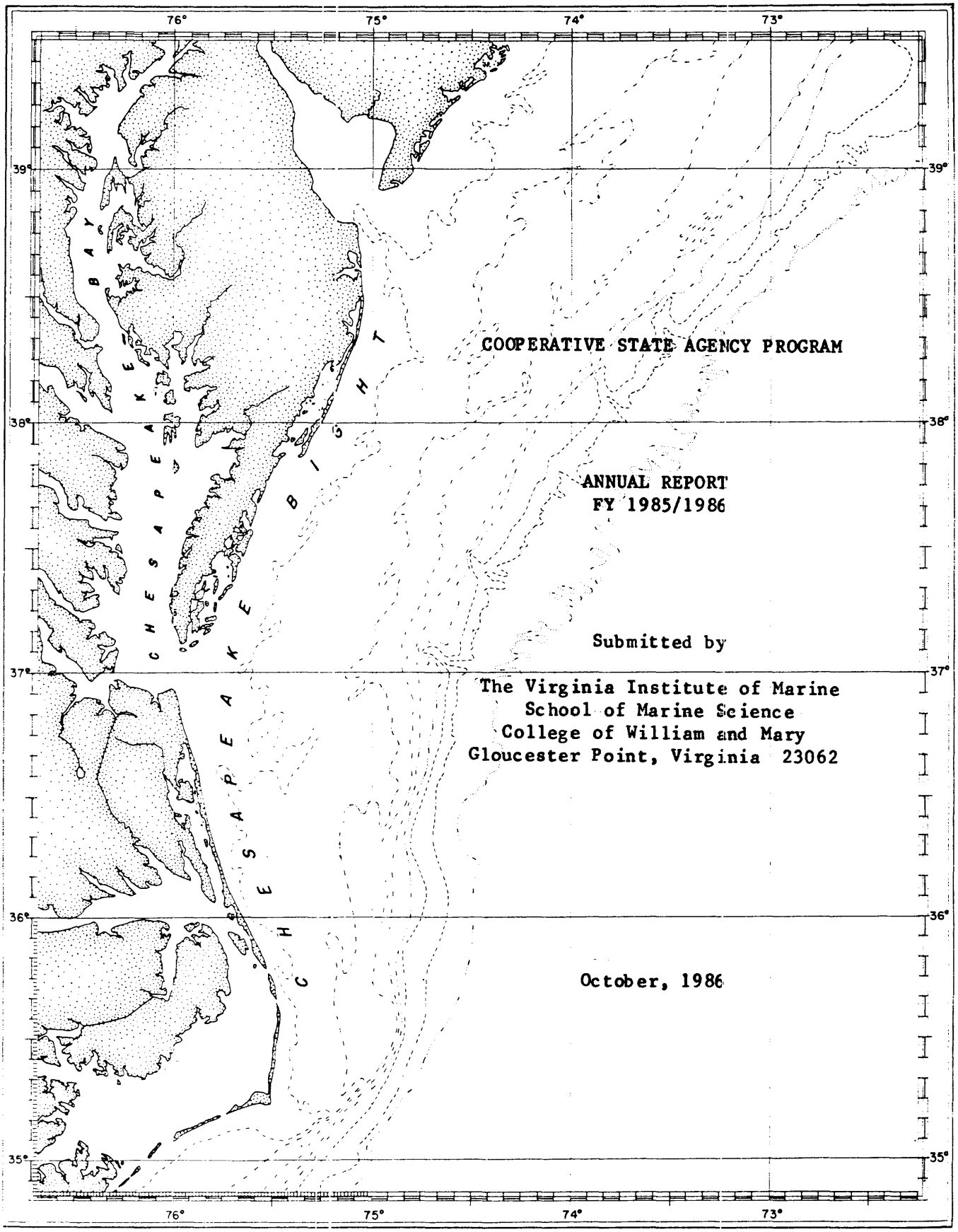
1986

Cooperative state agency program / annual report FY 1985-1986

Virginia Institute of Marine Science



COOPERATIVE STATE AGENCY PROGRAM

ANNUAL REPORT
FY 1985/1986

Submitted by

The Virginia Institute of Marine
School of Marine Science
College of William and Mary
Gloucester Point, Virginia 23062

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B. MANUAL FOR THE TIDAL PRISM MODEL

Work on the manual was not begun until the spring of 1986. The projected time table is to have a rough draft available by early August and to submit a "polished" draft to the WCB in September of 1986. If the review of the manual can be completed quickly, it should be possible to print the report by the end of the calendar year.

C. STATE OF THE RIVERS SURVEYS AND ANALYSIS

Slackwater surveys were conducted in the James, York, and Rappahannock rivers from July through November of 1985. During the spring of 1986, only the James River was monitored. A report summarizing the 1986 data from the James was issued in early July.

Analysis and interpretation of the historical data sets has focused primarily on the James River. Temperature, salinity and dissolved oxygen data have been reviewed and the results summarized in a report submitted to the WCB for use in the 305(b) report. Seasonal variations and spatial patterns of other water quality measures have been determined and graphs prepared. Interpretation of those results was not completed by the end of the fiscal year. Additional plots are believed necessary to highlight both spatial patterns and temporal trends.

It is anticipated that summary reports on temperature, salinity, and dissolved oxygen can be prepared for all three estuaries in the coming year. Interpretation of the other water quality data should be completed for the James and possibly also for the Rappahannock.

D. ADVISORY SERVICES

A range of advisory activities occurred during the year. The models of the Elizabeth River and the Pagan River were run to test particular waste loadings relative to NPDES permit studies. The models of the Potomac embayments were transferred to the Northern Virginia Planning District for their use in waste load allocation studies.

Scientists were available to review and comment on materials submitted by WCB staff, and a laboratory instrument maker, an electronics technician, and a computer systems engineer worked with WCB staff on problems of instrument calibration and repairs.

E. SEDIMENT-WATER COLUMN NUTRIENT FLUXES

Measurements of sediment-water column nutrient exchanges focused on phosphorus fluxes in Gunston Cove and in the Chowan River. Measures in Gunston Cove were conducted from June to August 1985. Results indicate that sediment phosphorus releases occur during periods of high water column pH and when water column nitrate concentrationsare low. Low nitrate and high pH occur simultaneously in Gunston Cove and the individual effects of these variates are difficult to discern. Additional research is needed to examine the individual roles of pH and nitrate. A report "Relation of Sediment Phosphorus Release to Water Column Nitrate Concentration in Gunston Cove" has been submitted to the Water Control Board (Attached).

Measures of sediment phosphorus flux in the Chowan and Perquimons Rivers were conducted in January and February of 1986. Since the Chowan has higher dissolved phosphorus than the Perquimons, sediments in the Chowan were expected to take up more phosphorus. Phosphorus fluxes in both rivers were below detection level, however. A report on all work completed in the Chowan will be available by late fall of 1986.

RELATION OF SEDIMENT PHOSPHATE RELEASE TO WATER COLUMN NITRATE CONCENTRATION IN GUNSTON COVE

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INTRODUCTION

Estuarine bottom sediments are becoming recognized as an important source or sink of nutrients in the water above. Sediment release of nutrients, especially phosphorus, may frustrate attempts to alleviate eutrophication through management of anthropogenic nutrient inputs. Sediment phosphorus release is suspected of supporting a 1983 algal bloom in the tidal Potomac River and its tributaries (Thomann et al, 1985). One puzzling aspect of sediment phosphorus release is its variability in magnitude. Measures of phosphate release conducted in the freshwater portion of the Potomac Estuary in August, 1979, showed phosphate was released from the sediments at a mean rate of 6 $mg/m^2/day$ (Callender and Hammond, 1982). Mass balance calculations indicate a release of 40 to 80 $mg/m^2/day$ total phosphorus occurred during summer, 1983, however (Thomann et al, 1985). Similar calculations indicate phosphorus release of approximately 50 $mg/m^2/day$ (Thomann et al, 1985) occurs in Guston Cove, a Potomac tributary, during algal blooms. In contrast, measurements conducted in Gunston Cove during summer, 1984, indicated the sediments generally took up phosphate at a mean rate of 4.4 $mg/m^2/day$ (Cerco, 1985).

The hypothesis is proposed here that sediment phosphate release in Gunston Cove is dependent upon the nitrate concentration in the overlying water. When nitrate concentration is low (less than 1 mg/L) phosphate release is large. When nitrate concentration is high (greater than 1 mg/L) phosphate release is small or else phosphate moves into the sediments. Observations presented here suggest that sediment phosphate release may be induced by algal uptake of nitrate.

This report is an informal presentation of research in progress. Conclusions reached are subject to revision. Additional research is required to test the proposed hypothesis.

THE STUDY AREA

Gunston Cove is a tidal freshwater embayment located on the Virginia shore of the Potomac River, 26 km downstream of Washington D.C. Areal extent of the Cove is approximately 5 km^2 and depth is 1 to 2 m. A wastewater treatment plant with a capacity of 1.6 m^3/sec discharges into the headwaters of the Cove and provides much of the freshwater input during dry weather. Gunston Cove is highly eutrophic. Observations during summer months 1984 and 1985 indicate ammonium concentrations in the range 0.0 to 1.88 mg/L, nitrate concentrations in the range 0.01 to 3.88 mg/L and total phosphorus concentrations in the range 0.08 to 0.42 mg/L. During the summer, depth-average chlorophyll 'a' concentrations above 100 µmg/L are commonplace and daytime dissolved oxygen (DO) concentration is usually supersaturated. At night, however, respiration may draw dissolved oxygen down to 5 mg/L.

BACKGROUND OF STUDY

From late July to early October, 1984, a study was conducted to examine the effects of dissolved oxygen and temperature on sediment-water nutrient flux (Cerco, 1985). Water and sediment samples were collected from Gunston Cove at weekly intervals at the location shown in Figure 1. A subset of the sediment-water nutrient flux measures is examined here. The subset consists of nine phosphate flux measures conducted with water-column dissolved oxygen of 5 or 8 mg/L and temperature of 10 to 25°C (in 5° increments). Laboratory

oxygen and temperature were less than in-situ oxygen and temperature which ranged from 5.7 to 12.4 mg/L and 15 to 32°C during the survey period. Results of the study indicated, however, that phosphate flux was virtually independent of dissolved oxygen in the range 5 to 8 mg/L and did not depend on temperature (Cerco, 1985). Therefore the subset of phosphate flux measures selected for analysis here is regarded as typical of the fluxes which occurred in-situ during the study period.

Additional sediment and water samples were collected at weekly intervals from early June to early September, 1985. Samples were collected primarily from the second site shown in Figure 1 but two sediment samples were collected at the 1984 site. Purposes of the sampling were to examine if the results of the 1984 measures applied elsewhere in the Cove and to examine if the 1984 measures were repeatable. No significant difference was found in phosphate flux at the two stations. A set of fourteen phosphate flux measures conducted with water-column dissolved oxygen of 5 or 8 mg/L and temperature of 15 to 30°C (in 5° increments) is examined here. During the study period, in-situ oxygen and temperature ranged from 5.6 to 12.3 mg/L and 24 to 29°C. The reasoning applied to the 1984 measures suggests the 1985 measures are typical of the fluxes which occurred in-situ during the study period.

METHODOLOGY

All water and sediment samples were collected at mid-day. In-situ dissolved oxygen and temperature were measured with a Yellow Springs Istruments Model 5739 dissolved oxygen probe fitted to a Model 54A readout unit. The probe was air calibrated on site prior to the measures. Measures were taken 30 cm below the surface, at mid-depth, and 30 cm above the

bottom. In 1985, pH was measured with a Beckman Phi 21 probe and readout unit calibrated on site. Measures were conducted by collecting 0.5 L samples, in Nalgene bottles, from the aforementioned three depths. The probe was immediately inserted in the mouth of the bottle and a reading completed. No pH measures were conducted in 1984.

