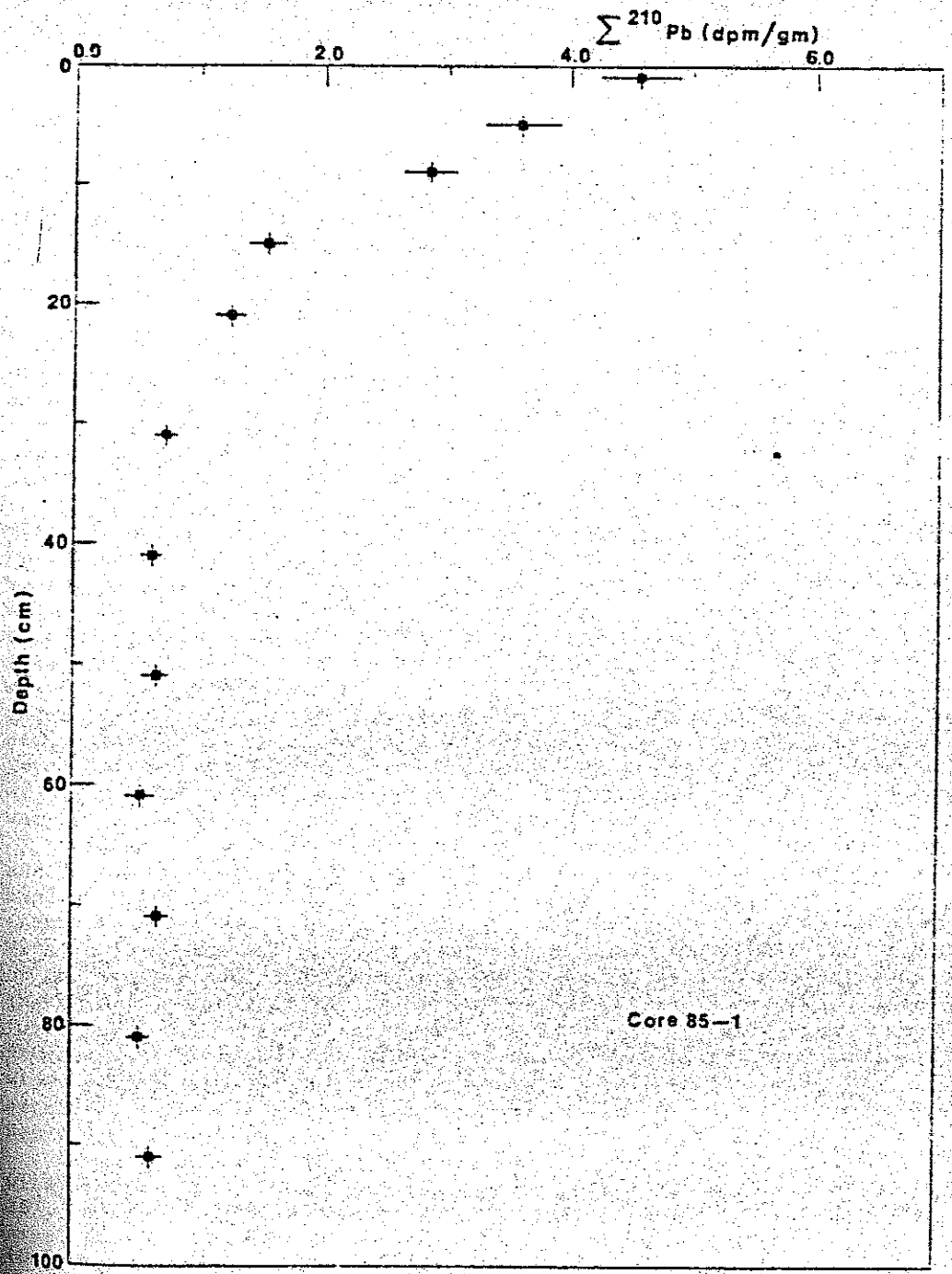


Figure 25. Total lead-210 vs. depth for core 85-1.

chronology as it is the only component which can be expected to change with time. The rate of change with time is dependent upon the decay constant of lead-210, $\lambda = 0.031$/year. At steady state conditions, this relationship is:

$$A_x = A_o e^{-\lambda t}$$

where A_x is the unsupported lead-210 activity at depth x, A_x the excess lead-210 activity at the sediment-water interface, and t the age corresponding to depth x. A plot of ln a as a function of depth yields a curve whose slope is proportional to the rate of change of age with depth, or the sedimentation rate. The exact relationship is:

$$S = -\lambda/m$$

where S is the sedimentation rate and m is the slope of the linear least squares line through the data.

Most of the lead-210 profiles from the Chesapeake Bay can be divided into three discrete regions: a surface layer with homogeneous activities, a central region where activities decrease logarithmically with depth in the core, and a lower region of constant low activities. The three regions; mixed surficial layer, zone of radioactive decay and background zone are variable in depth depending on core location. For example, the mixed surficial layer may vary from 0 - 10 cm depending on local physical and biological processes. Sediment accumulation rates were determined from the excess lead-210 activities in the zone of radioactive decay for each core. It was assumed that no turbation occurred in this zone. When a surficial mixed layer was observed it was assumed that the top of the zone of radioactive decay represented the present, and that each lower point in the sedimentary column represented a layer of sediment removed below the mixed layer in the past. Rates were calculated for sediments which showed signs of mixing in the surface layers by choosing only the part of the data which was below the mixed region.

Sedimentation rates calculated for the Chesapeake Bay sediment cores are listed in Table 10. The rates ranged from 0.7 to 42.6 mm/year. The highest rates were calculated for a Susquehanna River core and several cores collected near the mouth of the Potomac River (11 - 42.6 mm/year). With the exceptions of cores 6 and 55 (8.8 and 17.8 mm/year) the remainder of the core samples from the upper and lower portions of the Bay were in the several mm/year accumulation rate range. The lowest rate obtained was for core 14 (0.7 mm/year) collected in the proximity of Tilghman Island. Excess lead-210 activities (Table 11) do not exhibit any discernable Bay - wide trends, although the highest activity levels in the surficial estuarine sediments were measured in the central section of the Chesapeake Bay (cores 18, 60, 62, 83 and 86).

Comparisons can be made between several cores analyzed in this study with previously published lead-210 sedimentation rates (Table 12 and Figure 26). Although the collection locations are only from the same general area, the agreement is relatively good with only one exception. Core #14 (0.7 mm/year) lies in the vicinity of Schubel and Hirschberg's (1977) sediment sample (0.9 - 1.2 mm/year); Cores #83 and 85 (1.8 and 3.7 mm/year) are just south of Goldberg et al's (1978) sample location (3 mm/year); Core

Table 10. Chesapeake Bay Lead-210 Sedimentation Rates

Station	Latitude	Longitude	Sedimentation Rate* (mm/year)
52	39°29'15"N	75°56'30"W	2.0
4	39°19' N	76°14' W	3.1 (5.6)
6	39°09' N	76°23' W	8.7
55	38°48'30"N	76°23'30"W	17.9
14	38°39' N	76°25'30"W	0.7
18	38°19' N	76°20' W	3.6
60	38°11' N	76°19'30"W	2.3
62	38°10'30"N	76°14' W	12.6
63	38°11'30"N	76°07'45"W	6.6
64	38°12'30"N	75°57'50"W	11.2
24	38°00' N	76°13' W	12.2 (10.0)
83	37°41'30"N	76°14'30"W	1.9
85	37°41'15"N	76°04'30"W	3.7
86	37°43'15"N	75°55'15"W	5.2
102	37°24' N	76°04' W	2.3
99	37°00'30"N	76°14'15"W	3.8
4 (Sus. River)			42.6

* Average sedimentation rate derived from the cesium-137 time horizon is listed in parenthesis.

