COO-3292-28

PROGRESS REPORT

BIOGEOCHEMISTRY OF TRACE METALS IN CHESAPEAKE BAY

(Contract EY 76-S02-3292)

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ERDA PROGRESS REPORT

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Section 2: Work Completed

A. Holdren, G. R. 1977. Distribution and Behavior of Manganese in the interstitial waters of Chesapeake Bay Sediments During Early Diagenesis. Ph.D. Thesis, Johns Hopkins University (Abstract).

B. Eaton, A. 1976. Geochemistry of some trace metals in the San Francisco Bay estuary. Geol. Soc. Am. Abstracts 8(6): 849-50.

C. Eaton, A. 1977. Geochemistry of the turbidity maximum. Paper presented to the SEPM Research Group on Environmental Geology. AAPG-SEPM Meeting June, 1977 (abstract).

D. Gross, M. G., M. Karweit, W. B. Cronin, and J. R. Schubel. 1977. Suspended sediment discharge of the Susquehanna River to northern Chesapeake Bay 1966 to 1976. Chesapeake Science (in press).

PROGRESS REPORT

SECTION 1

A. General Introduction

This continuing project is concerned with biogeochemical cycling of selected trace elements in the Chesapeake Bay estuarine system. By examining different aspects of the biogeochemical cycles we are working to quantify the relative magnitude of various trace metal inputs to the Bay as background information by which one can estimate the impact of different energy related activities on metal fluxes in the Bay.

Our objectives for the contract period July 1, 1976 - September 30, 1977 were:

1. Initiate studies on metals associated with very fine grained suspended particles formed by reactions involving interstitial waters released from Chesapeake Bay sediments and other sources.
2. Continuation of research on distributions and behavior of selected metals in interstitial waters in undisturbed sediments.

This document reports the status of our program with respect to these objectives and several other related studies initiated during the year. It also reports on work completed in the form of reprints and abstracts of papers presented during the year financed by this contract.

B. The Fate of Particle-Associated Metals in the Chesapeake Bay.

Introduction

The Chesapeake Bay, the largest coastal plain estuary in North America, has been subject to increasing stress as the regional population increased and as the demand for energy increased. Future stresses include projected increases in the fluxes of heavy metals and suspended solids from the Susquehanna River basin due to increased coal mining activity. Increased fluxes of sediment and associated trace metals could have significant effects on the biota of Chesapeake Bay, particularly filter feeding organisms (Sherk, 1971; Frazier, 1975; 1976).

Little is known about the fate of Susquehanna River derived trace metals within the Chesapeake Bay estuary, although hypothetical models have been proposed (Helz, 1976). Schubel (1968, 1969, 1972) and Biggs (1970) have studied the transport of suspended sediment in the Chesapeake Bay and suggested generalized models as to its fate. Much recent work (Turekian, 1976; Sholkovitz, 1976) suggests that transport of trace metals is predominantly a uni-directional process, with particles being formed and trapping metals all through the estuary. Helz (1976) and Windom (1975) suggest that there are escape mechanisms for various trace metals from the normal sediment traps. In order to verify the suspended sediment pathways proposed by Biggs (1970) and Schubel (1968, 1969, 1972) and determine whether the trace metals do follow the suspended sediments, we initiated studies of the transport and fate of particulate associated metals found in the Susquehanna River as it discharges into the Chesapeake Bay.

Carpenter et al. (1975) demonstrated that the Susquehanna River discharges seasonally variable amounts of metals associated with particulate matter. We are utilizing these seasonal variations as a tracer for the fate of particle-associated metals entering the Bay. We reasoned that once we could demonstrate that there were seasonal variations which could be traced through the Bay it would subsequently be possible to investigate mechanisms for metal transport and removal similar to those postulated by Boyle (1976), Sholkovitz (1976) and Sholkovitz et al. (1977).

Carpenter et al. (1975) also demonstrated that there was a population of particles entering the Bay which were significantly enriched in various trace metals at different periods of the year. They speculated that the causes for these enrichments were decaying organic matter, although others (Lewis, 1976) have suggested that they are due to low temperatures slowing removal processes in the river. Regardless of the cause of the enrichment the fate of these "fine" particulates becomes important since they could be a major source of food for filter feeders. They could provide a mechanism for moving metals past the normal sediment traps and into the productive regions of the Bay. Consequently we initiated studies of these fine particles to characterize them further as they moved through the estuarine system.

Status

1. Methods

Our sample collection and processing techniques were similar to those of Carpenter et al. (1975). Samples of 20 to 50 liter volume were collected in acid-cleaned polyethylene carboys. Carboys were connected to polyethylene tubing via a swagelock fitting in the cap. The bottles were then evacuated with a vacuum pump connected to the carboy via a second swagelock fitting and the vacuum used to pull water samples through the tubing. Samples were taken from near-surface waters at 10 locations along the Bay axis at various seasons of the year. To avoid possible contamination of samples by surface films or the vessel itself, the tubing was lowered rapidly through the surface layer to a depth of approximately a meter. The tubing was attached to a nylon line and a plastic coated weight. All samples were taken at a minimum distance of about 5 meters from the ship. The tubing and bottle were rinsed with about half the sample bottle volume and a fresh sample was then collected and stored in the dark until returned to the lab. Between stations all open ends of the tubing were covered with polyethylene bags. We feel these precautions insure that the samples are not contaminated during collection.

Subsequent processing entailed letting the samples settle for periods of 10 to 21 days, depending upon bottle size, to allow material of Stoke's diameter 0.5 μm (density 2.65) to settle out of suspension. The supernatant was decanted and saved and the settled solids (hereafter referred to as heavies) were transferred onto clean weighed 3 μm Nucleopore filters. Due to clogging of the filters and probable particle coagulation less than 0.5% of the heavies passed a 3 μm filter. The supernatant was then filtered through a 0.2 μm nucleopore filter and the solids ("fines") saved. The filtrate was discarded.

There are numerous caveats regarding post-sampling changes during processing involving particle size changes, metal partitioning changes and oxidation of organic matter as a result of biological activity. Thus we are not completely happy with the technique but it provides a qualitative separation of two metal fractions. Alternative approaches would include addition of biological activity inhibitors (which we are currently investigating), filtration through two successive filters of different pore size (which has its own inherent difficulties, involving both reproducibility and the meaningfulness of arbitrary size fractions when the presence or absence of organic matter may be more important than the actual size of the particles), or continuous flow ultra-centrifugation (which has been used successfully in San Francisco Bay by Anderlini et al. (1975) and in stream suspended sediment in Tennessee (Perhac and Whelan, 1972) and which would be our method of choice (given sufficient funding).

We have investigated some of the possible post-collection changes using two techniques. To investigate possible loss of organic carbon through bacterial oxidation during storage we compared particulate organic carbon determinations on fresh filtered and aged settled samples from one cruise. The data are shown as Table 1. One change is quite dramatic. As much as 90% of the organic carbon may be oxidized during storage. It is possible that there is loss of metal to the solution as a result of such oxidation. But it is more likely that any released metal would be sorbed or co-precipitated on the remaining particulate matter. When we discuss our interpretations of the current data we present the calculated results of both hypotheses.

To investigate changes in metal partitioning as a result of storage we performed comparisons of analyses of 3 sets of samples taken simultaneously by ourselves and some colleagues in the region of the Conowingo Dam. We treated samples in the standard way described above. Another research program has used successive filtration through either 8 μm and 0.45 μm Millipore filters or 3 μm and 0.2 μm Nucleopore filters. Results for 4 metals, Cu, Zn, Fe, and Mn, are shown in Table 2. The only clear evidence for compositional changes is for Mn, where there is apparently significant precipitation of Mn during storage. The number of comparisons is insufficient to determine whether there are detectable changes occurring for the other metals. Manganese precipitates fairly rapidly within estuarine systems

(Sholkovitz, 1976; Sholkovitz et al., 1977) and would therefore be less of a problem in saline waters than at the dam.

These data suggest that in a system such as the Chesapeake where there are potentially large fluxes of soluble manganese from the river and the bottom sediments (Carpenter et al., 1975) we should treat our samples on board ship using a continuous flow centrifuge. We have now sampled for soluble manganese at several locations within the Bay and found that although the soluble manganese at Conowingo Dam may reach high levels (Table 2), within the turbidity maximum, only 30 km downstream from the dam, soluble Mn is usually less than 5 ppb.

We have also investigated various techniques of analysis of our suspended sediment samples to be able to determine the maximum number of elements as useful tracers. These included optical emission spectroscopy, x-ray fluorescence (XRF), and atomic absorption determinations on digests of the suspended sediment. Although emission spectroscopy gave useful results for sediment samples, the accuracy was deemed insufficient for work on the suspended sediment samples (See Section F). Thin film x-ray fluorescence techniques have been successfully used for analysis of aerosol and suspended sediment particulates (Brady and Cahill, 1973; Subramanian and D'Anglejan, 1976). Thus we decided to apply these techniques to analysis of our suspended particulates, using facilities available at the University of California at Davis Crocker Nuclear Lab. Preliminary results on blind standards (Table 3) were quite promising, when the technique involved pelletizing samples with cellulose to form an effective matrix with a low Z number and therefore low mass absorption coefficients. However, results on another blind standard using suspensions of particles on a Nucleopore filter

Table 1

Concentration of Organic Carbon* in Suspended Solids from Chesapeake Bay samples, December, 1976

	FRESH	SETTLED
	collected on GF/F filter (effective pore size 0.7μm)	collected by gravity settling and filtration onto 0.2 μm filter
	μG/L	μG/L
Station 858	730	240
834	1200	225
818	1400	127+
804	1100	260
744	790	140

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*Samples analyzed with a Perkin Elmer CHN analyzer

Table 2

Comparison of metals in fine and coarse fraction of solids collected in lower Susquehanna River using two different sample processing techniques

FRESH FILTERED

	μG Fe/L	μG Mn/L	μg Zn/L	μG Cu/L
K-18-XII-76				
diameter > 8.0 μm	330	14	3.3	.6
diameter <8>.45μm	153	1.3	1.5	.6
"soluble" (<.45μm)	161	174	-	-
P.D.-2-XII-76				
diameter > 8 μm	560	29	5.9	.8
diameter < 8 >.45μm	97	.7	.8	.07
"soluble" (<.45μm)	89	161	-	-
K-1-III-77				
diameter > 3μm	3500	80	25	3.9
diameter < 3 >.2μm	320	6	3	.7

AGED SETTLED

	μg Fe/L	μG Mn/L	μG Zn/L	μG Cu/L
K-18-XII-76				
calculated Stokes* diameter >.5μm	240	47	2.7	1.3
still-suspended particles >0.2μm	240	43	4.5±2.3	.6±.3
P.D.-2-XII-76				
calculated Stokes* diameter >.5μm	350	60	4.6	.5
still suspended particles >.2μm	255	40	2.4	.4
K-1-III-77				
calculated Stokes* diameter >.5μm	3500	350	20.0	3.7
still suspended particles >.2μm	370	11	6.0	.9

All analyses by flame atomic absorption of filter digestions

*assuming 2.5 G/cc density

Table 3

Comparison among Analytical Methods Applied to Standard Samples

U.S.G.S. G-2 granite

	Nominal(1) Concentration	Emission Spectroscopy	XRF Cellulose Matrix	6N HCl Acid Extraction Atomic Absorption
% Fe	1.8	1.8	1.4	1.5
ppm Mn	260	290	305	250
ppm Zn	85	<400	93	
ppm Cu	12	12	17	14
ppm Ni	5	<9	<25	<10
ppm Ti	2800	4500	2600	
ppm Pb	31	<100	47	
ppm CR	7	30	<100	

U.S.G.S. BCR-1 Basalt

% Fe	9.4		3.7	8.3
% Mn	1.4		1.0	.93
ppm Zn	120		67	107
ppm Cu	18		12	20
ppm Ni	16		<12	
ppm Ti	13000		5900	
ppm Pb	18		36	
ppm Cr	18		–	

(1)Flanigan, F. J., 1973.

suggest that there are still severe matrix interferences for some elements of interest (see Section F). Rather than pursue this problem we elected to perform all analyses using atomic absorption spectrophotometry. Atomic absorption results on the standard are also shown in Table 3. Although much more tedious than x-ray fluorescence, it is the most accurate technique we have used. We will continue to use occasional x-ray fluorescence analyses as a low-cost tool for semi-quantitative scanning. In addition, we are encouraging the Crocker Nuclear Lab to investigate the sources of the matrix interferences so that x-ray fluorescence data obtained can be more useful.

