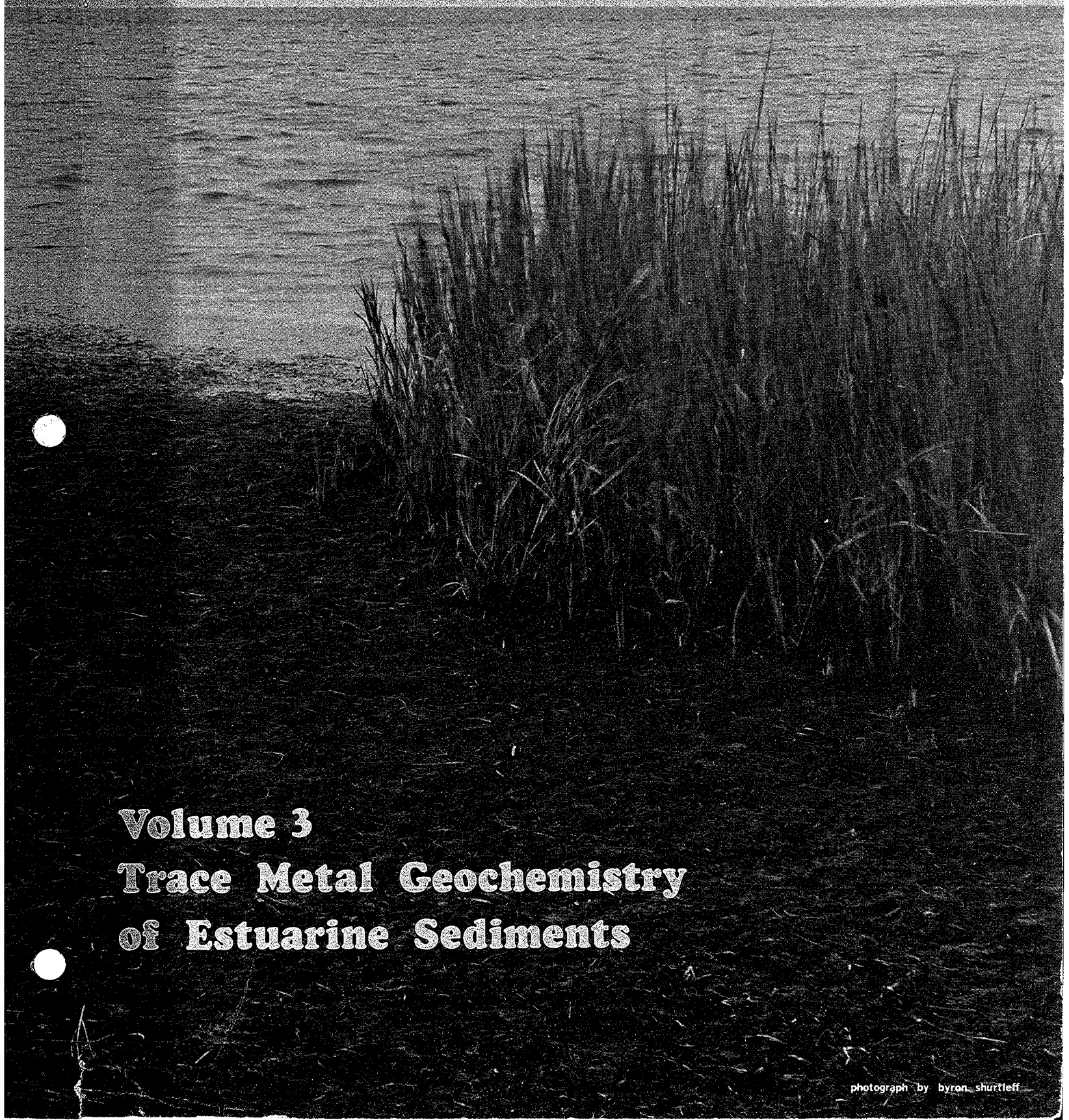
DELAWARE BAY REPORT SERIES



Volume 3
Trace Metal Geochemistry of Estuarine Sediments

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DELAWARE BAY REPORT SERIES

Volume 3

TRACE METAL GEOCHEMISTRY OF ESTUARINE SEDIMENTS

Report No. 1.
Richard N. Strom

Report No. 2.
Frederick Bopp, III and Robert B. Biggs

Report No. 3.
Frederick Bopp, III, Frederick K. Lepple, and Robert B. Biggs

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INTRODUCTION

For many years it has been known that colloidal and clay mineral particles act as scavengers for cations in solution in the marine and estuarine environment. The combination of high levels of industrial activity in the Delaware River watershed, the resurgence of the commercial oyster industry in Delaware Bay, and the tendency of oysters to remove metals from the environment and store them in their body tissues, stimulated an inquiry into the distribution of trace metals in the vicinity of oyster beds in Delaware Bay.

The first report in this section relates to the general distribution and composition of fine-grained sediments in the bay. In the second report, the relationship between the character of the fine-grained sediments and trace metal levels is developed, while in the third report, we have attempted to evaluate domestic sewage discharge as a source of metals in the estuarine environment.

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Report No. 1

CLAY MINERAL DISTRIBUTION IN THE DELAWARE BAY AND ESTUARY

Richard N. Strom

This report is the result of work funded in part by the University of Delaware.

SOURCES OF INFORMATION

Several investigations have been carried out on the distribution of fine grained sediments in the Delaware estuary. The U.S. Army Corps of Engineers has conducted extensive sediment sampling programs in an effort to alleviate some of the problems associated with channel maintenance. Neiheisel (1970) has reported on a recent, comprehensive program.

Oostdam (1971) studied the material in suspension at the mouth of the bay; and Jordan (1968), and Jordan and Oostdam (1969), have reported on the clay minerals in both suspended and bottom sediments in Delaware Bay.

Jordan and Groot (1962) analyzed a set of cores taken from a test boring which reaches into the Cretaceous Potomac group sediments at the site of the Delaware Memorial Bridge. Their report includes data on pollen analysis from this boring.

Strom (1970, unpublished data), investigated the clay minerals in transport in the headwaters of the Mispillion River and in the tidal portion of the Mispillion River, Cedar Creek and Slaughter Neck Creek.

Most of the data with the exception of Strom (1970), are reviewed in Oostdam (1971).

AERIAL DISTRIBUTION OF CLAY MATERIAL

The most comprehensive study of the clay materials in the estuary was conducted by the U.S. Army Corps of Engineers and reported by

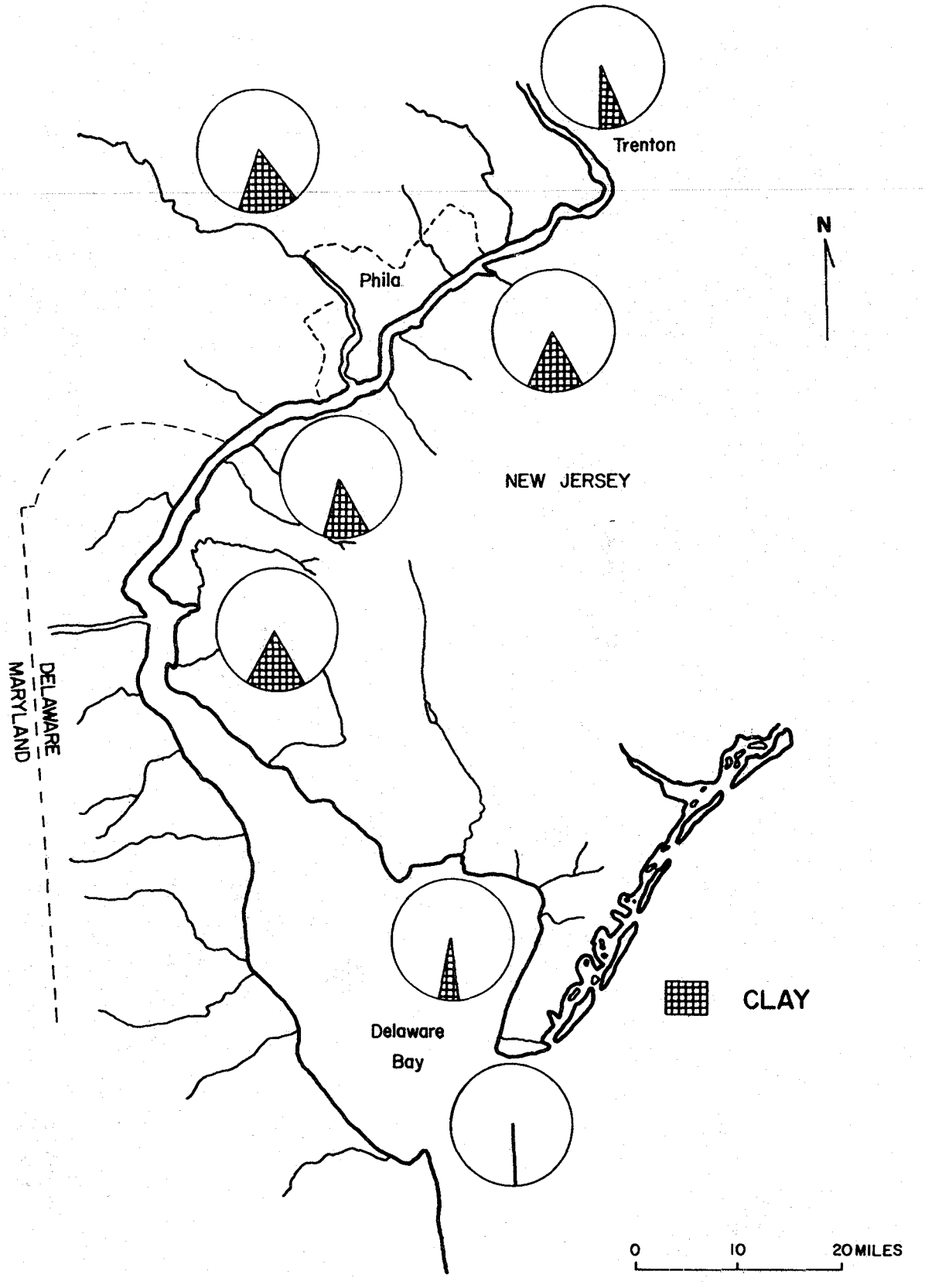

FIGURE 1: % CLAY in Delaware Bay and Estuary Bottom Sediments
(after Neiheisel, 1970)

Neiheisel (1970). Table 1 is a breakdown of the data from that report and shows the average texture and composition of the bottom sediments in the estuary. The data pertaining to the clay minerals has been extracted from this table and are shown in Table 2 and illustrated in Figures 1 and 2.

Clay sized inorganic material makes up only a small fraction (average = 4%) of the sediments in the open bay (Figure 1). The studies conducted by Jordan (1968), Jordan and Oostdam (1969), and Oostdam (1971) on the bottom and suspended sediments in the bay show that the bottom sediments are finer in the northern end of the bay than in the southern end and that the Holocene sediments have a thoroughly mixed clay fraction. The suspended clays are indistinguishable from the sedimented clays and they are homogeneous in composition throughout the bay.

The tidal estuary portion of the Delaware River contains considerable amounts of clay material (see Figure 1). Jordan and Groot (1962) have reported on the composition of Holocene sediments in cores taken in mid-channel at the Delaware Memorial Bridge. On the basis of pollen analysis and heavy mineral analysis, they tentatively conclude that the river was flushed of previously deposited Pleistocene river sediments by melt water from the retreating glaciers at the end of the Wisconsin glacial age. Since that event, the clay minerals deposited have had the same order of abundance as the present day clays being deposited in the channel. In the Delaware River north of Trenton, the clay content of the bottom sediments decreases significantly.

TABLE 1

Average Texture : Composition of Bottom Sediments in Delaware River from Trenton to the Capes (Neiheisel, 1970)

Constituents	At the Capes	Capes to Ship John Light	Ship John Light to Wilmington	Wilmington to Philadelphia	Philadelphia to Trenton	Delaware River North of Trenton	Schuykill River
Sample >44μ	98	81	37	45	25	80	28
Sample <44μ	2	19	63	55	75	20	72
			Average Composition of the >44μ Size Fraction				
Quartz	96.2	86.2	70.8	79.7	84.0	87.0	62.0
Feldspar	3.3	3.6	6.2	1.9	1.6	2.0	3.0
Mica	Trace	1.2	2.1	1.8	2.4	3.0	4.5
Coal	-	-	1.0	2.0	2.0	2.0	27.0
Heavy Mineral	0.5	3.5	3.0	3.0	2.0	4.0	3.0
Others	-	5.5	16.9	11.6	8.0	2.0	0.5
			Average Composition of the <44μ Size Fraction				
Quartz	77.3	51.8	44.9	47.4	51.0	66.0	40.0
Feldspar	11.2	16.3	12.8	12.4	11.5	3.0	10.0
Organics	0.7	2.5	2.0	5.8	7.8	5.0	19.0
Diatoms	Trace	1.7	3.0	6.0	3.5	Trace	2.0
Fe_2O_3	0.3	0.5	1.1	1.4	0.9	1.9	2.0
Clay	7.1	21.2	26.2	22.3	21.0	26.0	21.0
Coal	-	-	0.3	1.9	0.1	0.1	6.0
			Average Composition of the Clay Fraction				
Illite	72	59	65	65	57	50	65
Chlorite	23	26	20	15	29	26	18
Kaolinite	3	8	10	15	8	19	11
Montimorillonite	2	7	5	5	6	5	6
No. of Samples	3	15	11	20	5	1	13

TABLE 2

Clay Composition of Delaware Estuary Bottom Sediments*

	At the Mouth of Delaware Bay	The Capes to Ship John Light	Ship John Light to Wilmington	Wilmington to Philadelphia	Philadelphia to Trenton	Delaware River North of Trenton	Schuykill River
No. of Samples	3	15	11	20	5	1	13
Clay	0.14	4.0	16.5	12.3	15.8	5.2	15.1
Composition of Clay Fraction							
Illite	72	59	65	65	57	50	65
Chlorite	23	26	20	15	29	26	18
Kaolinite	3	8	10	15	8	19	11
Montmorillonite	2	7	5	5	6	5	6

* After Neiheisel (1970)

The composition of the clays is relatively uniform. Illite is by far the largest constituent. It makes up between 50 and 75% of the clay fraction. Smaller quantities of chlorite, kaolinite and montmorillonite are found. The minor variations between samples are probably not significant. Methods used to determine composition of samples, such as x-ray defraction techniques, are repeatable to only 5% (Biscaye, 1965). The larger variations, i.e. those over 10% are probably significant however, and reflect real differences in the composition of the clays and the influence of source areas and/or diagenesis.

The mineralogy of the clay portion of the tidal marsh sediments bordering on the Delaware side of the bay is essentially that of the bay itself (Strom, 1970). Volumetrically, the bay appears to have much larger sediment input into the salt marshes than the upland drainage and consequently, the clay minerals deposited in the salt marshes do not reflect the clay minerals in transport in the nontidal portion of the creeks emptying into them.

CATION EXCHANGE CAPACITY

No systematic studies of the cation exchange capacity of the clays in Delaware Bay appear to have been made up to the present time. The U.S. Army Corps of Engineers (1968) has analyzed 20 samples from the Marcus Hook shoal. Details of the procedure are not reported however, so that it can only be assumed that the clay fraction of the bulk sediment is the primary constituent entering into the reaction as

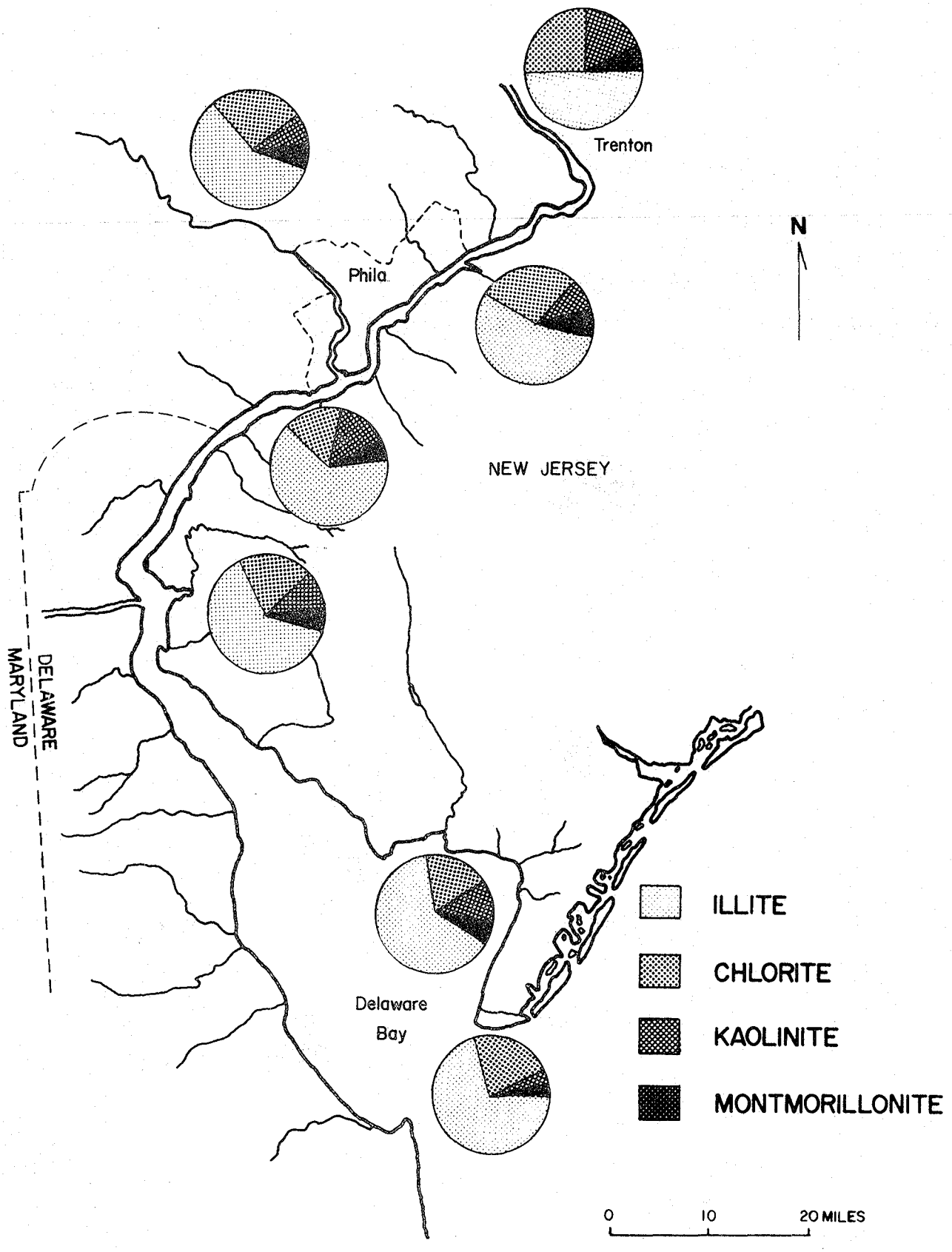

FIGURE 2: Composition of Clay Portion of Bottom Samples from Delaware Bay and Estuary (after Neiheisel, 1970)

suggested in Grim (1968, p. 188). The average value for the base-exchange capacity reported is 42.7 meg./100g. and they have a range of 35.7 - 47.6 meg./100g.

SOURCES

There appears to be no unique source of the clay material in the Delaware estuary. The relative contribution of the suspended sediments to shoaling in the channel has been estimated by the U.S. Army Corps of Engineers as follows (U.S. Army Corp of Engineers, 1968):

Source	Percent	(Dry) Tons/Year
1. Headwaters*	28	1,232 x 10^3
2. Tributaries*	22	968 "
3. Industry	15	660 "
4. Utilities		
Sanitary	11	484 "
Storm	2	88 "
5. Bay and ocean*	4	176 "
6. Miscellaneous		
Channel side slope	2	88 "
Mud flats & swamps	2	88 "
Estuary bank	2	88 "
Estuary erosion	10	440 "
Dredging	2	88 "
	100%	4,400 x 10^3 to NS/Y

According to this estimate, natural sources exterior to the system (*) contribute only 54% of the shoal material. Of these sources the headwaters of the Delaware contribute 52%, tributaries contribute 41% and the bay and ocean contribute 7%. Analyses of the composition of the clays in the bed load of headwaters and the major tributaries have been performed by the U.S. Army Corps of Engineers (1968) and are shown in Table 3.

TABLE 3

	Illite	Chlorite	Kaolinite	Vermiculite Montmorill
1. Delaware River at Yardley, Pa.	50	30	10	10
2. Schuylkill River	60	25	12	3
3. " "	63	16	18	3
4. Brandywine River	54	25	16	5

Tributary and headwater sources have also been studied in great detail by Neiheisel (1970), and he reports the following values for the composition of the clay fraction of suspended sediments:

TABLE 4

	Illite	Chlorite	Kaolinite	Vermiculite Montmorill
1. Delaware River north of Trenton	50	26	19	5
2. Schuylkill River	55	20	20	5
3. Other Piedmont streams (averaged)	46	18	30	6
4. Coastal Plain streams (Delaware - averaged)	57	20	16	7
5. Coastal Plain streams (New Jersey - averaged)	56	22	15	7

Data on the clays minerals in shelf sediments in the vicinity of Delaware Bay are not available. Reports for the mineralogy of clays on the continental slope indicate the relative abundance of

the clay species is approximately that of Delaware Bay (see Biscaye 1965, and Neiheisel, 1966).

The illite content in the bottom sediments of the estuary is high when it is compared to the reported mineralogy of the major source areas, i.e. the headwaters and the tributaries. Several explanations might account for this:

1. preferential deposition of illite by flocculation (?) or more rapid settling velocities in the estuary;
2. enhancement of the illite peak on x-ray defraction patterns by absorption of K from seawater as poorly crystallized (degraded ?) illite enters the estuary;
3. the contribution of clay sized material from the continental shelf has been underestimated.

SUMMARY

There is very little published data on the clay minerals in the Delaware Bay and estuary. The published data of Jordan, Jordan and Groot and Oostdam, all indicate that the clays are relatively homogeneous in composition within Delaware Bay. Studies by the U.S. Army Corps of Engineers (Philadelphia District), indicate that the maximum concentration of clays is within the estuarine portion of the Delaware River (from Ship John Light to Philadelphia). The salt marshes are also depositories of clay minerals. The major source of clays in the marshes is from the estuary system, rather than the headwaters of the creeks draining into them.