Table 11. Excess Lead-210 Activity in Chesapeake Bay Surficial Sediments

Station	Total ^{210}Pb	Excess ^{210}Pb (dpm/gram ± 1)	^{226}Ra
52	2.33 ± .21	1.06 ± .11	0.65 ± .03
4	4.07 ± .36	2.71 ± .24	1.54 ± .06
6	4.56 ± .32	3.15 ± .23	1.49 ± .09
55	4.91 ± .37	4.07 ± .31	0.85 ± .05
14	5.79 ± .44	4.96 ± .38	0.89 ± .07
18	8.02 ± .37	7.49 ± .34	0.71 ± .04
60	7.51 ± .61	6.77 ± .55	0.70 ± .04
62	7.61 ± .46	7.01 ± .42	0.58 ± .03
63	2.86 ± .22	2.19 ± .17	0.62 ± .03
64	3.97 ± .20	3.25 ± .17	0.66 ± .03
24	6.07 ± .28	5.50 ± .26	0.53 ± .03
83	7.41 ± .52	6.89 ± .48	0.48 ± .03
85	4.74 ± .30	4.24 ± .27	0.48 ± .03
86	6.72 ± .52	6.15 ± .48	0.57 ± .03
102	1.57 ± .11	1.32 ± .10	0.26 ± .02
99	1.18 ± .08	0.86 ± .06	0.33 ± .03
4 (Sus. River)	3.49 ± .27	1.55 ± .14	1.79 ± .10

Table 12. Chesapeake Bay Lead-210 Sedimentation Rates (Previously Reported Studies)

Authors	Latitude	Longitude	Sedimentation Rate (mm/year)
Schubel & Hirschberg (1977)	38°41'30"N	76°24'00"W	0.9 - 1.2
Goldberg et al. (1978)	39°14'12"N	76°14'18"W	80
	38°57'43"N	76°22'49"W	30
	38°56'80"N	76°25'18"W	10
	38°34'00"N	76°27'00"W	5
	37°47'00"N	76°11'00"W	3
Hirschberg & Schubel (1979)	39°22'47"N	76°05'32"W	4.5

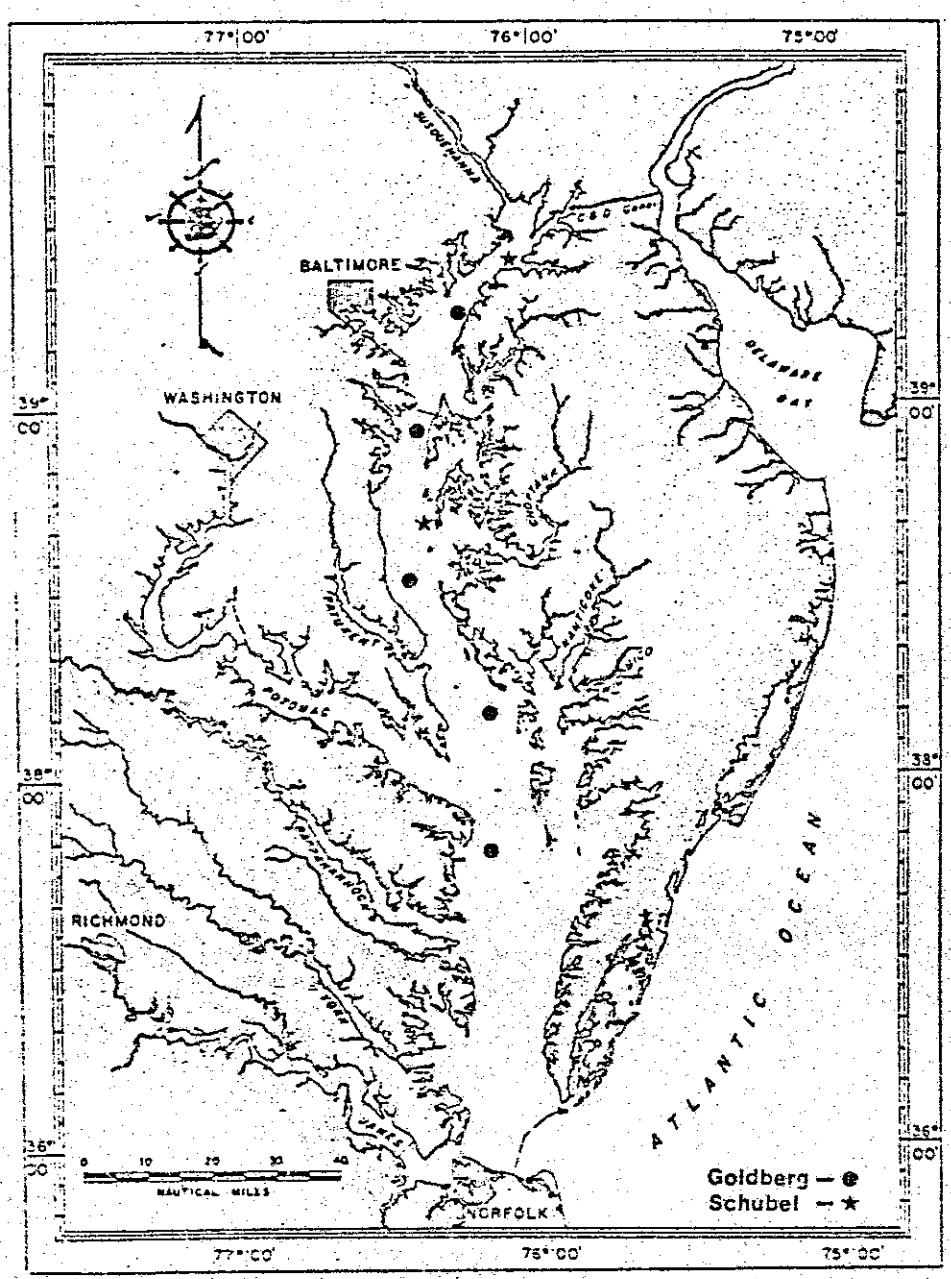


Figure 26. Location of dated cores described in published literature.

#18 (3.8 mm/year) is also south of another Goldberg et al. sediment core (5 mm/year); and core #52 (2.0 mm/year) is located north of a Hirschberg and Schubel (1979) coring site (4.5 mm/year). The one anomaly is between core #4 (3.1 mm/year) and a Goldberg et al. (1978) sample having an extremely high sedimentation rate (80 mm/year).

The ability of lead-210 geochronology to estimate sediment accumulation rates is a function of the natural local variability of sedimentation rates and its analytical reproducibility. To test the latter, core #85 was analyzed both in the fall of 1979 and the spring of 1980. The analytical precision (duplicate analyses were performed at the same core depths) between the samples is tabulated in Appendix C. Sedimentation rates calculated from the excess lead-210 data differed by 0.1 mm/yr.