The final analytical technique entails digestion of suspended sediments on Nucleopore filters in 6N HCl at 60° for 3 days, which produces reproducible and apparently complete leaching of those trace metals we have analyzed. We have used USGS rock standards as tests of our accuracy, but we are awaiting certification of new NBS standards for further checks.

All samples are digested in volumes of 3 to 5 mls of acid and metals determined using the method of small injections (Manning, 1975). Where concentrations are too low for flame atomic absorption determinations we are performing analyses by carbon rod techniques. We have found severe interferences with carbon rod techniques in a 6N HCl matrix which requires matrix modifications and attendant blank corrections. Thus our method of choice has been to optimize the sensitivity of our AA flame methods as far as possible. Thus far we have analyzed samples by atomic absorption only for Fe, Mn, Cu, and Zn. We are now performing analyses for Ni since x-ray fluorescence data indicates that element would be a useful tracer.

2. Results

a. "Heavy" particle associated metals

We initially proposed to determine whether the seasonal variations in metal composition of the heavy particulates observed by Carpenter et al. (1975) were reproducible and, therefore, useful as a tracer. Our data for a series of samples taken at Conowingo Dam at the head of Chesapeake Bay at approximately bi-weekly intervals are shown (Table 4). It appears from these data as though there is a winter enrichment for Fe and possibly other metals which could prove useful to follow metal transport in the bay.

Having demonstrated that the composition of the suspended sediment varies within reasonable limits over an extended period of time (sufficiently long to provide us with a chance to detect it when mixed with other suspended matter) we can then examine the distribution of suspended metals along the axis of the Bay (Figure 1) at selected times to trace the particle-associated metal transport. Data from different cruises (December, 1976; early March, 1977 and late March, 1977) are shown in Table 5. We are now processing samples obtained in April and June, 1977. Severe ice cover on the Bay in January and February prevented us from taking samples so we could not study the winter conditions.

The December and early March data appear to demonstrate that the unique Susquehanna metal tag is traceable throughout the northern Bay to a distance at least 100 km from the mouth of the Susquehanna. There is some suggestion that additional enrichment occurs for some elements below another source, Baltimore Harbor. A significant compositional change is not detected until we are some 100 km below the mouth where average salinities are about 10‰. In that region metals are sharply depleted in the solids. For the

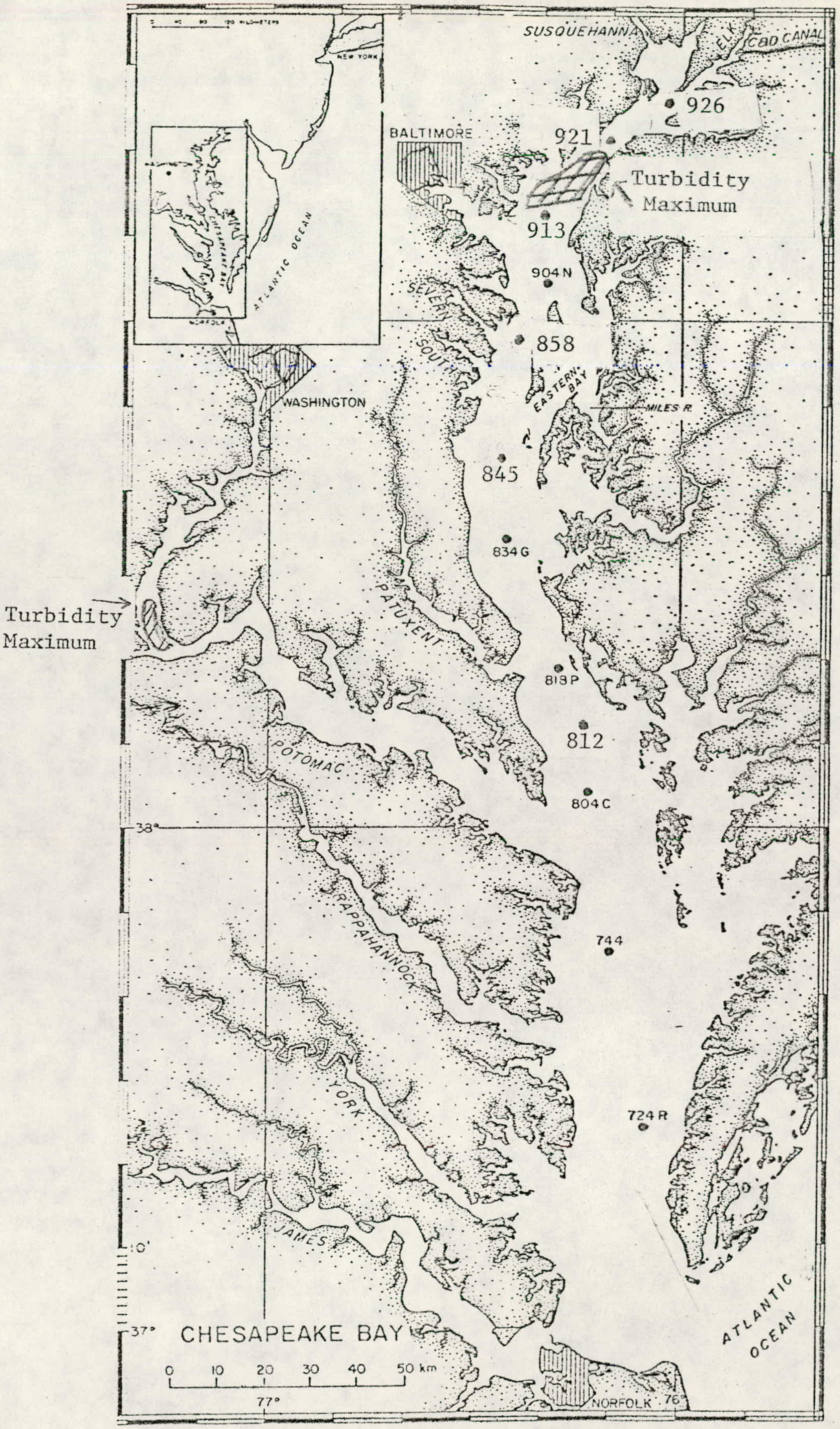


Figure 1. Chesapeake Bay

Table 4

Composition of Settled Solids from Samples taken at Conowingo Dam

	Fe (%)	Mn (%)	Zn (ppm)	Cu (ppm)
Dec. 9, 1976	8.1	2.7	940	-*
Dec. 21, 1976	8.0	2.8	1100	140
Jan. 5, 1977	9.5	1.1	1100	150
Jan. 19, 1977	8.3	.8	1400	110
Feb. 1, 1977	5.7	1.1	980	56
Feb. 14, 1977	5.9	2.0	1200	-*
Mar. 18, 1977	5.2	2.2	230	60

*determinations made; omitted due to possible contamination of sample

All determinations by atomic absorption.

Table 5

Composition of "Heavy" Suspended Solids in Chesapeake Bay

Station	Km Downstream	MG Fe / G	MG Mn / G	μG Zn / G	μG Cu / G
Dec. 11-17, 1976					
Susquehanna R.					
921	27	64	4.3	520	29
Turbidity Maximum					
913	43	66	4.0	450	31
Baltimore Harbor					
904	62	58	5.1	610	130
903	64	55	6.3	520	63
858	73	65	6.2	630	82
834	121	31	2.5	330	120
818	149	25	1.7	210	64
Potomac River					
804	172	24	1.2	220	95
747	211	20	.7	300	40
724	260	37	.9	260	20
Mar. 3-10, 1977					
Susquehanna R.					
926	17	58	6.3	320	65
Turbidity Maximum					
918	35	55	7.1	370	60
913	43	58	5.8	310	63
Baltimore Harbor					
904	62	62	9.4	630	160
845	100	67	7.4	390	85
Potomac River					
804	177	19	1.9	240	60
Mar. 22-25, 1977					
914	41	33	3.1	390	48
858	73	44	7.3	440	68
812	162	31	4.6	300	42

late March data there is no sign of a Susquehanna tag and we cannot use it as a tracer. We conclude on the basis of the change between early and late March that the residence time of particles in the northern Bay is relatively short, particularly during periods of high river flow.

Although there is no observable compositional change for metals during a given cruise in the upper Bay, there is still an efficient metal trap operating. The turbidity maximum (Schubel, 1968) acts to significantly reduce the suspended load entering the Bay and thus also affect the flux of particle associated metals to the mid-Bay. Up to 85% of the particle-associated metals are apparently caught in this trap (Figure 2). The lack of observed compositional variations immediately below the turbidity maximum suggests that riverine-derived metals still dominate the suspended matter even though the load has been significantly reduced. The load of individual metals as a function of distance downstream is shown in Table 6.