Samples for analysis of chlorophyll 'a' were collected at three depths in 0.5 L Nalgene bottles. Samples were composited and a 0.5 L subsample placed in a clean bottle and preserved with $MgCO_3$. Chlorophyll concentrations reported here represent a depth-average measure and do not include surface mats.

Water for nutrient analysis and for use in the sediment flux measures was collected by dipping 25 L Nalgene Carboys approximately 30 cm below the surface. Subsamples were collected from the carboys for analysis of ammonium, nitrate, phosphate, and total phosphorus. Ammonium, nitrate, and phosphate samples were filtered on site through 0.45 μm millipore filters. During 1985, the remaining carboy water was filtered on site through 1 μm string filters to remove most particulate matter. During 1984, the carboy water was filtered upon return to the lab.

Intact sediment cores and their overlying water were collected in transparent acryllic columns 60 cm long and 10 cm in diameter. Sediments occupied roughly half the length of the column. Cores, carboys, and water samples were placed on ice and transported back to the lab. Upon return to the lab, cores were placed in a constant-temperature bath set at the temperature specified for the experiment. Water overlying the sediments was replaced with 2.3 liters of filtered water. Each sediment-water column was topped with an air-tight cap fitted with a stirrer and DO probe. Dissolved oxygen concentration was initially brought to the desired level by bubbling

gaseous oxygen or nitrogen through the water. During the course of the flux measurement, DO was monitored and maintained by an automated system. A micro-processor read the probes and opened a valve which introduced oxygen to the columns whenever respiration reduced dissolved oxygen below a present level. This system maintained DO within ± 0.25 mg/L of the nominal value for the measure.

Sediment nutrient fluxes were indicated by concentration changes in the overlying water. Measurement of nutrient flux commenced when the sediment columns reached the desired DO and temperature. Approximately 12 hours elapsed between collection of the cores and initiation of the measure. Duration of each experiment was 18 to 24 hours during which water samples were collected at six-hour intervals. The volume withdrawn was replaced with ambient, filtered water of known nutrient concentration.

During 1985, the pH of the initial and final water samples was measured with the Beckman meter. The pH typically declined by one unit during the experiments. The mean of initial and final pH is referred to in subsequent analyses. In four 1985 experiments, pH was maintained, through addition of NaOH, within ± 0.1 units of the reported value. The pH was not recorded during 1984 experiments.

Flux rates per unit sediment area were determined through division of the cumulative nutrient change in the water by the sediment surface area and by the duration of the experiment. Flux rates were corrected for sample withdrawal and replacement. In the event a substance in the water became depleted or rose to a saturation concentration, the measurement duration was considered to be only that time interval during which the rate of change of concentration with respect to time was roughly linear.

Replicate sediment cores were run in each experiment. A single column filled with only water served as a blank used to correct the flux in the sediment columns for substance tranformations in the overlying water. Reported fluxes are the average of flux in the replicate sediment cores minus the apparent flux in the blank.

Ammonium was analyzed by an automated phenate method. Nitrate plus nitrite (subsequently referred to simply as nitrate) was analyzed by the cadmium reduction method. Phosphate was analyzed via an ascorbic acid method. Total phosphorus was subjected to acid persulfate digestion followed by analysis as for phosphate. Chlorophyll 'a' was analyzed via an acetone extraction method. All analyses were according to the American Public Health Association (1976). Sample holding time and preservation (if necessary) were in accordance with recommendations of the United States Environmental Protection Agency (1981).

PRESENTATION OF RESULTS

Phosphate flux measures are presented in Table 1 (1984) and Table 2 (1985). Also tabulated are dissolved oxygen and temperature of the experiment, mean pH (if available), and nitrate concentration at the initiation of the measure. In-situ nitrate and chlorophyll 'a' concentrations are shown in Figure 2.

Several trends are apparent in the data. Notably, sediments generally took up phosphate in 1984 but released phosphate in 1985. Mean flux in 1984 was -4.4 $mg/m^2/day$ (uptake). Mean flux in 1985 was 29.6 $mg/m^2/day$ (release). Chlorophyll concentrations during 1985 exceeded 200 µgm/L on several occasions but chlorophyll was limited during 1984 to approximately 125 µgm/L. Nitrate during 1984 was generally above 1 mg/L while nitrate was

generally below 1 mg/L during 1985.

ALTERNATE HYPOTHESES

Two hypotheses may be formed in order to explain the difference in phosphate flux between 1984 and 1985. The first hypothesis is that high pH during 1985 induced sediment phosphate release. The second hypothesis is that low nitrate concentration during 1985 permitted sediment phosphate release.

The pH hypothesis was originally formed by the Expert Panel convened to examine the causes of the 1983 Potomac River algal bloom (Thomann et al, 1985). The first step in the hypothesis is the link between chlorophyll concentration and pH. As the algal population increases, CO_2 is removed from the water and an increase in pH occurs. An empirical relationship between chlorophyll concentration and pH in Gunston Cove has been shown (Thomann et al, 1985). The second step in the hypothesis is the pH-mediated desorption of phosphate from particles in the surficial sediments. Decreased sorption capacity in the surficial sediments may also permit diffusion to the water column of dissolved phosphate from deeper sediments. The notion that phosphate sorption capacity of solids decreases as pH increases is supported, for example, by Edzwald et al (1976) who found the sorption capacity of two clay minerals decreased as pH increased from 4 or 5 to 10.

The nitrate hypothesis is based on results of several European investigations. Bostrom and Pettersson (1982) found that phosphorus release from anoxic lake sediments could be suppressed by nitrate concentrations in the water column of 5 mg/L. Anderson (1982) noted phosphate release from anoxic lake sediments was eliminated when the nitrate concentration was 1

mg/L or higher. He explained that nitrate in the water acts similarly to dissolved oxygen. The reduction of nitrate, concurrent with the oxidation of organic matter, maintains that oxidation-reduction potential (ORP) of the sediments at a level such that desorption of phosphate from particulates does not occur.

No evidence exists that Gunston Cove waters become anoxic. Anderson (1982) found, however, that nitrate in the water column supressed phosphorus release from oxic as well as anoxic sediments. How can nitrate suppress phosphorus release from oxic sediments? A conceptual model, applied to Gunston Cove, is as follows. Gunston Cove sediments may be divided into two layers: a thin oxygen-bearing layer in contact with the water and an anoxic layer beneath the first layer. Color transition from brown to black sediments (found to coincide with a transition from oxidized to reduced sediments by Vanderborght et al, 1977) suggests the oxygenated layer is approximately 1 to 2 cm thick. Due to the different sorption capacity of phosphate on to sediment particles in oxic and anoxic environments (e.g. Krom and Berner, 1980), phosphate in the upper layer exists primarily sorbed to sediments while in the lower layer the interstitial water is rich in dissolved phosphate. Diffusion causes dissolved phosphate to migrate from the region of high concentration (the lower sediment layer) to the region of low concentration (the upper sediment layer). By sorption on to sediment particles, the upper layer may trap phosphate diffusing from the lower layer or may allow phosphate to pass into the water column. If the upper layer is relatively thick and undisturbed, little phosphate escapes to the water. If the upper layer is thin, however, bioturbation (Holdren and Armstrong, 1980; Callender and Hammond, 1982) and physical disturbance of the sediments (Bates and Neafus, 1980) promote phosphate release. The theory is proposed

here that diffusion of nitrate from the water into the sediments and subsequent denitrification in the sediments leads to a relatively thick, impervious surface layer in which phosphate is sorbed to particulates. Dissolved phosphate found deeper in the sediments cannot penetrate this thick surface layer. In the absense of nitrate, the layer in which phosphate sortion occurs is thinner and is easily breached leading to sediment phosphate release.

EXAMINATION OF HYPOTHESES

Sediment phosphate release measured during 1985 is plotted versus laboratory pH in Figure 3. The observations display an abrupt increase in phosphate release at approximately pH 9.5. An anomalous, large flux is shown at pH 8, however, which suggests some variable other than pH can induce phosphate release.

Figure 4 shows phosphate flux measured during 1984 and 1985 as a function of nitrate concentration at the initiation of the measurement. The figure indicates that nitrate concentration during 1984 was 1 mg/L or more and that phosphate moved primarily into the sediments. During 1985, nitrate concentration was generally less than 1 mg/L and phosphate moved out of the sediments. An exponential function, fit by non-linear regression (Robinson, 1985), indicates the relation of phosphate flux to nitrate concentration is described

$$F = 90\ e^{-1.61\ NO3} - 10.8 \qquad (1)$$

in which F = phosphate flux at initiation of experiment ($mg/m^2/day$) and NO3 = nitrate concentration (mg/L). R^2 for the relationship is 0.71. This indicates that 71% of the variability in 23 phosphate flux measures

collected during two summers can be explained by a simple model in which nitrate is the only variable.

Interpretation of the available data is hampered by the covariance, observed during 1985, of nitrate concentration and pH ($r = -0.75$). Nitrate tends to be low when pH is high and high when pH is low. One approach to isolating the effects of the two variables is examination of residuals. Equation 1 is assumed to describe the relationship of phosphate flux to nitrate concentration. The difference (or residual) between each observed flux and the flux predicted by Equation 1 is next examined for a correllation with pH. The residuals are shown as a function of pH in Figure 5. Below pH 9.5, the residuals tend to be negative and indicate that below pH 9.5, phosphate release is less than predicted based on nitrate concentration. At pH 9.5, an abrupt shift to positive residuals occurs and indicates that at pH 9.5, phosphate release is larger than predicted based on nitrate concentration. A positive though lesser residual occurs at pH 10. The lesser residual may be due to experimental error or the influence of an unknown variable.

DISCUSSION

The preceeding analysis indicates that two conditions can promote sediment phosphate release: (1) nitrate concentration less than 1 mg/L. (2) pH greater that 9.5. Can either of these factors be indentified as contributing to the 1985 algal bloom? Examination of in-situ pH, nitrate chlorophyll 'a', and total phosphorus (Figure 6) suggests that nitrate-related phosphate release occurred during the period of bloom formation.

One phenomenon evident in the data is the vertical gradient of pH. Bottom pH is often 1 unit lower than surface pH. In this discussion, bottom rather than surface pH is regarded as influential on sediment processes.

The period from early June to mid-July is of most interest. During this interval, nitrate declined almost continuously. Nitrate fell below 1 mg/L, the threshold for promotion of phosphate release, in mid June. The decline in nitrate was matched by a concurrent increase in chlorophyll 'a' and total phosphorus. The mechanism proposed here to explain these observations is that nitrate was taken up as a nutrient by algae. As the nitrate concentration declined, sediment release of phosphate increased.

From June to mid-July, pH was limited to a maximum value of 9, one-half unit less than the threshold for promotion of phosphate release. The pH did achieve 9.5 about mid-August, coincident with maximum chlorophyll and total phosphorus observations. By this time, the bloom was several weeks old, however. Chlorophyll 'a' concentrations of approximately 200 µgm/L had been observed since early July. Therefore it appears that during the period of bloom formation, nitrate-related sediment phosphate release was more important than pH-mediated release.

CONCLUSIONS

Examination of available data indicates that sediment phosphate release in Gunston Cove is induced when nitrate in the water column falls below 1 mg/L or when pH of the water overlying the sediments equals or exceeds 9.5. If these indications are correct, then nitrate-related phosphate release was more important than pH-induced release during formation of the 1985 algal bloom.