Additional checks on the lead-210 accumulation rates were provided by obtaining pollen and cesium-137. The cesium-137 activity maximum in the cores is assumed to represent the 1963 nuclear fallout maximum which occurred after the 1961-1962 period of intensive nuclear weapons testing by the United States and the Soviet Union. For core #4 this cesium-137 peak occurs in the 8-10 centimeter interval. Assigning the 1963 date to the mid-point of this interval yields a sedimentation rate of 5.6 mm/year versus the lead-210 rate of 3.1 mm/year. For core #24 the cesium-137 peak is less definite and may have been spread out by physical processes (i.e. current and wave activity) or biological disturbances (i.e. burrowing benthic organisms). Assigning the 1963 date the mid-point of the 14-18 centimeter interval yields an average accumulation rate of 10 mm/year versus the lead-210 derived rate of 12.4 mm/year.

SECTION 7

GEOCHEMISTRY OF THE CORES

MAIN BAY CORES

The same cores that were analyzed for ^{210}Pb were analyzed for a number of major and minor elements. The data are presented in Appendix D. Crustal enrichments factors are also presented. Since Al was determined in the cores, the enrichment factors in Appendix D are placed on an aluminum basis, rather than an iron basis. Iron-based enrichment factors, for comparison with those discussed in Section 5, can be computed simply by dividing the enrichment factor of any element in Table D-2 by the corresponding enrichment factor for iron.

$$EF^{X}_{FE\ Basis} = \frac{EF^{X}_{Al\ Basis}}{EF^{FE}_{Al\ Basis}}$$

Table 13 gives the weight ratios of carbon to nitrogen. These ratios have been used in the past as indicators of the origin of the organic matter in sediments (Williams, 1968; Nissenbaum and Kaplan, 1972). Organic matter produced by marine algae tends to be more nitrogen-rich than that produced by terrestrial plants and transported into the estaurine zone by rivers. The data in Table 13 reveal high C/N ratios north of Baltimore where most of the Susquehanna suspended load is deposited. The C/N values south of Baltimore are similar to those found in marine sediments. An exception is core 99 near Norfolk where a very low concentration of organic matter makes the analyses somewhat uncertain but also where the C/N ratio might be modified by petroleum or coal contamination in the sediments.

Many of the cores contain much higher concentrations of some elements near the surface than at depth. This is summarized for all cores in Table [illegible] and illustrated for one core in Figure 27. These changes in sediment composition most likely are produced by a variety of processes. In the case of upward increases in Si, Ti or Zr (e.g. cores Sus, 52, 102, 99), changes in proportions of sand, clay and heavy minerals over a period of [illegible] seems to be the only reasonable explanation, because anthropogenic sources would be too small compared to natural sources to account for the changes. Furthermore there are also cores in which these elements decrease [illegible] (e.g. cores 4, 18).

On the other hand, in the case of upward enrichments in elements such [illegible], Co, and Zn, variation in the proportions of clay to sand is probably [illegible] the controlling factor, because the upward enrichments are apparent [illegible] in the enrichment factor tables (Appendix D) where normallization to [illegible] would largely compensate for clay/sand variations. For those elements, [illegible]netic remobilization or enrichment from anthropogenic sources is a [illegible] explanation.

[illegible]anganese is the best-known example of an element that becomes [illegible]ized during diagenesis. Under the reducing conditions that exist at [illegible] in many of the cores (see Md. Geological Survey data presented in

Table 13. C/N Weight Ratio in Cores

Core	No. Analyses	Max.	Min.	Mean
Susquehanna	1	–	–	15.4
52	8	26.4	4.9	14.0
4	23	46.5	5.4	11.9
6	7	9.9	4.4	7.3
55	9	9.1	6.2	7.5
14	6	11.3	6.0	8.6
18	9	7.4	3.6	5.7
62	4	9.8	9.2	9.5
24	32	10.6	7.2	8.8
102	1	–	–	4.4
99	4	29.5	4.8	17

Table 14. Elements Showing Upward Enrichment in Cores

Core	Elements
Susquehanna	Si, Ti, V, Ni
52	Si, Zr
4	Mn, Co, Ni, Cu, Zn
6	V, Cr, Mn, Fe, Co, Ni, Zn
55	Mn, Fe, Co, Ni, Cu, Zn
14	Mn, Fe, Co, Cu, Zn
18	Al, Ti, V, Cr, Mn, Fe, Co, Ni, Zn
60	V, Cr, Mn, Co, Cu, Zn
62	Fe, Co
63	Ti, Zn
64	Ti, Cr, Cu, Zn, Zr
24	Zn
83	Cr, Co, Zn
85	Co, Cu, Zn
86	Zn
102	Ti, Mn, Fe, Zn, Zr
97	Ti, Zr

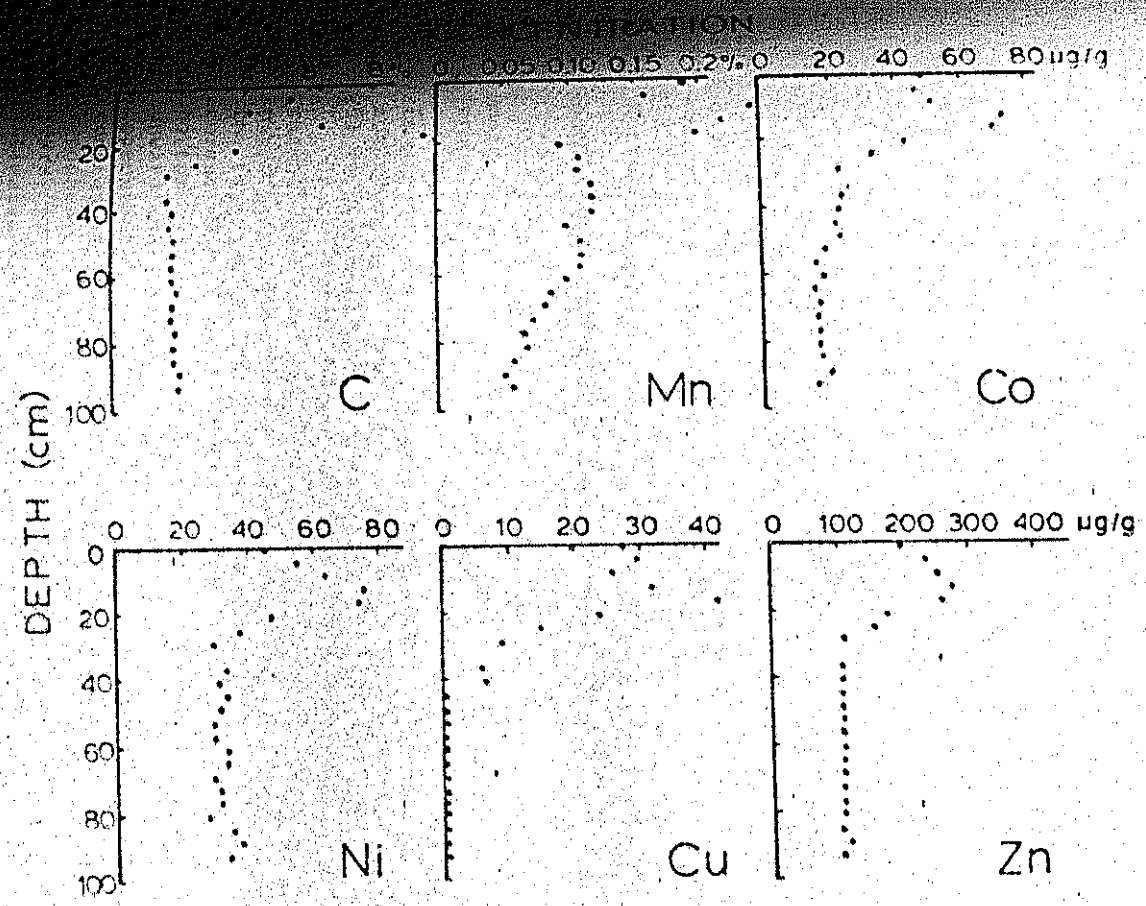


Figure 27. Vertical profiles for elements showing upward enrichment in core 4 (C and Mn are %; Co, Ni, Cu, and Zn are µg/g).

other Chesapeake Bay Program reports) manganese dissolves and can diffuse upwards toward the oxic-anoxic interface where it can re-oxidize and precipitate. This process will produce Mn enrichment near the sediment surface. Other elements that readily coprecipitate with Mn (e.g. Co, Ni and Cu) may migrate in a similar fashion, especially if sulfide is absent.