There are several hypotheses which can explain our observations of compositional changes in the mid-Bay. The simplest hypothesis to consider is dilution of river-derived material with other trace-element-poor solids derived from shore erosion or in situ productivity. Schubel (1969) and Biggs (1970) suggested that for the middle Bay 92% of the suspended sediment mass is due to these two sources, compared to 17% from those sources in the Northern Bay. The second hypothesis which might explain the distribution of composition variations would be an active removal hypothesis, similar to the flocculation proposed for a number of constituents by Sholkovitz (1976) and Sholkovitz et al. (1977). Under this hypothesis rather than seeing progressive dilution with trace metal poor material, one would expect to see an entirely new population of particles becoming dominant following

Figure 2. µg Zinc Extracted from all Suspended Solids/Liter

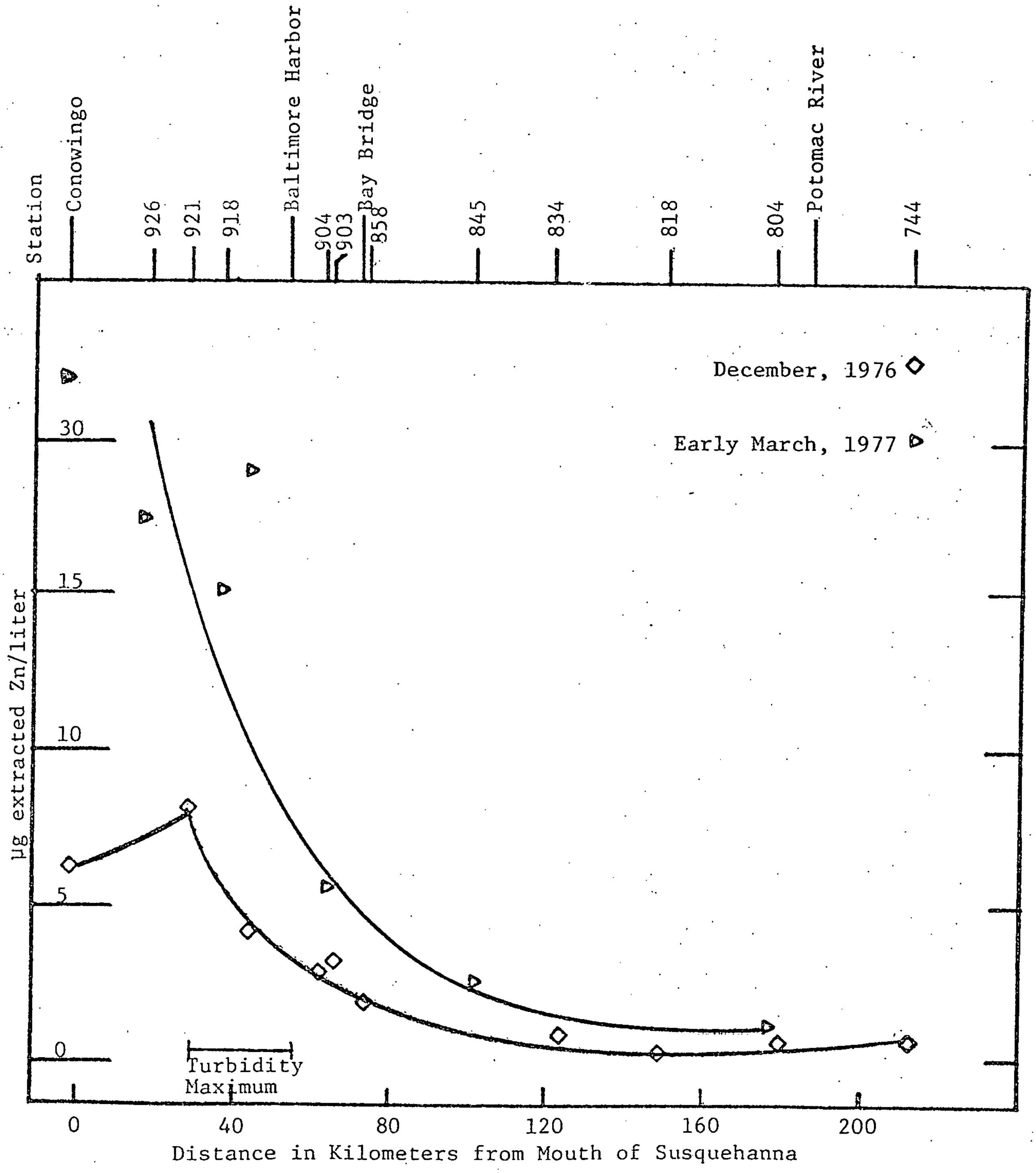


Table 6

Total Metal Load and Percent of Particulate Transport Associated with "Heavies"

Winter Samples			Sediment Load		Fe		Mn		Zn		Cu	
Station	Date	Km from Mouth of Susqu.	Total MG Solids / L	% from "Hv"	Total Partic µG Fe / L	% from "hv"	Total Partic µG Mn / L	% from "hv"	Total Partic µG Zn / L	% from "hv"	Total Partic µG Cu / L	% from "hv"
Conowingo	9-12-76	-4	5.1	69	540	52	120	79	4.3	77		
Conowingo	21-12-76	-4	5.1	57	550	42	110	74	6.2	52	.83	50
921	11-12-76	27	16.0	96	1020	97	66	100	8.3	96	.49	92
913	11-12-76	43	9.3	95	600	97	35	100	4.2	75	.32	81
904	15-12-76	62	3.4	87	210	96	17	100	2.8	75	<.49	>90
903	11-12-76	64	4.3	92	730	96	25	100	2.5	84	<.29	>86
858	15-12-76	73	3.1	83	180	94	16	100	1.9	84	.27	> 8
834	15-12-76	121	1.4	56	28	89	2	100	.8	32	<.14	>71
818	17-12-76	149	1.3	69	27	86	2	75	∿.2	-	<.10	>60
804	16-12-76	177	1.8	68	34	85	2	70	.5	52	<.15	>73
747	16-12-76	211	2.2	79	39	88	1	100	.8	64	<.11	>64
724	16-12-76	260	2.7	79	93	77	22	100	11.0	62	<.09	>56
Spring Samples - early March												
Conowingo	1-2-77	-4	5.4	67	560	38	63	63	11.0	32	1.0	70
Conowingo	14-2-77	-4	5.3	75	480	50	110	73	9.8	49	2.4	70
926	3-3-77	17	53.0	87	3700	87	330	91	17.5	86	3.9	79
918	4-3-77	35	37.0	92	2200	86	250	96	15.0	87	<2.5	>80
913	3-3-77	43	55.0	95	3400	88	310	97	19.0	84	4.3	74
904	4-3-77	62	7.6	83	500	78	60	99	5.8	69	1.5	67
845	10-3-77	100	5.9	88	380	92	39	97	2.6	77	.6	71
804	8-3-77	177	1.2	67	21	71	1.7	88	1.0	19	.3	14
Spring Samples - late March												
Conowingo	18-3-77	-4	76.0	87	4.2	81	150	99	21.0	71	5.3	81
914	23-3-77	41	101.0	98	3600	89	305	99	39.0	97	5.0	94
858	22-3-77	73	6.9	94	310	94	59	80	4.5	64	.50	88
812	25-3-77	162	4.1	95	130	92	19	95	1.4	86	.36	44

All analyses by atomic absorption on 6N HCl digests of filters.

flocculation and removal of river-borne detritus. The two hypotheses have different implications for the fate of anthropogenically derived metals. Confirmation of a simple dilution hypothesis would suggest that if man increases the flux of trace metals to the Northern Bay through energy-related activities such as increased mining the impact will be felt as a gradual increase in particle-associated metal concentrations progressively farther down the Bay. On the other hand, confirmation of a trapping hypothesis would suggest that impacts could be predicted on the basis of salinity distributions.

Ferri (1977) has presented data for the trace element composition of material conceivably reaching the central Bay from shore erosion (Table 7). It is apparent that this material is highly depleted in trace elements compared to the river-derived material. Assuming that shore erosion material was acting as the dilutant it does not seem to become significant until station 834, where observed suspended sediment compositions change. However, Biggs (1970) suggests that shore erosion is dominant throughout the mid-Bay, including regions much farther north than station 834. Shore erosion is undoubtedly an infrequent process and that may explain in part the discrepancy between our observations and those of Biggs (1970). The fact that we have observed metal enrichments as far as 100 km from the mouth of the river does suggest that significant amounts of particle-associated metals can travel that far. Simple dilution with shore erosion materials in the region below station 834 should result in progressive dimunition of the metal content of the suspended sediments since the shore erosion component remains relatively constant whereas river-derived material would be diluted into an increasing volume of water. We do not see such dimunition, so we

Table 7

Composition of Shore Erosion Derived Material Contributing to Suspended Sediment in the Central Bay (Ferri, 1977)

Element	ppm
Mn	89
Fe	31,500
Ni	20
Cu	12
Zn	60
Ti	11,000

conclude that simple two end member mixing of river detritus and shore-erosion material does not account for the observed metal distributions.

The other potential source of compositional alterations by dilution is biogenous material. Martin and Knauer (1973) have given typical values of different metals in phytoplankton associated with the organic and inorganic fractions, respectively (Table 8). Using their data we calculate the effective trace metal composition of phytoplankton remains assuming different organic matter to ash ratios. Estimates for the ash weight to organic carbon ratio of phytoplankton range from over 2.7 (Biggs, 1970) to less than 0.20 (Martin and Knauer, 1973). Calculated metal compositions of whole phytoplankton for these two extremes are shown in Table 9. We stated earlier that as a result of sample processing up to 90% of the organic material is oxidized. We have assumed that there is no concommitant loss of trace metals. Thus one can calculate the apparent metal composition of biologically derived material in our suspended solids (Table 9b). We can utilize these probable end member compositions and the organic carbon data we have obtained for the December 1976 samples to determine whether two end member mixing between biological material and river borne detritus could explain our observed metal distributions. Using an ash weight/dry weight ratio of 0.10 as a reasonable estimate for phytoplankton (Martin and Knauer, 1973), the primary production contribution to our observed sediment weights in the central bay are shown in Table 10. As we travel from station 858 to 834 and 818, the percentage of observed solids due to biota rises from about 13% at 858 to 54% at 834 and 818. Using Ti as an indicator element for lithogenous particles (Ti is strongly depleted in plankton compared to clay materials), we can independently calculate the fraction of biological material needed to account for observed Ti distributions. Our only Ti data

Table 8

Median Metal Concentration in Phytoplankton

(Martin and Knauer, 1973)

	ppm metal in organic fraction	ppm metal in silica fraction
Fe	224	220
Mn	6	< 1
Cu	3	6
Ni	2	< 0.5
Zn	19	5
Ti	<6	115

Table 9a

Calculated Composition of Whole Phytopalnkton
Assuming Different Organic Matter/Ash Weight Ratios
(composition of ash and organic fractions taken from Table 8)

	Fe	Mn	Cu	Ni	Zn	Ti
10% ash wt	220	6	3.6	2	19	∿11
50% ash wt	220	3	4.5	∿1	12	55

Table 9b

Calculated Apparent Composition of Biogenous Materials Added to
Suspended Sediment Assuming Complete Oxidation of Organic
Matter, But Trapping of Associated Metals and Ash Material

	Fe	Mn	Cu	Ni	Zn	Ti
10% ash wt	2200	60	36	20	190	110
50% ash wt	440	6	9	2	24	110

Table 10

Fraction of Measured Heavy Suspended Sediment Derived from Biota, Assuming Ash Weight Equals 20% of Raw Particulate Organic Carbon (Data from December, 1976)

Station	(a) Measured Suspended Sediment (heavies) (mg/ℓ)	(b) Fresh Particulate Organic Carbon (POC) (mg/ℓ)	(c) Calculated Ash Based on Fresh POC (mg/ℓ)	(d) Observed Organic Carbon on heavies (mg/ℓ)	(e) % of Observed Solids Due to Organism (c+d)/a
858	2.6	0.7	0.14	0.2	13
834	0.8	1.2	0.24	0.2	55
818	0.9	1.4	0.28	0.2	53
804	1.2	1.1	0.2	0.3	42
744	1.7	0.8	0.16	0.1	15

All organic carbon determinations performed with a Perkin Elmer CHN Analyzer.

is from x-ray fluorescence and its accuracy is in question (Table 3). However, based on the apparent precision of the analyses we can still apply the technique. The measured Ti goes from about 0.6% at all stations north of 834 to 0.3% at 834 and 818 (Table 11). This suggests an approximately 50% dilution, which is close to our other calculation of 54%. We are verifying these calculations by determining Ti by atomic absorption methods.