Validation, through additional measurements, of the findings relative to nitrate and pH is highly recommended. The experiments described were not designed to explore the influence of nitrate and pH on sediment phosphate release. As a result, measures at some critical values of variables (e.g. pH > 9.5) are sparse and covariance between variables exists. A series of

measurements in which both nitrate and pH are controlled should be performed. Nitrate and pH in each experiment should be specified so that the series of measurements encompasses the range of the variables commonly encountered. Covariance between nitrate and pH should be avoided.

Validation of the proposed mechanism by which nitrate suppresses phosphate release should also be performed. Measures of sediment oxidation-reduction potential are recommended. The vertical distribution of ORP in the sediments, as a function of nitrate in the water, should be explored. Investigation of temporal variation in ORP due to variation in water-column nitrate is also desirable.

Experiment	Phosphate Flux	Dissolved Oxygen	Temperature	pH	Nitrate
2-84	-16.4	8	10	n.m.	1.39
3-84	-2.30	8	15		1.01
4-84	0.19	8	10		1.37
5-84	-3.98	5	20		1.43
6-84	-0.02	8	25		2.81
7-84	-9.29	8	20		1.25
8-84	-1.61	5	25		2.39
9-84	-4.27	5	30		1.81
10-84	-1.90	5	15		2.09

Table 1. 1984 Phosphate Flux Measures. Phosphate flux in $mg/m^2/day$. Negative flux indicates sediment uptake of phosphate. Dissolved oxygen in mg/L. Temperature in ^{o}C. n.m. indicates not measured. Nitrate in mg/L.

Experiment	Phosphate Flux	Dissolved Oxygen	Temperature	pH	Nitrate
1-85	3.17	8	25	8.0	0.97
2-85	2.35	5	25	7.9	0.79
3-85	6.02	8	20	8.8	1.03
4-85	18.8	5	20	9.3	0.66
5-85	14.8	8	20	9.1	0.55
5-85	11.4(1)	8	20	9.0	0.55
6-85	70.3	5	30	9.5	0.42
6-85	74.9(1)	5	30	9.6	0.42
7-85	18.0	5	15	8.8	0.64
8-85	23.4	8	30	9.2	0.44
9-85	84.7	8	25	10.0(2)	0.03
9-85	50.9	8	25	8.0(2)	0.03
10-85	17.5	8	25	9.0(2)	0.86
10-85	18.4	8	25	8.0(2)	0.89

Table 2. 1985 Phosphate Flux Measures. Phosphate Flux in $mg/m^2/day$. Positive flux indicates sediment release of phosphate. (1) indicates sample collected at 1984 station. Dissolved oxygen in mg/L. Temperature in ^{o}C. pH is mean of initial and final value. (2) indicates pH regulated within $\pm$ 0.1 units of stated value. Nitrate in mg/L.

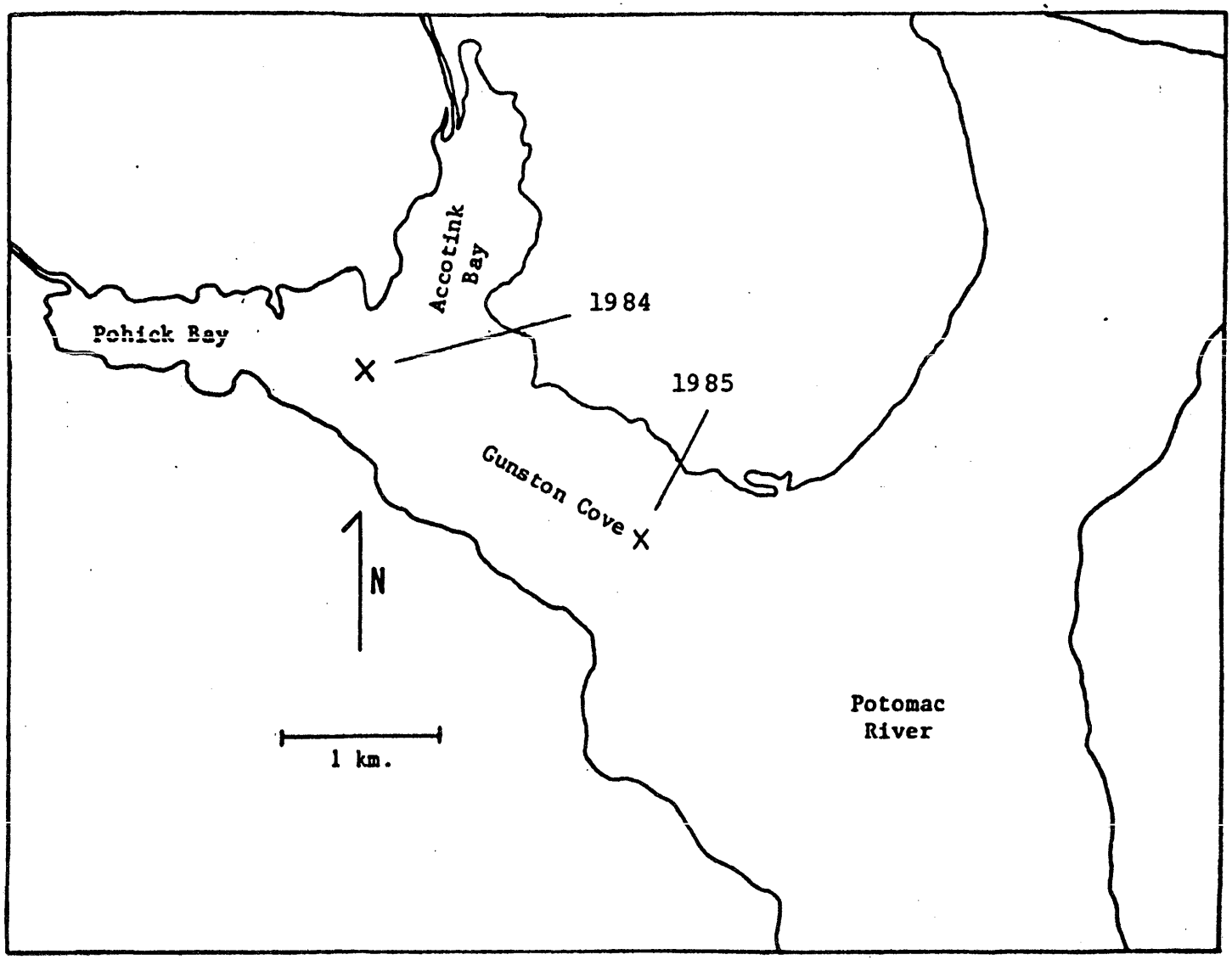


Figure 1. Gunston Cove Sample Stations.

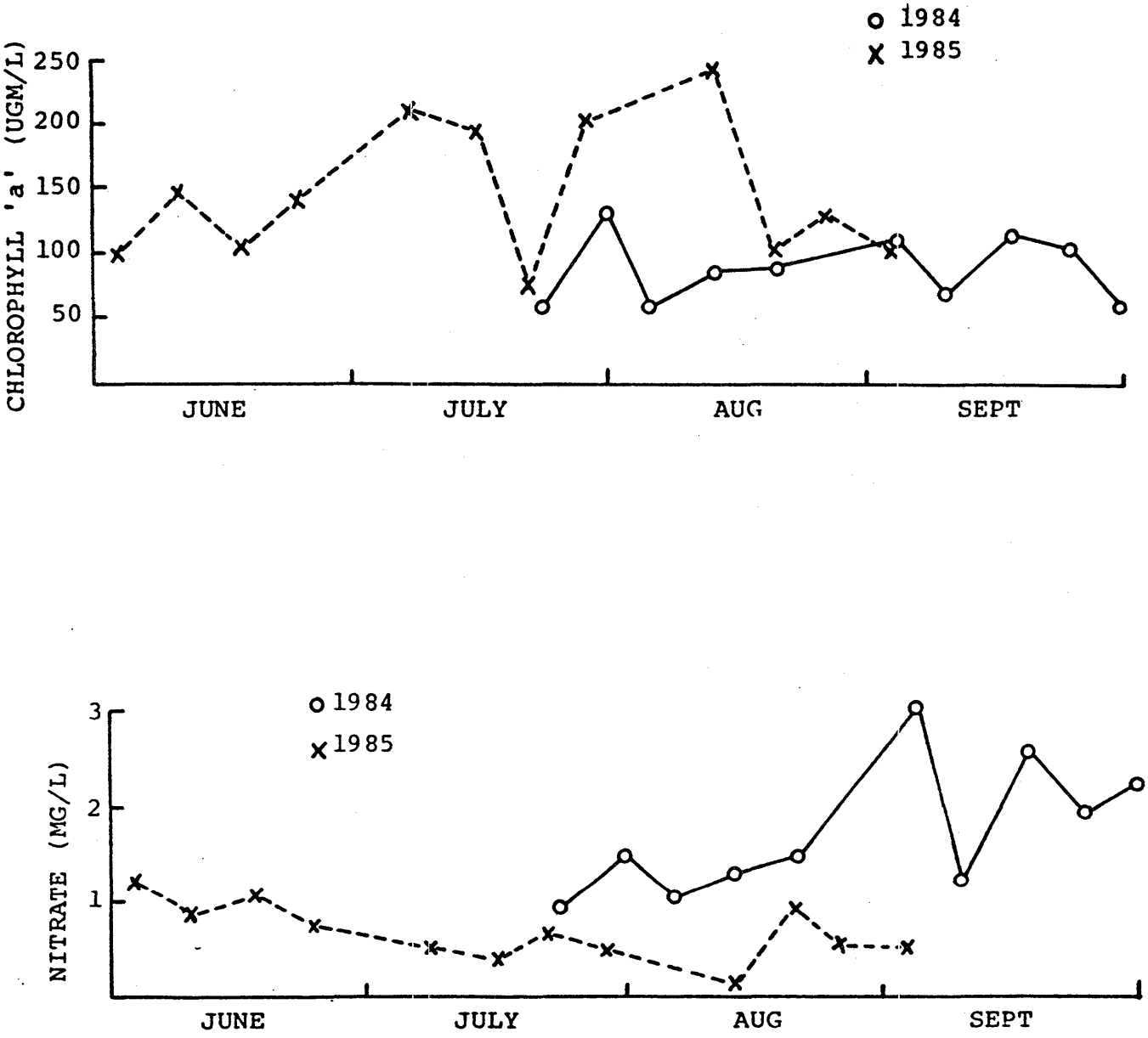


Figure 2. Nitrate and Chlorophyll Concentrations in Gunston Cove.