Zinc is one of the elements that was found in Section 5 to be enriched relative to continental crust over much of the Bay's bottom. It is also the element that most consistently shows upward enrichment in the cores, and does so even in cores where no upward enrichment in Mn occurs. Since the upward enrichment in Zn is clearly delineated in the enrichment factor tables in Appendix D, it probably is not explainable by changes in the clay/sand ratio. These lines of evidence suggest that the Zn profiles are reflecting anthropogenic contamination of Chesapeake Bay in recent decades. A similar conclusion has been reached by Goldberg, et al (1978).

In the specific case of core 4, data from which are plotted in Figure 26, the closely correlated profiles for six geochemically disparate elements suggest yet another mechanism for the enrichments near the surface. Since core 4 occurs near the turbidity maximum, a region where Schubel and Zabawa (1977) observed deposition of as much as 20 cm of sediment by Hurricane Agnes, the enrichment zone near the top of the core may simply reflect the Agnes event. In this case the enrichments relative to deeper sediment might be explained by arguing that Agnes brought anthropogenically contaminated materials into the Bay or simply that Agnes brought materials from different sources than normally contribute to the Susquehanna's suspended load. For example, the large concentration of carbon in the top 20 cm of core 4 may be due to scouring of the A horizon in soils during flooding of fields and forests such as occured during Hurricane Agnes.

BALTIMORE HARBOR AND ELIZABETH RIVER CORES

Most elements in Baltimore Harbor show erratic changes with depth in most cores. The sediments appear to have been jumbled by dredging, propeller wash, etc. The data for the Hampton Roads cores (Appendix D) are not as erratic and most show a systematic decrease in Zn with depth. Zinc is a good marker for anthropogenic contamination and the surface of both subestuaries are markedly contaminated even when the fining effect (Section 5) is eliminated by normalizing to Al.

Of the six cores collected from the Elizabeth River, two are in a channel area that undergoes regular maintenance dredging and are probably mixed from this process. The other cores are further upriver and out of the regularly dredged channel. Figure 28 is a plot of the data from these cores. The Zn concentrations have been normalized to the value at the bottom of the core. The four cores appear to record an exponentially upward increasing Zn concentration. This could be caused by an approximately exponential increase in Zn sources over time combined with a constant deposition rate or any downward mixing process. The former hypothesis is plausible if the sources have doubled approximately every 25 years, in keeping with the population growth rate. This leads to an estimated deposition rate of 0.3 - 0.6 cm/yr which is reasonable. This does not rule out the possibility, however, that the actual deposition rate is much slower and the Zn has been mixed downward.

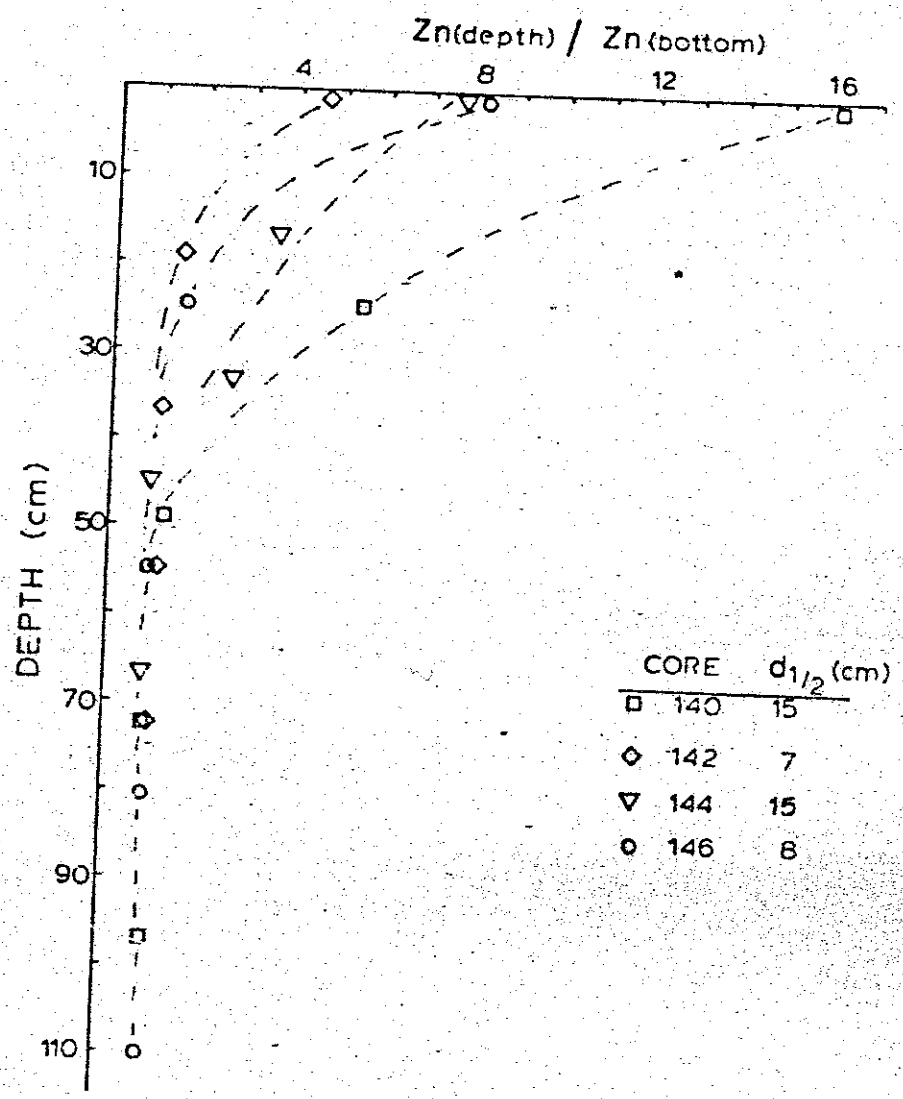


Figure 28. Zn in Elizabeth River cores ratioed to value in deepest sample. Estimate of depth at which excess Zn is half of surface value given as $d_{\frac{1}{2}}$ in cm.

Although the Zn profiles from Baltimore Harbor are erratic in the upper cores, there is usually a horizon below which Zn drops below 200 μg/g and settles down. Based on our study of the main Bay cores, 200 μg/g can be adopted as a background, or only mildly contaminated level. This will allow an estimation of the thickness of the contaminated layer in Baltimore Harbor.

Using the data from 12 cores from this study and 18 cores from an earlier EPA study (Anonymous, 1977), the depth to the 200 μg/g isopleth can be estimated by interpolation. In cases where it lies slightly below the bottom sample, the estimate was made by extrapolation provided the extrapolation was not more than half the core's length deeper. The depth in meters to the 200 ug/g Zn isopleth is shown in Figure 29. The most obvious feature is the massive area of contamination (>3 meters) in the inner Harbor area near Fort McHenry. This is the same area where Al is the highest and is also where very high depostion rates probably occur. The wedge of contamination slowly thins in a seaward direction. The contaminated zone is less than 0.5 meter at the harbor mouth.