Using the calculated and observed Zn and Fe data similar results are calculated for the degree of dilution, 40-50%. Thus much of our observed data in the lower Bay seems to be explainable on the basis of simple mixing of different end members. There is, however, some form of active removal occurring for river derived material, since for stations 858 through 818 there is no significant change in the amount of biological material present. Rather the change is due to a sharp reduction in the quantities of abiological material present, from about 2.4 mg/l at station 858 to 0.5 mg/l at 834 and 818. The salinity increases in this region from about 5 to 10‰ so on the basis of simple dilution one would only expect a 50% decrease in suspended matter. Thus there appears to be some removal mechanism operating such as flocculation. As noted earlier this salinity regime is the same as that noted by Sholkovitz (1976) for maximum removal of a number of dissolved constituents due to flocculation. It, therefore, appears as though we must invoke two hypotheses to account for our observed metal composition distributions; active removal of river-borne detritus due to increasing salinity and coagulation and mixing of the residue with biological material depleted in metals. Thus we cannot say with certainty without further study what the effect of increased metal fluxes in the Susquehanna would be on the mid-Bay region, but it appears as though future enrichments would be restricted by natural removal processes in the estuary. If so, this would mean that Bay

Table 11

Composition of Suspended Sediment Samples from December, 1976 as Determined by X-ray Fluorescence

		%		μg/g			
Station		Mn	Ti	Zn	Cu	Ni	Pb
921		0.44	0.54	368	40	86	160
913		0.36	0.56	369	45	59	162
904		0.47	0.61	506	73	43	208
903		0.45	0.43	386	47	31	116
858		0.61	0.56	558	78	82	218
834		0.21	0.30	232	74	44	155
818	replicates	0.11 0.17	0.35 0.26	247 241	22 30	14 24	81 62
804		0.06	0.20	157	32	14	70
744		0.12	0.38	448	39	28	49
724		0.10	0.41	197	14	18	61

waters and marine organisms are protected against the effects of human activities releasing metals in the river.

b. "Fine" particle-associated metals

We originally postulated that metals associated with the "fine" particulates might represent an important mechanism for metal uptake by biota and for escape of metals from the natural sediment traps in the Bay.

We are limited in our observations on these fine particles by sample size. In spite of the settling of "heavies", we still find our 0.2 μm filters clogging rapidly, restricting us to sample sizes of 1 mg or less. We are currently overcoming this problem by digesting multiple filters, although this increases the procedural blank and our uncertainty. We can still make some valid observations.

First, although up to 50% or more of the particulate metal transport may occur associated with this fraction in fresh waters, the partitioning for most metals changes rapidly within the estuary, to only about 10% or less of the particle associated transport (Table 6). Once we reach the biologically dominated region of the Bay this fraction again becomes important, although below the turbidity maximum of the Bay the total particulate metal transport is probably small compared to the dissolved fraction for both Cu and Zn (Cronin et al., 1974).

Second, this fraction is as much as 33% organic carbon (Table 12) and, therefore, highly mobile and perhaps significant as a source of metals to biota. We do not know on the basis of present data whether the metals are associated with the organic or inorganic fraction of this material nor have we yet characterized the organic matter.

Table 12

Organic Carbon* Content of "fines", December, 1976

Station	Particulate Organic Carbon on "fines" (mg/ℓ)	Total wt of "fines" (mg/ℓ)	% Organic Carbon in "fines"
921	0.12	0.6	20
913	0.11	0.5	22
904	0.08	0.5	16
903	0.07	0.3	23
858	0.08	0.5	16
834	0.14	0.6	23
818	0.13	0.4	32
804	0.13	0.6	21
744	0.08	0.5	16
724	0.09	0.3	33

*Analyses for organic carbon performed with a Perkin Elmer CHN Analyzer on material still in suspension after 10 days, but trapped by a GF/F glass fiber filter (nominal pore size 0.7 μm).

Third, on a mass basis, the "fines" are more enriched than the "heavies" in the trace metals we have analyzed thus far by a factor of 2 to 3 (Table 13). The composition does not show the same systematic variations downstream as the heavies. This is undoubtedly due in part to uncertainties in weights (which are extremely low), but it may also indicate that there is a fraction of particulate associated metals which is highly mobile and can indeed escape the normal sediment traps. In addition, the enrichment in the fines may be of biological significance if filter feeding organisms can sort particles by size (Sherk, 1971), since they would then be selectively exposed to high apparent concentrations of metals. This would contrast with unselective filtering of a variety of particle sizes where the metal composition would be lower.

We do not know whether the enrichment is restricted to the Susquehanna basin. Our enrichment factors for the fine fraction are certainly much greater than comparable enrichment factors observed in San Francisco Bay fine particulates (Anderlini et al., 1975) and may, therefore, be unique to the Chesapeake region. We still need to confirm this by examining comparable particles in other local estuary systems. Until we can determine the origin of the "fines" we cannot speculate as to their implication for future energy related activities. We cannot proceed further in answering these questions until we have overcome some of the sampling difficulties for these particles. We hope to utilize either radial flow filtration or continuous flow centrifugation to overcome the problem of lack of sufficient material.

Table 13

Typical Enrichments of Metals in "Fines" Relative to "Heavies"

(only samples where the weight of the fines is >1 mg are included)

	Zn			Cu		
Station	μg/g Composition of "fines" (a)	μg/g Composition of "heavies" (b)	Ratio (a/b)	Composition of "fines" (a)	Composition of "heavies" (b)	Ratio (a/b)
March 3-10, 1977						
921	530	320	1.7	170	60	2.8
918	720	350	2.1			
913	670	315	2.1	290	65	4.5
904	1340	630	2.1	350	150	2.3
845	940	400	2.4	320	85	3.8
804	1600	240	6.7	630	59	10.7
March 22, 1977						
914	430	390	1.1	107	48	2.2
C-18-III-77	600	230	2.6	138	60	2.3
C-14-II-77	3500	1150	3.0	744	350	2.1
C-I-II-77	4500	980	4.6	525	56	9.4
C-21-XII-76	1300	1100	1.2	90	140	0.6
Median Ratio			2.1			2.8

Median and range of comparable particle fractions observed in San Francisco Bay (Anderlini et al., 1975)

Zn = 1.3(1.2-1.5, n = 3)

Cu = 2.5(2.0-3.2, n = 5)

C. Behavior of Iron in the Potomac River Estuary

Introduction

As a subproject of this contract we have been investigating the behavior of iron in the Potomac River estuary. The Potomac is smaller than the Chesapeake and in its lower reaches is not affected to any great extent by acid mine drainage. It has a potential point source of metals near the low salinity tidal reaches, primarily the Blue Plains sewage treatment plant. It also has an apparent turbidity maximum. By studying the distribution of one element in that estuary, we felt we could examine in somewhat greater detail the processes going on in zones of the river such as the turbidity maximum. We elected to look at iron since analytical techniques are comparatively simple and contamination is not as great a problem as for some of the other metals. In addition, Boyle (1976) and Boyle et al. (1974) have demonstrated that iron consistently displays non-conservative behavior and that its behavior largely reflects coagulation of fine particles. Thus it may be a useful tracer for other materials affected by coagulation.

In addition, some knowledge of the behavior of metals in the Potomac as compared to the Susquehanna-Chesapeake Bay system would allow us to further determine the extent to which the Susquehanna may be unique.

Results

Thus far we have had two cruises in the Potomac. These cruises were in March and June, 1977. Samples were collected using a continuous flow hull mounted pump which we had previously found to produce no significant blank (less than 1 ppb "soluble" iron). On board ship the samples were immediately filtered through 3 μm Nucleopore and GF/F glass fiber filters (nominal pore size 0.7 μm). To prevent changes in iron concentration due to filter clogging (Kennedy et al., 1974), we used only minimum volumes of solution, just enough to rinse the filter and collect enough solution for analysis (25-50 cc). Samples which had passed through each of the filters were analyzed for total reactive iron, using a modification of the method of Stookey (1970). Reactive iron is considered that iron reduced upon standing for at least 30 minutes in the presence of the mixed acid-reducing reagent of Stookey (1970). The sample is then buffered with a sodium acetate buffer and the iron absorbance determined using a 10 cm cell. The data from these cruises are shown in Figures 3 and 4.

Several conclusions can be drawn from these data. "Soluble" iron is rapidly removed from solution in the Potomac River, being essentially completely gone within 30 miles from the probable source at high flow and 10 miles at low flow. The removal occurs before there is any evidence of salinity intrusion, suggesting that the mechanism of removal is some time dependent function rather than a salt effect. Filtration of several samples through 0.2 μm filters on the June cruise produced still lower values for soluble Fe, suggesting that we are seeing colloidal iron (Boyle, 1976). The iron passing a 3 μm filter shows the same general trend as the "soluble" iron, but the slope of the removal curve is different, and appears to be affected by the turbidity maximum. It may reflect trapping and enhanced coagulation of the iron as a result of increased water residence time in that region. The weak acid soluble iron reflects the presence of the turbidity maximum. Until we have obtained more data we do not want to speculate further as to the systematics of the acid soluble iron distribution.