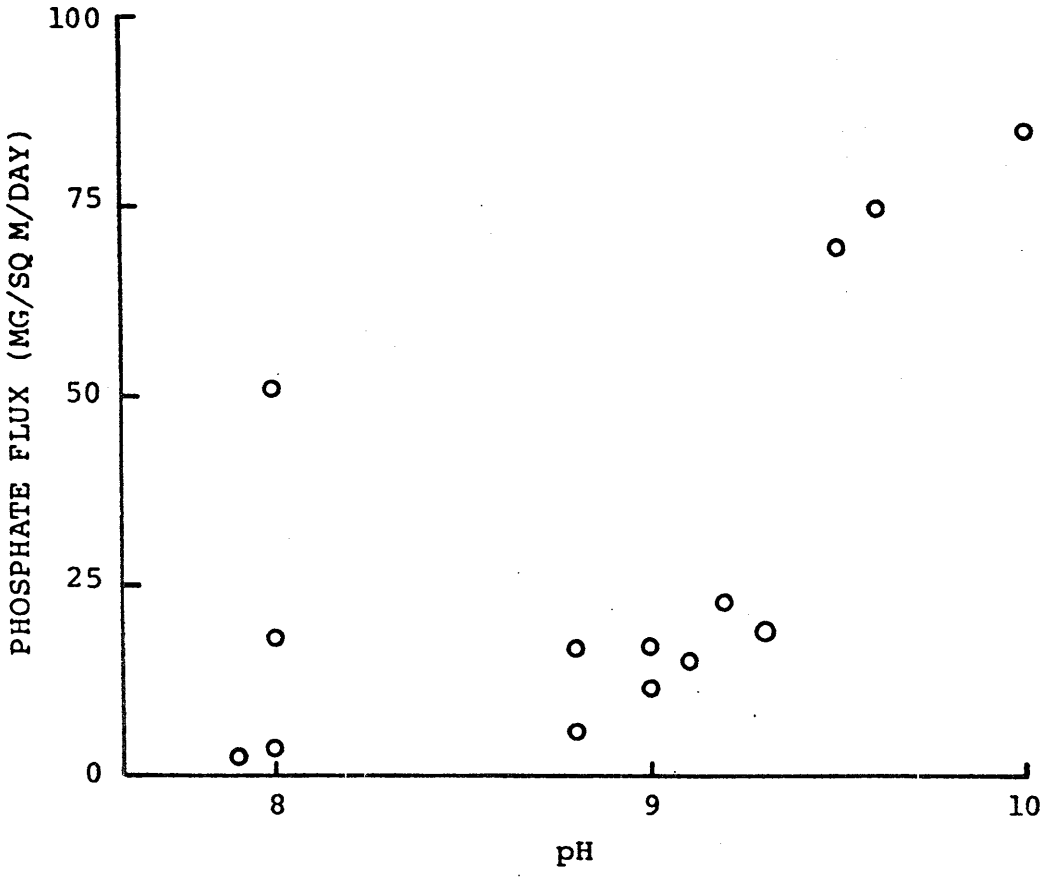


Figure 3. Phosphate Flux vs. pH. (1985 observations)

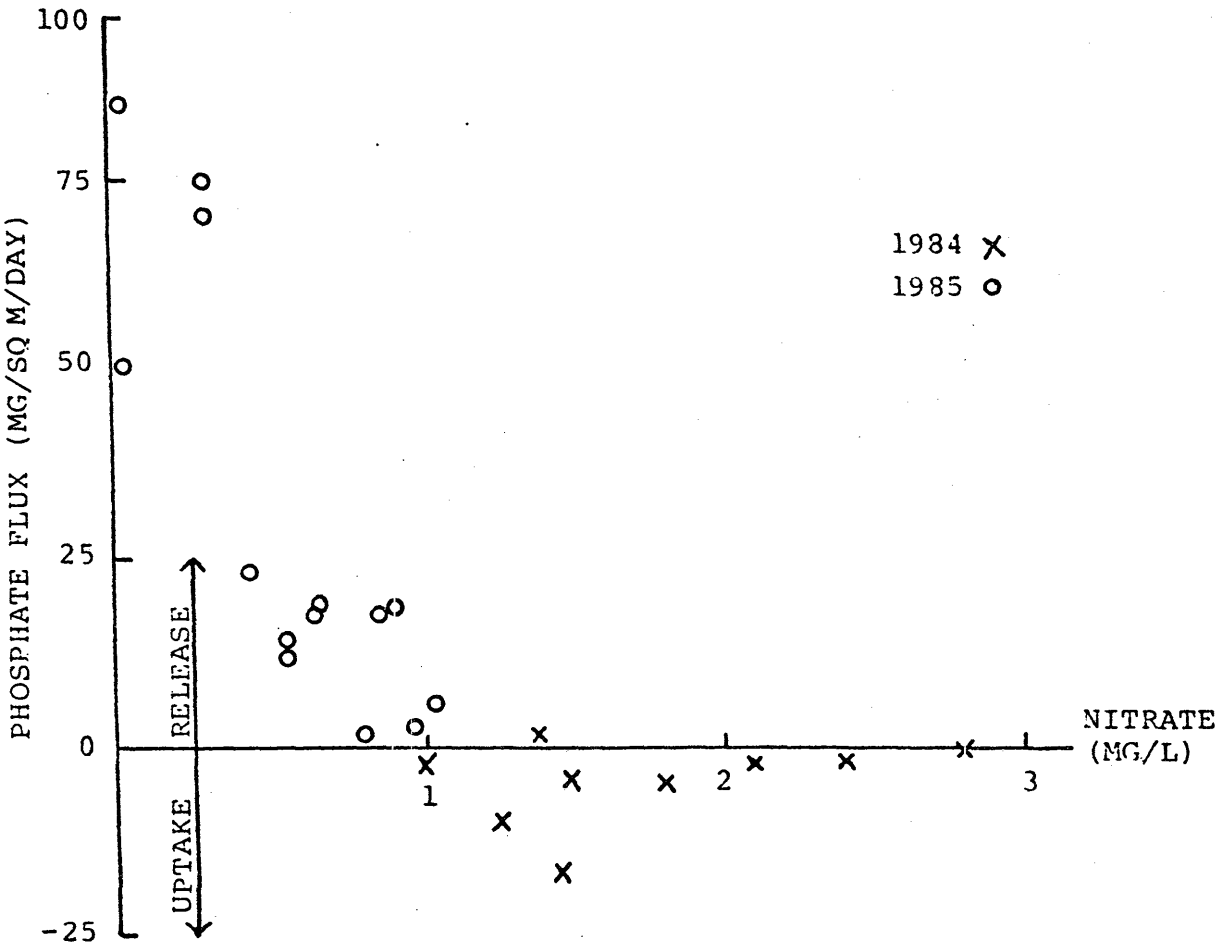


Figure 4. Phosphate Flux vs. Nitrate Concentration.
(1984 and 1985 observations).

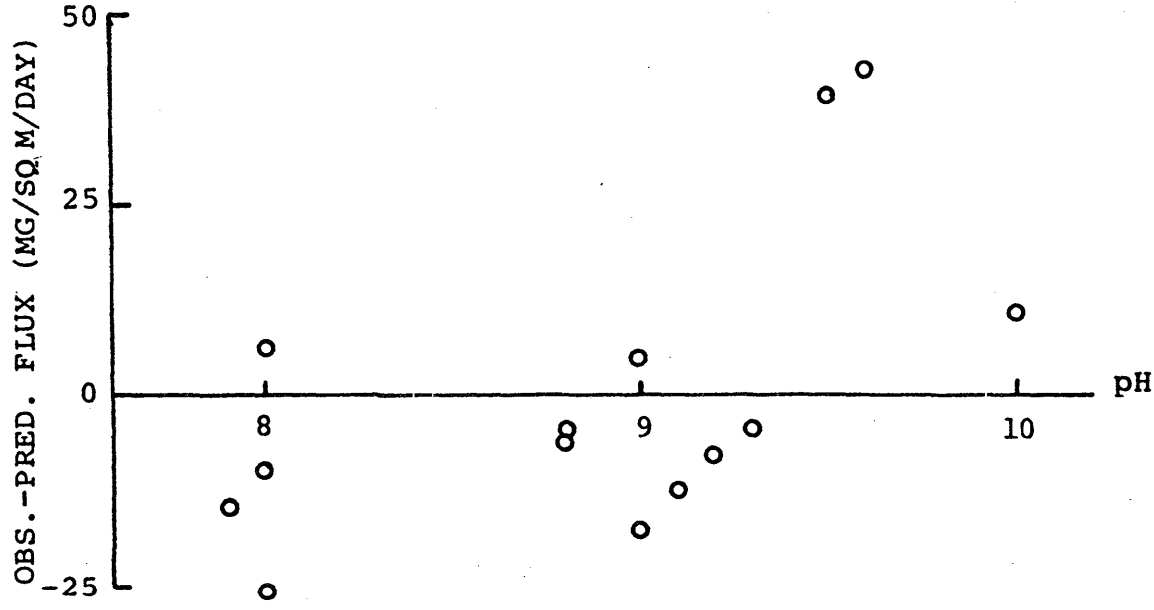
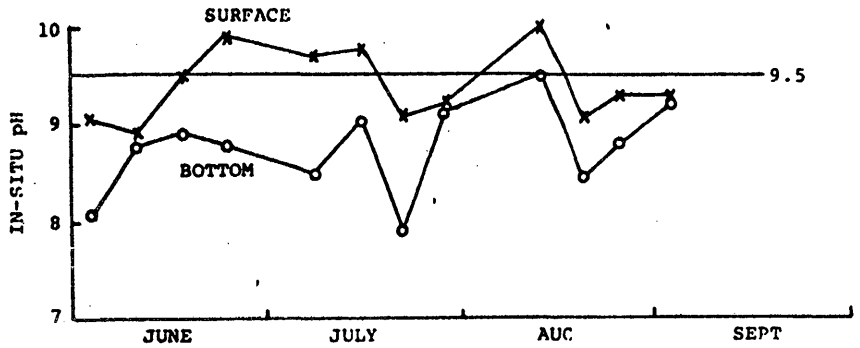
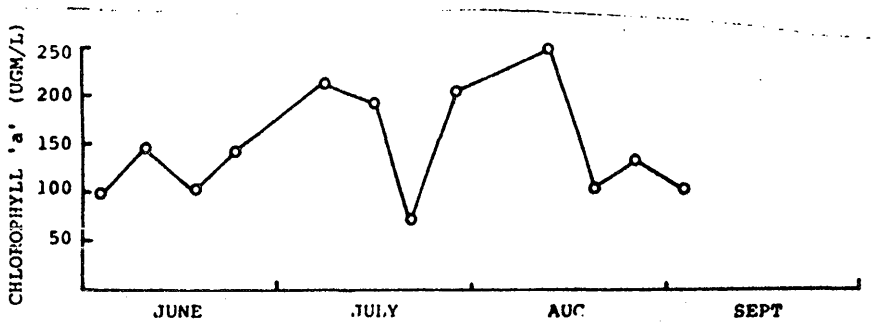
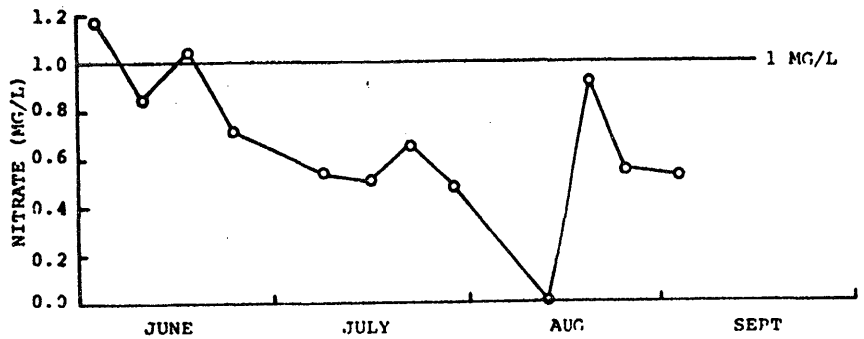


Figure 5. Residual Phosphate Flux (observed flux minus predictions based on Equation 1) vs. pH.







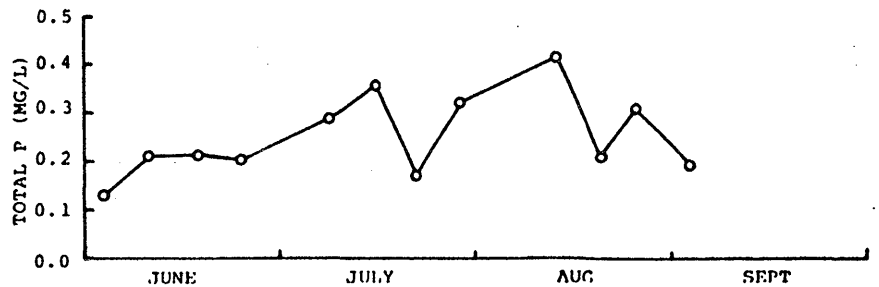


Figure 6. In-situ pH, Nitrate, Chlorophyll 'a' and Total Phosphorus. (1985 observations).