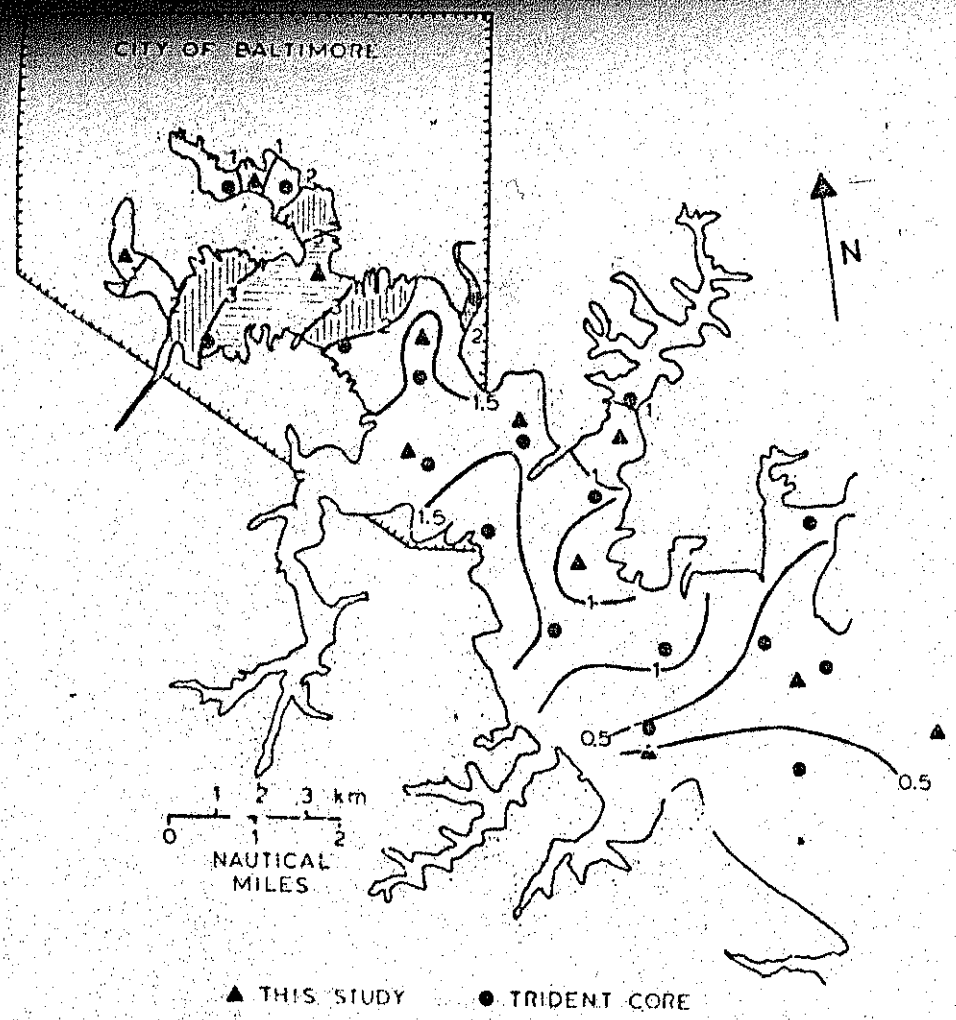


Figure 29. Depth in meters to 200 ppm Zn isopleth

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Appendix A

Surface Sample Data and Locations

For Main Bay Stations

Table A-1

Data for Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb with sample locations

All values are μg metal/g of dry sediment except Fe which is %. The values are good to only two significant figures. Additional zeroes in some cases result from computer format. Locations are given in degrees of latitude and longitude expressed as decimal fractions. The following codes are used:

-1.0 Trace
-2.0 Not Detectable
-3.0 Not Analyzed

TRAVERSE NUMBER 00
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
10	37.0	1800.0	2.30	21.0	33.0	18.0	80.0	.30	14.0	39	34.900	76	6.700
20	27.0	550.0	1.60	13.0	30.0	15.0	65.0	-1.00	10.0	39	35.100	76	6.900
30	14.0	300.0	1.10	17.0	29.0	15.0	99.0	.50	24.0	39	30.500	76	5.200

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
11	55.0	1800.0	5.20	42.0	79.0	49.0	230.0	.30	38.0	39	34.900	76	6.700
21	59.0	3300.0	5.20	47.0	88.0	49.0	240.0	.29	46.0	39	35.100	76	6.900
31	41.0	1600.0	5.00	45.0	90.0	49.0	280.0	1.30	92.0	39	30.500	76	5.200

TRAVERSE NUMBER 01
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
1010	15.0	590.0	1.10	13.0	24.0	18.0	64.0	-1.00	10.0	39	31.500	76	5.700
1020	11.0	250.0	.90	8.0	17.0	-2.0	50.0	-2.00	6.0	39	32.100	76	4.500
1030	7.0	180.0	.50	6.0	12.0	-2.0	50.0	-2.00	7.0	39	32.600	76	3.700

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
1011	66.0	6900.0	5.80	69.0	130.0	54.0	340.0	.90	58.0	39	31.500	76	5.700
1021	48.0	3800.0	5.20	59.0	120.0	55.0	350.0	.89	56.0	39	32.100	76	4.500
1031	63.0	5100.0	5.30	74.0	130.0	63.0	360.0	1.10	63.0	39	32.600	76	3.700

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 02

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
2010	37.0	1100.0	2.60	26.0	49.0	48.0	100.0	.90	34.0	39	28.800	76	3.800
2020	14.0	400.0	1.30	17.0	32.0	15.0	100.0	.40	9.0	39	29.100	76	3.200
2030	15.0	1500.0	1.30	23.0	43.0	22.0	180.0	.40	14.0	39	29.500	76	2.700
2040	26.0	1900.0	1.90	31.0	55.0	46.0	180.0	.80	31.0	39	29.800	76	2.100
2050	18.0	1100.0	1.30	25.0	45.0	28.0	120.0	.50	14.0	39	30.100	76	1.500
2060	27.0	1100.0	2.10	30.0	49.0	56.0	200.0	.80	41.0	39	30.400	76	1.000
2070	13.0	550.0	1.20	18.0	32.0	18.0	100.0	.30	10.0	39	30.800	76	.400
2080	51.0	1700.0	3.90	46.0	71.0	95.0	380.0	2.00	53.0	39	31.100	75	59.800
2090	57.0	2100.0	4.50	50.0	83.0	73.0	340.0	2.00	55.0	39	32.500	75	59.100

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
2011	48.0	1500.0	4.60	42.0	84.0	54.0	340.0	1.30	56.0	39	28.800	76	3.800
2021	45.0	3200.0	4.80	68.0	110.0	53.0	350.0	1.80	79.0	39	29.100	76	3.200
2031	53.0	4700.0	4.70	70.0	240.0	67.0	1600.0	1.20	78.0	39	29.500	76	2.700
2041	50.0	2200.0	4.70	50.0	100.0	65.0	410.0	1.30	57.0	39	29.800	76	2.100
2051	47.0	1800.0	4.30	49.0	110.0	58.0	410.0	1.30	53.0	39	30.100	76	1.500
2061	53.0	1600.0	4.90	44.0	100.0	67.0	430.0	1.30	65.0	39	30.400	76	1.000
2071	48.0	4300.0	4.80	76.0	130.0	54.0	370.0	1.20	57.0	39	30.800	76	.400
2081	52.0	1600.0	4.60	45.0	91.0	72.0	420.0	1.60	66.0	39	31.100	75	59.800
2091	51.0	1900.0	4.40	45.0	140.0	58.0	350.0	1.40	57.0	39	32.500	75	59.100