According to reports by the Corps of Engineers, there is little variation in the order of abundance of the clay mineral species. Illite predominates in all sediments and sediment sources. Chlorite is the next most abundant species with the exception of streams draining the Piedmont (Chester Creek and Brandywine Creek - Table 4), where kaolinite exceeds chlorite. Montmorillonite is relatively constant and usually less than 10%. The higher illite concentrations noted in estuarine samples have not yet been evaluated.

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Report No. 2

TRACE METAL ENVIRONMENTS NEAR SHELL BANKS IN DELAWARE BAY

Frederick Bopp, III

and

Robert B. Biggs

This report is the result of research sponsored by the National Oceanic and Atmospheric Administration, Office of Sea Grant, Department of Commerce, under Grant No. 2-35223.

PREFACE

This report represents an interim record of progress during Fiscal Year 1972 in one aspect of the geological investigation of Delaware Bay. Preliminary interpretations have been included as well as appendices presenting the raw data.

The authors felt that the inclusion of a layman's definition of "part per million" would be beneficial in order to emphasize to all readers the magnitude of the numbers with which we deal in trace metals. Dale W. Jenkins, director of the ecology program in the Office of Environmental Sciences of the Smithsonian Institute contributed this definition-- "The world's driest martini: one ppm of vermouth would be the equivalent of one ounce of vermouth in 7,800 gallons of gin." (Science, 177: pp. 476-77, 1972)

We thank Charles B. Weil and Roger D. Moose, of the Department of Geology, for taking the samples used, and Frederick K. Lepple, of the College of Marine Studies, for his assistance in the Laboratory and Data Reduction phases of this research.

The National Science Foundation, the National Oceanic and Atmospheric Administration, and agencies of the State of Delaware are free to use the contents in any way which serves the public interest, but are requested to respect the intention of the authors to publish the formal results of their investigation at a later date.

BACKGROUND

This paper reports the results of research for Fiscal Year 1972 into one aspect of the geological investigation of Delaware Bay. Biggs (1972) presented the results of a sedimentological survey of the oyster reef areas of Delaware Bay. Ninety-two discrete locations were sampled and analyzed for that study. The primary result of the survey was the observation that fine-grained sediments in Delaware Bay are concentrated to a large extent on the Delaware side of the bay. This led to the two-fold hypothesis that either the silts and clays have their source area along the Delaware shore, or there exist conditions for the preferential deposition of silt and clay sized particles along the Delaware shoreline, perhaps due to the Coriolis effect. While there is a vast amount of fine-grained material suspended in the coastal plain estuaries and in the nearshore waters of Delaware Bay, a reliable determination of its source has not yet been made. A corollary to the second hypothesis mentioned above provides the suggestion for a geochemical test of the hypothesis. That corollary was mentioned by Biggs (1972): "if extraneous materials (trace metals, pesticides, etc.) are attached to fine suspended particles, carried downriver, and deposited preferentially on the Delaware shore, then the Delaware side of the Bay is more susceptible to pollution sources from up-river."

INTRODUCTION

The primary objective of Fiscal Year 1972 research is to typify the trace metal geochemical aspects of the sedimentary environments which support oysters in Delaware Bay. These results would provide baseline information to be used in the oyster early-warning pollution monitoring system being developed by the State of Delaware and the University of Delaware under the auspices of the Sea Grant Program. A secondary objective of Fiscal Year 1972 research is to test the hypothesis outlined above. The tertiary objective of this project is an effort to characterize the trace metals determined with respect to 1) their generalized source (i.e., the Delaware River, the ocean, etc.), and 2) the primary factor(s) controlling their distribution.

Most of the original ninety-two samples used by Biggs (1972) had been kept frozen and were used for this research. In addition, twelve samples were obtained from viable oyster reefs in Delaware Bay (labelled B-1, B-2, and B-4 through B-13), and twenty-three samples were obtained which extended the area of investigation to the south and east (labelled SG-101-S-72 through SG-146-S-72). Table 1 is a listing of the positions of the samples from 118 discrete locations used in this project. Sampling and field handling techniques for all samples were those used by Biggs (1972). No sediment analyses are available for the newly procured samples. Figure 1 is a chart of the research area on which the sample positions are plotted.

Table 1: Positions in Latitude and Longitude for Delaware Bay Bottom Sediment Grab Samples.

SAMPLE	LAT.	LONG.	SAMPLE	LAT.	LONG.
SG-1A-W-71	39-15.40	75-15.40	SG-42-W-71	39-23.20	75-26.00
SG-1B-W-71	39-15.40	75-15.40	SG-43-W-71	39-21.20	75-23.85
SG-2-W-71	39-14.70	75-16.75	SG-44-W-71	39-20.50	75-24.55
SG-4A-W-71	39-14.00	75-18.25	SG-45-W-71	39-19.90	75-25.20
SG-4B-W-71	39-14.00	75-18.25	SG-46-W-71	39-19.65	75-25.50
SG-5-W-71	39-13.60	75-19.05	SG-47-W-71	39-15.00	75-23.40
SG-6-W-71	39-13.35	75-19.55	SG-48-W-71	39-15.35	75-22.30
SG-7-W-71	39-13.25	75-19.85	SG-49-W-71	39-15.65	75-21.75
SG-8A-W-71	39-13.10	75-20.20	SG-50-W-71	39-15.85	75-21.35
SG-8B-W-71	39-13.10	75-20.20	SG-51-W-71	39-16.10	75-20.60
SG-9-W-71	39-12.60	75-21.05	SG-52-W-71	39-16.65	75-19.75
SG-10-W-71	39-11.95	75-22.20	SG-53-W-71	39-17.25	75-18.95
SG-11-W-71	39-22.50	75.29.05	SG-55-W-71	39-17.35	75-17.80
SG-12-W-71	39-22.40	75-29.65	SG-56-W-71	39-15.35	75-15.50
SG-14-W-71	39-22.80	75-27.30	SG-57-W-71	39-13.95	75-18.35
SG-15-W-71	39-23.00	75-26.35	SG-59-W-71	39-13.00	75-20.35
SG-16-W-71	39-23.15	75-25.90	SG-60-W-71	39-13.90	75-21.10
SG-17-W-71	39-23.10	75-26.10	SG-61A-W-71	39-14.30	75.21.70
SG-18A-W-71	39-22.85	75-26.75	SG-61B-W-71	39-14.30	75-21.70
SG-18B-W-71	39-22.85	75-26.75	SG-62-W-71	39-14.80	75-21.90
SG-19-W-71	39-19.40	75-25.75	SG-63-W-71	39-15.85	75-22.70
SG-20-W-71	39-19.60	75-20.75	SG-64-W-71	49-16.25	75-23.00
SG-21-W-71	39-20.00	75-25.10	SG-65-W-71	39-16.70	75-23.40
SG-22-W-71	39-20.25	75-24.75	SG-66-W-71	39-13.30	75-19.70
SG-23-W-71	39-20.90	75-24.35	SG-67-W-71	39-12.35	75-22.75
SG-24-W-71	39-21.20	75-24.10	SG-68-W-71	39-13.05	75-22.40
SG-25-W-71	39-06.60	75-20.35	SG-70-W-71	39-13.60	75-21.70
SG-26-W-71	39-07.00	75-21.05	SG-71-W-71	39-13.25	75-21.30
SG-27-W-71	39-07.60	75-20.05	SG-72-W-71	39-11.75	75-20.75
SG-28-W-71	39-06.45	75-19.45	SG-73-W-71	39-10.95	75-20.60
SG-29-W-71	39-07.30	75-19.25	SG-74-W-71	39-06.90	75-19.10
SG-30-W-71	39-07.75	75-18.55	SG-75-W-71	39-06.15	75-18.85
SG-31-W-71	39-08,10	75-17.65	SG-76-W-71	39-03.95	75-16.95
SG-32-W-71	39-08.15	75-17,45	SG-77-W-71	39-02.85	75-16.90
SG-33-W-71	39-08.40	75-16.65	SG-78-W-71	39-02.05	75-15.65
SG-34-W-71	39-08.75	75-15.85	SG-80-W-71	39-04.95	75-16.50
SG-35-W-71	39-09.05	75-14.75	SG-81-W-71	39-05.20	75-16.85
SG-36-W-71	39-09.35	75-14.10	SG-82-W-71	39-06,00	75-16.80
SG-37-W-71	39-10.10	75-12.50	SG-83-W-71	39-07.20	75-17.20
SG-39-W-71	39-10.70	75-09.80	SG-84-W-71	39-08,75	75-18.25
SG-40-W-71	39-23.00	75-26.85	SG-85-W-71	39-09.70	75-19.10
SG-41-W-71	39-25.15	75-26.20	SG-86-W-71	39-09.80	75-17.40

Table 1 (cont.)

SAMPLE	LAT.	LONG.	SAMPLE	LAT.	LONG.
SG-87-W-71	39-11.15	75-18.60	SG-123-S-72	39-06.10	75-14.80
SG-88-W-71	39-21-70	75-23.80	SG-124-S-72	39-06.95	75-14.40
SG-89-W-71	39-20.35	75-27.10	SG-125-S-72	39-07.25	75-13.70
SG-90-W-71	39-21.20	75-24.10	SG-126-S-72	39-08.40	75-11.40
SG-101-S-72	38-59.80	75-16.90	SG-127-S-72	39-09.15	75-10.30
SG-102-S-72	39-00.50	75-17.45	SG-128-S-72	39-10.10	75-08.20
SG-103-S-72	39-00.80	75-16.80	SG-146-S-72	39-01.40	75-08.20
SG-104-S-72	39-01.35	75-16.25	B-1	39-17.40	75-23.50
SG-105-S-72	39-02.20	75-13.60	B-2	39-16.42	75-23.38
SG-107-S-72	39-02.70	75-12.20	B-4	39-12.87	75-22.57
SG-110-S-72	39-04.45	75-08.00	B-5	39-12.59	75-22.48
SG-111-S-72	39-07.40	75-08.00	B-6	39-12.32	75-22.32
SG-115-S-72	39-00.65	75-13.80	B-7	39-12.60	75-21.68
SG-116-S-72	39-03.00	75-18.90	B-8	39-04.50	75-20.25
SG-117-S-72	39-04.05	75-21.95	B-9	39-06.87	75-18.10
SG-118-S-72	39-04.60	75-20.50	B-10	39-09.70	75-20.92
SG-119-S-72	39-05.20	75-19.30	B-11	39-15.45	75-21.06
SG-120-S-72	39-05.50	75-18.30	B-12	39-13.64	75-20.55
SG-121-S-72	39-05.60	75-18.05	B-13	39-13.20	75-20.60
SG-122-S-72	39-05.70	75-17.70			

PHILOSOPHY, AND THE CONCEPT OF ENVIRONMENTAL ACTIVITY

The basic philosophy subscribed to in undertaking this research is that the trace metals which are of interest are only those which are available for introduction to the marine food web through naturally occurring biological or chemical processes; i.e., those trace metals which are "environmentally active." Those cations so firmly bonded to, or exchanged within, mineral grains that natural biochemical processes cannot remove them are of no concern to this investigation. The laboratory extraction procedure used was designed to approximate, however crudely, the severest conceivable naturally occurring biochemical conditions, without completely degrading the sediments.

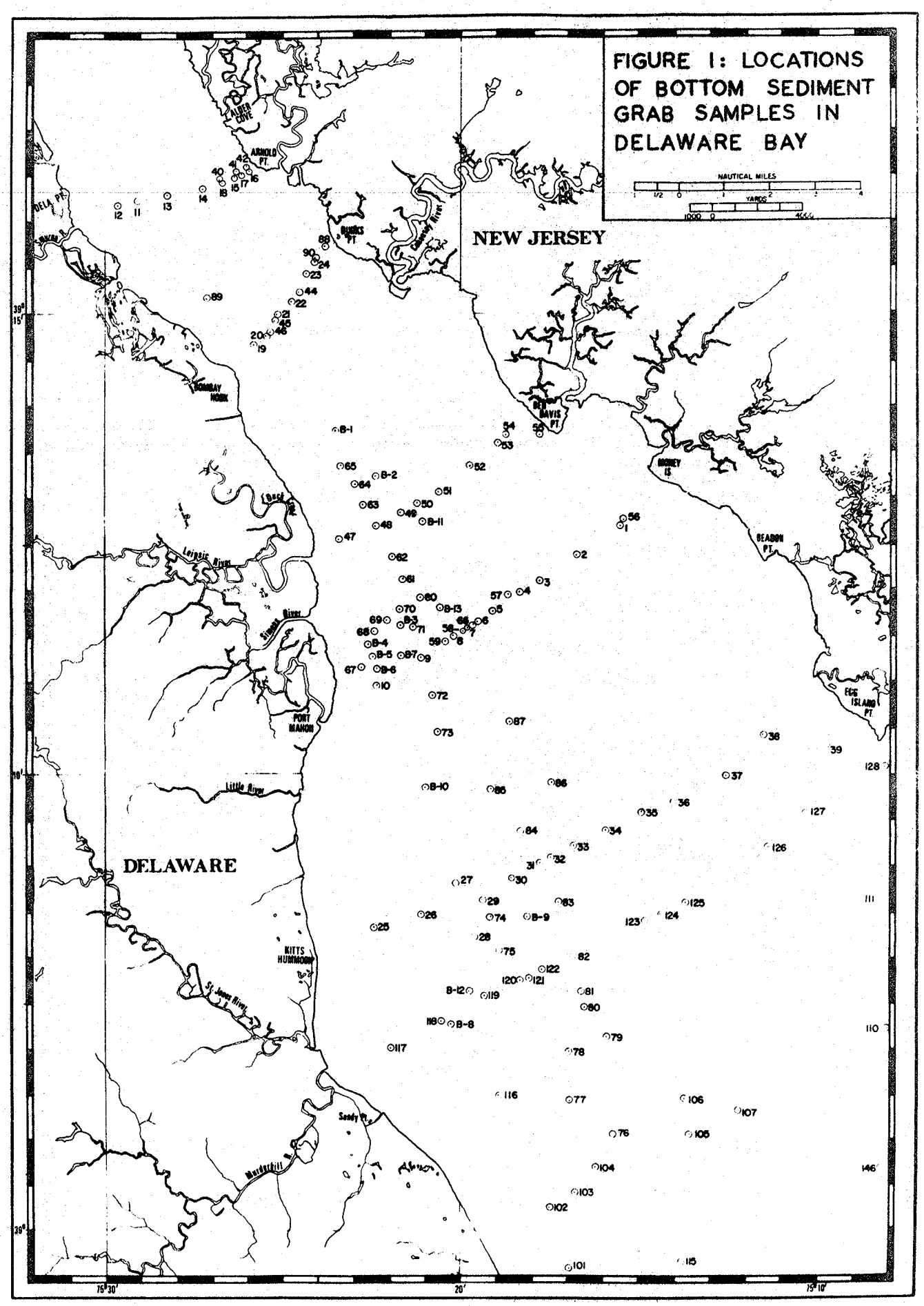

FIGURE 1: LOCATIONS OF BOTTOM SEDIMENT GRAB SAMPLES IN DELAWARE BAY

It must be borne in mind, however, that any given sediment particle enters our laboratory extraction system only once, and then is gone from consideration. In Delaware Bay it is possible for the resident epi- and infauna to recycle the top few centimeters of sediment several times each year, thereby making each particle in the natural habitat available for cation stripping at the very least more than once (see also: Gordon, 1966; and Rhoads, 1963, for examples in other estuarine systems). This is partial justification for making the treatment used here as severe as it is. In addition to this is the fact that the extraction technique used here is a simple, reproducible, inorganic process, whereas the gut-chemistry of even the simplest biological specimen is a complex scheme of enzymes, catalysts and organic acids. The results of the inorganic technique used here are generalized and have a wide range of applications, whereas the results of a biochemical extraction would be species-specific and, therefore, of limited use.

For the purpose of this research the environmentally active trace metals are defined to be those cations which can be separated from 3 grams of dried and disaggregated sediment, from the silt and clay fraction, by leaching with 500 mls, of 10% (vol/vol) HCl in distilled/deionized water at 70°C for 96 hours.

LABORATORY PROCEDURES

General: All solutions used in handling, separating, extracting and analyzing the samples were prepared using distilled/deionized

water, or Fisher Certified A.C.S. solvents. With the exception of a 3-inch, 63-micron sieve, all laboratory equipment and utensils used in the handling of the samples were made of polyethylene or other plastic, or of ceramic, in order to eliminate, insofar as is economically practical, the probability of outside contamination. All chemicals used in the analyses were Fisher Certified A.C.S. Reagents, and all standard solutions were prepared from Fisher Certified Atomic Absorption Standards.

Silt and Clay Separation: A subsample of each of the samples, wet weight approximately 250 grams, was transferred to an acid-washed, double AA-water-washed, 600 ml. plastic beaker. ("AA-water" is used interchangeably with "distilled/deionized water.") AA-water was added and the sample aggitated until suspended. The suspensate was passed through a U. S. Standard No. 230, 63-micron mesh sieve, and was collected in an acid-washed, double AA-water washed, 1 liter polyethylene bottle. Then the collected suspensate was centrifuged at maximum RPM in a Universal Model UV Centrifuge, using Nalgene tubes, for 30 minutes. The supernatant, containing some non-separable colloids, was discarded. The sediment particles were transferred to a 50 ml. plastic beaker and dried at 70°C. The dried sediment was milled to uniform size, determined only by visual approximation, in a Spex Industries Model 8000 Mixer Mill, using a ceramic powder vial and ball. The resulting powder was transferred to a plastic vial, capped and stored.

Trace Metal Extraction: Polyethylene 500 ml. bottles were pre-treated by leaching with 10% (vol/vol) HCl at 70°C for 96 hours immediately prior to use for trace metal extractions. Subsamples of the dried and disaggregated silts and clays were weighed out at 3.00 $\pm$ 0.001 grams using a Mettler Analytical Balance. The weighed samples were transferred to the acid-treated bottles and 500 mls. of 10% (vol/vol) HCl were added. The acid was prepared by diluting 50 mls. of concentrated HCl (sp. gr. = 1.19) to 500 mls. with AA-water, in order to avoid error due to the electrostriction of the AA-water by the addition of chloride ion. The bottles were capped tightly, shaken vigorously, and heated at 70 $\pm$ 4°C for 96 hours. The bottles were shaken and vented periodically during the course of the heated extraction. When 96 hours had elapsed the solutions were vacuum filtered while hot using a Millipore filtration apparatus with AAWP 0.8 micron filters. The supernatant was returned to the washed bottle in which it had been extracted, capped and stored in a cool place pending analysis.

ANALYTICAL CONDITIONS

General: All analyses were conducted using a Jarrell-Ash Model 800 Atomic Absorption Spectrophotometer in association with twin Honeywell Electronik 17 single-event pen recorders set for 15-inches per hour chart speed. Response of the recorders was 1 second for 1 millivolt full-scale deflection. Hollow cathode lamps used for atomic absorption were all single-element, high spectral output, Jarrell-Ash lamps.

The extraction technique used was designed to yield trace metal concentrations within the direct-reading limits of the spectrophotometer for most of the metals of interest. Background corrections were investigated on a routine basis, but no significant differences were noted between corrected and uncorrected readings. As the use of the background correction, B/A mode, reduced the signal-to-noise ratio, it was not used.