Figure 3. Filter Passing Iron in the Potomac River

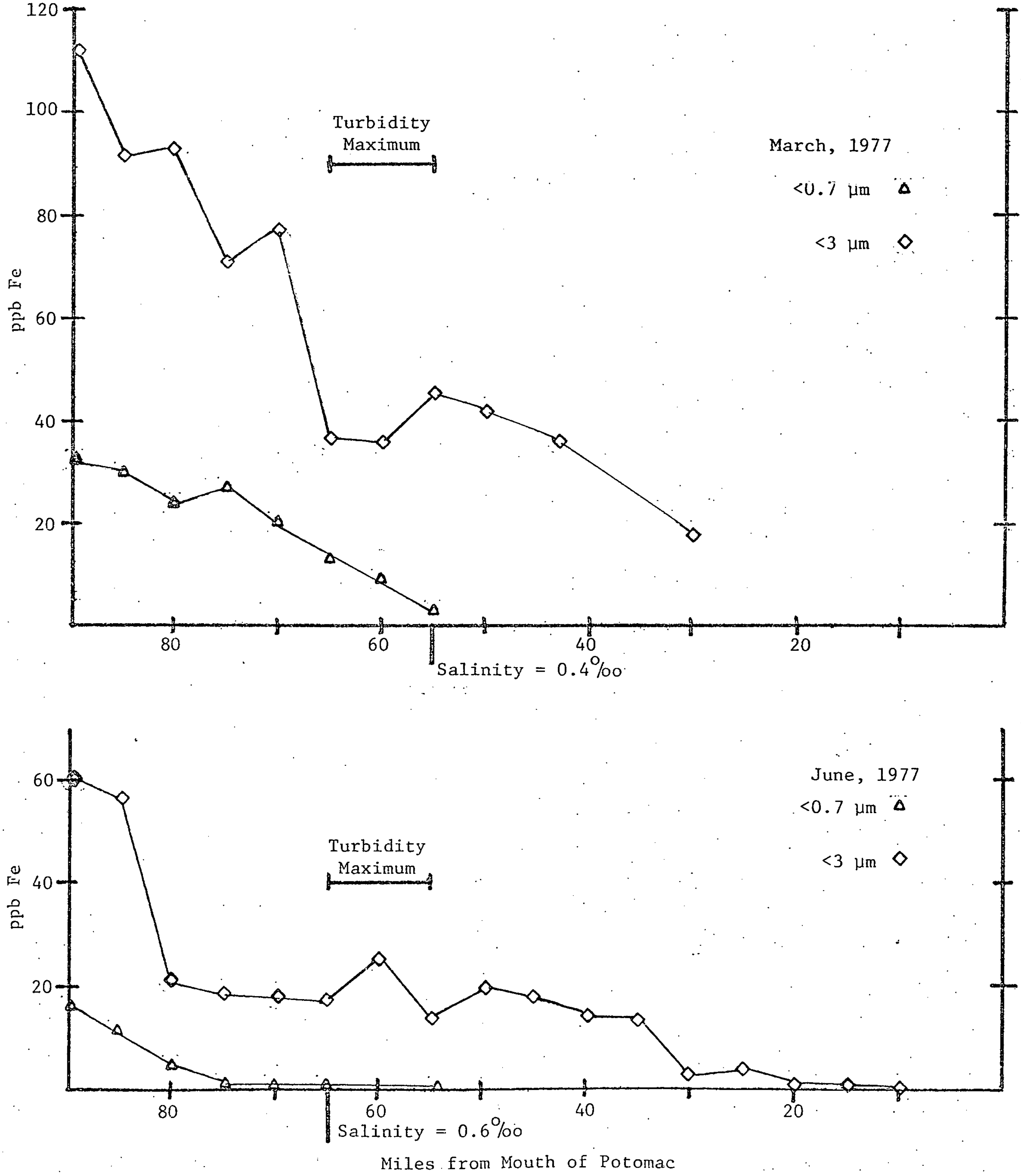
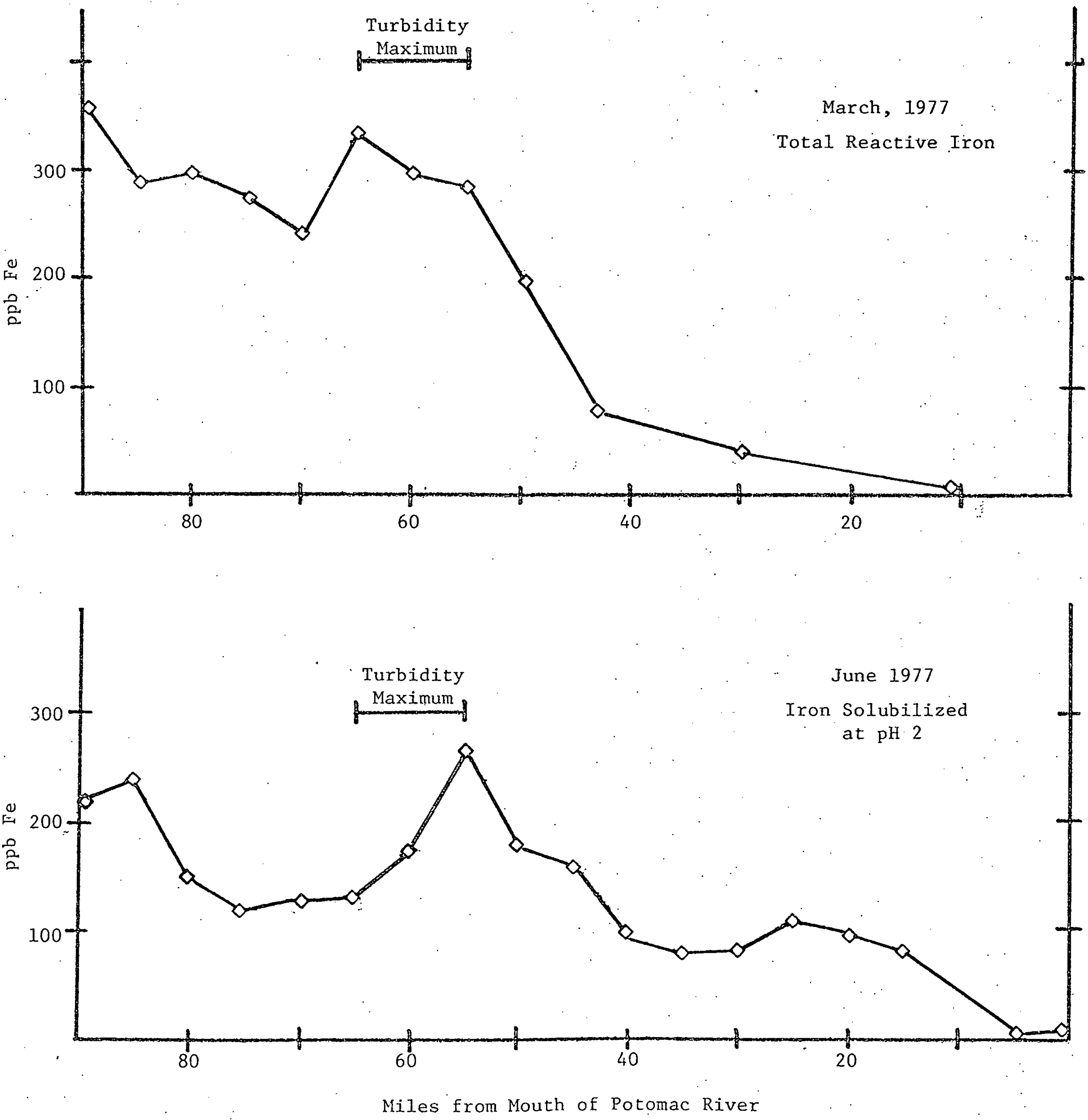


Figure 4. Total Iron in the Potomac River



D. Interstitial Water Investigations

Little work has been done in this area during the past year. Samples collected from a number of cores in past years and previously analyzed for copper by anodic stripping voltammetry (ASV) have been analyzed for the same element by atomic absorption graphite furnace techniques by a cooperating investigator at the USGS (E. Callender). His results are similar to ASV results mentioned in previous progress reports. Copper shows uniformly low values along the lengths of the cores. Because there is no evidence for either a trend with depth or high values relative to overlying waters we do not feel that the present data suggests significant diffusive or advective transfer of copper out of the sediments in the Bay. We will thus not try to investigate these cores further at the present time. We currently feel that external sources of metals such as riverine flow are much more important in this system. Investigations this summer when Bay bottom waters are likely to become anoxic should disclose whether metals other than manganese have any steadily detectable flux from the bottom.

E. Trace Metal Behavior in the San Francisco Bay Estuary

As a comparison to the metal distribution in the Susquehanna River Chesapeake Bay estuary we have been completing a study of the San Francisco Bay estuary begun while A. Eaton was a post-doctoral fellow in California. The Chesapeake Bay system has the potential for being significantly affected by coal mining activity in the Susquehanna drainage basin, whereas the San Francisco Bay estuary has no such input, draining agricultural lands. The general results of this study were discussed in a paper presented at the GSA meetings in November, 1976, but we are still continuing analyses of samples obtained in September, 1976. We expect to finish these analyses and have several manuscripts prepared by the end of the current contract year.

In contrast to the compositional changes observed in the Chesapeake Bay system as one goes downstream, there are no similar changes observed in the San Francisco Bay system (Figure 5). This probably reflects the lack of a unique input to the system and the fact that the turbidity maximum extends over a wider salinity range in San Francisco Bay (Peterson et al., 1975) and may therefore obscure any secondary removal effects. We see the same trapping action in San Francisco Bay as in the Chesapeake, with the turbidity maximum removing most of the particulate associated metal inputs.

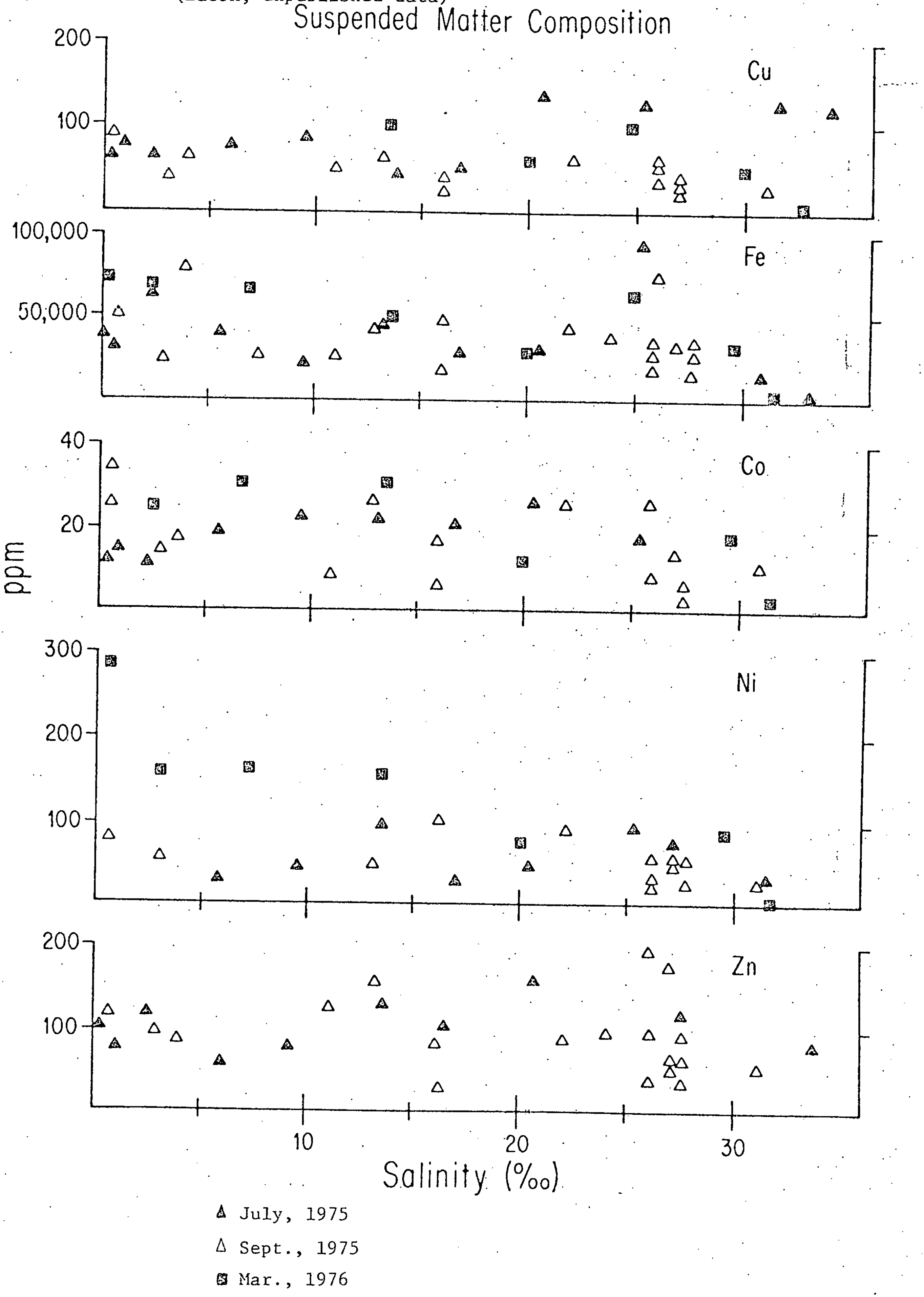
F. Investigations of Bottom Sediment Composition in the Chesapeake Bay

Introduction

As part of our investigations to determine the optimum technique to analyze suspended sediment in the Chesapeake we also spent some time in the past contract year analyzing bottom sediments from different regions in the Bay. In addition to providing a ready source of material for testing analytical techniques, there are currently few published data on the metal composition of bottom sediments (Goldberg et al., 1977; Helz, 1976; Cronin et al., 1974) and thus any additional data is significant. There are several studies commencing at the present time which should overcome this paucity of data, including systematic studies of metal distributions by the Maryland Geological Survey and the University of Maryland.