TRAVERSE NUMBER 03

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
3010	38.0	2100.0	3.70	35.0	59.0	52.0	330.0	1.60	51.0	39	26.600	76	3.100
3020	25.0	1500.0	2.90	32.0	48.0	51.0	230.0	.80	40.0	39	26.200	76	2.100
3030	41.0	1900.0	4.30	32.0	53.0	44.0	250.0	.90	46.0	39	25.900	76	1.400
3040	13.0	330.0	.70	6.0	12.0	4.0	41.0	.20	12.0	39	25.500	76	.500

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
3011	44.0	2100.0	1.50	44.0	91.0	54.0	350.0	1.10	50.0	39	26.600	76	3.100
3021	48.0	2400.0	4.70	53.0	97.0	57.0	370.0	1.40	66.0	39	26.200	76	2.100
3031	51.0	2000.0	4.50	36.0	73.0	50.0	270.0	.88	53.0	39	25.900	76	1.400
3041	54.0	1600.0	4.50	30.0	81.0	47.0	320.0	.86	53.0	39	25.500	76	.500

TRAVERSE NUMBER 04

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
4010	37.0	1800.0	3.60	38.0	57.0	56.0	310.0	1.00	55.0	39	23.200	76	8.600
4020	39.0	2000.0	3.80	38.0	81.0	56.0	290.0	1.00	57.0	39	22.800	76	7.700
4030	50.0	2400.0	4.30	34.0	55.0	44.0	250.0	.70	46.0	39	22.400	76	6.900

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
4011	44.0	1900.0	4.10	40.0	76.0	49.0	330.0	1.10	52.0	39	23.200	76	8.600
4021	41.0	2300.0	4.10	37.0	77.0	44.0	310.0	1.10	46.0	39	22.800	76	7.700
4031	44.0	2700.0	4.30	35.0	73.0	42.0	310.0	1.10	45.0	39	22.400	76	6.900

TRAVERSE NUMBER 05

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
5010	55.0	3000.0	5.00	52.0	100.0	65.0	480.0	2.00	92.0	39	18.000	76	21.800
5020	70.0	2800.0	5.50	45.0	88.0	60.0	390.0	.80	73.0	39	17.500	76	20.500
5030	62.0	5000.0	5.50	75.0	150.0	66.0	580.0	2.00	84.0	39	17.000	76	19.100
5040	92.0	3600.0	4.90	66.0	120.0	60.0	500.0	1.00	42.0	39	16.500	76	18.000
5050	94.0	2900.0	4.80	50.0	88.0	52.0	350.0	1.00	63.0	39	16.100	76	16.800
5060	85.0	2400.0	4.70	43.0	72.0	46.0	310.0	.80	54.0	39	15.600	76	15.500
5070	85.0	2300.0	4.90	42.0	70.0	44.0	310.0	.70	52.0	39	15.100	76	14.300

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
5011	52.0	2500.0	4.70	51.0	130.0	59.0	440.0	1.30	98.0	39	18.000	76	21.800
5021	55.0	1700.0	5.00	36.0	87.0	49.0	350.0	.59	73.0	39	17.500	76	20.500
5031	52.0	3700.0	5.20	61.0	160.0	59.0	770.0	.82	80.0	39	17.000	76	19.100
5041	54.0	2500.0	4.90	50.0	110.0	54.0	420.0	.73	65.0	39	16.500	76	18.000
5051	54.0	2600.0	4.30	44.0	100.0	52.0	350.0	.75	57.0	39	16.100	76	16.800
5061	46.0	1700.0	4.40	36.0	70.0	49.0	270.0	.45	53.0	39	15.600	76	15.500
5071	45.0	1900.0	4.40	37.0	77.0	47.0	310.0	.60	50.0	39	15.100	76	14.300

TRAVERSE NUMBER 06

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
6010	135.0	800.0	7.50	51.0	80.0	98.0	1100.0	1.00	250.0	39	11.500	76	27.100
6020	109.0	1600.0	6.30	26.0	51.0	51.0	400.0	.60	90.0	39	11.000	76	27.600
6030	-3.0	1300.0	10.30	81.0	82.0	126.0	1100.0	.80	210.0	39	10.400	76	28.100

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
6011	160.0	630.0	6.40	38.0	76.0	100.0	890.0	.88	170.0	39	11.500	76	27.100
6021	100.0	1400.0	4.80	25.0	59.0	66.0	470.0	.74	99.0	39	11.000	76	27.600
6031	-3.0	1200.0	11.20	80.0	110.0	160.0	1300.0	1.10	220.0	39	10.400	76	28.100

TRAVERSE NUMBER 07

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
7010	90.0	3600.0	6.00	54.0	75.0	56.0	740.0	.70	78.0	39	3.700	76	25.000
7020	65.0	1700.0	5.40	23.0	46.0	29.0	240.0	.40	43.0	39	3.500	76	23.800
7030	76.0	1800.0	5.50	37.0	61.0	54.0	370.0	.50	50.0	39	3.400	76	22.500
7040	68.0	2400.0	5.70	41.0	73.0	51.0	1000.0	.70	93.0	39	3.200	76	21.200
7050	41.0	790.0	3.40	14.0	29.0	25.0	140.0	-2.00	37.0	39	3.000	76	19.800
7060	48.0	1200.0	4.10	28.0	49.0	38.0	330.0	.50	54.0	39	2.600	76	16.900
7070	52.0	750.0	4.50	31.0	57.0	46.0	370.0	.50	58.0	39	2.500	76	16.100

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
7011	83.0	1700.0	5.00	36.0	76.0	68.0	600.0	.59	100.0	39	3.700	76	25.000
7021	57.0	1000.0	4.30	19.0	50.0	37.0	240.0	.35	38.0	39	3.500	76	23.800
7031	71.0	1500.0	4.70	26.0	52.0	50.0	250.0	.15	50.0	39	3.400	76	22.500
7041	64.0	1700.0	4.40	32.0	71.0	53.0	400.0	.59	69.0	39	3.200	76	21.200
7051	62.0	1200.0	4.40	22.0	46.0	44.0	280.0	.30	64.0	39	3.000	76	19.800
7061	52.0	940.0	3.90	24.0	61.0	44.0	650.0	.45	60.0	39	2.600	76	16.900
7071	54.0	650.0	4.40	28.0	60.0	52.0	350.0	.60	66.0	39	2.500	76	16.100

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 08

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
8010	114.0	1500.0	8.00	36.0	70.0	39.0	570.0	.60	70.0	38	59.330	76	26.370
8020	84.0	1700.0	6.00	37.0	54.0	46.0	490.0	.70	68.0	38	58.930	76	24.410
8030	76.0	3300.0	5.60	35.0	60.0	41.0	410.0	.70	63.0	38	58.690	76	23.770
8040	64.0	1100.0	5.00	17.0	53.0	44.0	390.0	.60	61.0	38	58.450	76	23.130
8050	72.0	3100.0	5.10	29.0	56.0	34.0	330.0	.50	56.0	38	58.230	76	22.520
8060	64.0	1100.0	4.50	28.0	50.0	34.0	350.0	.70	55.0	38	58.010	76	21.950
8070	12.0	450.0	.68	5.0	9.0	4.0	50.0	.20	6.0	38	57.830	76	21.460