Iron: Iron concentrations were extremely high in the extraction solutions. A secondary absorption line was selected to allow accurate determinations to be made. The following analytical conditions prevailed during the analysis for iron:

Lamp Current	8 ma
Wavelength	3720 Å
RB	2.00 (arbitrarily set)
MB	1.96
HVB	-311
Exit Slit Pair	900-1000μ
Mode	% Absorption--Direct
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = scfh
Detection Limit	0.01 μg/ml
Sensitivity	± 0.05 μg/ml

Magnesium: The magnesium concentrations encountered were too high to allow the use of the primary 2852 Å line, and they were too low to allow reliable use of the secondary 2025 Å line in the % Absorption mode. Therefore, the Absorbance mode was adopted using the primary wavelength to allow for raising the upper detection

limit. The following analytical conditions prevailed during the analysis for magnesium:

Lamp Current	10 ma
Wavelength	2852 Å
RB	2.00 (arbitrarily set)
MB	2.00
HVB	-340
Exit Slit Pair	75-100μ
Mode	Absorbance--Direct
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = 4 scfh
Detection Limit	0.0004 μg/ml
Sensitivity	± 0.004 μg/ml

Zinc: These analyses were routine with no unusual conditions. The following analytical conditions prevailed during the analysis for zinc:

Lamp Current	7.5 ma
Wavelength	2139 Å
RB	2.00 (arbitrarily set)
MB	2.00
HVB	-470
Exit Slit Pair	75-100μ
Mode	% Absorption--Direct
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = scfh aux. air = scfh
Detection Limit	0.003 μg/ml
Sensitivity	± 0.015 μg/ml

Chromium: The signal-to-noise ratio for chromium at the concentrations encountered in most of the extraction solutions made the use of the % Absorption Mode unreliable. The Concentration

mode with full signal expansion was adopted, along with maximum damping at the pen recorder in complement of the maximum damping at the spectrophotometer signal output. The following analytical conditions prevailed during the analysis for chromium:

Lamp Current	10 ma.
Wavelength	3579 Å
RA	2.00 (arbitrarily set)
MA	2.00
HVA	-390
Exit Slip Pair	150-200μ
Mode	Concentration--10 (maximum)
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = 4 scfh
Detection Limit	0.005 μg/ml
Sensitivity	± 0.06 μg/ml

Copper: The concentrations of copper encountered in the extract were in the lower end of the reliable detection range. In order to overcome the low signal-to-noise ratio, the lamp current was raised above the normal operating currents, and exit slits were opened wide to allow the maximum throughput of energy. The following analytical conditions prevailed during the analysis for copper:

Lamp Current	15 ma.
Wavelength	3247 Å
RA	2.00 (arbitrarily set)
MA	1.36
HVA	-330
Exit Slit Pair	900-1000μ
Mode	% Absorption--Direct
Damping	3 (1-3 scale of reducing noise)

Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = 4 scfh
Detection Limit	0.003 µg/ml
Sensitivity	± 0.04 µg/ml

Lead: The concentrations of lead encountered in the sediment extract were in the lower limits of reliable detection. However, use of the secondary 2833Å line was required because the signal-to-noise ratio on the primary 2170Å line approached unity. Despite the low signal-to-noise ratio, reproducible standard curves were recorded on three occasions using the secondary wavelength. No further steps were taken to enhance the signal. The following analytical conditions prevailed during the analysis for lead:

Lamp Current	5 ma
Wavelength	2833 Å
RA	2.00 (arbitrarily set)
MA	1.75
HVA	-490
Exit Slit Pair	150-200µ
Mode	% Absorption--Direct
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = 4 scfh
Detection Limit	0.03 µg/ml
Sensitivity	± 0.30 µg/ml

Cadmium: The concentrations of cadmium encountered were so low as to discourage any confidence in the data. Signal-to-noise ratio in these concentrations is virtually 1, with several samples registering concentrations equal to the Detection Limit for direct reading. Attempts to use the concentration mode only served to

lower the signal-to-noise ratio further. Despite the low level of confidence in the data, the method did yield reproducible standard curves, and so the results are presented. The following analytical conditions prevailed during the analysis for cadmium:

Lamp Current	8 ma
Wavelength	2288 Å
RB	2.00 (arbitrarily set)
MB	1.90
HVB	-540
Exit Slit Pair	425-500μ
Mode	% Absorption--Direct
Damping	3 (1-3 scale of reducing noise)
Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 4 scfh aux. air = 4 scfh
Detection Limit	0.003 μg/ml
Sensitivity	± 0.02 μg/ml

Mercury: Mercury analyses were performed using a flameless, cold vapor technique, in which a quartz cell replaces the burner head. The quartz cell is aligned in the optical beam path, and is attached to a compressed air circulatory system and a series of gages and stopcocks. The system was purged by running air through the plumbing into the quartz cell and venting while the spectrophotometer was tuned. Two-ml aliquots of the extraction solution were pipetted into ground glass reaction vessels. Mercury bound inorganically within the solutions was reduced to elemental Hg by the addition of 0.3 ml stannous chloride solution (20% wt/vol in concentrated HCl). The elemental mercury was carried by the air stream into the quartz cell. The flameless vapor technique is highly sensitive, and has an upper limit of reliability of

200 nannograms of mercury per aliquot. Reliable concentrations of Hg were read in the 0.2-5.0 ppb range. Calibration was accomplished with a 10 ppb standard, and linearity was assumed between zero and 10 ppb. The following analytical conditions prevailed during the analysis for mercury:

Lamp Current	5 ma
Wavelength	2537 Å
RB	2.00 (arbitrarily set)
MB	1.87
HVB	-395
Exit Slit Pair	900-1000μ
Mode	Concentration--10 (maximum)
Damping	3 (1-3 scale of reducing noise)
Air Pressure to Cell	0.5 scfh
Detection Limit	0.2 nannograms/ml
Sensitivity	± 0.15 nannograms/ml

Nickel: In trying to analyze for nickel by direct aspiration the signal-to-noise ratio approached 1 in all modes of operation. An evaporation was carried out which yielded a 2.5X concentrated solution. The flame was tuned down to extremely lean conditions, and no auxilliary oxidant was used. These measures brought the signal-to-noise ratio to within acceptable limits, and reliable results were obtained. The following conditions prevailed during the analysis for nickel:

Lamp Current	10 ma
Wavelength	2320 Å
RA	2.00 (arbitrarily set)
MA	1.80
HVA	-620
Exit Slit Pair	75-100μ
Mode	% Absorption-- Direct, 2.5X
Damping	3 (1-3 scale of reducing noise)

Burner Slot	10 cm.
Flame	air = 15 scfh acetylene = 2 scfh aux. air = 0 scfh
Detection Limit	0.01 µg/ml
Sensitivity	± 0.1 µg/ml

Strontium: Analysis for strontium was carried out in the flame emission mode, using a nitrous oxide/acetylene flame. The signal-to-noise ratio was moderately favorable and reasonable reproducibility of the standard curves was attained. However, a gradual decline in sensitivity was noted as analyses proceeded. The manufacturer provides no sensitivity specification for metals detected by flame emission--it was assumed that the sensitivity was one order of magnitude more coarse than the detection limit. The following analytical conditions prevailed during the analysis for strontium:

Wavelength	4607 Å
Mode	Flame Emission
Flame	nitrous oxide = 9 scfh acetylene = 6 scfh aux. N_2O = 4 scfh
Zero Setting	3.08
Sensitivity Setting	7.66
Detection Limit	0.005 µg/ml
Sensitivity	± 0.05 µg/ml

EMISSION SPECTROPHOTOMETRY

Prior to accomplishing the analyses outlined above, it was desirable to determine gross presence-absence, and rough approximations of concentrations, of the trace metals of interest here. Of the many methods available to determine total chemistry of a

sediment sample, emission spectrophotometry was chosen. The new samples from the oyster reefs were separated as described above, and small amounts of each of these samples were sent to the E. I. DuPont de Nemours Co., Wilmington, Delaware for emission spectrophotometric determinations. Along with these samples were sent samples of bottom sediments from each of the larger tributary tidal estuaries which empty into Delaware Bay, and samples of dried oyster tissues from each of the 25 sites sampled. The results of emission spectrophotometric determinations are tabulated here in Appendix A.

RESULTS

Table 2 contains a tabulation of all the concentrations of trace metals determined during Fiscal Year 1972 research. These concentrations are expressed as micrograms per gram, or parts per million, of sediments finer than 63 microns.

The values presented in Table 2 were used to plot the geographic variations among the ten metals determined on the chart of the research area presented as Figure 1. Figures 2 through 11 are plots of the geographic variations in Delaware Bay bottom sediments of iron, magnesium, zinc, chromium, copper, lead, cadmium, mercury, nickel and strontium, respectively. Contour intervals for each plot were chosen to satisfy the following conditions: 1) contour intervals had to be of a uniform interval, 2) they had to bracket approximately 90% of all the data, and 3) the intervals had to be broad enough to illustrate general trends without the introduction of specific

Table 2: Concentrations of Trace Metals in Delaware Bay Bottom Sediments, Expressed as Parts Per Million of the <63 micron Sediment Fraction. (Mercury listed in PPB)

SAMPLE	Fe	Mg	Zn	Cr	Cu	Pb	Cd	Hg	Ni	Sr
SG-1A-W-71	34500	6850	388	113	98	103	3.8	908	625	161
SG-1B-W-71	39350	8000	495	127	68	107	4.2	983	725	160
SG-2-W-71	43350	9400	475	133	43	103	2.5	975	895	130
SG-4A-W-71	44000	7950	168	100	34	73	2.5	708	600	117
SG-4B-W-71	32650	4150	78	33	9	50	0.8	113	625	56
SG-5-W-71	42350	7400	522	117	65	167	3.3	1142	850	117
SG-6-W-71	49150	6650	363	113	58	127	2.2	958	1167	70
SG-7-W-71	42650	7150	435	100	40	117	2.7	792	175	110
SG-8A-W-71	45000	6500	400	92	86	167	2.5	1291	1035	83
SG-8B-W-71	44000	7950	413	86	62	113	2.5	917	225	94
SG-9-W-71	42850	8500	500	111	47	103	4.2	917	770	114
SG-10-W-71	37150	7550	317	80	34	83	2.2	783	592	105
SG-11-W-71	28500	4400	278	130	50	157	2.5	750	478	53
SG-12-W-71	33150	3850	290	113	43	162	1.7	825	492	40
SG-14-W-71	33000	6850	1875	119	163	250	8.3	1783	650	48
SG-15-W-71	42150	5400	875	150	108	200	3.8	792	675	46
SG-16-W-71	33650	3700	67	95	86	54	1.0	133	525	32
SG-17-W-71	32500	4250	345	108	43	93	2.5	358	358	52
SG-18A-W-71	46350	6900	1100	133	74	208	2.2	1350	775	67
SG-18B-W-71	47500	7050	558	161	102	152	1.0	783	775	59
SG-19-W-71	17350	2650	48	80	50	25	0.8	133	295	48
SG-20-W-71	39350	4050	287	150	50	78	1.6	783	500	53
SG-21-W-71	43150	8400	100	83	18	25	0.8	86	417	56
SG-22-W-71	26850	4850	80	62	18	20	0.8	108	342	48
SG-23-W-71	41500	4100	1200	150	75	205	2.5	2275	925	155
SG-24-W-71	57650	7400	2667	282	98	1083	3.3	975	1717	121
SG-25-W-71	37150	6250	288	120	25	73	2.2	725	545	62
SG-26-W-71	37650	7550	317	153	40	107	1.0	558	403	59
SG-27-W-71	32650	5850	357	133	43	88	2.5	1292	425	80
SG-28-W-71	37250	7000	400	192	115	184	3.7	536	592	77
SG-29-W-71	32000	7300	342	153	40	54	0.8	583	367	210
SG-30-W-71	24500	4650	217	168	28	44	0.8	500	283	56
SG-31-W-71	35650	7250	442	175	43	68	1.7	725	358	75
SG-32-W-71	36650	7500	353	212	43	73	2.5	808	462	75
SG-33-W-71	38150	9150	310	247	52	103	0.5	583	545	267
SG-34-W-71	52000	10250	683	268	65	157	4.3	2150	873	155
SG-35-W-71	41250	8650	312	209	41	96	2.5	863	717	144
SG-36-W-71	41150	9150	412	187	51	113	2.2	766	808	94
SG-37-W-71	27350	8150	435	199	209	167	4.3	1199	617	506
SG-39-W-71	35350	8100	637	139	40	100	4.5	833	650	205
SG-40-W-71	47150	5150	222	167	62	63	3.2	371	833	45

Table 2 (cont.)

SAMPLE	Fe	Mg	Zn	Cr	Cu	Pb	Cd	Hg	Ni	Sr
SG-41-W-71	36000	6250	100	179	86	73	2.0	86	583	40
SG-42-W-71	37850	6300	110	158	123	78	1.5	200	378	38
SG-43-W-71	45650	7500	833	249	77	267	2.3	1625	1045	148
SG-44-W-71	50000	7800	5833	447	252	890	11.3	1666	3633	520
SG-45-W-71	27000	5750	83	208	18	47	2.2	166	608	43
SG-46-W-71	28500	4250	203	216	86	142	1.5	725	608	32
SG-47A-W-71	33500	5550	267	159	68	217	2.3	600	617	32
SG-47B-W-71	26500	4400	192	148	28	68	2.2	408	625	27
SG-48-W-71	34000	7600	305	193	33	78	1.5	642	637	112
SG-49-W-71	31500	6650	383	185	43	73	1.5	600	762	107
SG-50-W-71	43350	8450	525	258	58	225	3.5	875	925	121
SG-51-W-71	41850	10150	408	205	56	183	3.2	2058	750	235
SG-52-W-71	32000	6100	167	148	22	59	1.0	183	670	70
SG-53-W-71	44000	8900	440	277	171	375	2.3	1750	943	154
SG-55-W-71	31250	4400	95	250	260	250	1.5	938	463	23
SG-56-W-71	36850	7050	105	227	135	37	0.8	100	550	15
SG-57-W-71	33350	6550	90	256	34	21	1.5	128	508	32
SG-59-W-71	28850	5750	333	184	40	88	1.5	750	537	43
SG-60-W-71	37000	7850	442	362	80	208	2.2	1058	692	93
SG-61A-W-71	37000	7550	422	280	68	131	2.2	1917	---	74
SG-61B-W-71	28850	4650	125	110	47	88	1.0	371	667	23
SG-62-W-71	30850	5200	325	200	71	63	2.0	630	500	27
SG-63-W-71	40650	8700	375	185	47	88	2.3	558	492	83
SG-64-W-71	38350	6900	103	128	77	37	1.0	228	570	27
SG-65-W-71	41350	7000	595	174	250	242	1.0	825	775	32
SG-66-W-71	45150	8350	1042	265	71	200	3.2	2916	767	88
SG-67-W-71	26000	5600	325	143	40	47	1.5	350	453	37
SG-68-W-71	25000	4600	242	167	38	83	0.8	433	442	78
SG-70-W-71	24150	3700	96	178	47	68	1.0	175	375	74
SG-71-W-71	28650	4700	588	216	68	146	1.7	458	528	74
SG-72-W-71	31000	6900	350	188	40	124	2.5	562	428	78
SG-73-W-71	29150	6300	458	158	28	93	2.5	562	442	78
SG-74-W-71	15900	4100	267	145	49	56	2.5	197	183	146
SG-75-W-71	44500	9150	483	206	89	155	2.7	96	603	205
SG-76-W-71	38350	9050	262	193	56	88	2.7	1458	508	205
SG-77-W-71	42000	8200	420	276	49	131	3.3	1442	558	140
SG-78-W-71	20650	2050	138	227	25	66	2.0	1033	303	41
SG-80-W-71	54850	9900	372	392	100	183	3.3	1708	742	215
SG-81-W-71	67250	10500	560	196	109	300	3.8	4413	1038	219
SG-82-W-71	55150	9150	640	267	63	241	3.3	1375	903	230
SG-83-W-71	41150	8350	373	267	63	111	2.0	691	658	109
SG-84-W-71	23850	4400	237	160	46	88	2.0	113	370	157
SG-85-W-71	26650	4450	222	250	35	66	1.7	408	433	99
SG-86-W-71	26750	4900	200	250	48	91	2.5	267	363	125

Table 2 (cont.)

SAMPLE	Fe	Mg	Zn	Cr	Cu	Pb	Cd	Hg	Ni	Sr
SG-87-W-71	31833	5500	292	203	73	138	1.7	475	475	93
SG-88-W-71	38500	8050	800	348	94	208	4.0	4700	455	522
SG-89-W-71	31650	5100	90	160	53	26	1.3	161	425	60
SG-90-W-71	46500	5100	212	232	143	292	1.0	875	742	50
SG-101-S-72	30850	6850	233	118	49	83	1.3	250	475	50
SG-102-S-72	38350	8450	290	227	63	118	2.0	475	478	125
SG-103-S-72	32350	7150	230	232	59	99	1.7	350	403	125
SG-104-S-72	37000	7200	295	238	86	188	1.7	250	478	140
SG-105-S-72	42350	7600	283	203	63	111	2.0	313	608	161
SG-107-S-72	32250	8050	243	205	84	99	3.8	345	438	763
SG-110-S-72	27650	6350	217	155	333	155	1.3	325	403	93
SG-111-S-72	30500	9000	300	355	95	138	2.0	590	510	535
SG-115-S-72	36500	8050	225	197	49	83	1.3	313	542	140
SG-116-S-72	42350	10850	525	214	225	188	1.7	396	692	297
SG-117-S-72	26000	5000	202	113	32	83	1.0	650	303	64
SG-118-S-72	26650	5200	203	190	39	88	1.0	288	358	97
SG-119-S-72	24650	5600	205	125	49	99	1.0	458	342	64
SG-120-S-72	23000	5100	175	118	35	99	0.7	371	358	69
SG-121-S-72	35650	7400	300	178	53	208	1.0	350	487	178
SG-122-S-72	63500	9700	420	313	84	400	2.0	433	905	140
SG-123-S-72	36350	7050	343	208	56	131	1.7	360	525	89
SG-124-S-72	43000	9650	485	303	93	250	2.5	417	542	272
SG-125-S-72	26500	6150	223	143	39	105	1.3	325	342	125
SG-126-S-72	40850	8650	400	130	76	124	1.0	408	600	248
SG-127-S-72	24850	6350	303	178	89	105	3.3	313	320	751
SG-128-S-72	33650	6650	183	150	76	105	1.7	350	283	78
SG-146-S-72	44150	8650	313	197	80	175	1.3	328	537	156
B1	28350	4700	143	140	18	31	1.7	208	403	45
B2	36500	5150	372	184	46	118	1.3	550	512	64
B4	32850	6900	283	124	35	83	1.3	338	467	64
B5	33850	6950	338	103	39	118	1.3	328	428	74
B6	32350	6400	280	130	39	105	1.7	242	353	89
B7	31000	5900	338	178	53	83	1.0	208	320	69
B8	30350	6500	237	103	35	77	1.7	383	342	93
B9	29850	6600	265	114	56	72	2.0	733	458	115
B10	34850	7400	327	187	49	118	2.0	405	487	93
B11	34350	6200	77	130	25	41	1.7	153	492	55
B12	35650	6600	362	145	56	111	1.7	478	475	60
B13	25850	5400	205	140	25	66	1.3	277	392	60

trends which may or may not be capable of substantiation.

SOURCES OF ERROR

With any tedious and repetitive laboratory process there are always ample opportunities for contamination of a sample or two by simple human error. The errors which are most costly, however, are those arising from faulty design of the test procedures. In the procedures used here there are at least five places where significant error may be introduced, either in the form of contaminants or in analytical error. The four major sources of consistent contamination probability are as follow: 1) use of distilled/deionized water which has been contaminated or improperly distilled, 2) contamination due to contact of the sample with the metal sieve during sample preparation, 3) loss of metals due to the discarding of the colloid-containing supernatant after centrifuging, and 4) contamination from the millipore filter during the filtration of the hot extraction solutions. Each of these four sources was tested for detectable contaminant levels.

Five hundred ml aliquots of the solutions from each of the possible contaminating steps were measured into 1 liter volumetric flasks. The pH was adjusted to 2.8 by the addition of Bromphenol Blue indicator and the dropwise addition of concentrated HCl. A chelation-extraction yielded a fifty-fold concentration of the metals present due to contamination. Ten ml of 1% Ammonium Pyrrolidine Dithiocarbamate (APDC) were added, shaken vigorously

and allowed to react for 15 minutes. The metal-APDC chelates were extracted with 10 ml of Methyl Isobutyl Ketone (MIBK) and the ketone layer aspirated directly into the flame of the spectrophotometer. Several of the metals with high concentrations in the bay were analyzed for--iron, magnesium, zinc, and nickel--with negative results in all but the colloid-discarding sample. However, the level noted was not inordinately high--on the order of several hundred ppb iron, several tens of ppb magnesium, traces of zinc and no nickel. Considering that the sample preparation was carried out on samples still containing bay water, these metal levels probably represent ions from the bay pore waters taken into solution during sample preparation.

A one-liter aliquot of the colloid-discarding supernatant solution was vacuum filtered using a Millipore filtration apparatus with an HAWP 0.45 micron filter. The retained particulate material weighed 0.0017 grams, or 0.006% of the nominal yield of 30 grams of fine grained material from the sample preparation procedure previously described. This is well below the 0.03% error already found acceptable in the extraction technique previously described, and, therefore, is not considered to be an important source of error.

The last source of error is the machine error caused by resolution limitations inherent in the design of the atomic absorption spectrophotometer. Listed in the analytical conditions for each metal was the "sensitivity," or resolution limit of the machine. In converting the concentration readings determined for the extraction

solutions into concentrations in the finer than 63-micron fraction, the conversion factor of 1/3 was used. Table 3 is a tabulation of the manufacturer's specifications for sensitivity. These specifications were met for all metals except Fe and Mg, since all readings were made by direct determination.

Table 3: Sensitivities for the Data Presented in Table 2, Expressed as ± Parts Per Million of the <63 Micron Sediment Fraction.