The bottom sediments of the Bay represent a long term average reflection of the fate of suspended material in the estuary. They are thus a further indicator of the processes of mixing and removal of river-borne trace metals.

Figure 5. Suspended Sediment Composition of San Francisco Bay Particulates (Eaton, unpublished data)



Status

Bottom samples and blind standards were analyzed by 3 techniques, optical emission spectroscopy, x-ray fluorescence analysis, and atomic absorption following digestion in hot 6N HCl as described in section B. The first two techniques should provide total metal levels, whereas the third method should only approach totals under optimum conditions. As shown in Table 3 (section B) results for both total techniques on a blind standard were promising for a number of metals. However, comparison of actual core samples for the two techniques gave drastically different results (Table 14). The results of the x-ray fluorescence analyses are much closer to other published results on Bay sediments from similar areas (Goldberg et al., 1977) and are thus assumed to be more accurate for most of the samples. On the basis of this preliminary comparison we can see some patterns in the bottom sediments similar to those seen by Goldberg et al. (1977), namely a decrease in metal levels as one proceeds down the Bay (Table 15). The number of samples we have analyzed is insufficient to determine whether the compositional changes along the axis are as marked as they appear to be in the suspended sediments (section B) and in the sediment samples we have analyzed. We do not feel that it is possible with the present data to determine unequivocally the mechanisms for the compositional changes.

The sediment work was intended in part as a test of the various analytical techniques. On the basis of this work we analyzed a number of suspended sediment samples by x-ray fluorescence. Results for another blind standard were presented in Table 3. We presented the summarized data for suspended sediment samples (Table 11) which can be compared with atomic

Table 14.

X-ray Fluorescence (XRF) and Emission Spectroscopy (ES) results on Selected Metals in Core Samples Taken in May, 1976

		%			ppm		
Sample		Fe	Ti	Mn	Cu	Pb	Ni
92200T	ES	3.2	0.39	0.22	100	200	110
	XRF	4.1	0.59	0.16	44	100	<36
92200B	ES	2.1	0.64	0.098	170	<100	26
	XRF	3.6	0.59	0.11	<24	54	<23
922Y	ES	2.1	0.86	0.23	140	400	130
	XRF	4.4	0.62	0.18	46	90	59
914ST	ES	4.9	0.81	0.24	120	240	120
	XRF	3.7	0.52	0.18	33	65	44
914SB	ES	3.9	0.67	0.11	120	460	85
	XRF	3.7	0.49	0.064	57	120	<43
913R	ES	5.9	1.2	0.26	76	300	120
	XRF	4.0	0.51	0.14	40	100	<30
904NT	ES	6.1	0.73	0.42	130	390	95
	XRF	3.9	0.45	0.23	38	115	<57
904NB	ES	5.8	0.65	0.29	170	670	93
	XRF	3.8	0.47	0.25	62	140	<45
834T	ES	4.0	0.67	0.07	37	<100	40
	XRF	2.8	0.39	0.06	<25	38	<39
834B	ES	3.6	0.67	0.06	18	<100	47
	XRF	3.3	0.43	0.05	<30	47	<46

Table 15

Trace Metal Concentration in Bay Sediments

CBI Station	KM Downstream from Mouth of Susqu. R.	MG Fe / G-Sed	MG Mn / G-Sed	µG Zn / G-Sed	µg Cu / G-sed
A. E. Goldberg Data*- May, 1975 samples, acid extraction, atomic absorption					
914	41	44	3.7	400	65
858	73	45	1.2	340	55
834	121	44	.7	250	40
747	211	39	.5	120	25
B. C.B.I. Data - May, 1976 samples, XRF Analyses					
92200	36	40	1.6	340	45
914	41	37	1.8	260	35
904	62	39	2.3	260	40
834	121	28	.6	70	<25

*Goldberg et al., 1977

absorption data where available (Table 5). It is clear that there are still matrix interferences present in the x-ray fluorescence analyses, particularly for the low Z elements. We are chiefly concerned with the accuracy of our methods since a great deal of cost and effort goes into collection and preparation. Therefore, we abandoned x-ray fluorescence as a final technique. It is worth noting that for the x-ray fluorexcence data where results on standards are close to known values and precision is adequate, namely Ni, Pb, Cu, and Mn, we see the previously observed pattern of a sharp compositional change in going from the Northern to Southern Bay. We can, therefore, utilize x-ray fluorescence as a valuable screening technique to determine what elements are fruitfully investigated in more detail using atomic absorption.

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PROGRESS REPORT

Section 2

Work Completed

COO-3292-29

Distribution and Behavior of Manganese in the Interstitial Waters of Chesapeake Bay Sediments during Early Diagenesis

by

George Richard Holdren, Jr.

A dissertation submitted to The Johns Hopkins University in conformity with the requirements for the Degree of Doctor of Philosophy

Baltimore, Md.

1977

ABSTRACT

The distribution and behavior of manganese in the anoxic pore waters of Chesapeake Bay sediments are investigated as functions both of position along the salinity gradient within the Bay and of season of the year. Based on the results of the study, the Chesapeake Bay is divided into three geochemical provinces. In the northern province (north of 38°40'N), dissolved manganese concentrations vary seasonally. During the summer, the maximum concentration, which usually occurs in the upper ten to fifteen centimeters of the sediment column, rarely exceeds 800 μM, and most concentrations lie in the range 50 μM to 300 μM. The highest concentration observed to date has been 955 μM. During the winter, dissolved manganese concentrations decrease dramatically in the northern Bay. Concentrations generally lie in the range 10 μM to 50 μM, with the maximum values rarely exceeding 300 μM. In the central Bay province, dissolved manganese concentrations do not vary seasonally. Here, concentrations rarely exceed 300 μM and most concentrations lie in the range 10 μM to 50 μM. In the southern Bay (south of 38°10'N), dissolved manganese concentrations do not vary seasonally, and, generally, they are the lowest observed in the Bay. Concentrations generally range from < 1 μM to 10 μM over most of the sediment column.

Using an ion pairing-activity model, the state of saturation of pore waters with respect to manganous carbonate, phosphate, sulfide and hydroxide phases was determined. Results indicate that pore waters in the northern Bay province during the winter and in the central Bay province throughout the year approach equilibrium with a manganous carbonate phase similar to rhodocrhosite ($MnCO_3$). During the summer in the northern Bay, pore waters are oversaturated with respect to this phase by more than an order-of-magnitude. The oversaturation is attributed to the activity of microorganisms within the sediment. In the southern Bay, pore waters are undersaturated with respect to all of the phases considered. Possible explanations for this observed undersaturation are considered.

Finally, a model is developed to describe the behavior of manganese during early diagenesis. The sediment is divided into two zones. In the upper zone, diffusion, advection and chemical reactions are used to describe the distribution of dissolved manganese. In the lower zone, however, only a precipitation reaction is considered. Results indicate that diffusion, advection, adsorption, and other common sedimentary processes are not needed to describe adequately the distribution of dissolved manganese over most of the sediment column. The model is then used to calculate, on an *a priori* basis, the distribution of manganese in sediment solids. The model cannot be used in areas such as the Chesapeake Bay because the steady state assumption used in the model is not valid. However, the profiles obtained using the model are qualitatively similar to observed distributions of manganese in some oceanic sediments.

Geochemistry of Some Trace Metals in the San Francisco Bay Estuary

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Geol. Soc. Am. Abstracts 8(6): 849-50.

Observations of the distribution of dissolved and suspended metals (Fe, Cu, Ni, Zn, Cd, and Co) in the San Francisco Bay estuary in 1975 and 1976 suggest that physical processes are the main controls on metal levels. Average dissolved concentrations in the river and oceanic end member are as follows: Cu 4 and 0.2 ppb, Ni 2 and 0.1 ppb, Zn 5 and 0.5 ppb, Cd 0.2 and 0.05 ppb, Co 0.5 and 0.04 ppb. Cu and Ni both show large excesses of dissolved metals (relative to conservative mixing) in that the probable source of this excess is municipal and industrial waste discharge to the Bay. Excesses for the other metals are not as marked.

Suspended metal distributions reflect both the composition of bottom sediments and the gradual sedimentation of particulates within the estuary. In spite of the fact that the area is highly developed, suspended metal compositions are not noticeably different from crustal material.

Biogeochemical processes acting to control metals in the estuary are largely restricted to the low salinity waters. There is little evidence for significant exchange between waters and suspended particles in the estuary with the exception of metals supplied from sewage outfalls.

The Geochemistry of the Turbidity Maximum
Andrew D. Eaton
Abstract of invited paper presented at the 1977 SEPM-AAPG Annual Meeting
to the Environmental Geology Research Group.

The turbidity maximum is a ubiquitous feature of many estuaries. Either as a result of the presence of the turbidity maximum itself or the hydrodynamic processes responsible for its formation there are a number of geochemical consequences which are associated with the turbidity maximum. These include trapping of particle-associated contaminants such as metals and chlorinated hydrocarbons; increased productivity with consequent nutrient removal as a result of the long water residence time in the turbidity maximum region; removal of dissolved constituents via sorption reactions on the large quantities of suspended sediment; flocculation of "dissolved" constituents such as has been observed by Sholkovitz (1976) and Sholkovitz et al (1977) as a result of both the salinity gradient which occurs in the region of the turbidity maximum and the effect of increased turbidity on removal processes; and more rapid sediment-water exchange processes due to increased resuspension of bottom sediments.

The turbidity maximum has other utilities also. LANDSAT imagery can often identify the turbidity maximum of an estuary, thereby allowing one to rapidly determine without extensive field work the 0-5‰ salinity region. Furthermore the sediment trap aspects of the turbidity maximum make it a possible place to overwhelm biological mixing processes by high sedimentation rates. It may, therefore, be the most useful place in estuaries to core to establish anthropogenic flux patterns.

Evidence for each of the above geochemical effects can be found in various coastal plain or west coast estuaries, suggesting that more research should be oriented around the turbidity maximum.

COO-3292-32

Suspended sediment discharge of the Susquehanna River to Northern Chesapeake Bay, 1966 to 1976

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INTRODUCTION

The Susquehanna River is the major sediment source to northern Chesapeake Bay and one of the largest sediment sources for the Bay as a whole (Wolman, 1968). From 1966 through 1975 estimates of suspended sediment discharged at the mouth of the Susquehanna River were made by Carpenter et al (1975), Biggs (1970), Schubel (1968, 1972), and Palmer, Schubel and Cronin (1975). Data were also collected at Harrisburg, Pennsylvania, by the U.S. Geological Survey. Thus we can evaluate the river discharge over a decade which included two large floods and the end of the drought period of the 1960s.

The hydroelectric dam at Conowingo, Maryland, the last of three dams on the Susquehanna River, provides a useful location to study suspended sediment transport. The dam is about 15 kilometers from the head of Chesapeake Bay. Thus the estimate of suspended sediment discharge at Conowingo provides the best available estimate of Susquehanna River sediment discharge to Chesapeake Bay now available. No data are available on bed load transport between Conowingo Dam and Chesapeake Bay.

Suspended sediment samples have been collected daily from the discharge on the downstream side of the dam since 1969 (Schubel, 1969, 1971; Palmer and Schubel, 1976; and in this report) using techniques described by Schubel (1969). Carpenter et al (1975) collected samples in the Susquehanna River just below Conowingo Dam as did Biggs (1970).