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FINAL REPORT

Polynuclear Aromatic Hydrocarbon Residues in Oysters and Brackish Water Clams from Virginia Estuaries

Results of the Fall 1985 Survey

to

Virginia State Water Control Board

by

Michael E. Bender

Virginia Institute of Marine Science
School of Marine Science
College of William and Mary
Gloucester Point, Virginia

August 1986

Objectives

The objectives of this program were to:

(1) update and expand the data base for polynuclear aromatic hydrocarbon residues in oysters and brackish water clams from Virginia's major estuaries;

(2) determine if differences in residues occur between years;

(3) determine if residues vary between species and/or river systems; and

(4) determine whether any unusual compounds and/or inputs can be detected

Methods

Samples of oysters (*Crassostrea virginica*) and clams (*Rangia cuneata*) were collected between 15-30 October of 1985 from the stations shown in Figure 1. Two composite samples, of 5-8 animals each, were analyzed for polynuclear aromatic hydrocarbon residues from each station.

A detailed account of the methods utilized for this study can be found in Bieri, et al. (1986) and Huggett, et al. (1986). Briefly, they include: Soxhlet extraction with methylene chloride; gel permeation chromatographic fractionation; compound separation by glass capillary chromatography; quantification relative to an internal standard by GC/FID; tentative compound identification by relative retention indices with mass spectral confirmation on selected samples.

Results

The residues of total resolved aromatics in the fall of 1984 and 1985 surveys are tabulated in Table 1. Figure 2 compares the two sampling periods. The two surveys yielded generally similar results:

(1) decreasing levels in oysters as one moves upstream from the first station for about 20 kilometers; and

(2) higher residues in Rangia as one moves upstream with declining residues at the most upstream station.

Relatively large differences in residues of total resolved aromatics in Rangia were noted at two stations. Residues were much lower at the station in Cobham Bay (RJ9) in 1985 and considerably higher in 1985 at Weyanoke Point (RJ12). Total aromatics in Rangia at Weyanoke Point are nearly as high as those found in oysters in the Elizabeth.

In the York River considerably lower residues in both oysters and Rangia were observed at the upstream stations during 1985. Resin acids although still present in Rangia were much lower than in 1984.

Residues in oysters from the Poquoson and Back rivers were below 1 ppm.

Tables 2 and 3 present data on the most common PAHs detected in the survey.

Figure 3 shows the concentrations of unresolved aromatics as a function of distance from the James River mouth. Relatively low residues were observed in the lower 80 kilometers of the river in both oysters and Rangia. Residues in the Rangia reached a peak at Station RJ12 and then declined at the two most upstream stations.

Substituted naphthalenes were generally higher in oysters in the lower river and similar residues were found in both oysters and Rangia at Station 8 (Figure 4). Perylene residues were also similar in oysters and Rangia at Station 8 then increased to almost 2 ppm at Station RJ12.

A paper to be published in the Ocean 86 Conference on monitoring which describes results of the first year effort is appended.

Table 1

River	Station	Species	Total Resolved ppm-dry wt. Fall 85	Fall 84	$\bar{x}$
York	1	Oyster	3.90	3.24	3.57
York	2	Oyster	1.16	2.00	1.58
York	3	Oyster	0.16	NS	--
York	4	Oyster	1.03	7.61	4.32
Pamunkey	1	Rangia	4.95	7.52	6.24
Pamunkey	2	Rangia	2.42	4.42	3.42
Mattaponi	1	Rangia	3.17	8.35	5.76
Mattaponi	2	Rangia	--	4.27	--
Poquoson	1	Oyster	0.44	NS	--
Back River	1	Oyster	0.77	NS	--
Back River	2	Oyster	0.39	NS	--
Lynnhaven	1	Oyster	2.31	NS	--
Elizabeth	HP	Oyster	16.32	NS	--
Elizabeth	LP	Oyster	13.40	NS	--
Nansemond	1	Oyster	0.80	1.45	1.12
James	2	Oyster	4.15	NS	4.15
James	3	Oyster	3.02	5.15	4.08
James	4	Oyster	1.13	3.95	2.54
James	5	Oyster	1.73	3.18	2.46
James	6	Oyster	2.54	2.90	2.72
James	7	Oyster	3.96	2.67	3.32
James	8	Oyster	1.28	NS	1.28
James	8	Rangia	1.89	NS	1.89
James	9	Rangia	1.55	6.38	3.97
James	10	Rangia	7.41	5.75	6.58
James	11	Rangia	5.92	6.88	6.40
James	12	Rangia	12.02	5.02	8.50
James	13	Rangia	4.46	4.41	4.44
James	14	Rangia	3.60	NS	3.60
Chickahominy	1	Rangia	1.42	1.92	1.67
Pagan	1	Oyster	2.07	NS	--
Pagan	2	Oyster	1.19	NS	--

Table 2.

Compound	Station 0J1	0J2	0J3	0J4	0J5	0J6	0J7	0J8	RJ8	RJ9
Naphthalene	<2	<3	52	<3	<1	4	<2	<2	<1	<1
Sub-naphthalenes	18	35	807	"	225	170	239	35	33	3
Dibenzofuran	14	67	<5	"	20	15	30	9	2	<1
Fluorene	7	28	<5	"	9	14	54	4	10	5
Methylfluorene	<2	15	<5	"	<1	<2	<2	<2	<1	<1
Phenanthrene	14	30	<5	27	42	34	66	34	25	12
Anthracene	<2	50	<5	<3	1	<2	<2	<2	<1	<1
Methylphenanthrene	4	10	<5	20	45	20	85	29	75	10
Phenylnaphthalene	<2	<3	<5	11	17	2	<2	<2	13	<1
C2-phenanthrene	23	52	61	32	85	27	26	53	37	13
Flouranthene	37	92	<5	<3	65	43	<2	48	57	34
Pyrene	37	82	46	124	52	47	32	52	80	52
Methylphenylnaphthalene	8	<3	<5	<3	10	24	41	28	39	21
Benzo(a+b)fluorene	3	<3	<5	50	22	50	24	35	40	65
Retene	<2	8	<5	11	<1	<2	<2	6	16	4
Methyl(pyrene/fluoranthene)	8	<3	"	6	24	24	22	28	39	21
Benzo(ghi)fluoranthene	8	<3	"	<3	<1	<2	37	<2	19	7
Benz(a)anthracene	<2	<3	"	"	8	4	5	5	<1	<1
Chrysene/Triphenylene	10	9	"	23	30	14	25	13	69	78
Trimethyltetrahydrochrysene	4	<3	"	<3	5	7	7	11	25	23
Benzofluoranthenes	<2	<3	"	"	15	6	<2	<2	<1	<1
Benz(e)pyrene	<2	<3	"	"	9	8	15	"	<1	<1
Benz(a)pyrene	<2	<3	"	"	2	9	13	"	4	4
Perylene	152	245	77	78	52	687	772	212	69	106
Total Resolved	803	4184	3020	1125	1729	2542	3961	1286	1890	1547
UCM	550	1400	1140	1510	2000	1815	3300	1720	4400	5600

Table 2 (continued)

Compound	Station RJ10	RJ11	RJ12	RJ13	RJ14	Check.	ERLP	ERHP
Naphthalene	30	9	27	2	7	9	30	4
Sub-naphthalenes	<2	15	77	79	105	46	41	215
Dibenzofuran	8	15	32	100	21	35	28	40
Fluorene	56	2	44	10	20	<1	269	107
Methylfluorene	<2	8	<2	26	<1	<1	<2	<3
Phenanthrene	14	4	387	28	34	7	54	61
Anthracene	<2	6	<2	15	14	<1	20	32
Methylphenanthrene	107	102	21	85	98	15	186	329
Phenylnaphthalene	<2	110	<2	17	30	<1	235	136
C2-phenanthrene	16	97	272	106	98	3	473	380
Flouranthene	54	122	58	94	67	17	560	636
Pyrene	45	160	116	139	111	44	546	782
Methylphenylnapthalene	72	125	37	104	68	13	460	211
Benzo(a+B)fluorene	365	208	1517	105	83	76	874	1083
Retene	<2	33	65	61	57	3	<2	<3
Methyl(pyrene/fluoranthene)	13	40	26	24	42	22	240	563
Benzo(ghi)fluoranthene	8	26	15	5	2	<1	135	356
Benz(a)anthracene	<2	<1	<2	13	<1	<1	65	134
Chrysene/triphenylene	55	128	246	130	120	64	175	429
Trimethyltetrahydrochrysene	20	87	108	97	82	20	<2	93
Benzofluoranthenes	<2	<1	<2	<2	<1	<1	196	800
Benz(e)pyrene	<2	6	<2	9	<1	<1	102	384
Benz(a)pyrene	<2	11	<2	17	4	4	52	112
Perylene	1846	909	428		65	80	1073	178
Total Resolved	7406	5913	12280	4464	3607	1414	13400	16322
UCM	3400	16810	52400	16400	15500	750	58100	62000

Table 3.

Compound	Station 0Y1	0Y2	0Y3	0Y4	RP1	RP2	RM1	Pagan 1	Pagan 2	Poquoson	Back 1	Back 2	Lynnhave
Naphththalene	<4	<5	<3	<4	<5	<5	<5	<2	<2	<3	3	<3	11
Sub-naphthalenes	16	"	"	37	99	21	147	20	"	"	<1	"	89
Dibenzofuran	<4	"	"	<4	<5	<5	<5	6	"	"	11	"	13
Fluorene	"	"	"	"	"	"	"	11	"	"	6	"	12
Methylfluorene	"	"	"	"	"	"	"	<2	"	"	<1	"	<1
Phenanthrene	"	23	"	"	21	"	"	63	18	"	14	10	29
Anthracene	"	<5	"	"	<5	"	"	<2	<2	"	<1	<3	<1
Methylphenanthrene	"	"	"	11	46	18	58	25	34	"	20	"	53
Phenylnaphthalene	25	"	"	<4	195	49	12	13	10	"	4	"	12
C2-phenanthrene	47	30	6	"	50	11	41	80	138	151	171	16	184
Flouranthene	10	22	11	42	115	63	115	79	72	23	52	55	191
Pyrene	37	86	14	54	117	72	27	80	51	68	79	67	99
Methylphenylnaphthalene	<4	<5	15	15	79	32	62	4	23	<3	39	<3	38
Benzo(a+b)fluorene	"	"	<3	51	57	96	87	<2	17	"	<1	"	8
Retene	"	"	"	<4	<5	25	43	<2	20	"	"	"	73
Methyl(pyrene/fluoranthene)	"	"	"	10	33	11	36	14	<2	"	"	"	12
Benzo(ghi)fluoranthene	"	"	"	<4	<5	<5	<5	<2	<2	"	"	"	<1
Benz(a)anthracene	"	"	"	"	<5	"	<5	<2	6	"	"	"	9
Chrysene/Triphenylene	"	"	"	"	95	91	120	25	28	"	26	"	54
Trimethyltetrahydrochrysene	15	18	"	"	60	89	57	11	19	"	3	19	<1
Benzofluoranthenes	<4	<5	"	"	<5	<5	<5	<2	<2	"	<1	<3	"
Benz(e)pyrene	"	"	"	"	"	"	"	<2	10	"	"	"	"
Benz(a)pyrene	"	14	"	"	"	"	"	58	<2	"	"	"	"
Perylene	2167	299	85	205	196	214	213	540	74	94	78	41	244
Total Resolved	3913	1158	261	1031	4954	2423	3170	2071	1184	438	765	389	2306
UCM	200	0	0	400	2500	2000	4000	500	1800	0	0	0	2000