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
8011	100.0	1200.0	6.70	39.0	74.0	48.0	530.0	.75	73.0	38	59.330	76	26.370
8021	77.0	1500.0	4.70	33.0	58.0	50.0	450.0	1.80	71.0	38	58.930	76	24.410
8031	67.0	3600.0	4.60	42.0	62.0	43.0	340.0	.60	52.0	38	58.690	76	23.770
8041	63.0	1300.0	4.20	39.0	59.0	49.0	420.0	.74	59.0	38	58.450	76	23.130
8051	63.0	2600.0	4.20	35.0	49.0	40.0	280.0	.59	55.0	38	58.230	76	22.520
8061	56.0	1300.0	4.20	45.0	60.0	47.0	350.0	1.10	54.0	38	58.010	76	21.950
8071	50.0	1500.0	4.00	24.0	40.0	30.0	270.0	.45	33.0	38	57.830	76	21.460

TRAVERSE NUMBER 09

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
9010	120.0	850.0	8.60	13.0	29.0	33.0	240.0	-2.00	-2.0	38	54.960	76	26.980
9020	120.0	2000.0	8.70	19.0	35.0	26.0	370.0	.60	43.0	38	54.740	76	26.350
9030	76.0	1500.0	6.30	30.0	52.0	58.0	460.0	.70	79.0	38	54.530	76	25.730
9040	62.0	1100.0	5.90	31.0	53.0	59.0	440.0	.50	78.0	38	54.310	76	25.120
9050	58.0	1200.0	5.10	22.0	41.0	51.0	330.0	.40	61.0	38	54.070	76	24.500
9060	57.0	950.0	4.70	22.0	43.0	51.0	320.0	.50	59.0	38	53.840	76	23.900
9070	52.0	1100.0	4.00	18.0	36.0	41.0	280.0	.70	50.0	38	53.600	76	23.320
9080	4.3	170.0	.15	1.0	2.0	3.0	11.0	-2.00	2.0	38	53.340	76	22.670

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
9011	89.0	930.0	6.00	20.0	49.0	34.0	260.0	.15	47.0	38	54.960	76	26.980
9021	78.0	2900.0	5.90	29.0	61.0	43.0	450.0	1.10	69.0	38	54.740	76	26.350
9031	74.0	1900.0	5.50	38.0	74.0	53.0	440.0	.58	69.0	38	54.530	76	25.730
9041	72.0	1100.0	5.40	32.0	74.0	55.0	420.0	.58	64.0	38	54.310	76	25.120
9051	58.0	1500.0	4.40	25.0	53.0	44.0	280.0	.30	49.0	38	54.070	76	24.500
9061	60.0	1400.0	4.20	32.0	57.0	37.0	400.0	.73	47.0	38	53.840	76	23.900
9071	60.0	1100.0	4.00	22.0	41.0	37.0	260.0	.72	50.0	38	53.600	76	23.320
9081	68.0	4000.0	3.40	25.0	47.0	38.0	280.0	-1.00	38.0	38	53.340	76	22.670

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 10
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.
10010	6.0	350.0	.45	3.5	5.0	-1.0	40.0	.37	7.0	38	48.720	76	29.120
10020	53.0	1200.0	5.00	31.0	44.0	55.0	400.0	1.30	64.0	38	48.490	76	28.450
10030	55.0	1200.0	5.40	32.0	49.0	61.0	440.0	.88	73.0	38	48.260	76	27.850
10040	58.0	1000.0	5.40	33.0	49.0	64.0	410.0	1.60	73.0	38	48.000	76	27.230
10050	55.0	850.0	4.90	29.0	45.0	59.0	400.0	1.80	68.0	38	47.710	76	26.600
10060	47.0	600.0	4.40	19.0	35.0	44.0	220.0	.75	43.0	38	47.420	76	26.020
10070	48.0	850.0	4.20	21.0	38.0	48.0	250.0	1.40	47.0	38	47.110	76	25.450
10080	41.0	650.0	3.50	16.0	35.0	34.0	200.0	.75	34.0	38	46.790	76	24.880
10090	5.0	130.0	.33	2.0	3.3	-1.0	21.0	.81	1.3	38	46.470	76	24.360
10100	6.0	150.0	.68	1.5	3.0	-1.0	19.0	-1.00	2.4	38	46.100	76	23.800
10110	8.0	120.0	.67	3.5	8.4	-1.0	50.0	1.10	5.5	38	45.490	76	21.450

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.
10011	63.0	2800.0	4.20	25.0	45.0	36.0	380.0	3.50	48.0	38	48.720	76	29.120
10021	66.0	1100.0	4.70	35.0	58.0	41.0	380.0	.59	62.0	38	48.490	76	28.450
10031	70.0	1600.0	5.00	41.0	73.0	50.0	650.0	.74	67.0	38	48.260	76	27.850
10041	68.0	1100.0	5.00	37.0	59.0	48.0	370.0	.57	68.0	38	48.000	76	27.230
10051	67.0	640.0	4.20	28.0	59.0	49.0	350.0	.74	56.0	38	47.710	76	26.600
10061	54.0	590.0	3.80	18.0	41.0	29.0	170.0	.30	31.0	38	47.420	76	26.020
10071	54.0	750.0	3.50	21.0	49.0	40.0	240.0	.73	45.0	38	47.110	76	25.450
10081	45.0	500.0	2.80	18.0	42.0	31.0	230.0	.60	36.0	38	46.790	76	24.880
10091	39.0	2500.0	2.40	19.0	36.0	26.0	190.0	2.00	19.0	38	46.470	76	24.360
10101	40.0	2100.0	3.20	15.0	33.0	23.0	160.0	.97	23.0	38	46.100	76	23.800
10111	28.0	830.0	1.90	16.0	45.0	16.0	340.0	-3.00	14.0	38	45.490	76	21.450

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 11

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
11010	24.0	400.0	1.50	9.9	17.0	16.0	150.0	1.70	20.0	38	38.050	76	30.300
11020	53.0	840.0	4.80	27.0	50.0	59.0	410.0	.74	65.0	38	38.100	76	28.900
11030	52.0	640.0	4.80	23.0	49.0	53.0	380.0	.73	60.0	38	38.120	76	27.510
11040	49.0	500.0	4.50	13.0	35.0	26.0	120.0	-1.00	1.8	38	38.100	76	26.170
11050	43.0	500.0	3.80	14.0	35.0	32.0	180.0	.60	2.9	38	38.140	76	24.800
11060	5.0	100.0	.29	2.0	4.2	-1.0	16.0	.04	.8	38	38.160	76	23.400
11070	4.0	25.0	.28	1.7	4.2	3.0	16.0	.04	.8	38	37.640	76	22.040
11080	18.0	83.0	1.50	6.7	14.0	11.0	83.0	.25	1.1	38	37.640	76	20.660
11090	31.0	500.0	2.50	9.9	23.0	25.0	120.0	.45	2.0	38	37.640	76	19.270