Metal	Sensitivity
Fe	0.05 ppm
Mg	0.004 ppm
Zn	0.015 ppm
Cr	0.06 ppm
Cu	0.04 ppm
Pb	0.30 ppm
Cd	0.02 ppm
Hg	0.15 ppb
Ni	0.10 ppm
Sr	0.05 ppm

DISCUSSION

When one looks over Table 2 and Figures 2 through 11, one is immediately struck by the extremely high values obtained for iron and magnesium. There are a number of factors influencing the high levels of iron and magnesium, and also their distribution around the Bay. The greatest influence is the fact that chlorite, which is one of the more common clay minerals in Delaware Bay bottom sediments, is soluble in hydrochloric acid. One would expect that iron and magnesium would be in high concentration because both are primary constituents of chlorite. However, one is struck by the great

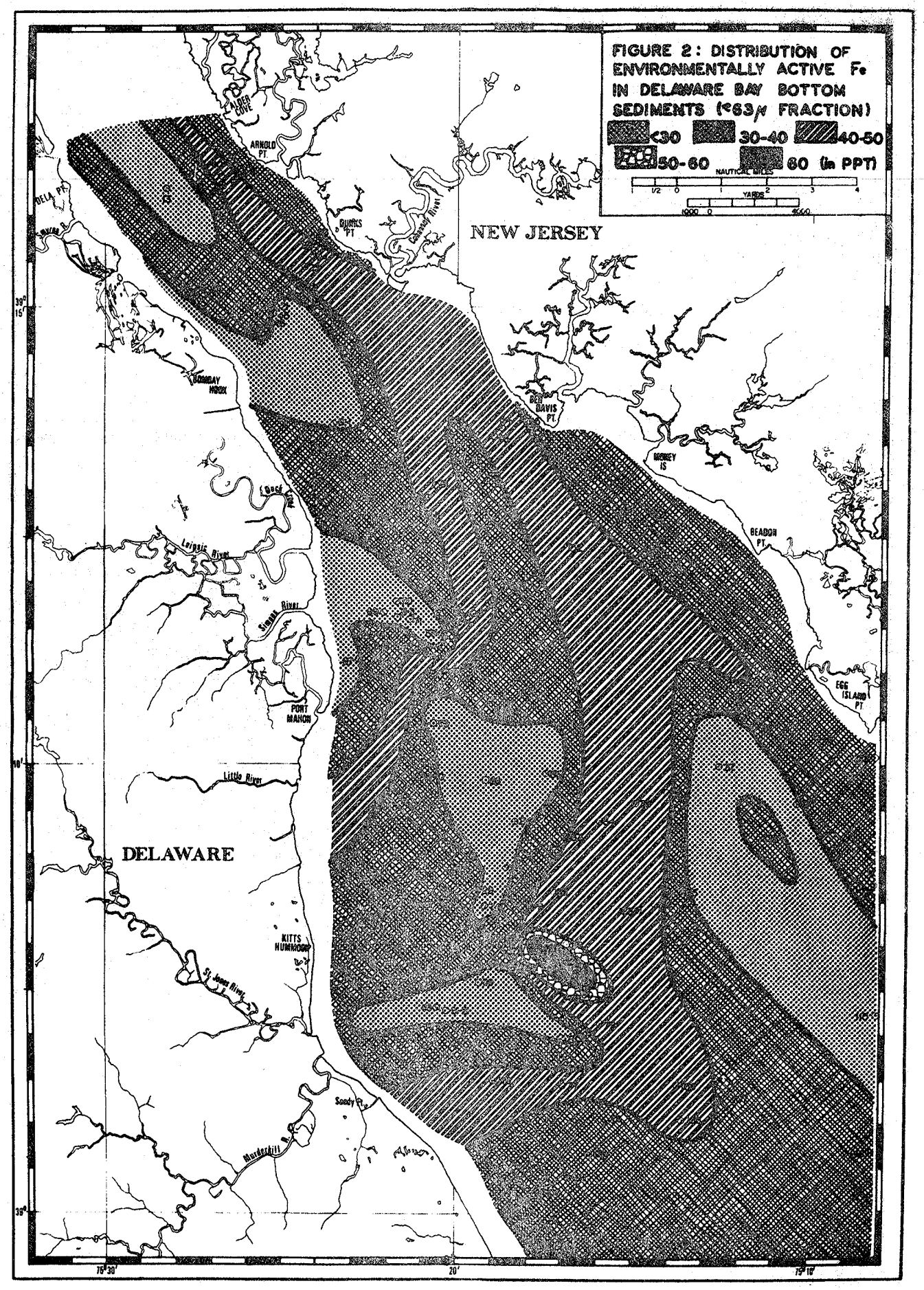
FIGURE 2: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Fe IN DELAWARE BAY BOTTOM SEDIMENTS (<63μ FRACTION)
<30
30-40
40-50
50-60
60 (in PPT)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ARNOLD PT.
ALLOWAY CREEK
BUCKS PT.
Cohansey River
DELA. PT.
MAURICE RIVER
BOWERS BEACH
BROADKILL BEACH
DEAD DAVIS PT.
MONEY IS.
BEADON PT.
EGG ISLAND PT.
Leipsic River
Simons River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt.
Murderkill
39° 15'
10'
39°
75° 30'
20'
75° 10'

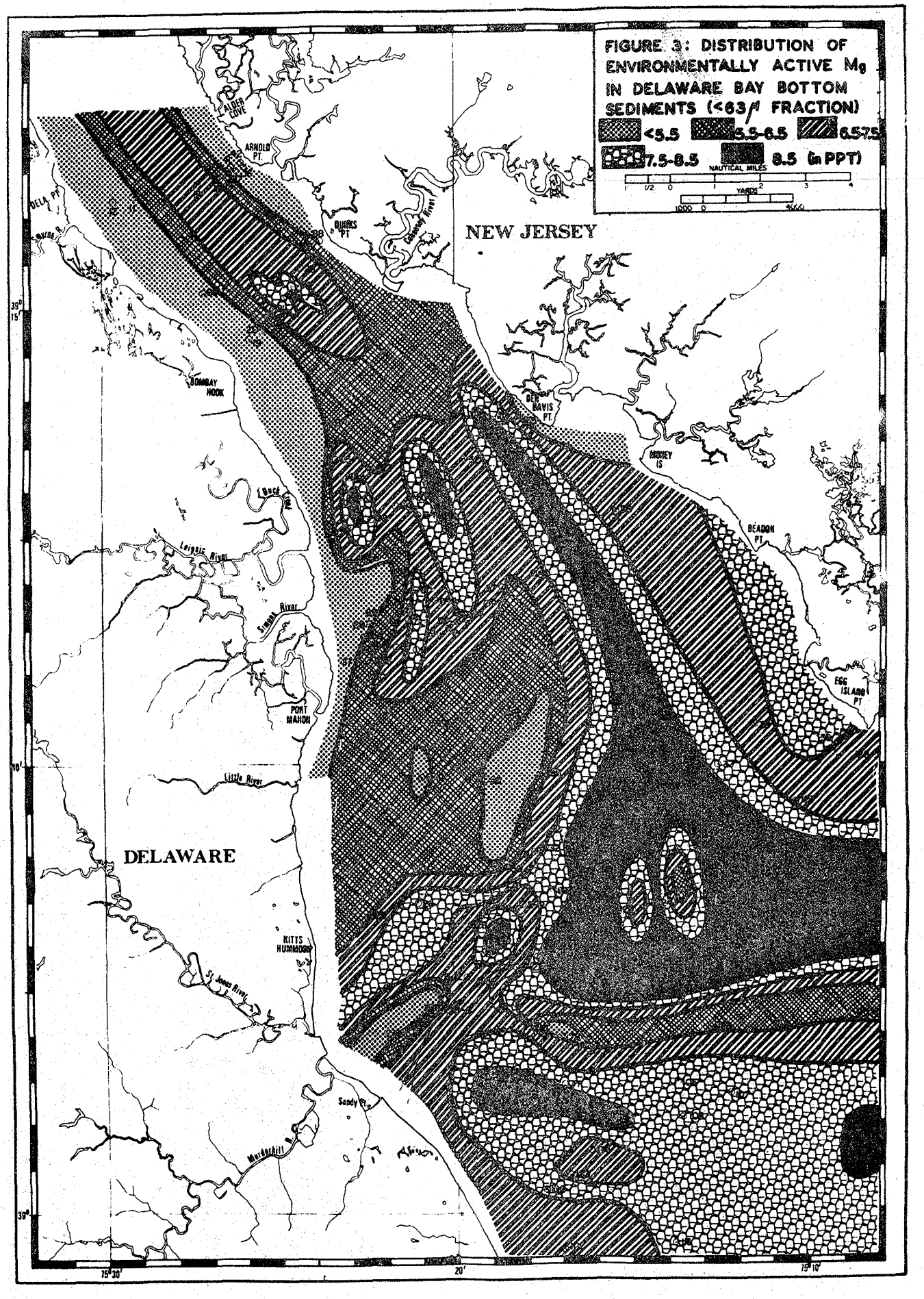
FIGURE 3: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Mg IN DELAWARE BAY BOTTOM SEDIMENTS (<63μ FRACTION)
<5.5
5.5-6.5
6.5-7.5
7.5-8.5
8.5 (in PPT)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT.
DELA PT
QUARKS PT
Cohansey River
BOMBAY HOOK
BEN DAVIS PT.
BROSEY IS
BEADON PT
EGG ISLAND PT
Leipsic River
Simons River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt.
Murderkill
39° 15'
39° 10'
39°
75° 30'
20'
75° 10'

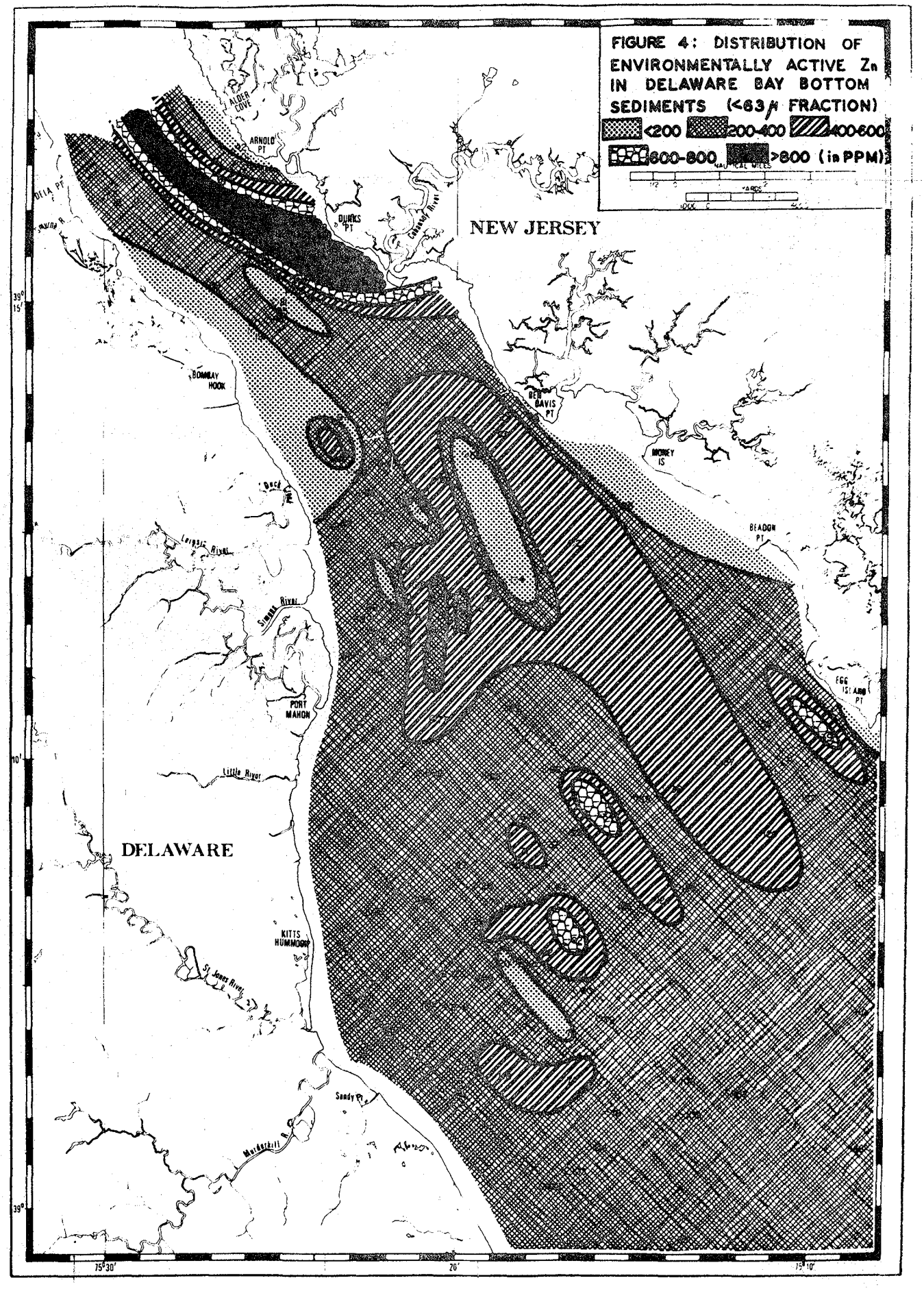
FIGURE 4: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Zn IN DELAWARE BAY BOTTOM SEDIMENTS (<63μ FRACTION)
<200
200-400
400-600
600-800
>800 (in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT
DELA PT
DUNKS PT
Cohansey River
BOMBAY HOOK
BEN DAVIS PT
MONEY IS
BEADON PT
EGG IS
Lavinia River
Smyrna River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt
Murderkill
39° 15'
10'
39°
75°30'
20'
75°10'

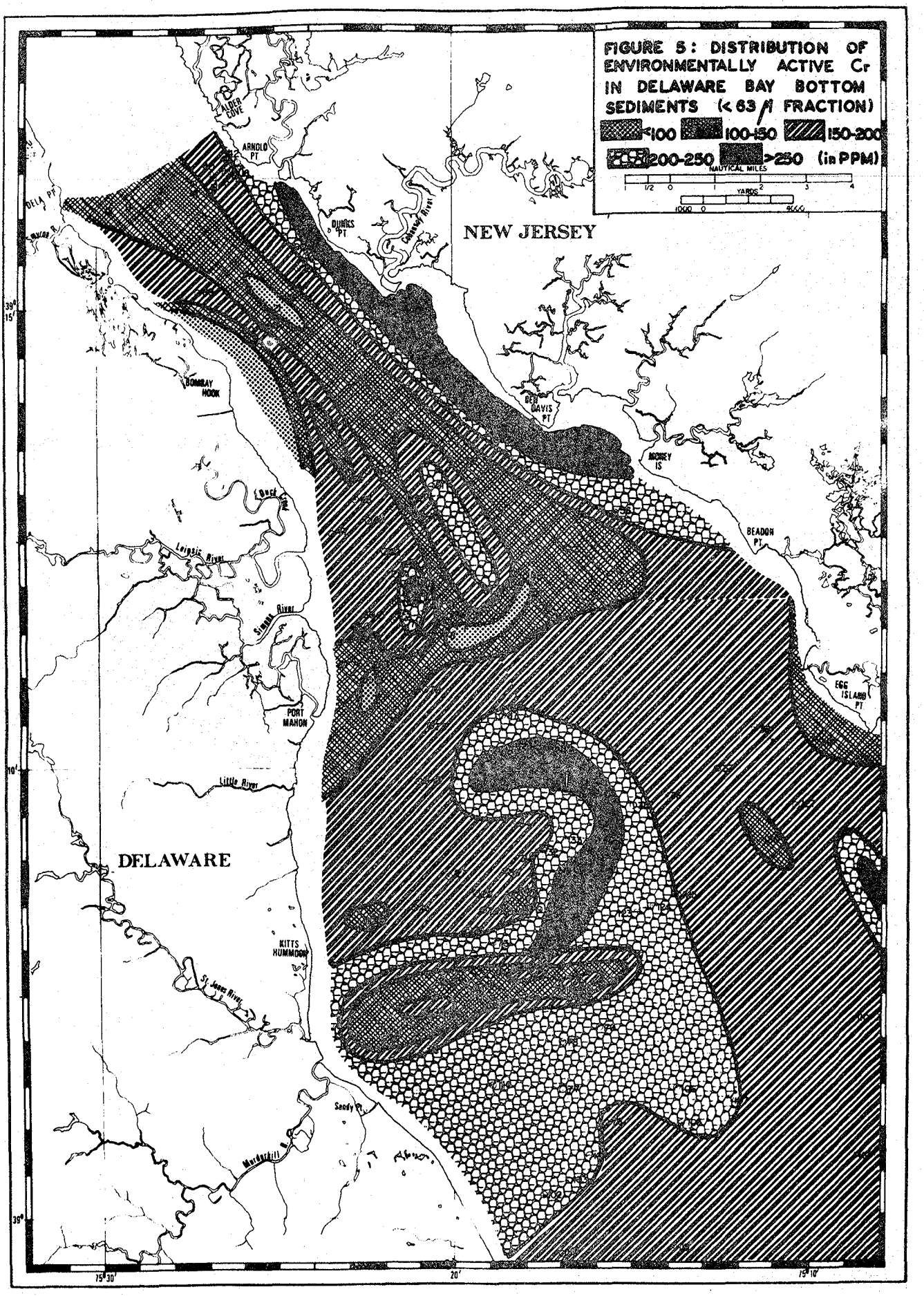
FIGURE 5: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Cr IN DELAWARE BAY BOTTOM SEDIMENTS (< 63 μ FRACTION)
<100
100-150
150-200
200-250
>250 (in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT
DELA PT
DUNKS PT
Cohansey River
BOMBAY HOOK
BEAR
DAVIS PT
MONEY IS
BEADON PT
EGG ISLAND PT
Leipsic River
Simons River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt
Murderkill R
75° 30'
20'
75° 10'
39°
10'
15'

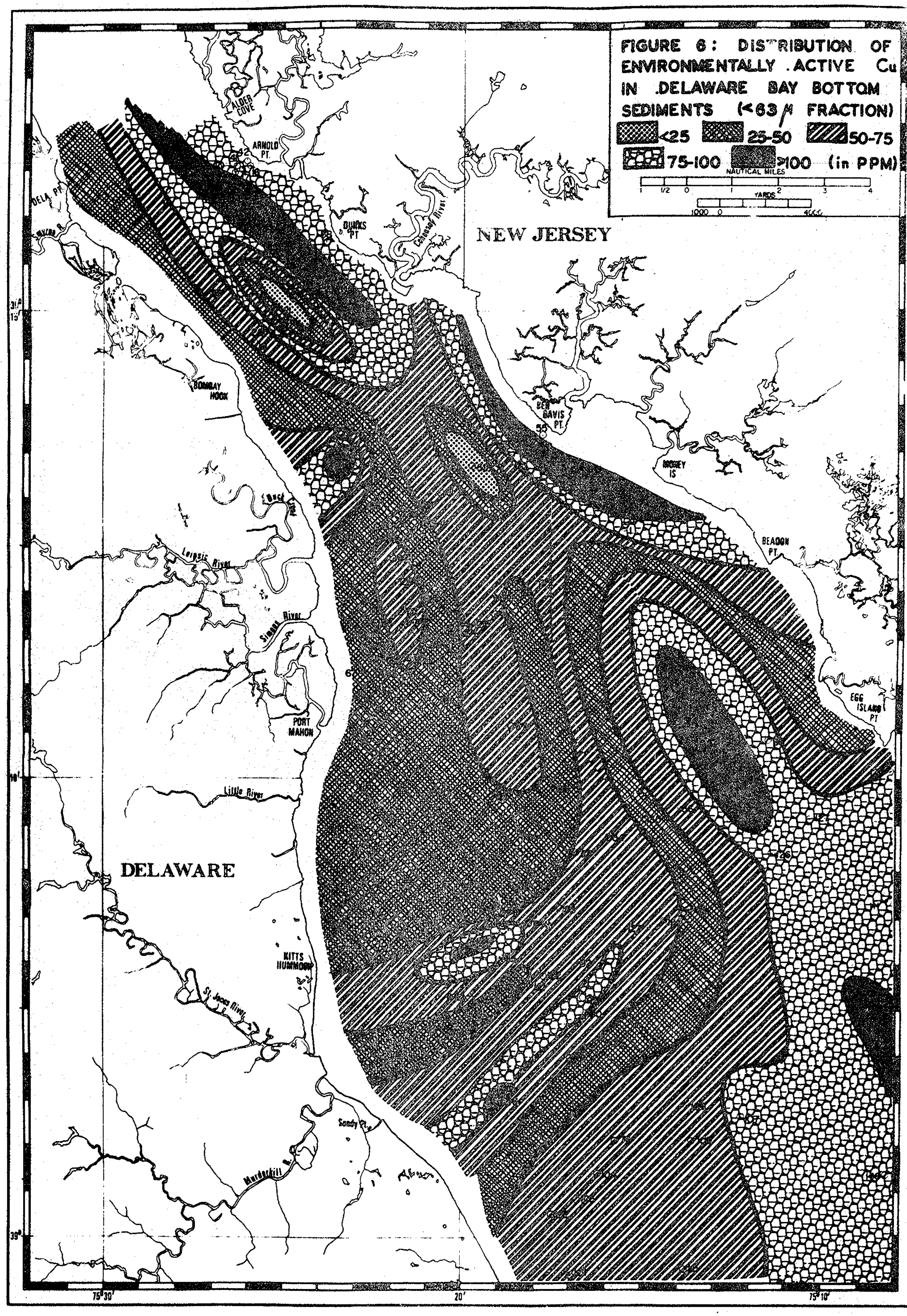
FIGURE 6: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Cu IN DELAWARE BAY BOTTOM SEDIMENTS (<63 μ FRACTION)
<25
25-50
50-75
75-100
>100 (in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT.
DUNKS PT.
BEN DAVIS PT.
BOMBAY HOOK
BEADON PT.
EGG ISLAND PT.
PORT MAHON
Little River
Leipsic River
Simons River
KITTS HUMMOCK
St. Jones River
Sandy Pt.
Murderkill R.
75°30'
20'
75°10'
39°

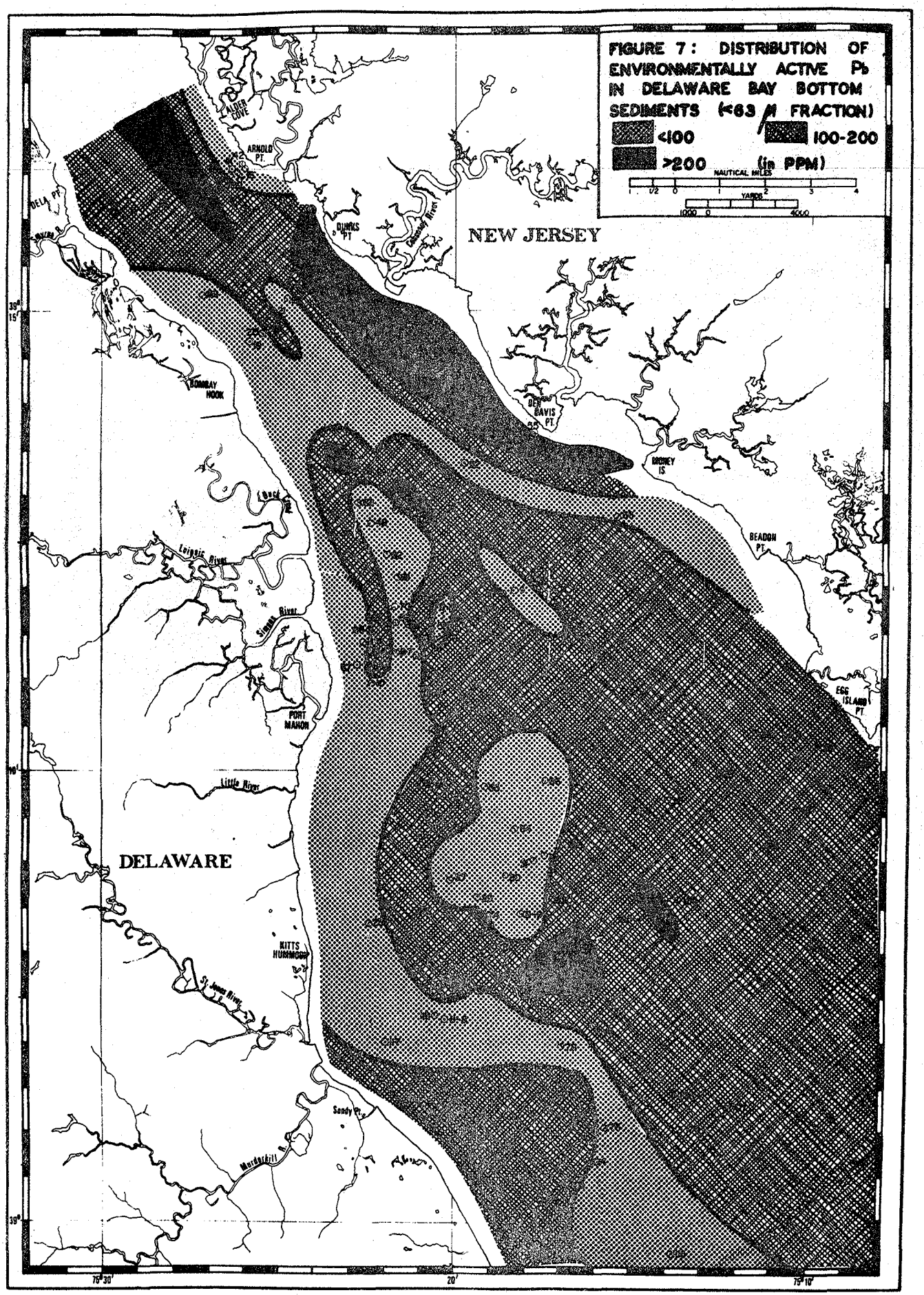
FIGURE 7: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Pb IN DELAWARE BAY BOTTOM SEDIMENTS (<63 μ FRACTION)
<100
100-200
>200 (in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT.
BOMBAY HOOK
BEAR BAVIS PT.
BROWNS PT.
BRADEN PT.
EGG ISLAND PT.
PORT MAHON
KITTS HUMMOCK
Sandy Pt.
Little River
Leipsic River
Simons River
Murderkill
Cohansey River
39°15'
39°
75°30'
20'
75°10'