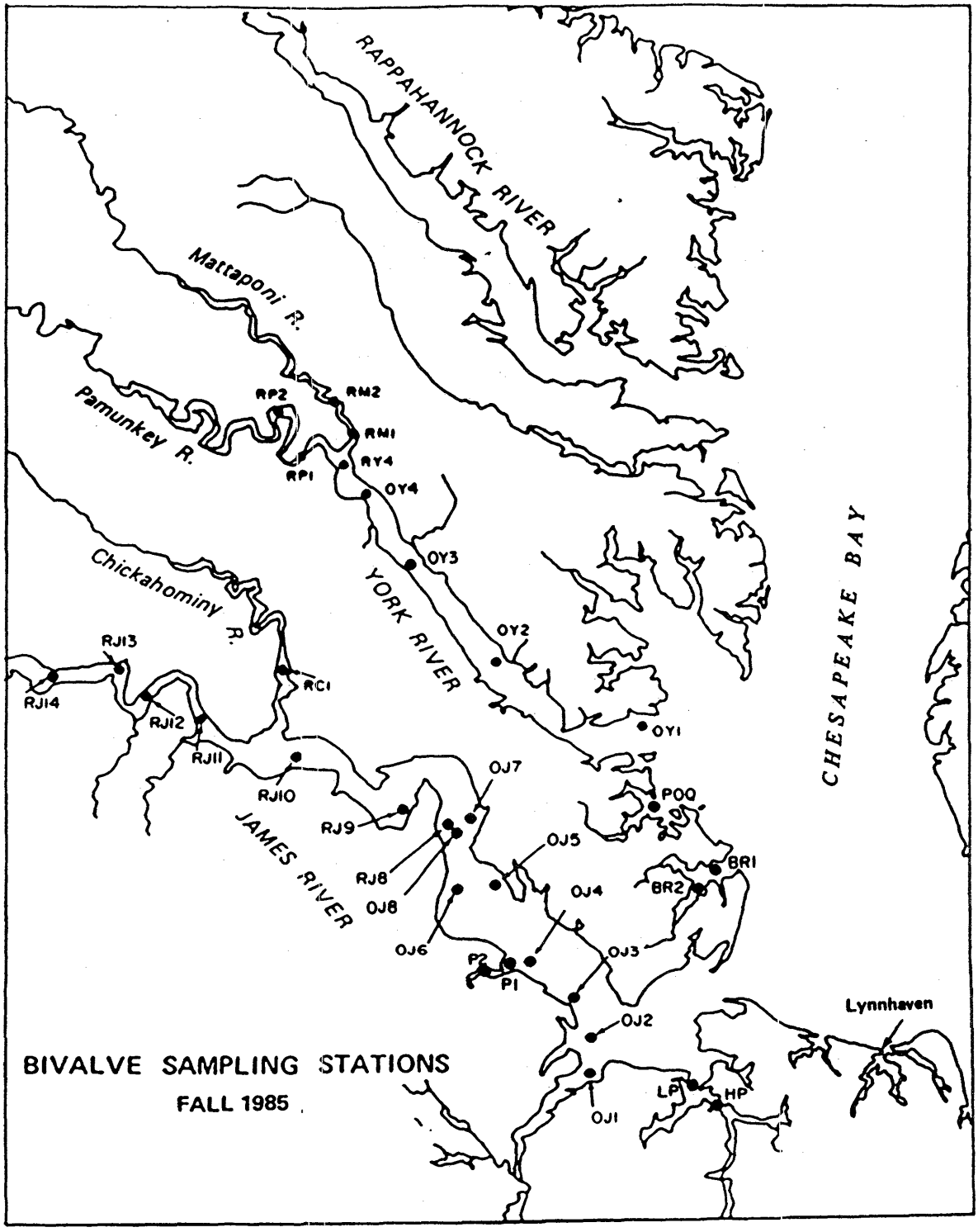

RAPPAHANNOCK RIVER
Mattaponi R.
Pamunkey R.
RP2
RM2
RM1
RP1
RY4
OY4
OY3
OY2
OY1
YORK RIVER
CHESAPEAKE BAY
Chickahominy R.
RJ13
RJ14
RJ12
RJ11
RJ10
RC1
RJ9
RJ8
OJ8
OJ7
OJ6
OJ5
OJ4
OJ3
OJ2
OJ1
P2
P1
P00
BR1
BR2
JAMES RIVER
Lynnhaven
LP
HP
BIVALVE SAMPLING STATIONS
FALL 1985

Fig. 1

Fig. 2

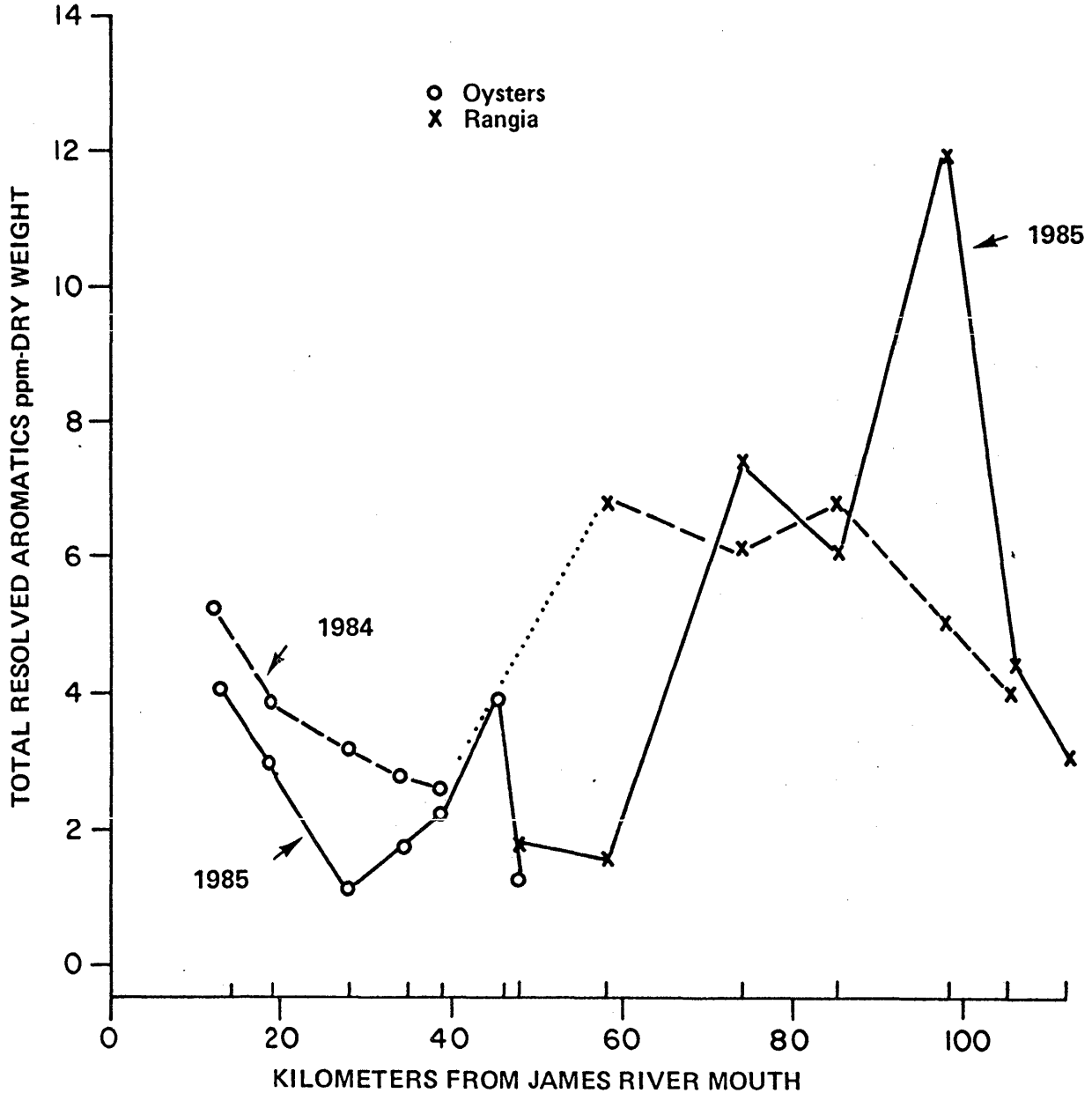

Oysters
Rangia
1984
1985
1985
TOTAL RESOLVED AROMATICS ppm-DRY WEIGHT
KILOMETERS FROM JAMES RIVER MOUTH
0
2
4
6
8
10
12
14
0
20
40
60
80
100

Fig. 3

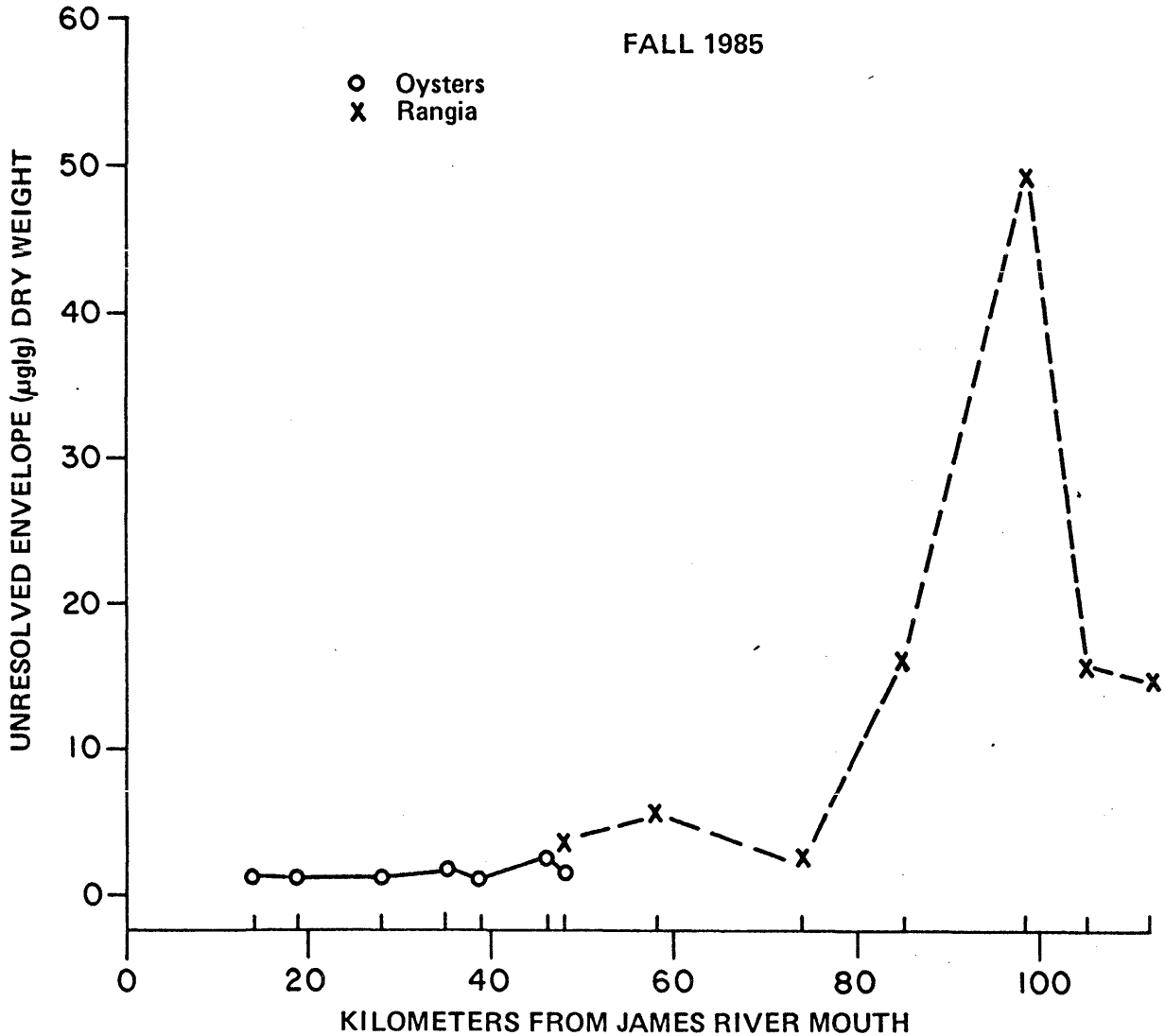

FALL 1985
Oysters
Rangia
UNRESOLVED ENVELOPE (µg/g) DRY WEIGHT
60
50
40
30
20
10
0
0
20
40
60
80
100
KILOMETERS FROM JAMES RIVER MOUTH