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
11011	61.0	770.0	4.10	26.0	47.0	37.0	340.0	.74	50.0	38	38.050	76	30.300
11021	69.0	800.0	4.60	35.0	59.0	45.0	400.0	.70	64.0	38	38.100	76	28.900
11031	64.0	550.0	4.20	30.0	53.0	42.0	340.0	.45	61.0	38	38.120	76	27.510
11041	53.0	480.0	3.90	15.0	35.0	21.0	120.0	-2.00	16.0	38	38.100	76	26.170
11051	52.0	500.0	3.40	17.0	35.0	25.0	140.0	.45	28.0	38	38.140	76	24.800
11061	51.0	820.0	3.40	35.0	43.0	29.0	220.0	.61	31.0	38	38.160	76	23.400
11071	49.0	570.0	3.40	16.0	37.0	24.0	180.0	.49	28.0	38	37.640	76	22.040
11081	30.0	300.0	2.30	12.0	24.0	15.0	130.0	.28	14.0	38	37.640	76	20.660
11091	36.0	490.0	2.80	12.0	28.0	19.0	140.0	.30	20.0	38	37.640	76	19.270

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 12
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
12010	54.0	650.0	4.00	20.0	47.0	46.0	280.0	1.10	43.0	38	26.300	76	26.300
12020	53.0	570.0	4.00	18.0	45.0	37.0	230.0	.74	33.0	38	26.800	76	24.600
12030	11.0	70.0	1.10	4.2	8.2	3.2	30.0	-1.00	3.4	38	27.100	76	23.900
12040	4.6	57.0	.37	1.5	3.8	2.9	15.0	.03	2.9	38	27.600	76	21.200

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
12011	51.0	640.0	3.90	18.0	43.0	43.0	250.0	1.00	40.0	38	26.300	76	26.300
12021	48.0	490.0	3.60	15.0	39.0	32.0	190.0	.44	28.0	38	26.800	76	24.600
12031	46.0	290.0	3.80	13.0	35.0	33.0	170.0	.47	27.0	38	27.100	76	23.900
12041	27.0	260.0	2.20	8.6	24.0	19.0	95.0	.14	14.0	38	27.600	76	21.200

TRAVERSE NUMBER 13
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
13010	4.0	28.0	.16	.7	2.5	3.0	12.0	.11	3.0	38	19.000	76	26.600
13020	58.0	1000.0	4.00	14.0	30.0	36.0	210.0	.74	40.0	38	18.400	76	26.600
13030	44.0	490.0	3.70	11.0	23.0	27.0	150.0	.59	30.0	38	17.800	76	26.700

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
13011	43.0	560.0	3.30	11.0	29.0	35.0	220.0	1.00	40.0	38	19.000	76	26.600
13021	48.0	770.0	3.50	13.0	35.0	32.0	190.0	.60	33.0	38	18.400	76	26.600
13031	45.0	350.0	3.90	10.0	31.0	25.0	150.0	.45	29.0	38	17.800	76	26.700

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 14
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.
14010	47.0	590.0	3.50	13.0	30.0	33.0	200.0	.89	32.0	38 19.400	76	23.200
14020	58.0	590.0	4.00	17.0	38.0	40.0	240.0	1.10	49.0	38 18.100	76	20.300
14030	57.0	490.0	3.80	15.0	37.0	39.0	190.0	.87	44.0	38 18.100	76	19.000
14040	57.0	630.0	3.60	12.0	34.0	35.0	140.0	.58	35.0	38 18.300	76	17.600
14050	4.0	25.0	.22	1.5	4.2	-2.0	16.0	.07	2.7	38 18.300	76	16.200

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.
14011	44.0	500.0	3.60	12.0	37.0	31.0	180.0	.71	28.0	38 19.400	76	23.200
14021	48.0	610.0	3.20	20.0	52.0	39.0	230.0	1.00	40.0	38 18.100	76	20.300
14031	47.0	440.0	3.10	14.0	45.0	34.0	210.0	.89	32.0	38 18.100	76	19.000
14041	41.0	420.0	2.60	8.9	33.0	23.0	140.0	.45	23.0	38 18.300	76	17.600
14051	20.0	180.0	1.40	4.9	18.0	12.0	62.0	-1.00	11.0	38 18.300	76	16.200

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 15

BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
15010	4.0	20.0	.14	.8	1.9	-1.0	9.4	.06	2.1	38	8.200	76	18.300
15020	33.0	280.0	2.40	9.7	22.0	21.0	120.0	.48	21.0	38	8.200	76	16.300
15030	45.0	370.0	3.30	11.0	29.0	25.0	160.0	.61	28.0	38	8.300	76	14.600
15040	26.0	170.0	1.80	8.3	19.0	13.0	83.0	.37	15.0	38	8.300	76	13.100
15050	8.0	33.0	.40	2.6	5.6	5.0	26.0	.15	5.0	38	8.300	76	11.200
15060	6.0	79.0	.41	2.4	5.4	3.0	20.0	-1.00	3.0	38	8.100	76	9.200
15070	6.0	68.0	.54	1.8	4.5	3.0	16.0	-1.00	2.9	38	8.200	76	7.000

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
15011	41.0	360.0	3.20	11.0	29.0	27.0	200.0	.27	27.0	38	8.200	76	18.300
15021	48.0	400.0	3.60	13.0	37.0	30.0	180.0	.57	28.0	38	8.200	76	16.300
15031	41.0	390.0	3.10	12.0	33.0	22.0	150.0	.44	22.0	38	8.300	76	14.600
15041	50.0	390.0	3.40	14.0	38.0	29.0	160.0	.44	23.0	38	8.300	76	13.100
15051	35.0	210.0	2.50	11.0	34.0	27.0	130.0	.43	28.0	38	8.300	76	11.200
15061	33.0	350.0	2.60	9.9	27.0	20.0	120.0	.30	20.0	38	8.100	76	9.200
15071	30.0	220.0	2.20	7.0	25.0	11.0	110.0	-1.00	14.0	38	8.200	76	7.000

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed

TRAVERSE NUMBER 16
BULK ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
16010	.0	.0	.00	.0	.0	.0	.0	.00	.0	0	.000	0	.000
16020	39.0	300.0	2.80	9.8	27.0	26.0	150.0	.59	44.0	38	.800	76	19.400
16030	46.0	380.0	3.80	12.0	29.0	30.0	180.0	.58	27.0	37	59.800	76	19.600
16040	51.0	440.0	4.10	14.0	67.0	50.0	640.0	.73	45.0	37	58.600	76	19.500
16050	13.0	120.0	.87	3.9	10.0	10.0	53.0	.29	9.7	37	57.500	76	19.300
16060	2.0	9.0	.06	.2	-1.0	-2.0	-3.0	-1.00	4.0	37	56.600	76	19.100

FINES ANALYSIS

ID	CR	MN	FE(%)	CO	NI	CU	ZN	CD	PB	LAT.		LONG.	
16011	27.0	370.0	2.20	6.0	24.0	12.0	190.0	-2.00	18.0	38	1.800	76	19.300
16021	42.0	440.0	3.00	11.0	35.0	24.0	190.0	.58	30.0	38	.800	76	19.400
16031	45.0	490.0	3.30	11.0	34.0	25.0	160.0	.44	23.0	37	59.800	76	19.600
16041	45.0	450.0	3.40	12.0	39.0	30.0	170.0	.59	60.0	37	58.600	76	19.500
16051	41.0	370.0	3.10	11.0	56.0	30.0	570.0	.59	29.0	37	57.500	76	19.300
16061	20.0	150.0	1.20	3.9	18.0	16.0	98.0	-1.00	12.0	37	56.600	76	19.100

-1.00 Trace -2.00 Not Detectable -3.00 Not Analyzed