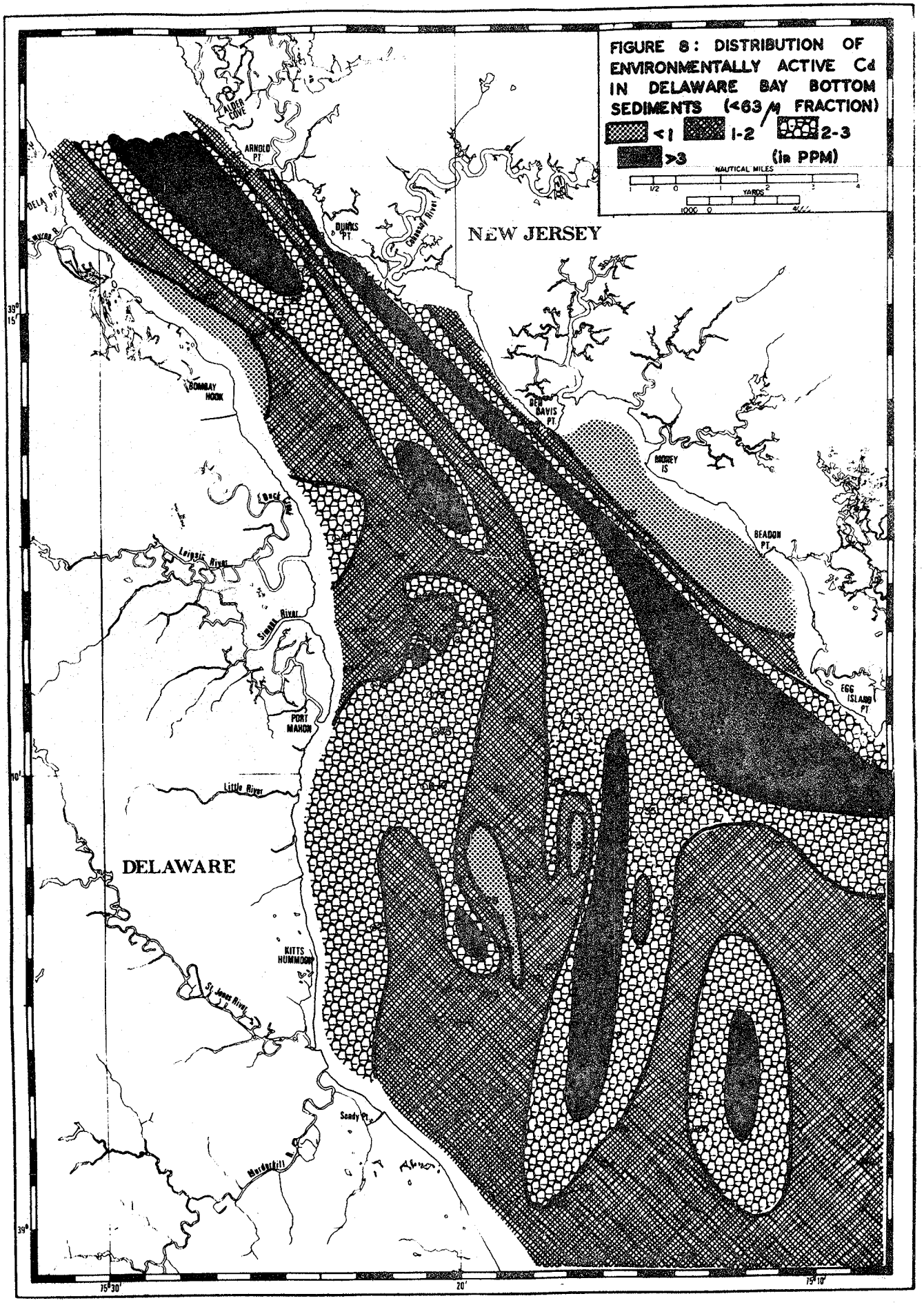
FIGURE 8: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Cd IN DELAWARE BAY BOTTOM SEDIMENTS (<63 μ FRACTION)
<1
1-2
2-3
>3
(in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT.
DELA PT.
MAGAR
DUNKS PT.
Cohansey River
BOMBAY HOOK
BEN DAVIS PT.
BADGLEY IS.
BEADON PT.
EGG ISLAND PT.
Duck Creek
Leipsic River
Simons River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt.
Murderkill
Abbott
39° 15'
10'
39°
75°30'
20'
75°10'

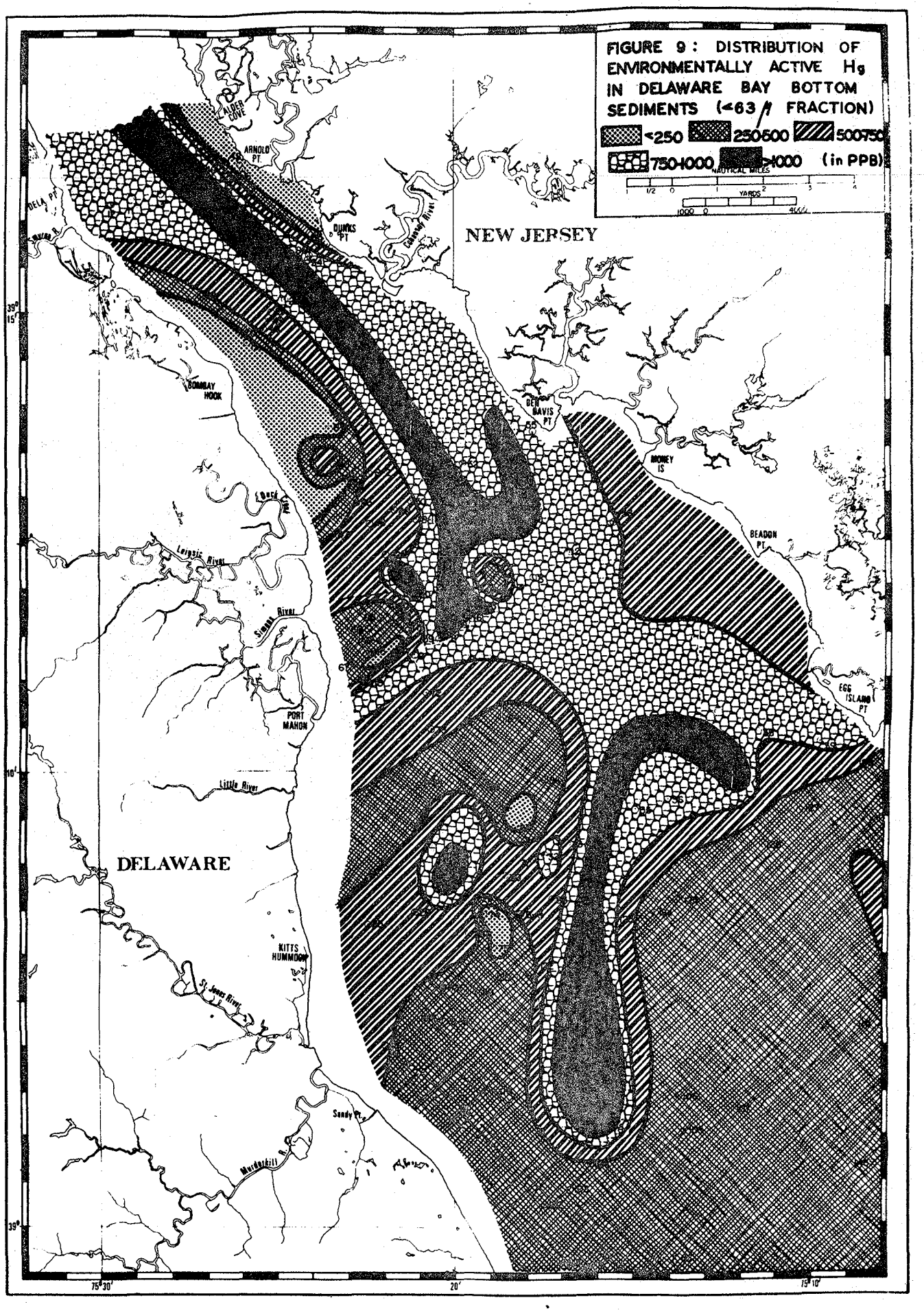
FIGURE 9 : DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Hg IN DELAWARE BAY BOTTOM SEDIMENTS (<63 μ FRACTION)
<250
250-500
500-750
750-1000
>1000
(in PPB)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT.
DELA. PT.
QUINNS PT.
Cohansey River
BOMBAY HOOK
BEN DAVIS PT.
MONEY IS.
BEADON PT.
EGG ISLAND PT.
Leipsic River
Simons River
PORT MAHON
Little River
KITTS HUMMOCK
St. Jones River
Sandy Pt.
Murderkill R.
39° 15'
10'
39°
75°30'
20'
75°10'

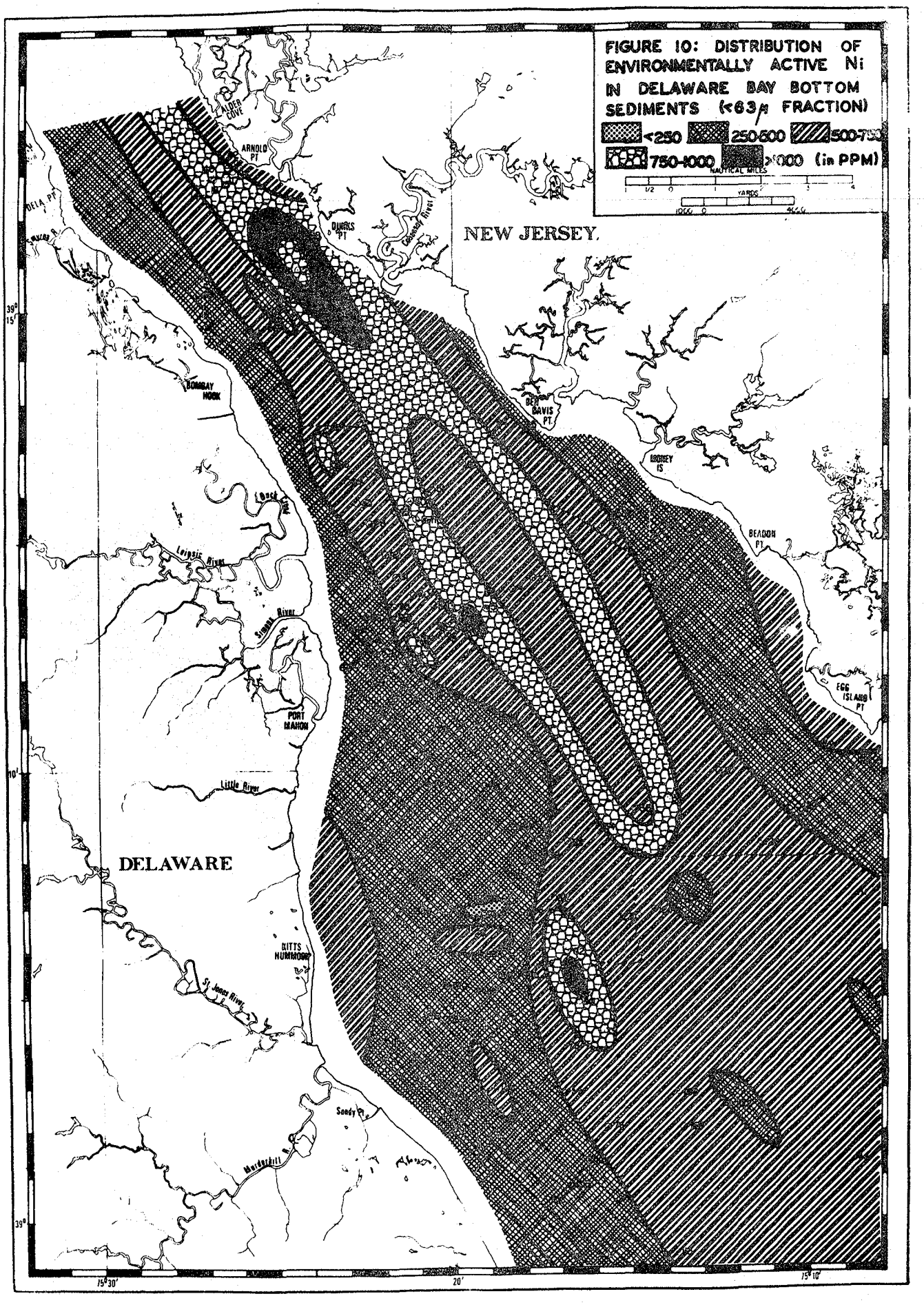
FIGURE 10: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Ni IN DELAWARE BAY BOTTOM SEDIMENTS (<63μ FRACTION)
<250
250-500
500-750
750-1000
>1000 (in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ARNOLD PT
ALDER COVE
DELA PT
DUNKS PT
Delaware River
BOMBAY HOOK
BEN DAVIS PT
BIDDEY IS
BEACON PT
EGG ISLAND PT
Duck Creek
Leipsic River
Simons River
PORT MAHON
Little River
GITTS HUMMOCK
St. Jones River
Sandy Pt
Murderkill
39° 15'
10'
39°
75° 30'
20'
75° 10'

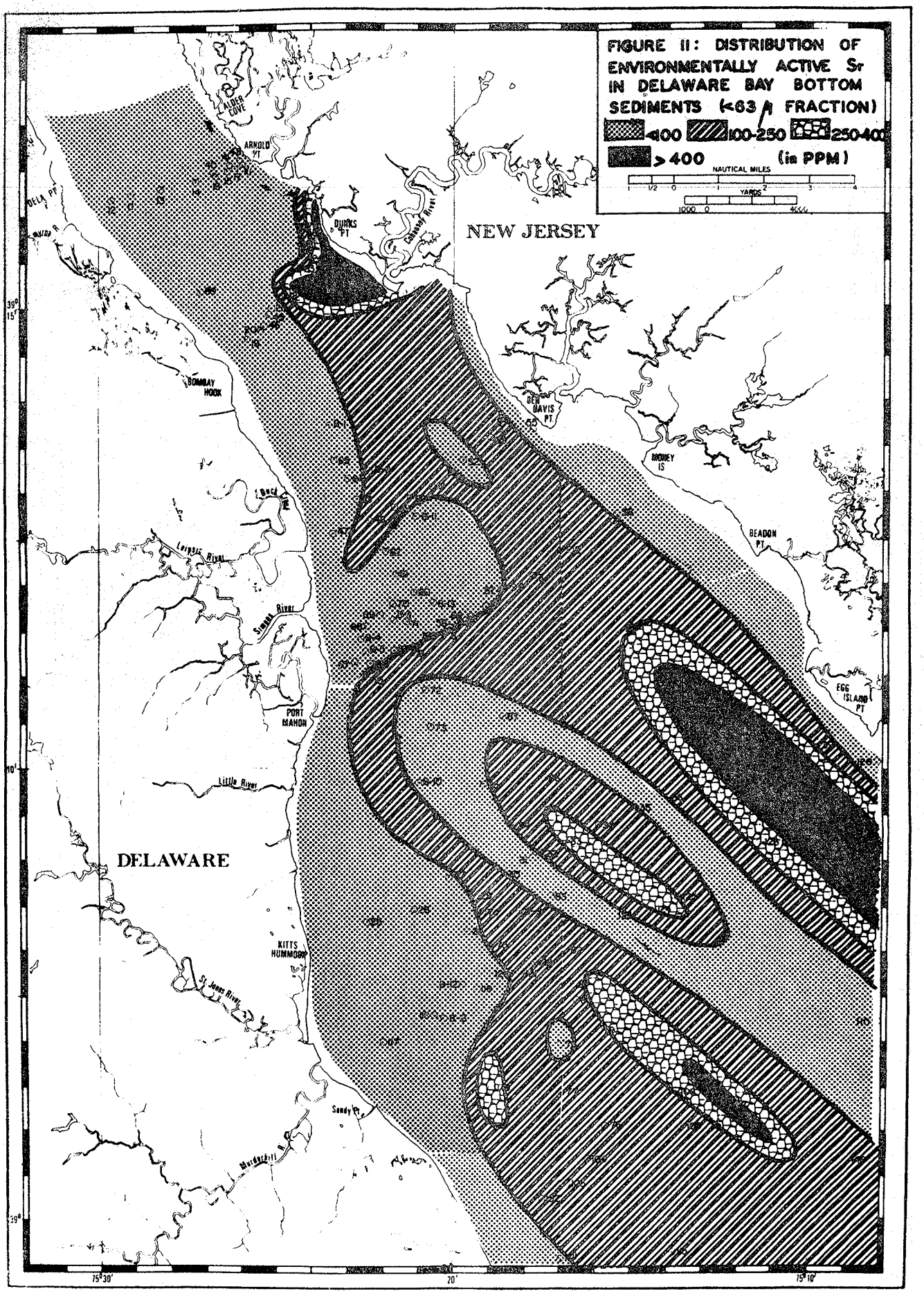
FIGURE II: DISTRIBUTION OF ENVIRONMENTALLY ACTIVE Sr IN DELAWARE BAY BOTTOM SEDIMENTS (<63 μ FRACTION)
<400
100-250
250-400
>400
(in PPM)
NAUTICAL MILES
YARDS
NEW JERSEY
DELAWARE
ALDER COVE
ARNOLD PT
DUNKS PT
Cohansey River
BOMBAY HOOK
BEN DAVIS PT
MONEY IS
BEADON PT
EGG ISLAND PT
Leipsic River
Smyrna River
PORT MAHON
Little River
KITTS HUMMOCK
St Jones River
Sandy Pt
Murderkill R
39° 15'
10'
39°
75°30'
20'
75°10'

dissimilarity of the two regional diagrams presented as Figures 2 and 3. It seems apparent that the iron source is from the Delaware River, while the magnesium source is primarily the ocean.

Figure 4 indicates an exceptionally straightforward pattern in the distribution of zinc. It would seem that the primary source of the zinc is the Delaware River. This is not hard to believe for two reasons: 1) the high concentration of heavy industry in the vicinity of Philadelphia, and 2) the prevalence of economic zinc ore deposits in the Delaware drainage basin, most notably the huge deposit in Franklin, New Jersey.

Figure 5 appears to indicate a predominantly seaborne source for chromium, although high values in the upper reaches of the area would suggest that there is also a substantial contribution from the Delaware River. This also appears to be the case in Figure 6, illustrating the distribution of copper in the Bay. Figure 7 indicates that most of the lead in Delaware Bay sediments has its source in the Delaware River, and that there is a substantial amount of mixing in the middle reaches of the bay.

Although the data which comprise Figure 8 are the most suspect in this report, it would appear that there is a cogent story to be gleaned from the regional distribution of cadmium. It seems that the principle source is the Delaware River, and that the mixing which occurs in the lower and middle areas of this study has created a "sink" of cadmium in the vicinity offshore from the points of entry into the Bay of the Murderkill and St. Jones Rivers.

Judging by the distribution pattern for mercury in Figure 9, there is no doubt that the primary source of mercury is the Delaware River. Here again, mixing is occurring in the middle and lower reaches of the study area, although more restricted mixing than that experienced with cadmium. The same "sink" is also shown in Figure 9.

Figure 10, illustrating the distribution of trace nickel, indicates a primary source for nickel in the Delaware River, with a very straightforward distribution pattern. In Figure 11 one also sees a very straightforward pattern, although one which would indicate that the source of strontium in the Bay is the ocean with some limited mixing into the ebb tide side of the Bay along the Delaware shoreline.

In trying to answer the question of how much of any one of these metals is dangerous, toxic or lethal, one is hard pressed to quote rock-solid figures, even to the point of not wishing to hazard a guess. So little is currently known about the biochemistry of trace metals, that it is impossible to state what the danger levels are. One hopes that work on this type of an environmental problem is being pressed with all possible speed.

CONCLUSIONS

1) Trace metal geochemical aspects of the sedimentary environments which support oysters in Delaware have been typified for ten common trace metals. It is hoped that further work may

be accomplished in the foreseeable future which will expand the results of this work.

2) The two hypotheses mentioned in the BACKGROUND section of this report have been tested, and have been found not to be mutually exclusive. That is, both of the processes mentioned appear to be in operation. Fine-grained materials are being eroded from the tidal marshes and are accumulating in the near-shore bay area, where there are consistently low geochemical measurements. There also exist conditions for the preferential deposition of fine-grained materials carried into the Bay by the Delaware River, although their deposition does not occur where originally hypothesized. Deposition of river-borne materials occurs near the middle of the navigational channel, and up to the New Jersey side of the Bay in the uppermost reaches, and then approaches the Delaware side of the Bay in the area between Port Mahon and the Murderkill and St. Jones River mouths.

3) The characterization of the trace metals as to their primary source and the major factor influencing their distribution was made possible by Figures 2 through 11. It appears obvious that iron, zinc, lead, cadmium, mercury and nickel have their primary sources in the Delaware River, while magnesium, chromium, copper and strontium have predominantly seaborne sources. It also seems obvious that water currents are the principle factor influencing the distribution of all of these metals, irrespective of source area.

4) From Figures 5, 6, 7, and 11, it appears that there is a "hot spot" of high concentrations of chromium, copper, lead and strontium associated with the mouth of the Cohansey River in the northern extreme of the study area. Further investigation of this area should be undertaken to determine whether the area is a source for metal pollutants or a sink for metals borne by the Delaware River.

5) From Figures 2 through 11, it appears that there is a "sink" of trace metals being formed in the vicinity offshore from the mouths of the Murderkill and St. Jones Rivers. Further investigation of this area should be undertaken in order to ensure that shellfish taken from the region are within the U.S. Public Health Service limits of trace metals content.