Fig. 4

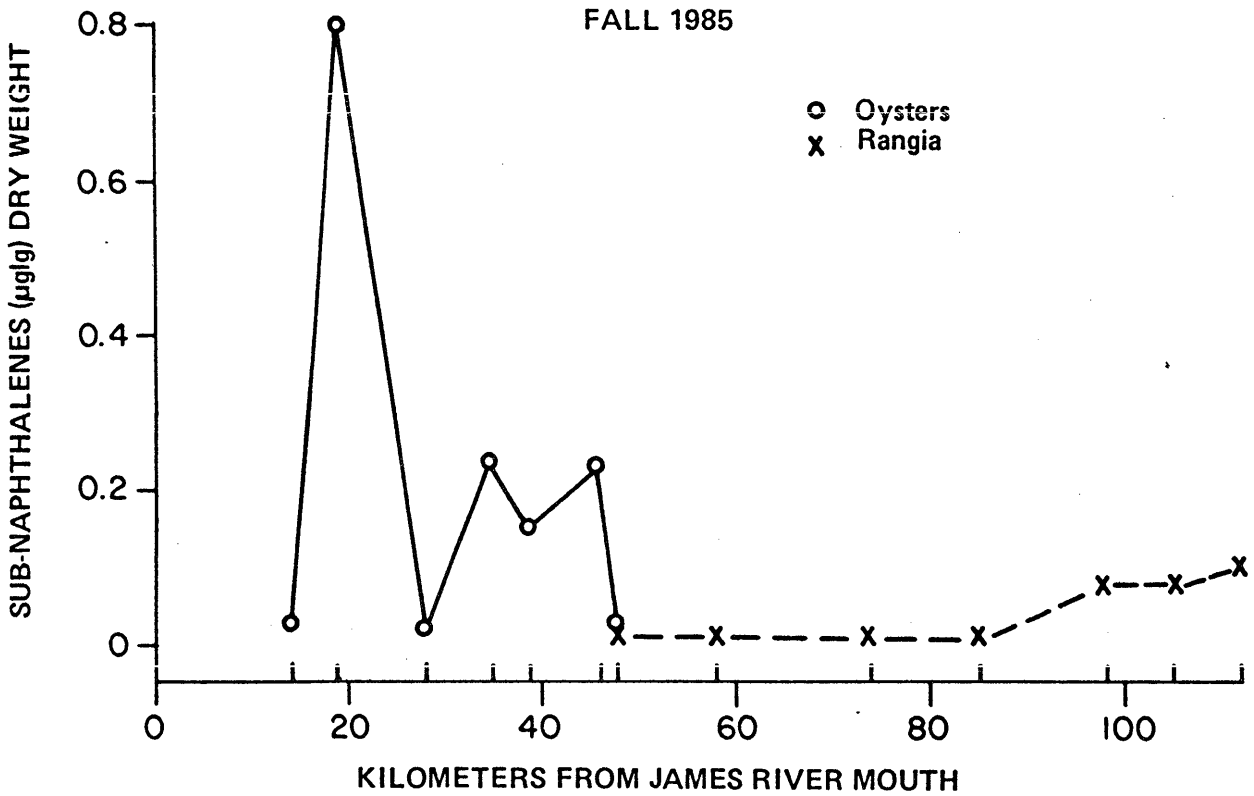
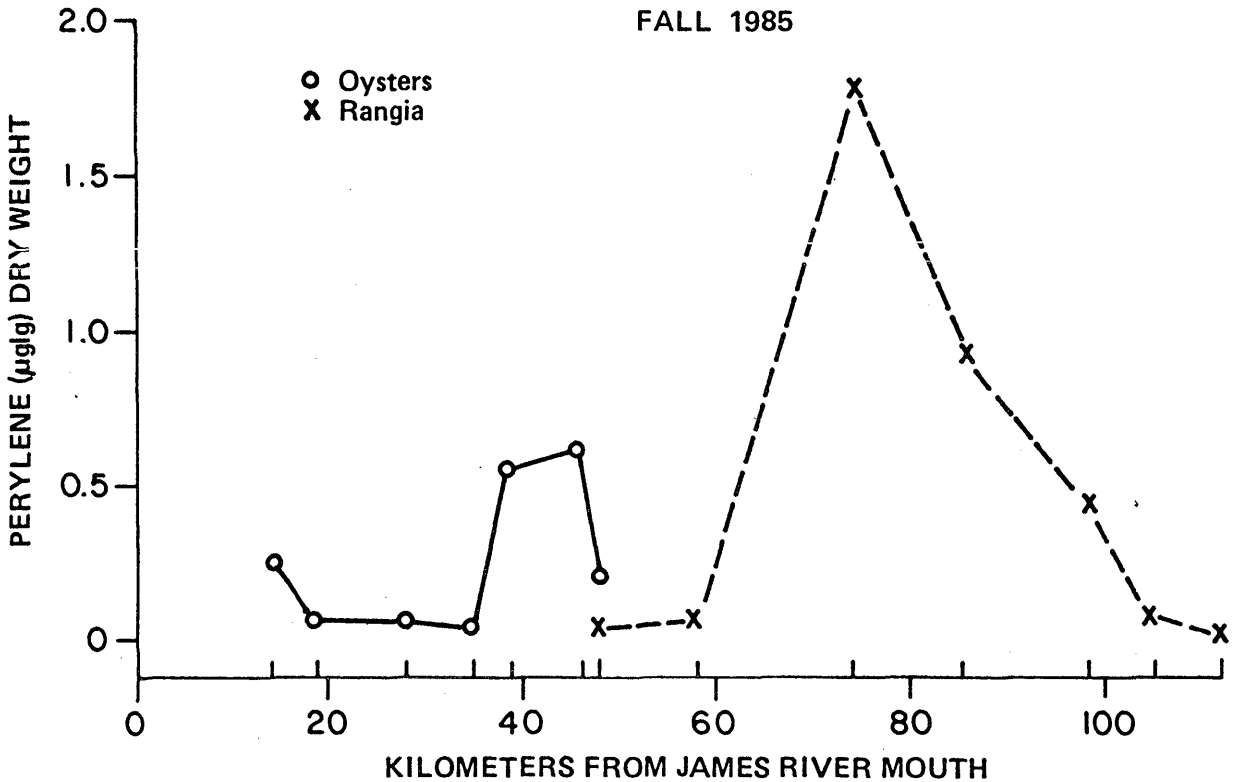

FALL 1985
Oysters
Rangia
SUB-NAPHTHALENES (µg/g) DRY WEIGHT
0.8
0.6
0.4
0.2
0
0
20
40
60
80
100
KILOMETERS FROM JAMES RIVER MOUTH

Fig. 5


FALL 1985
Oysters
Rangia
PERYLENE (µg/g) DRY WEIGHT
2.0
1.5
1.0
0.5
0
0
20
40
60
80
100
KILOMETERS FROM JAMES RIVER MOUTH

Polynuclear Aromatic Hydrocarbon Monitoring in Estuaries Utilizing: Oysters, Brackish Water Clams and Sediments

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Abstract

The monitoring of contamination from polynuclear aromatic hydrocarbons (PAH) in estuarine animals is complicated by the necessity of utilizing different species as one progresses upstream along the salinity gradient. In the Chesapeake Bay, most tributary sub-estuaries contain two bivalve species, the oyster, Crassostrea virginica, and the brackish water clam, Rangia cuneata, which frequently have overlapping distributions. This paper describes the use of these species and sediments as monitors for PAH contamination in the James, York and Rappahannock rivers. Seasonal, species and source related differences are discussed.

INTRODUCTION

Monitoring water for organic chemical contamination is difficult because the compounds of interest are usually present in very low concentrations due to low solubilities and affinity for sediment particles. The dynamic nature of the water column adds to the difficulty. To overcome these problems sediments and/or sessile animals are preferred as a sampling medium.

In the case of polynuclear aromatic hydrocarbons (PAH) Neff [1] estimated that sediments will always contain concentrations greater by a factor of 1,000 than the overlying water. Hence, he concluded that "sediment samples have a substantial integrating effect on temporal patterns of PAH input and offer good geographic resolution".

Shellfish have been used to monitor various pollutants such as bacteria, viruses, metals, pesticides and hydrocarbons for many years [2 and 3]. Several authors, including Lee [4] and Neff [1] have indicated that one of the advantages of using mollusks for monitoring PAH is their limited ability to metabolize these compounds.

The objectives of the studies reported here were to: (1) assess the level of potentially toxic organic compounds in sediments of Virginia's major tributaries of the Chesapeake Bay; (2) establish a baseline for PAH residues in oysters and brackish water clams; (3) determine if seasonal differences in residues occur; (4) determine if residues vary between species and/or river systems and (5) determine whether any unusual compounds and/or inputs could be detected.

METHODS

Sediments were collected from the stations shown in Figure 1 during the spring of 1985. The samples were collected with a stainless steel Smith-MacIntyre grab sampler. The grab was rinsed with water and methanol prior to deployment. The top two centimeters of the undisturbed sediment was transferred to clean glass jars which were stored on ice until they were returned to the laboratory and frozen.

Samples of oysters (Crassostrea virginica) and clams (Rangia cuneata) were collected, by dredge, in the fall of 1984 and spring of 1985 from the stations shown in Figure 2. Two composite samples, of 5-8 animals each, were analyzed for polynuclear aromatic hydrocarbon residues from each station.

A detailed account of the methods utilized for this study can be found in Bieri et al. [5] and Huggett et al. [6]. Briefly, they include: sample desiccation; Soxhlet extraction with methylene chloride; gel permeation chromatographic fractionation; high pressure liquid chromatographic fractionation; compound separation by glass capillary chromatography; quantification relative to an internal standard by GC/FID; tentative compound identification by relative retention indices with mass spectral confirmation on selected samples.

RESULTS

Bivalves

Table 1 summarizes the levels of total resolved aromatics detected by river, station, species and season.