RESULTS

None of the investigations evaluated the sources and possible magnitude of errors in estimating sediment discharge. The major variable in estimating sediment discharge on the Susquehanna River is the water flow which varied between 200 and 1,120,000 cubic feet per second (cfs) whereas suspended sediment concentrations ranged from 5 to 1500 milligrams per liter from 1966 to 1975. We consider the order of magnitude of the sediment discharge, and perhaps one significant figure, to be statistically significant.

Between 1966 and 1976 (Table 1), Susquehanna sediment discharge was approximately 50 million metric tons. More than 40 million metric tons were transported during two floods caused by hurricanes or tropical storms: the Agnes floods of June 1972 (approximately 30 million metric tons) and the Eloise floods of September 1975 (approximately 10 million metric tons). Spring freshets generally transported far less suspended sediment than the hurricanes (Table 2).

The data (Table 1) indicate that the suspended sediment discharge of the Susquehanna River at Conowingo was 0.9±0.3 million metric tons per year between 1966 and 1976 (in absence of major floods). During normal years 50 to 60% of the sediment discharge at Conowingo comes during the annual spring flood or freshet, usually in March and April (Table 1), which is caused by snowmelt.

Two floods occurred during 1975 (Figure 1). The spring freshet in February 1975 had a flow (peak discharge on February 26, 1975, of 369,900 cubic feet per second, 10,470 cubic meters per second) which would be expected to occur only every 5 years (Figure 2), while the runoff caused by Tropical Storm Eloise (peak discharge on 27 September 1975 of 584,000 cubic feet per second, 16,750 cubic meters per second) has a recurrence period of approximately 30 years (Page and Shaw, 1974). Because of these floods, sediment discharge during 1975 was abnormally large, approximately 11 million metric tons (Figure 3). During the Agnes (June 1972) and the Eloise (September 1975) floods, approximately 40 million metric tons of sediment were discharged to the Bay (Table 2). The Agnes flood has a recurrence period of at least 200 years (Page and Shaw, 1974).

Typical suspended sediment concentrations at Conowingo were between 10 and 30 milligrams per liter with no obvious correlation between concentrations and river discharge, at flows less than 100,000 cfs.

At river discharges more than 100,000 cubic feet per second (2,800 cubic meters per second) there was a definite correlation (Fig. 2) based on 117 observations made during 28 flood events (discharges exceeding 100,000 cubic feet per second) between 1969 and 1974.

DISCUSSION

Using data based on sediment yields resulting from present land use and average runoff conditions, Williams and Reed (1972) estimated that the Susquehanna River transports 3 million tons of sediment annually - typically 10% sand, 50% silt, and 40% clay. Using the estimated trapping efficiency curves of Brune (1953), Williams and Reed (1972) estimated that approximately 1.2 million tons of sediment is trapped behind the three hydroelectric dams of the lower Susquehanna with an annual discharge of 1.8 million tons of sediment each year to Northern Chesapeake Bay.

Our data indicate that at least half, and usually two thirds, of the suspended sediment transported past Harrisburg (U.S. Geological Survey Data) does not pass Conowingo for flows (peak daily discharges) of 400,000 cubic feet per second (11,300 cubic meters per second or less). This suggests that Williams and Reed (1972) underestimated the trapping efficiency of the three hydroelectric dams. Some of these sediments may accumulate in channel deposits of the lower Susquehanna River.

During the Agnes flood, the suspended sediment discharge at Conowingo was much greater than the sediment transport at Harrisburg (see Table 1) suggesting that these deposits are eroded during major floods. There was no evidence of major erosion resulting from the Agnes floods in Pennsylvania streams (Ritter, 1974) upriver from Harrisburg. We have no data on the Susquehanna River channel between Harrisburg and Conowingo, or the reservoirs at the three hydroelectric dams.

Even if 22×10^6 metric tons of sediment were eroded from the three dam reservoirs on the lower Susquehanna, the changes in bottom topography might be difficult to document without careful study. The entire sediment discharge could be derived by eroding approximately 0.5 meter (1.5 feet) from the three reservoirs (L. Reed and J. R. Ritter, written communication, 11 November 1976).

Because of the floods during 1966-1976, the annual sediment yield of the Susquehanna River to Chesapeake Bay was equivalent to 71 tons per square kilometer (180 tons per square mile) per year, which is substantially greater than the 25 tons per square kilometer (65 tons per quare mile) per year estimated by Williams and Reed (1972), based on their analyses of sediment yields of small tributary basins in the Susquehanna basin.

The period 1966-1975 was a time of unusually high sediment discharge by the Susquehanna River. The Agnes flood, which alone accounted for about 60 per cent of the sediment discharge, had a recurrence interval of more than 200 years (Figure 4). The largest flood before Agnes occurred in 1936 (Hoyt and Langbein, 1955), but we have no data on the suspended sediment discharges caused by that flood.

We still do not know the long-term sediment discharge of the Susquehanna River to Chesapeake Bay or the role of major floods. Particular attention should be given to determining the amount of sediment that remains on the Susquehanna River Flats (the shallow area of the Bay near the river mouth), the amount that is trapped in the turbidity maximum zone, and the amount that moves into the middle and southern portions of Chesapeake Bay.

IMPLICATIONS

From these data it seems obvious that human alteration of the Susquehanna River can have major effects on sediment discharge to the Bay. There was no compelling evidence that coal mining (surface or subsurface) has any present large scale effects on sediment yields of the drainage basin (Williams and Reed, 1972). Future increases in levels of coal mining activity or in urbanization could increase the local sediment yield and might eventually effect the Bay.

On the other hand, the evidence is strong that the three hydroelectric dams influence the suspended sediment discharge of the river. One-half to two-thirds of the suspended sediment discharge is apparently deposited behind the dams or in the lower reaches of the river during years of relatively low discharge and no major floods. During major floods (discharges exceeding 10^4 cubic meters per second or about 400,000 cubic feet per second) these deposits are apparently eroded and transported into Northern Chesapeake Bay. Thus the dams are effectively increasing the amount of sediment discharged under flood conditions relative to the amount discharged in an average or a low-flow year.

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Table 1. Suspended sediment transport and discharges of Susquehanna River

Calendar Year	Annual Suspended Sediment Discharge (millions of metric tons per year)	
	Harrisburg, PA[1]	Conowingo, MD
1966	1.5	0.7[2] (60%)*
1967	1.7	>0.3[3] **
1968	> 1.7 **	nd
1969	nd	0.32 (60%)
1970	> 2.0 **	>1.1**
1971	> 1.4 **	1.0 (51%)
1972	11.3	33[5]
Agnes, 24-30 June 1972	7.6	30[5]
1973	3.2	1.2[6] (54%)
1974	1.7	0.8[6] (53%)
1975	>3.8 **	11
Eloise, 26-30 Sept. 1975	1.6	9.9
1976	nd	1.2

nd = no data

*Percent discharged during annual spring flood
**Records incomplete for the year

[1] U. S. Geological Survey Water Resources Data for Pennsylvania, Part 2. Water Quality Records, Harrisburg, PA. Published for each year.
[2] Biggs (1970)
[3] Schubel (1968)
[4] Schubel (1972)
[5] Schubel (1974)
[6] Palmer, Schubel, and Cronin (1975)

Table 2. Some major floods and their water and suspended sediment discharges at Conowingo, MD., 1966-1975.

Date (Peak flow)	Peak daily discharge[3] $10^3 m^3/sec$	 $(10^3 ft^3/sec)$	Suspended Sediment Peak Concentration (mg/liter)	 Discharge (10^6 tonnes[1])
22 June to 3 July 1972 (Hurricane Agnes) (24 June 1972)	31.7	(1,120)	∿10,000[2]	∿30[2]
26 September to 2 October 1975 (Hurricane Eloise) (27 September 1975)	16.5	(584)	2,800	10
25 February to 3 March 1975 (26 February 1975)	10.5	(370)	240	0.56
29 March to 28 April 1970 (4 April 1970)	9.82	(347)	250	0.77
3 - 8 March 1972 (4 March 1972)	9.29	(328)	190	0.40

[1] Tonne is 2205 lbs or one metric ton.

[2] Schubel (1974)

[3] Susquehanna Electric Co.

LIST OF FIGURES

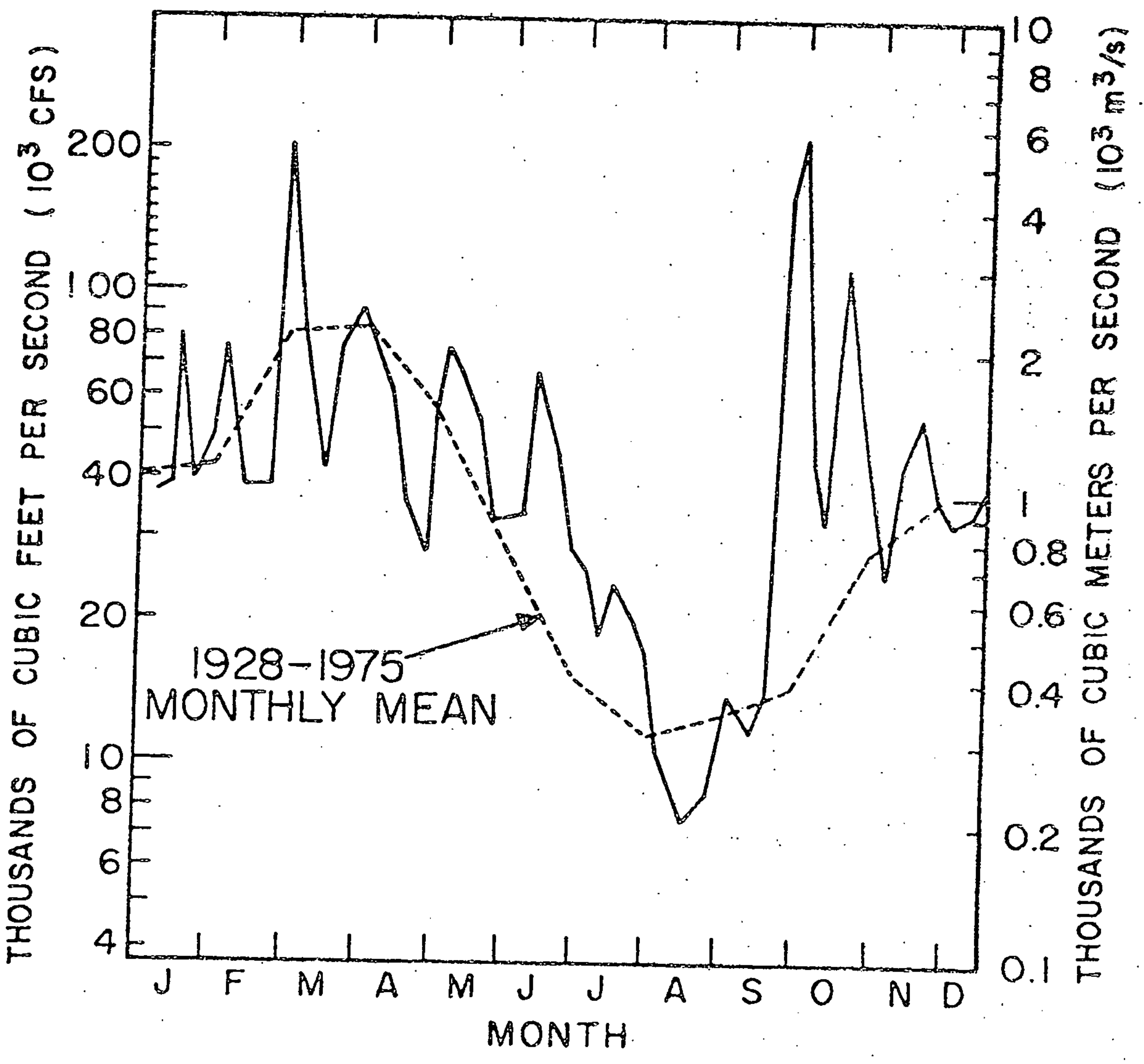

Figure 1. Weekly average flow of the Susquehanna River at Conowingo, Maryland in 1975 as compared to the average flow 1928-1975.