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Gordon, D. C., (1966) The effects of the deposit feeding polychaete Pectinaria gouldii on the intertidal sediments of Barnstable Harbor. Limnol. & Oceanog., 11: 327-32.

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APPENDIX

Results of Emission Spectrophotometry, Reported in Parts Per Million of the Finer than 63 Micron Sediment Fraction

SAMPLE ABBREVIATION KEY

Sample (from Table)	Sample Location
1	Bay Oyster Reef, B-1
2	Bay Oyster Reef, B-2
3	Bay Oyster Reef, B-3
4	Bay Oyster Reef, B-4
5	Bay Oyster Reef, B-5
6	Bay Oyster Reef, B-6
7	Bay Oyster Reef, B-7
8	Bay Oyster Reef, B-8
9	Bay Oyster Reef, B-9
10	Bay Oyster Reef, B-10
11	Bay Oyster Reef, B-11
12	Bay Oyster Reef, B-12
13	Bay Oyster Reef, B-13
14	Leipsic River West
15	Leipsic River East
16	Simon's Creek West
17	Simon's Creek East
18	St. Jones River West
19	St. Jones River East
20	Murderkill River East
21	Murderkill River West
22	Mispillion River West
23	Mispillion River East
24	Broadkill River West
25	Broadkill River East

"A" after a sample number indicates that it is a sediment sample from the finer than 63 micron fraction. "B" after a sample number indicates that it is a sample of dried and powdered oyster tissues from that location.

LOWER LIMITS OF DETECTION

Listed below are some of the lower limits of detection for some of the elements not listed in the accompanying table due to insufficient concentrations.

10,000 PPM:	Li
5,000 PPM:	Dy
1,000 PPM:	As, Te, Ta, Tl, W
500 PPM:	Ga, In, Ra, Tb
100 PPM:	Hg, Sb, Pb, Mo, Th, Sn, V, Bi, Cd, Co
50 PPM:	Pt, Pd, Ru, Hf, Rh, Ir, Y, Lu, La, Se, Gd, Tm, Er
10 PPM:	Ge, Nb
5 PPM:	Au, Yb, Ho
1 PPM:	Be

SAMPLE	Fe	Mg	Ti	Ba	Mn	V	P	Zn
1A	>100,000	20,000	10,000	1,000	50,000	1,000	1,000	10,000
1B	1,000	5,000	100	<100	100	---	10,000	50,000
2A	>100,000	20,000	10,000	1,000	2,000	1,000	1,000	300
2B	3,000	10,000	300	<100	100	---	10,000	50,000
3A	---	---	---	---	---	---	---	---
3B	3,000	10,000	300	<100	200	---	10,000	30,000
4A	>100,000	20,000	10,000	1,000	2,000	1,000	<1,000	300
4B	3,000	5,000	300	<100	100	---	10,000	30,000
5A	>100,000	20,000	10,000	1,000	2,000	1,000	<1,000	300
5B	3,000	5,000	300	<100	100	---	10,000	50,000
6A	>100,000	30,000	10,000	1,000	20,000	1,000	1,000	2,000
6B	3,000	5,000	100	<100	100	---	10,000	50,000
7A	>100,000	20,000	10,000	1,000	1,000	1,000	<1,000	200
7B	3,000	10,000	100	<100	300	---	10,000	30,000
8A	---	---	---	---	---	---	---	---
8B	3,000	10,000	100	<100	100	---	10,000	10,000
9A	>100,000	20,000	10,000	1,000	1,000	1,000	<1,000	200
9B	20,000	10,000	200	<100	100	---	10,000	20,000
10A	>100,000	20,000	10,000	1,000	1,000	1,000	<1,000	200
10B	2,000	10,000	200	<100	100	---	10,000	20,000
11A	---	---	---	---	---	---	---	---
11B	2,000	10,000	200	<100	100	---	10,000	>100,000
12A	---	---	---	---	---	---	---	---
12B	2,000	10,000	200	<100	100	---	10,000	>100,000
13A	>100,000	15,000	10,000	1,000	1,000	1,000	<1,000	200
13B	2,000	10,000	200	<100	100	---	10,000	10,000
14A	100,000	10,000	10,000	1,000	800	1,000	<1,000	<100
14B	2,000	10,000	200	<100	100	---	10,000	>100,000
15A	>100,000	30,000	10,000	1,000	1,000	1,000	<1,000	<100
15B	2,000	10,000	200	<100	100	---	10,000	>100,000
16A	>100,000	20,000	10,000	1,000	1,000	1,000	<1,000	100
16B	2,000	10,000	200	<100	100	---	10,000	>100,000
17A	100,000	10,000	10,000	1,000	3,000	1,000	<1,000	200
17B	2,000	10,000	100	<100	100	---	10,000	60,000
18A	>100,000	20,000	10,000	1,000	500	1,000	<1,000	200
18B	5,000	20,000	100	<100	100	---	10,000	20,000
19A	>100,000	20,000	10,000	1,000	800	1,000	<1,000	200
19B	50,000	20,000	200	<100	100	---	10,000	20,000
20A	100,000	10,000	10,000	800	500	1,000	<1,000	<100
20B	5,000	20,000	200	<100	100	---	10,000	3,000
21A	>100,000	20,000	10,000	1,000	2,000	1,000	<1,000	<100
21B	5,000	20,000	200	<100	100	---	10,000	20,000
22A	---	---	---	---	---	---	---	---
22B	5,000	20,000	200	<100	100	---	10,000	10,000
23A	100,000	10,000	10,000	1,000	1,000	1,000	<1,000	100
23B	5,000	20,000	200	<100	100	---	10,000	10,000
24A	>100,000	20,000	10,000	1,000	600	1,000	<1,000	<100
24B	5,000	20,000	500	<100	100	---	10,000	10,000
25A	>100,000	20,000	10,000	1,000	500	1,000	<1,000	200
25B	5,000	20,000	100	<100	100	---	10,000	10,000

SAMPLE ABBREVIATION KEY

Sample (from Table)	Sample Location
1	Bay Oyster Reef, B-1
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3	Bay Oyster Reef, B-3
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11	Bay Oyster Reef, B-11
12	Bay Oyster Reef, B-12
13	Bay Oyster Reef, B-13
14	Leipsic River West
15	Leipsic River East
16	Simon's Creek West
17	Simon's Creek East
18	St. Jones River West
19	St. Jones River East
20	Murderkill River East
21	Murderkill River West
22	Mispillion River West
23	Mispillion River East
24	Broadkill River West
25	Broadkill River East

"A" after a sample number indicates that it is a sediment sample from the finer than 63 micron fraction. "B" after a sample number indicates that it is a sample of dried and powdered oyster tissues from that location.

LOWER LIMITS OF DETECTION

Listed below are some of the lower limits of detection for some of the elements not listed in the accompanying table due to insufficient concentrations.

10,000 PPM:	Li
5,000 PPM:	Dy
1,000 PPM:	As, Te, Ta, Tl, W
500 PPM:	Ga, In, Ra, Tb
100 PPM:	Hg, Sb, Pb, Mo, Th, Sn, V, Bi, Cd, Co
50 PPM:	Pt, Pd, Ru, Hf, Rh, Ir, Y, Lu, La, Se, Gd, Tm, Er
10 PPM:	Ge, Nb
5 PPM:	Au, Yb, Ho
1 PPM:	Be

SAMPLE	Pb	B	Cr	Ni	Cu	Sn	Ga	Co	Nb	La	Ag
1A	2,000	100	800	1,000	500	100	500	500	≤10	50	1
1B	---	10	<100	<100	2,000	---	---	---	---	--	100
2A	800	100	500	200	200	100	500	100	<10	50	1
2B	---	10	<100	<100	2,000	---	---	---	---	--	100
3A	---	---	---	---	---	---	---	---	---	--	---
3B	---	10	<100	<100	3,000	---	---	---	---	--	100
4A	800	100	300	200	200	100	500	100	<10	50	1
4B	---	≤10	<100	<100	1,000	---	---	---	---	--	100
5A	800	100	500	200	200	100	500	100	<10	50	≤1
5B	---	10	<100	<100	2,000	---	---	---	---	--	100
6A	1,000	100	500	500	300	100	500	100	<10	50	1
6B	---	10	<100	<100	3,000	---	---	---	---	--	100
7A	200	100	500	200	500	100	500	100	≤10	50	1
7B	---	10	<100	<100	1,000	---	---	---	---	--	50
8A	---	---	---	---	---	---	---	---	---	--	---
8B	---	10	<100	<100	1,000	---	---	---	---	--	50
9A	200	100	500	200	500	100	500	100	≤10	50	≤1
9B	---	10	<100	<100	500	---	---	---	---	--	10
10A	200	100	500	200	300	100	500	100	≤10	50	≤1
10B	---	10	<100	<100	500	---	---	---	---	--	10
11A	---	---	---	---	---	---	---	---	---	--	---
11B	---	10	<100	<100	2,000	---	---	---	---	--	100
12A	---	---	---	---	---	---	---	---	---	--	---
12B	---	10	<100	<100	1,000	---	---	---	---	--	100
13A	250	100	500	150	250	100	500	100	≤10	50	1
13B	---	10	<100	<100	1,000	---	---	---	---	--	10
14A	100	100	200	200	200	<100	500	100	<10	50	<1
14B	---	10	<100	<100	1,000	---	---	---	---	--	100
15A	200	100	500	200	300	<100	500	100	<10	50	<1
15B	---	10	<100	<100	1,000	---	---	---	---	--	100
16A	300	100	400	200	500	100	500	100	<10	50	1
16B	---	10	<100	<100	1,000	---	---	---	---	--	100
17A	400	100	400	200	500	100	500	100	<10	50	1
17B	---	10	<100	<100	1,000	---	---	---	---	--	50
18A	200	100	500	200	1,000	100	500	100	<10	50	<1
18B	---	10	<100	<100	500	---	---	---	---	--	10
19A	200	100	500	200	500	≤100	500	100	≤10	50	2
19B	---	10	<100	≤100	500	---	---	---	---	--	10
20A	200	100	200	200	1,000	100	500	100	<10	50	<1
20B	---	10	<100	<100	200	---	---	---	---	--	10
21A	200	100	500	200	200	100	500	100	<10	50	<1
21B	---	10	<100	<100	500	---	---	---	---	--	10
22A	---	---	---	---	---	---	---	---	---	--	---
22B	---	10	<100	<100	500	---	---	---	---	--	10
23A	200	100	200	200	200	<100	500	100	<10	50	<1
23B	---	10	<100	<100	1,000	---	---	---	---	--	20
24A	200	100	200	200	100	<100	500	100	<10	50	<1
24B	---	10	<100	<100	500	---	---	---	---	--	20
25A	200	100	500	200	500	100	500	100	≤10	50	1
25B	---	30	<100	<100	500	---	---	---	---	--	10

Report No. 3

TRACE METAL BASELINE STUDIES ON THE MURDERKILL AND ST. JONES RIVERS DELAWARE COASTAL PLAIN

Frederick Bopp, III

Frederick K. Lepple

and

Robert B. Biggs

This report is the result of research sponsored by the National Oceanic and Atmospheric Administration, Office of Sea Grant, Department of Commerce, under Grant No. 2-35223.

PREFACE

This report represents an interim record of progress during Fiscal Year 1972 in one aspect of the geological investigation of Delaware Bay. Preliminary interpretations have been included.

We thank Holly Bopp for her assistance in doing the major sampling efforts for this study, and William Treasure of the Department of Geology for his assistance in doing the remainder.

The National Science Foundation, the National Oceanic and Atmospheric Administration, and agencies of the State of Delaware are free to use the contents in any way which serves the public interest, but are requested to respect the intention of the authors to publish the formal results of their investigation at a later date.

BACKGROUND

Numerous studies of the Murderkill River have been instituted in the past few years since the decision to construct a regional sewage treatment facility for Kent County, Delaware. This new facility, with a design capacity of approximately 10 million gallons per day (which will account for up to 37% of the fresh water daily volume during periods of low runoff), will deposit its 48-hour, extended aeration treated effluent into the Murderkill River approximately 7.3 miles upstream from the river mouth at Bowers, Delaware. The studies done have concerned themselves mainly with the hydrography, biochemistry and ecological balance of the estuary in its present state (see, for example: Daiber, 1972; DeMichele, 1972). The DeMichele study attempted to model the estuary and predict the long-range effects of the sewage treatment facility on the Murderkill River. None of the studies encountered by these authors, however, has established a baseline of the trace metals levels in the riverbed of the as yet virtually unpolluted Murderkill. In view of the significant amounts of lead, copper, chromium, zinc and other metals known to be in sewage treatment wastes, it would seem that the establishment of such a baseline datum is needed in order to make a complete background study of the river in its present condition.

INTRODUCTION

It is the principal purpose of this study to establish a trace metal baseline for the Murderkill River prior to commencement of operation of the Kent County Regional Sewage Treatment Plant, presently under construction near Frederica, Delaware. Baselines will be established for iron, magnesium, zinc, chromium, copper, lead, cadmium, mercury, nickel and strontium. In addition to the establishment of these baselines, the second purpose of this study is to contrast the Murderkill River baseline with a similarly established baseline for the St. Jones River, which has been the recipient of domestic sewage and industrial and other organ wastes for a number of years. By comparing the results of these two river systems' baselines, it is hoped that some projection may be made of those metals which should be reasonably closely monitored after commencement of operation of the sewage treatment facility.

For a discussion of project philosophy, the concept of environmental activity, and laboratory procedures used, see pages 30 to 34 (Report No. 2). For an analysis of possible sources of error, see page 46.

SAMPLING

All samples for this research were taken from a small outboard runabout, R/V Ariadne, with a modified Forster-Anchor Dredge (see Kraft, 1971). Samples were taken at approximately every half- to three-quarters of a mile from the mouth of the rivers to well above the limit of salt intrusion on all branches of the rivers. The

Forster-Anchor Dredge was washed with river water at the sampling site, dropped overboard with approximately 30 feet of line attached, and pulled back aboard manually with a thin veneer of sediments (approximately the top 5 to 10 cm) inside it. These sediments were transferred to heavy gauge plastic sample bags, sealed, and kept cool. Upon return to the laboratory the samples were frozen. Figure 1 is a map of the Murderkill and St. Jones Rivers showing the locations of the samples for each river, along with some of the salient features and landmarks. Sample numbers are preceded by "M" for the Murderkill River, and by "SJ" for the St. Jones River in order to differentiate similarly numbered samples.

ANALYTICAL CONDITIONS

All analyses, except those for mercury, were conducted using a Jarrell-Ash Model 800 Atomic Absorption Spectrophotometer in association with twin Honeywell Electronik 17 single-event pen recorders set for 15-inches per hour chart speed. Response of the recorders was 1 second for 1 millivolt full-scale deflection. Hollow cathode lamps used for atomic absorption were all single-element, high spectral output, Jarrell-Ash lamps. The extraction technique used was designed to yield trace metal concentrations within the direct-reading limits of the spectrophotometer for most of the metals of interest. Background corrections were investigated on a routine basis, but no significant differences were noted between corrected

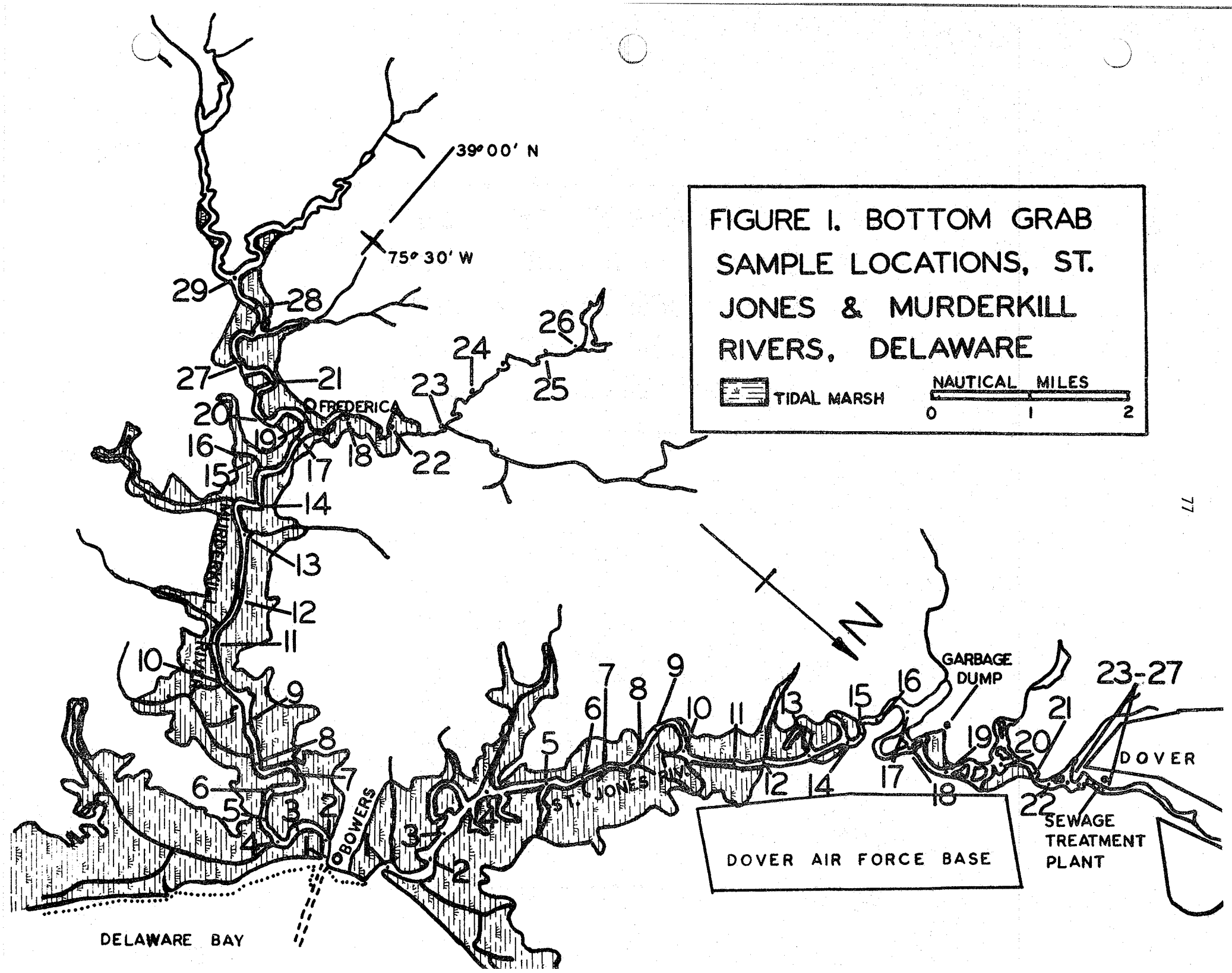

FIGURE 1. BOTTOM GRAB SAMPLE LOCATIONS, ST. JONES & MURDERKILL RIVERS, DELAWARE

and uncorrected readings. As the use of the background correction, B/A mode, reduced the signal-to-noise ratio, it was not used. For specific spectrophotometer operational parameters as applied to individual metals analyses, the reader is referred to Bopp and Biggs (1972).

Mercury was measured by flameless atomic absorption spectrophotometry using a Coleman Model MAS-50 Mercury Analyzer System and Coleman "Mercury-Free" Reagents. Standards were prepared daily from a stock solution of 1µg/ml mercury which had been stabilized in an aqueous acid permanganate solution. The chemistry of the mercury determination is based on the method developed by Hatch and Ott (1968), which measures total mercury (inorganic plus organic forms). However, in our acid treatment, HCl was substituted in place of HNO_3 and H_2SO_4 and no $KMnO_4$ was added to the leachate. For this reason, oxidation of organic compounds present in the HCl leachate might be incomplete and thus the values reported here are minimum mercury concentrations.

In the analysis procedure, stannous chloride (5ml of 10% solution) was added to 100ml of leachate in order to reduce all of the dissolved mercury to the metallic form. The mercury is then vaporized and circulated by the bubbler system through an absorption cell. The 2537 nm mercury spectral line emitted by a mercury lamp is absorbed by the vapor and the change in transmittance is detected by the phototube. Over the concentration range of 0 to 10ppb, the limit of detection is approximately 0.01ppb mercury.

RESULTS

Tables 2 and 3 contain tabulations of all of the trace metal concentrations determined during Fiscal Year 1972 research. These concentrations are expressed as micrograms per gram, or parts per million, of the sediment fraction finer than 63 microns.

The values presented in Tables 2 and 3 were used to plot the graphs presented as Figures 2 through 11, which illustrate the variations among the trace metals along the length of the riverbeds.

DISCUSSION

From Figures 2 through 11 several patterns make themselves apparent. These patterns appear to assist in the understanding of the sources and distribution of the various pollutive trace metals.