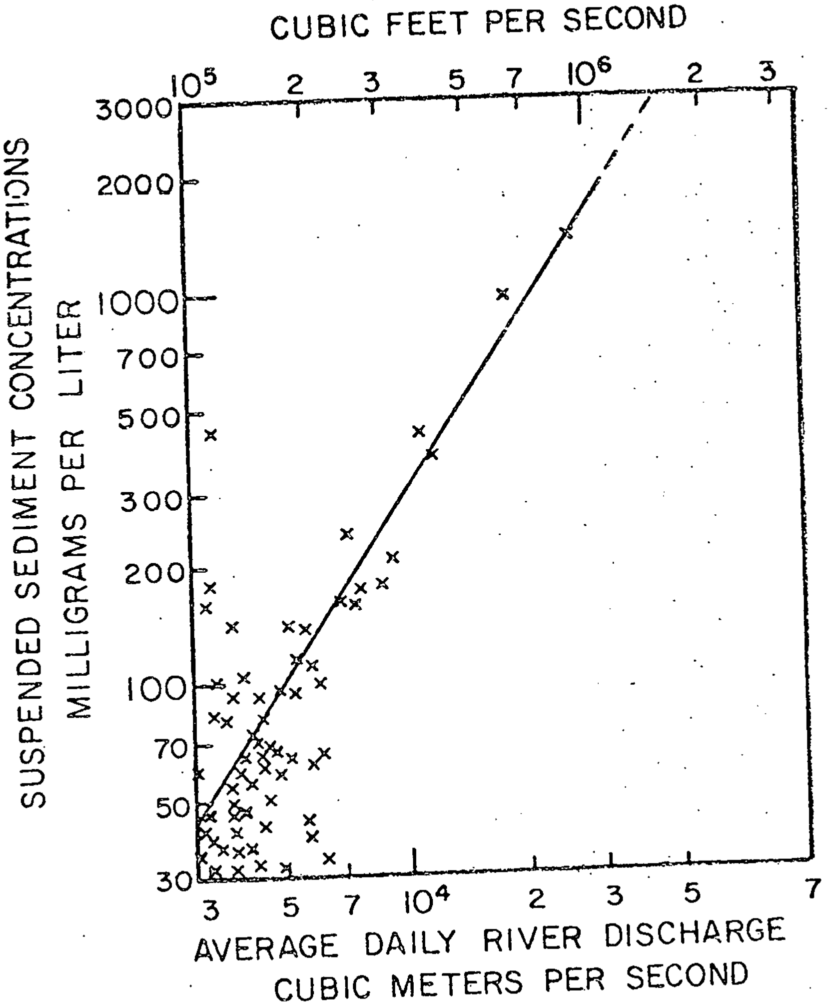

Figure 2. Suspended sediment concentrations at Conowingo, Md. at various flood-stage discharges of the Susquehanna River, 1969-1974.

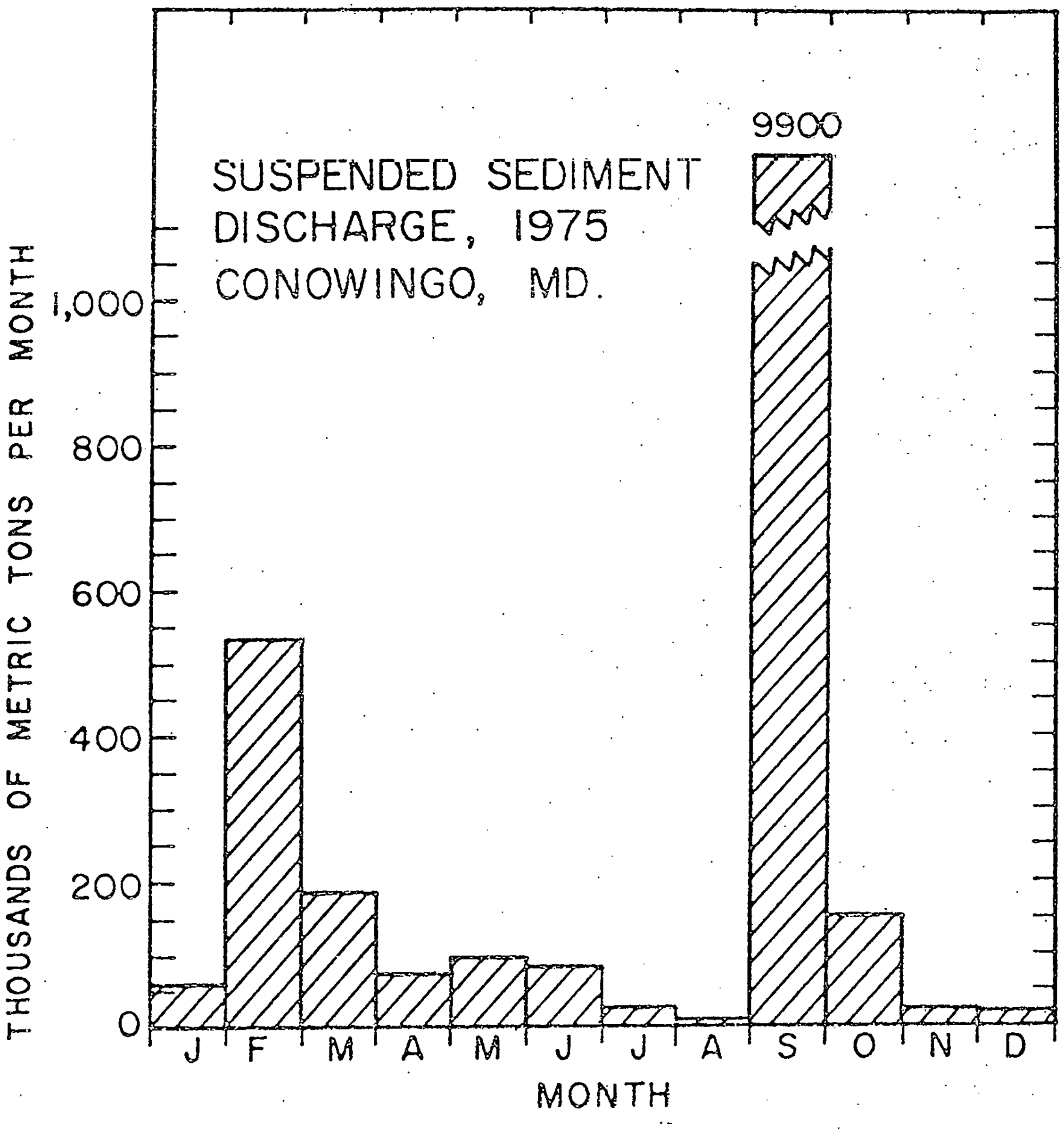

Figure 3. Monthly suspended sediment discharge at Conowingo, Md. in 1975.

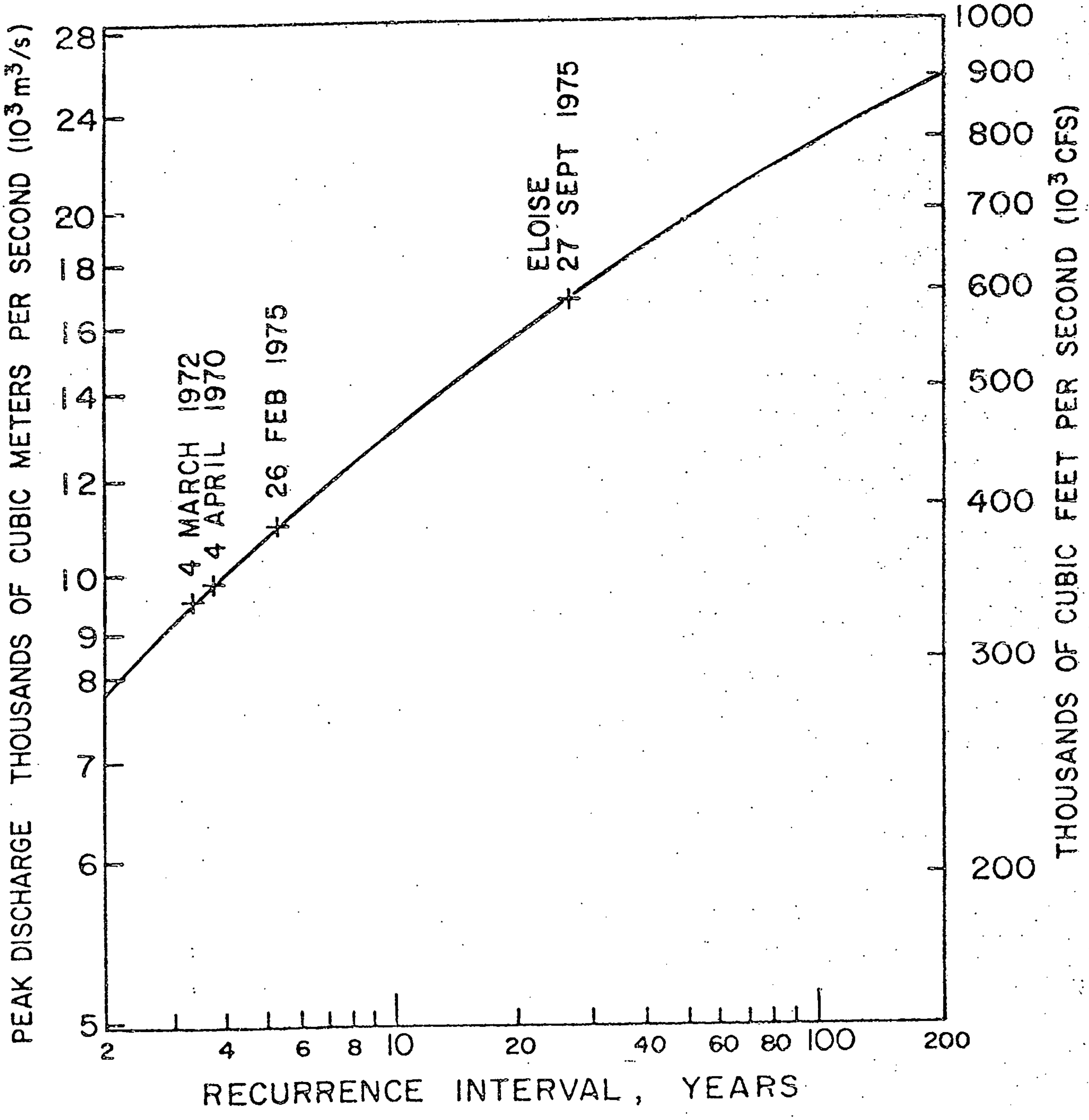

Figure 4. Recurrence intervals of peak river flows at Conowingo, Maryland (natural flow). (after Page and Shaw, 1974)