Table 2: Concentrations of Trace Metals in the Murderkill River Bottom Sediments, Expressed as Parts Per Million of the <63-Micron Sediment Fraction. (Mercury Expressed as Parts Per Billion)

SAMPLE	Fe	Mg	Zn	Cr	Cu	Pb	Cd	Hg	Ni	Sr
M1	36250	5700	362	128	35	355	5.7	711	654	206
M2	44850	7250	405	130	50	217	8.7	984	680	275
M3	35600	7500	278	92	50	92	2.7	332	425	123
M4	54300	7400	219	138	26	95	2.8	198	733	134
M5	34000	7350	100	128	38	75	2.7	87	395	72
M6	35500	7850	110	128	38	55	4.0	70	412	58
M7	42150	8000	220	128	22	92	5.0	205	408	60
M8	40350	7850	190	128	22	55	3.7	195	470	73
M9	33150	7100	97	92	22	45	4.0	77	533	73
M10	38350	6500	262	120	33	75	4.0	317	361	75
M11	24500	5150	77	83	30	55	4.5	88	250	78
M12	39150	6800	313	107	50	83	2.7	318	478	72
M13	29000	7000	90	83	12	42	1.8	73	245	78
M14	37150	6650	133	128	38	42	1.8	163	408	68
M15	34000	5150	225	113	67	67	3.7	262	433	58
M16	32000	5100	202	92	67	83	3.2	255	325	65
M17	35150	5500	190	92	55	62	2.3	222	328	53
M18	34650	6250	102	113	55	50	1.3	67	550	62
M19	33500	5000	203	100	38	67	1.8	262	378	75
M20	34650	5000	178	90	30	80	2.8	222	435	58
M21	25000	5650	85	92	22	38	1.3	102	258	58
M22	20000	4600	77	60	72	33	1.3	97	250	58
M23	31150	4600	172	83	38	42	1.3	213	300	60
M24	8500	1150	74	59	202	53	1.7	272	195	51
M25	21000	2550	145	113	92	50	1.3	265	400	42
M26	5100	650	48	56	191	51	0.8	183	178	53
M27	28850	4350	170	92	33	42	1.3	242	400	53
M28	19000	2700	104	104	37	74	1.1	261	372	67
M29	26900	3600	150	111	37	37	2.0	198	695	61

Table 3: Concentrations of Trace Metals in the St. Jones River Bottom Sediments, Expressed as Parts Per Million of the <63-Micron Sediment Fraction. (Mercury Expressed as Parts Per Billion)

SAMPLE	Fe	Mg	Zn	Cr	Cu	Pb	Cd	Hg	Ni	Sr
SJ1	23150	3150	88	145	38	67	1.0	233	417	60
SJ2	44350	8350	360	183	55	133	1.3	467	662	122
SJ3	44000	8000	373	162	47	133	1.3	500	662	107
SJ4	44650	8000	358	200	50	87	0.5	383	453	108
SJ5	42500	7500	368	192	42	117	1.0	500	458	105
SJ6	39350	6500	213	162	25	58	1.0	233	292	92
SJ7	41850	7150	267	162	55	100	1.0	350	408	90
SJ8	38650	5500	277	145	62	100	1.0	375	595	93
SJ9	39350	7350	298	173	47	95	0.5	342	642	82
SJ10	40350	7850	335	162	50	117	1.3	355	628	58
SJ11	45850	8500	335	183	38	87	1.3	272	450	50
SJ12	33850	6650	367	157	42	100	2.3	337	317	42
SJ13	34350	5350	255	140	62	95	1.3	300	312	58
SJ14	33150	4350	227	107	38	95	1.8	262	275	63
SJ15	22650	5000	127	80	30	42	1.0	138	208	77
SJ16	30350	4750	310	107	33	125	2.3	347	403	52
SJ17	33150	4850	333	127	68	133	2.3	375	312	52
SJ18	29500	3650	270	87	38	113	2.7	342	350	30
SJ19	25850	3500	347	100	55	133	2.3	450	292	45
SJ20	25850	3600	355	107	72	130	2.3	467	287	60
SJ21	24500	3350	438	100	88	142	2.3	550	320	50
SJ22	24000	3650	505	120	130	142	1.8	750	353	53
SJ23	23850	3250	457	127	92	155	2.7	667	383	58
SJ24	23000	3350	505	133	117	237	2.3	867	312	77
SJ25	21000	4650	833	113	183	350	3.7	2833	308	73
SJ26	25850	3150	740	167	125	583	2.7	1267	342	77
SJ27	25000	5000	467	120	162	687	7.7	3083	353	103

In the graphs illustrating the distribution of strontium, mercury, cadmium, lead and zinc, the samples from the Murderkill River indicate high values in association with Bowers, Delaware. It seems obvious from these high values that the town of Bowers has a significant local pollutive effect upon the river. This effect is definitely local, however, dissipating less than one mile upstream, with the exception of cadmium which appears to be much more mobile than the other metals.

In most cases, there is a subtle but definite gradual lowering of metal levels from rivermouth to headwaters, as one would surmise would be the case with a tidal estuary. This trend would suggest that at least several of the pollutive metals are being transported into the lower reaches of the rivers by the tidal movement of the bay waters. Sea Grant Report No. DEL-SG-9-72 indicated that there is a trace metal "sink" in the vicinity offshore from the mouths of the Murderkill and St. Jones Rivers, so this net inshore and upriver transport of metals by tidal fronts is not entirely unreasonable.

In two cases, the upper reaches of the Murderkill River show unusually high values. In the one case, the Main Channel above Frederica indicates unusually high concentrations of nickel, and in the other case, the Spring Creek Branch indicates unusually high concentrations of copper. It is difficult to associate these anomalies with a direct cause by simple observation. However, in both cases there are farming activities closely associated with the

area sampled, and this might provide a possible explanation.

The most obvious trend one is struck with from Figures 2 through 11 is the extreme trend in the values of trace metals in the uppermost 3 miles of the St. Jones River. These 3 miles are the section of the St. Jones most closely associated with urban activity centered in Dover. Indeed, the last four samples in the series approach the sewage effluent outflow for the treatment plant currently servicing Dover. One can see that there are varying degrees of effect from the urban activities, although, in almost all cases, the effect is one of heightening the trace concentrations in the area. For zinc the heightened concentration is quite obvious: the effect of the urbanity is not necessarily a local one, with higher zinc concentrations noticeable for at least five miles downstream. A similar phenomenon, although not so extreme, is notable for the distribution of chromium. The heightened concentrations are marked for copper, lead, cadmium, and mercury. The downstream effects from the sources of trace metals associated with Dover are such that the general trace metal levels for the St. Jones River are higher than those of the Murderkill River for the following metals: zinc, chromium, copper, lead, and mercury. For these metals, it is significant that if there are common values in both rivers, they occur at 7-8 miles above the rivermouths, the approximate location of Frederica on the Murderkill.

CONCLUSIONS

1) Trace metal baselines have been established for the Murderkill River and the St. Jones River with respect to iron, magnesium, zinc, chromium, copper, lead, cadmium, mercury, nickel and strontium. It is hoped that further work may be accomplished in the forseeable future which will expand the results of this work.

2) Local pollution sources along the Murderkill River may be identifiable by their associated trace metal accumulations--most notable here is Bowers, Delaware--but the Murderkill River appears to have extremely low trace metal concentrations along most of its course. This bears out the reputation of the river as being virtually unpolluted.

3) The effects of large-scale urban population concentrations can be demonstrated by their associated trace metal concentrations. The large-scale effects of urban trace metal pollution have been demonstrated by the comparison of the baselines of the two rivers.

4) It is recommended that the Kent County Regional Sewage Treatment Plant be monitored for trace metal output, and that the river bottom sediments be similarly monitored in order to trace the growth of any front which may arise due to effluent dumping practices at the new facility.

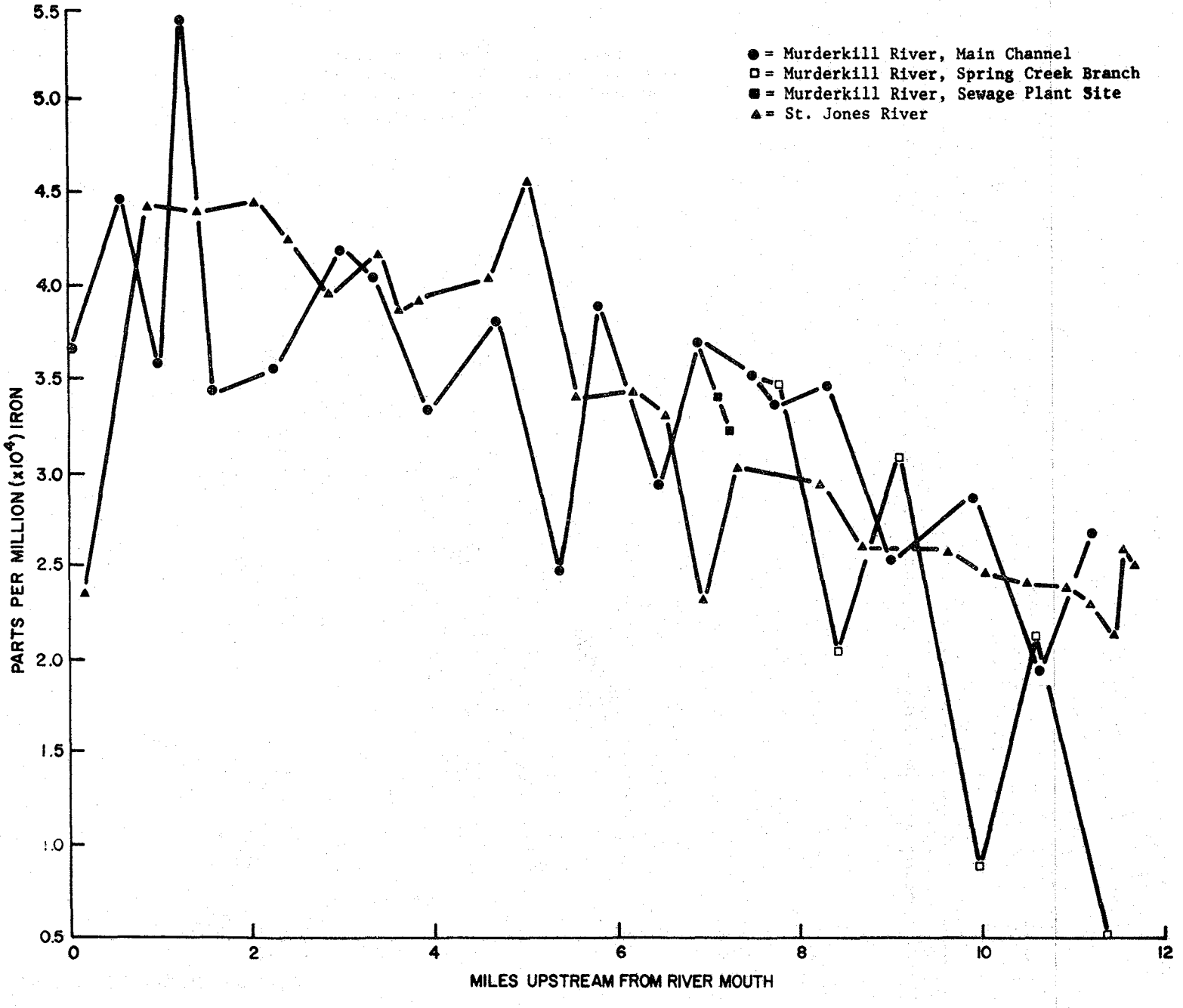

FIGURE 2: Distribution of Environmentally Active Fe in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

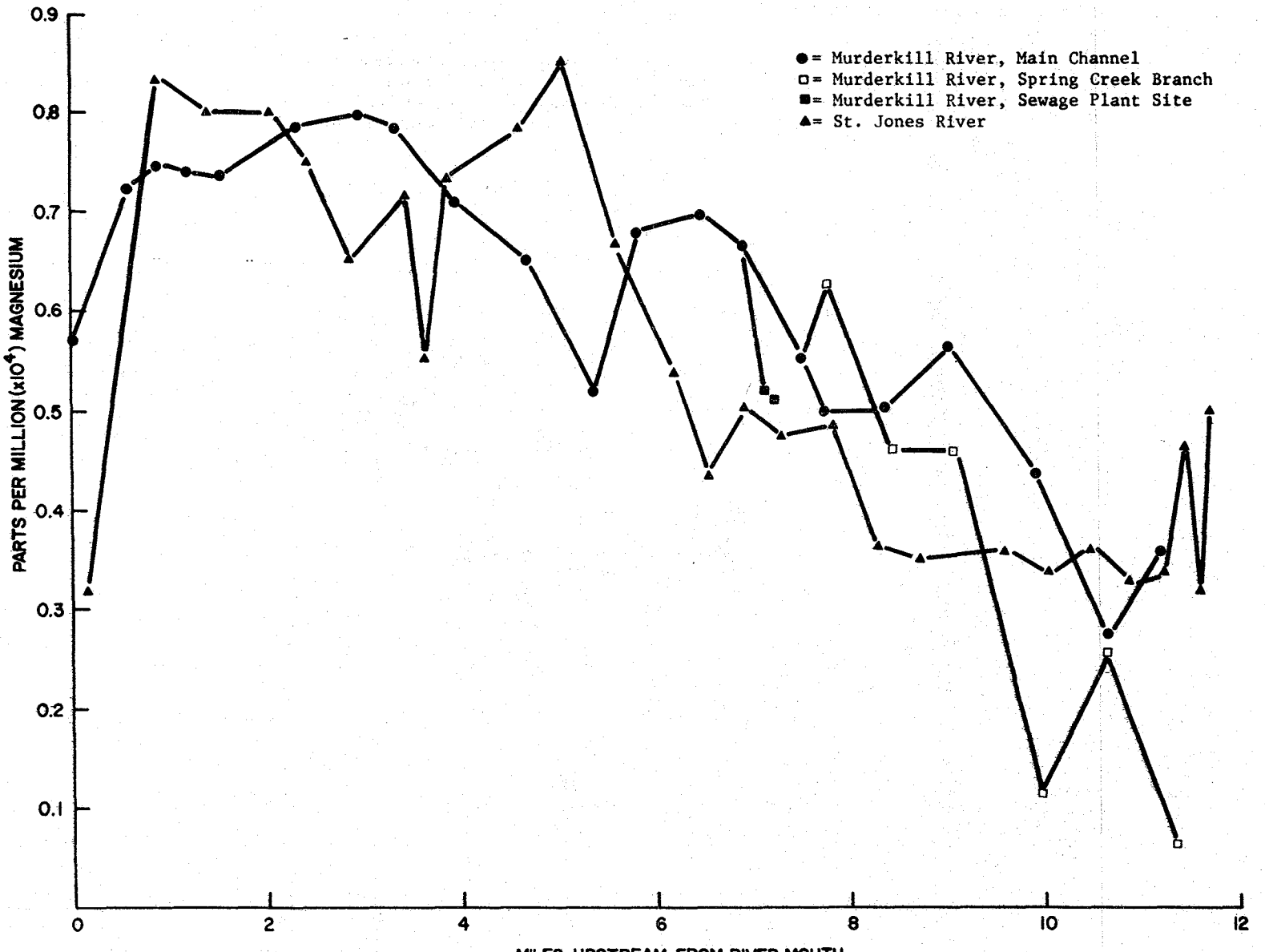

FIGURE 3: Distribution of Environmentally Active Mg in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

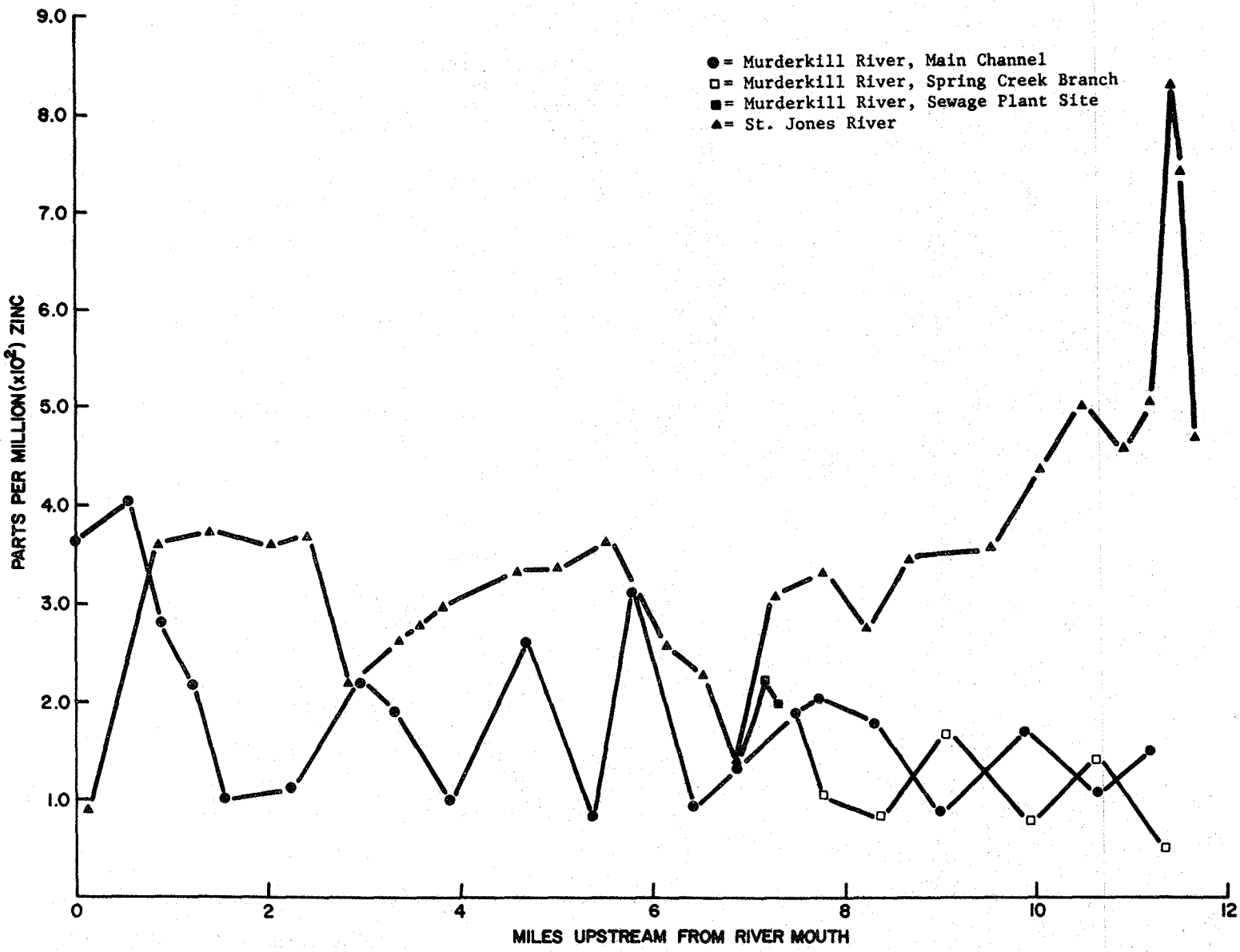

FIGURE 4: Distribution of Environmentally Active Zn in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

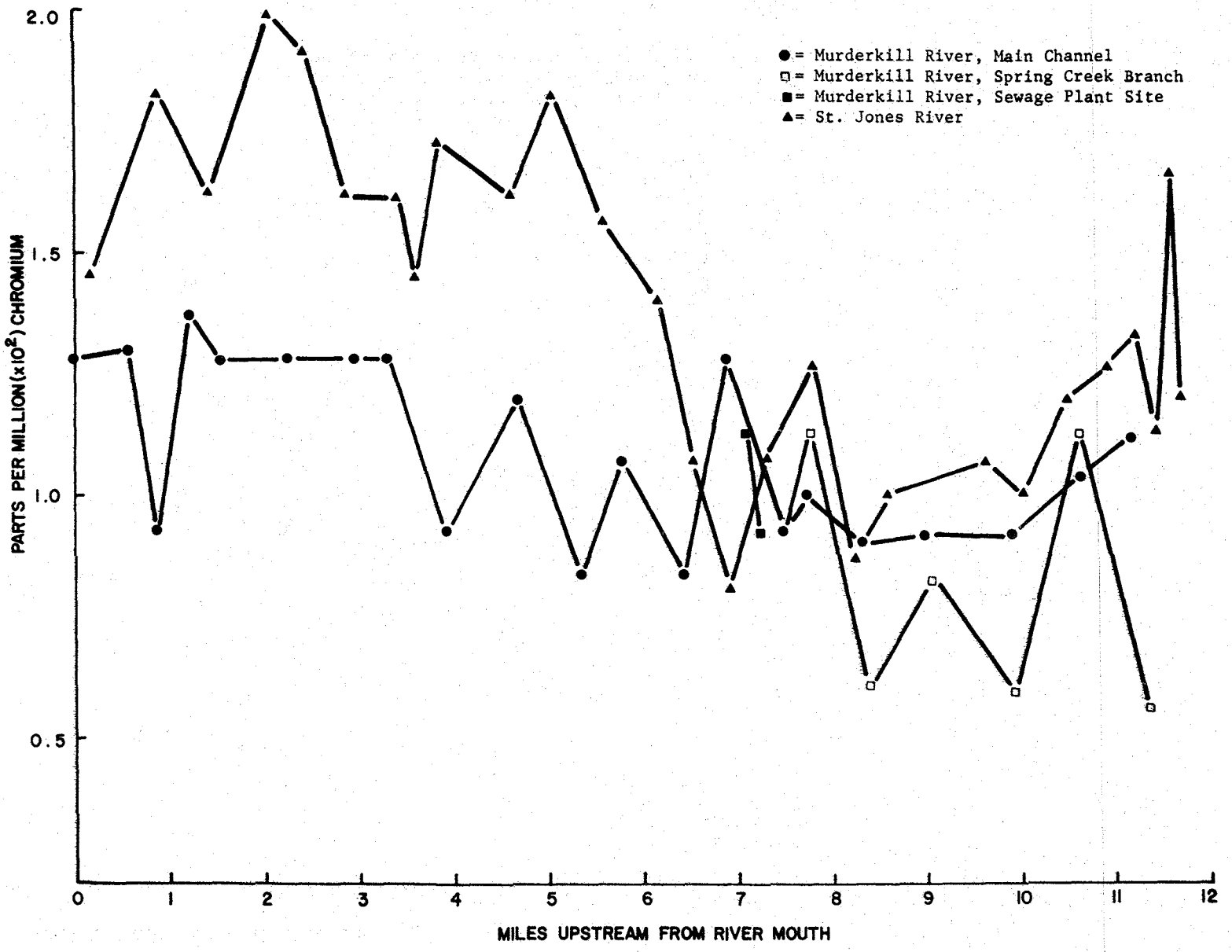

FIGURE 5: Distribution of Environmentally Active Cr in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

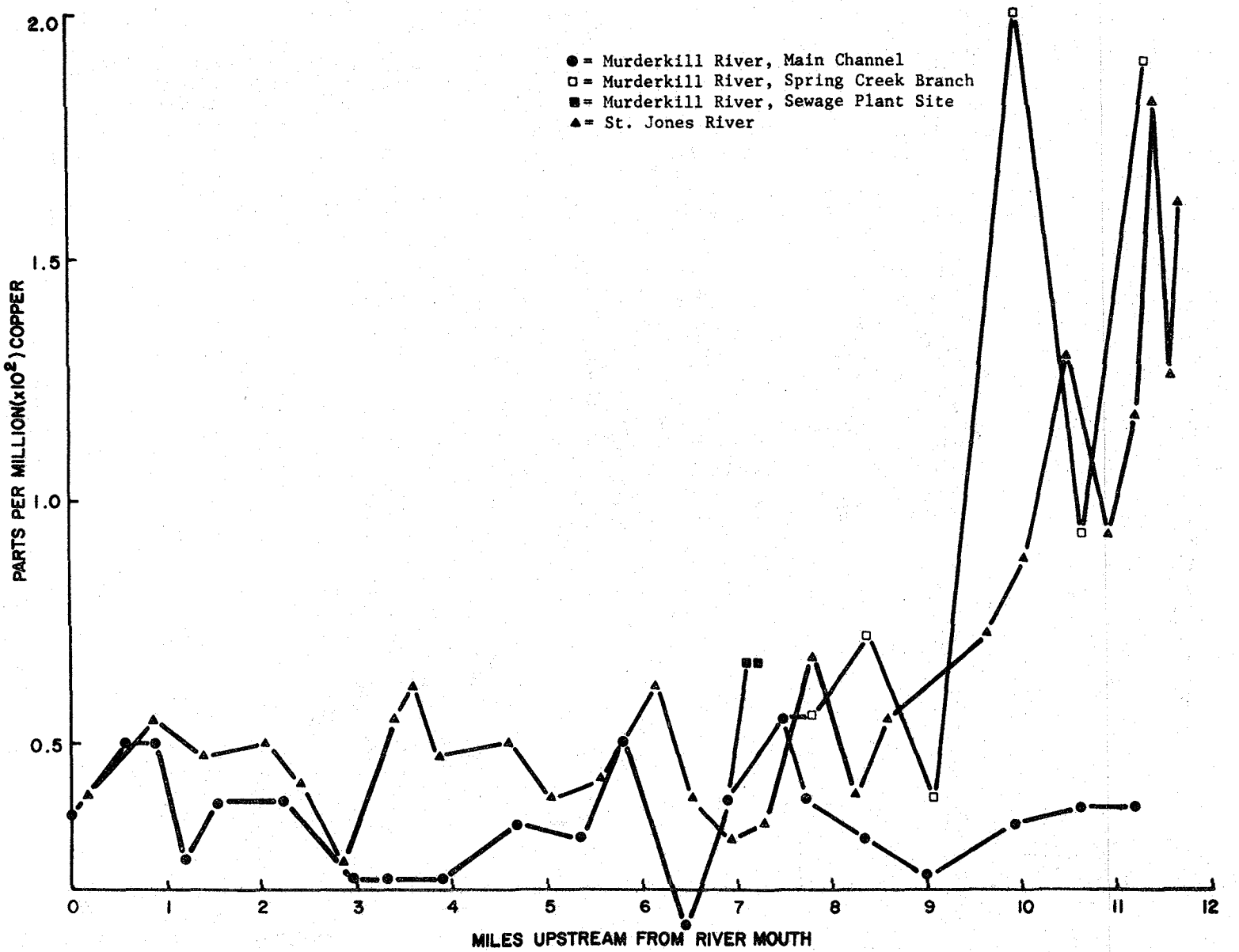

FIGURE 6: Distribution of Environmentally Active Cu in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

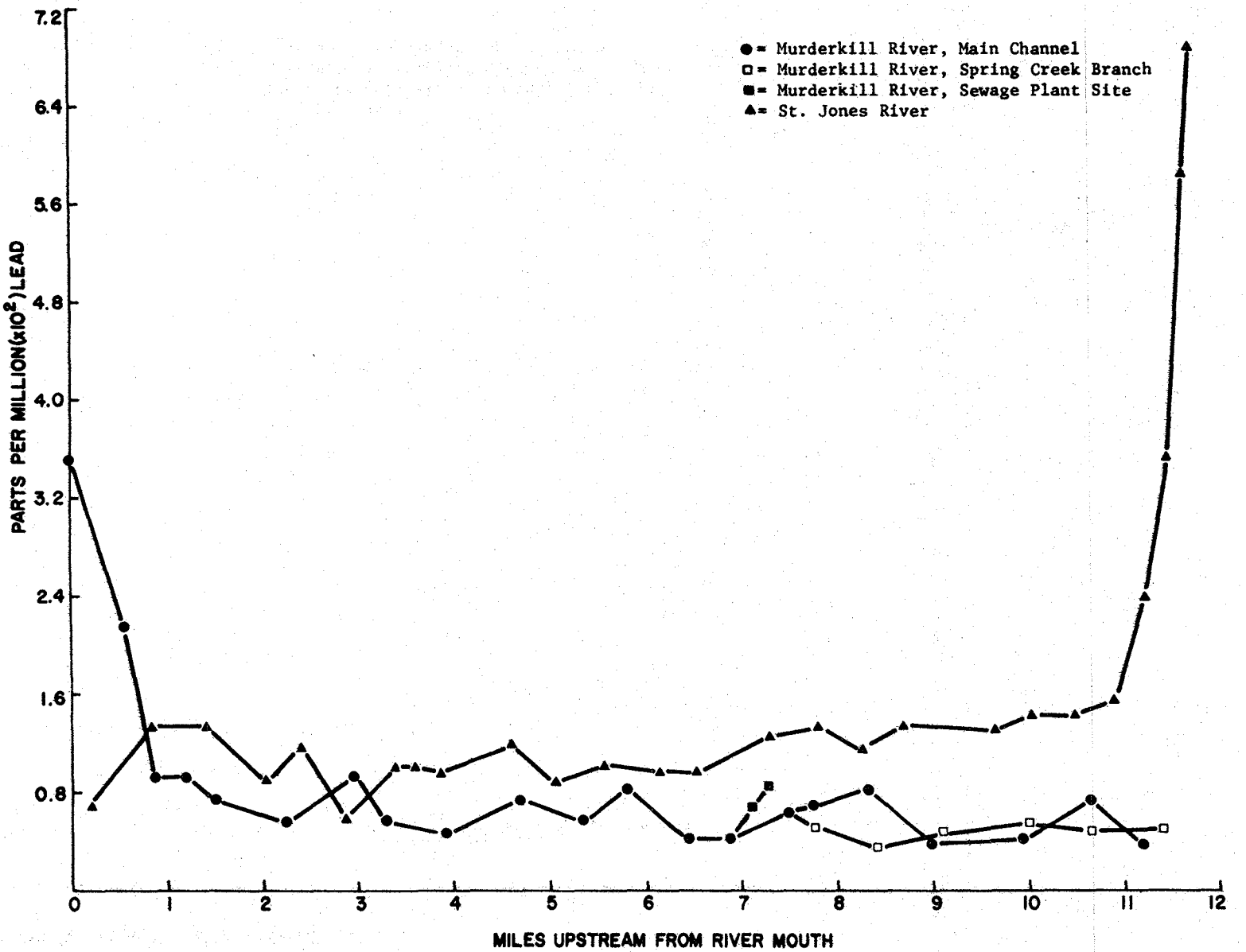

FIGURE 7: Distribution of Environmentally Active Pb in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

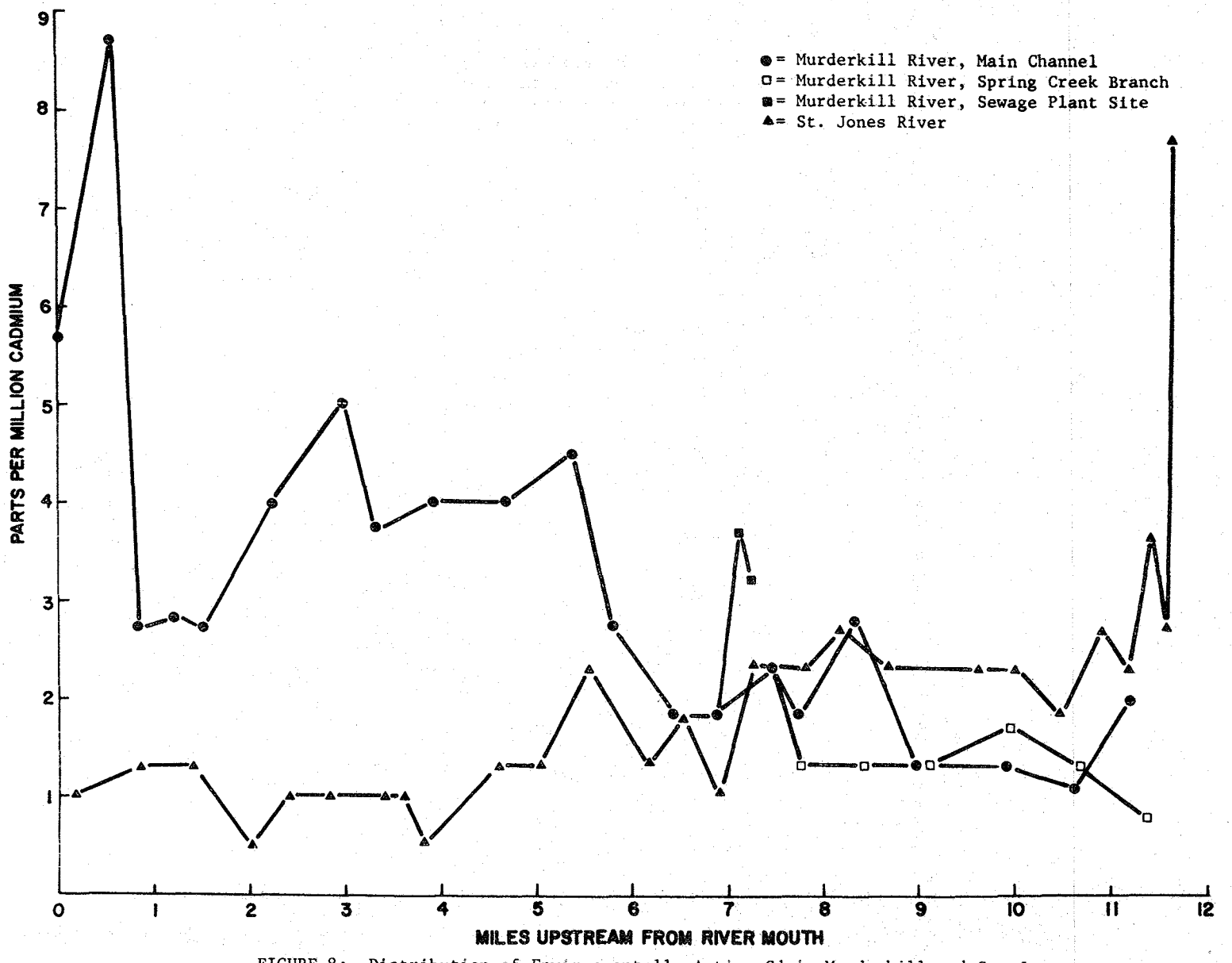

FIGURE 8: Distribution of Environmentally Active Cd in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

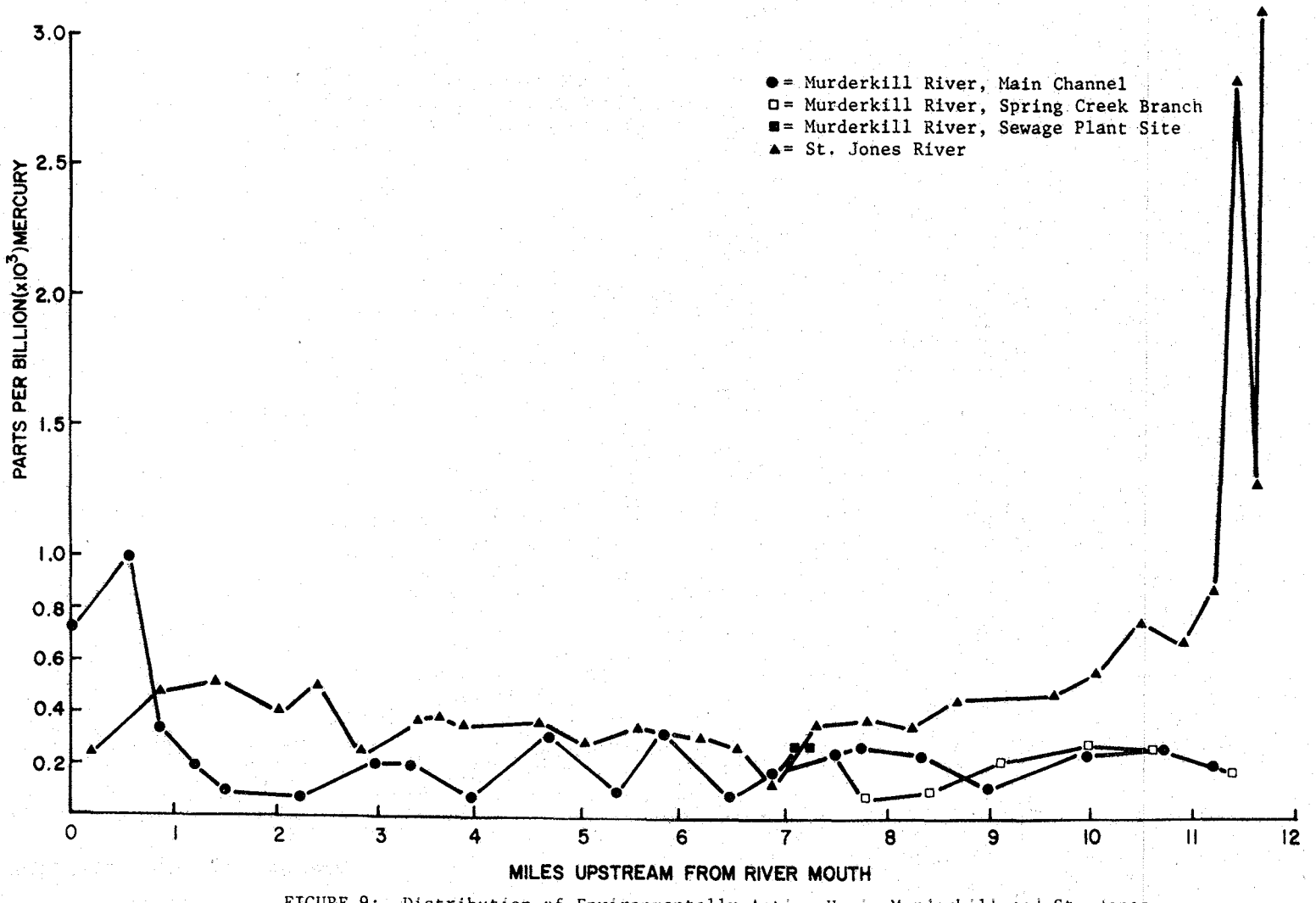

FIGURE 9: Distribution of Environmentally Active Hg in Murderkill and St. Jones River Bottom Sediments, Expressed in PPB of the <63 Micron Sediment Fraction.

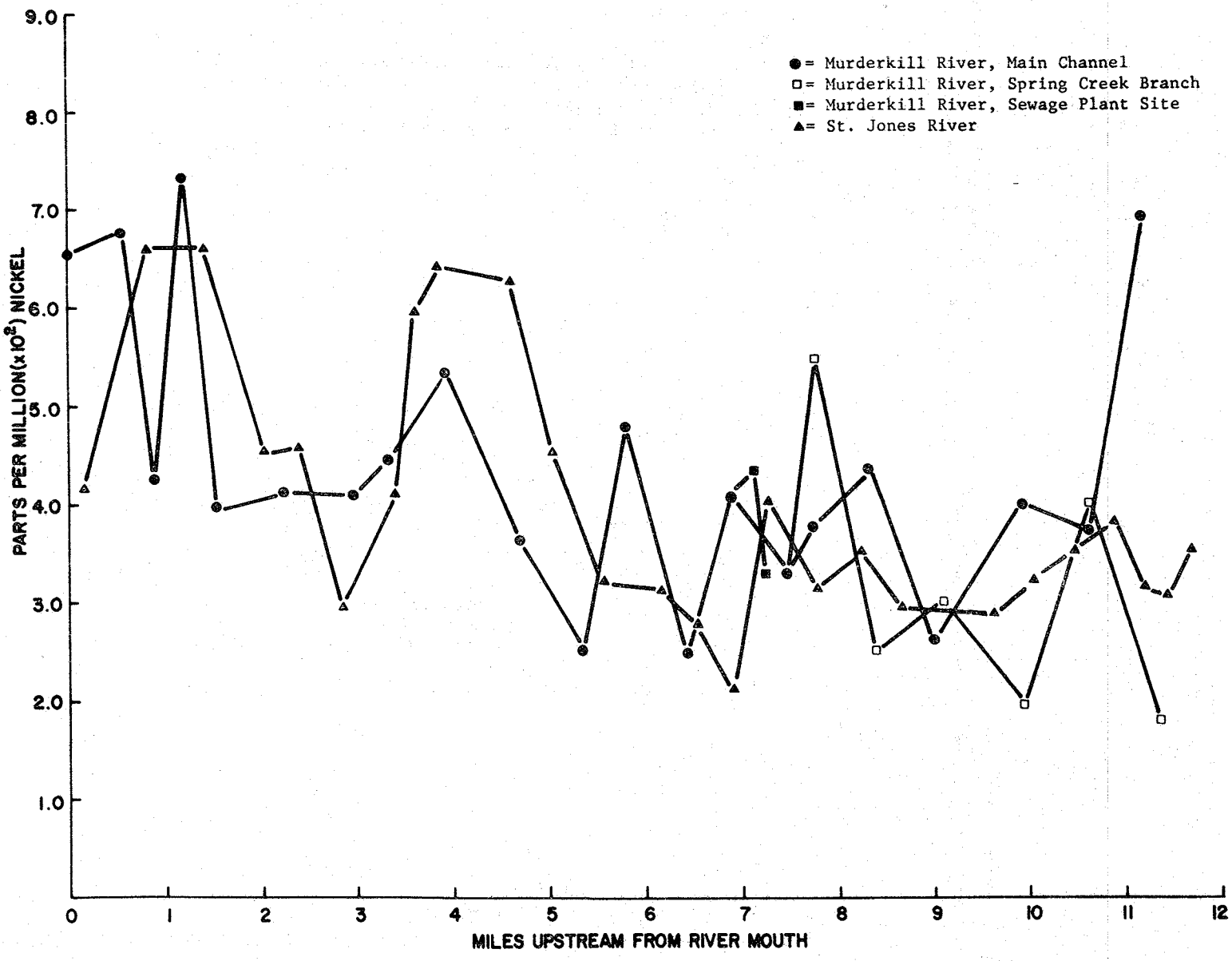

FIGURE 10: Distribution of Environmentally Active Ni in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the <63 Micron Sediment Fraction.

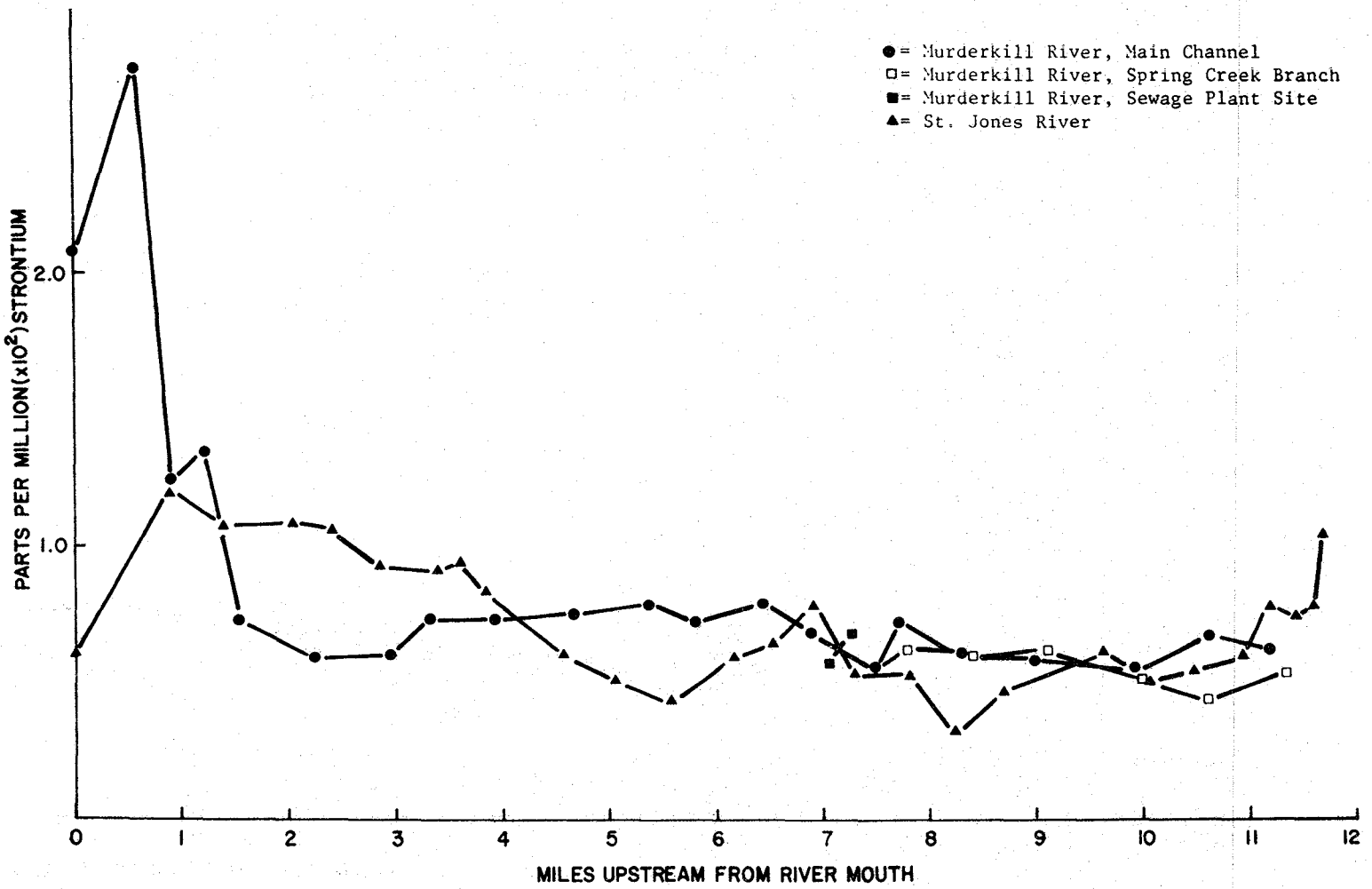

FIGURE 11: Distribution of Environmentally Active Sr in Murderkill and St. Jones River Bottom Sediments, Expressed in PPM of the < 3 Micron Sediment Fraction.

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