In the fall 1984, James River survey residues of total PAH in oysters declined with increasing distance from the river mouth (Figure 3). Residues in clams were relatively constant between

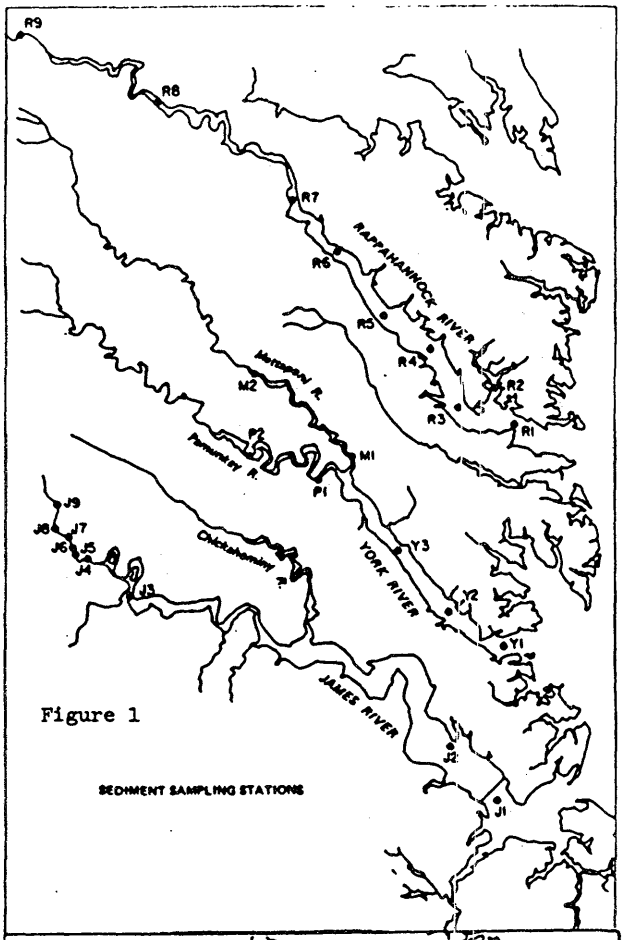

Figure 1

SEDIMENT SAMPLING STATIONS

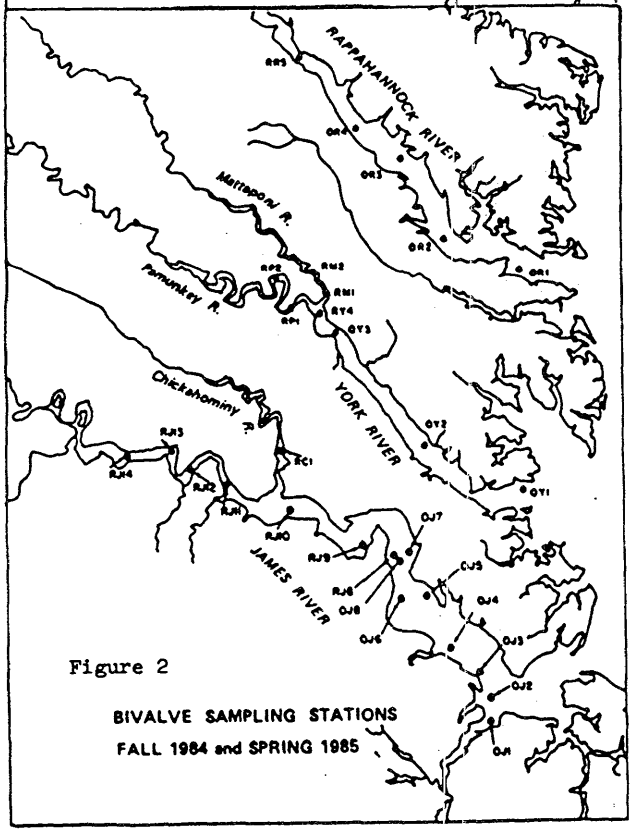

Figure 2

BIVALVE SAMPLING STATIONS
FALL 1984 and SPRING 1985

Table 1

River	Station	Species	Total Resolved Aromatics ppm - dry weight Fall 84	Spring 85	x̄
York	1	Oyster	3.24	1.85	2.55
	2	Oyster	2.00	0.51	1.25
	3	Oyster	7.61	2.36	5.00
	4	Rangia	15.70	2.92	9.30
Pamunkey	1	Rangia	7.52	1.71	4.60
	2	Rangia	4.42	0.87	2.66
Mattaponi	1	Rangia	8.35	9.93	9.14
	2	Rangia	4.27	1.88	3.10
Rappahannock	1	Oyster	1.83	0.29	1.06
	2	Oyster	1.72	0.25	0.99
	3	Oyster	1.30	0.65	0.98
	4	Oyster	1.48	0.69	1.09
	5	Rangia	1.56	0.74	1.15
Nansemond	1	Oyster	1.45	0.31	0.88
James	2	Oyster	-	0.42	-
	3	Oyster	5.15	0.61	2.88
	4	Oyster	3.95	0.64	2.30
	5	Oyster	3.18	0.69	1.94
	6	Oyster	2.90	0.89	1.90
	7	Oyster	2.67	1.76	2.22
	8	Oyster	-	1.10	-
	8	Rangia	-	1.34	-
	9	Rangia	6.38	1.07	3.73
	10	Rangia	5.75	2.05	3.90
	11	Rangia	6.88	3.91	5.40
	12	Rangia	5.02	5.30	5.15
	13	Rangia	4.41	4.37	4.40
	14	Rangia	-	1.81	-
Chickahominy	1	Rangia	1.92	0.90	1.40

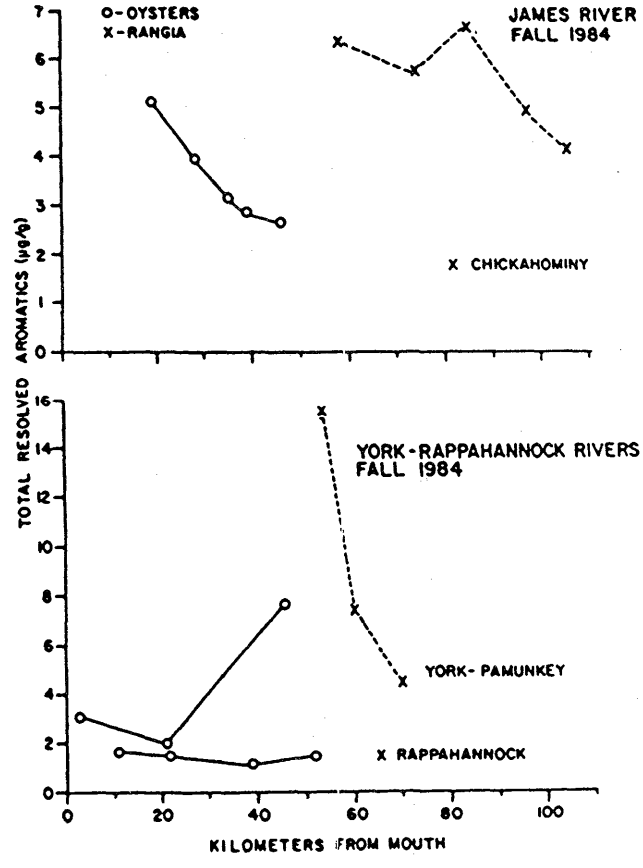

Figure 3

60 and 90 kilometers from the river mouth and then declined at the upriver sites. Residues in Rangia collected from the Chickahominy, a relatively pristine tributary of the James, were considerably lower than those from any of the James River stations.

In the York River, concentrations of total aromatics increased dramatically at the most upstream oyster rock sampled and clams collected from just below West Point had the highest residues observed during the survey (Figure 3). A detailed examination of the clam samples from the York, Pamunkey and Mattaponi indicated that compounds derived from resin acids of plants accounted for a significant proportion of the resolved aromatics in these samples. A large pulp and paper mill is located at West Point and discharges from its waste treatment system appear to be the most likely source of these compounds.

Concentrations of hydrocarbons in the unresolved complex mixture (UCM - unresolvable mixtures of aromatic hydrocarbons) from these samples are shown in Figure 4. Oysters and clams collected from the Rappahannock showed no evidence of UCM. In both the York and James rivers substantial increases in the UCM were observed in both oysters and clams collected near the turbidity maximum zone. The lack of a UCM in the Rappahannock samples and the relatively low concentration observed in the Chickahominy samples suggest anthropogenic origins for the UCM.

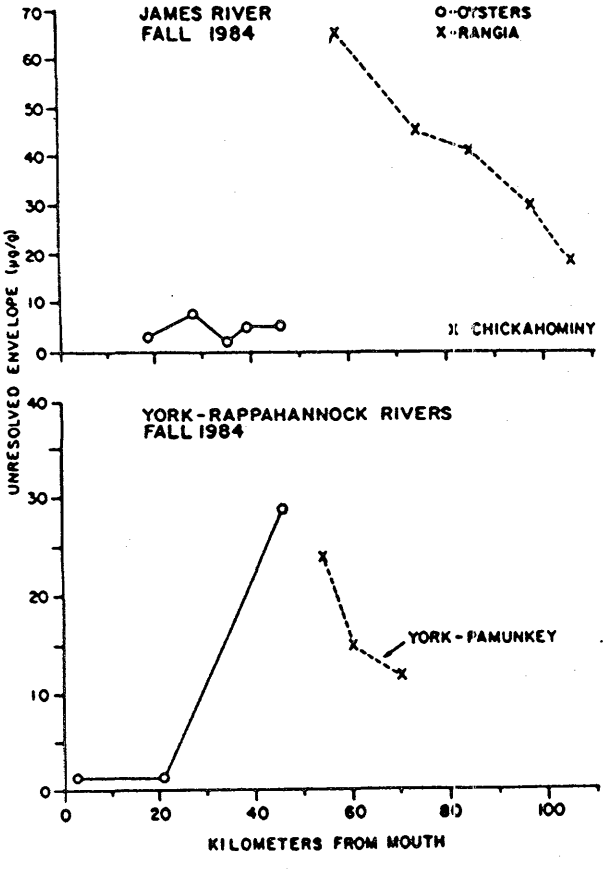

Figure 4

Figure 5 illustrates different sources for hydrochrysenes and dibenzofurans in the James River, an upriver source for hydrochrysenes and a downstream origin for dibenzofurans.

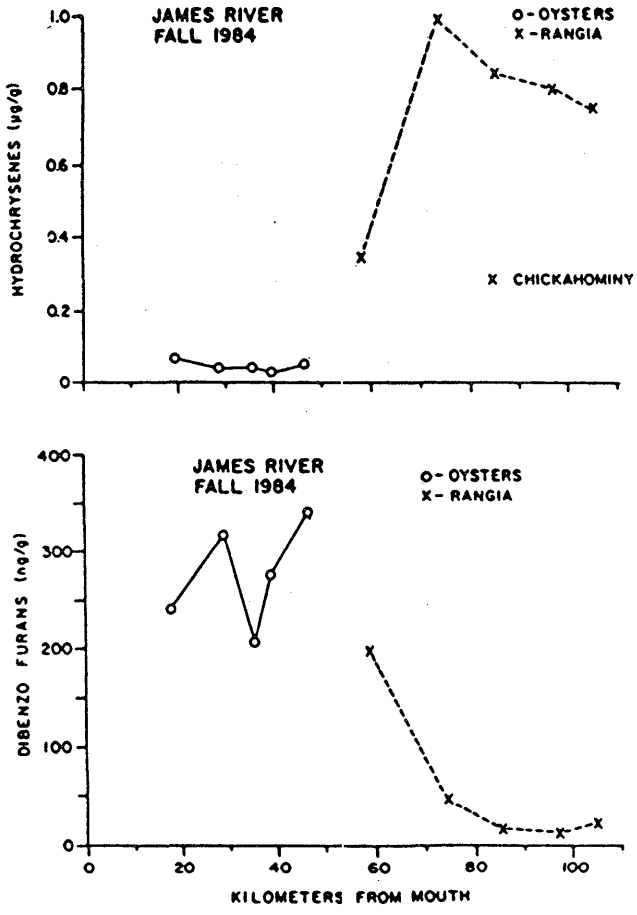

Figure 5

Figure 6 shows the residues of total resolved aromatics as a function of distance in the three rivers surveyed during the spring of 1985. Important to note from this figure are the following:

(1) the York system has the highest concentrations;

(2) oysters and Rangia collected from about the same locations in the James had very similar residue levels; and,

(3) oysters and Rangia from the Rappahannock and Rangia from the Chickahominy showed the least contamination.

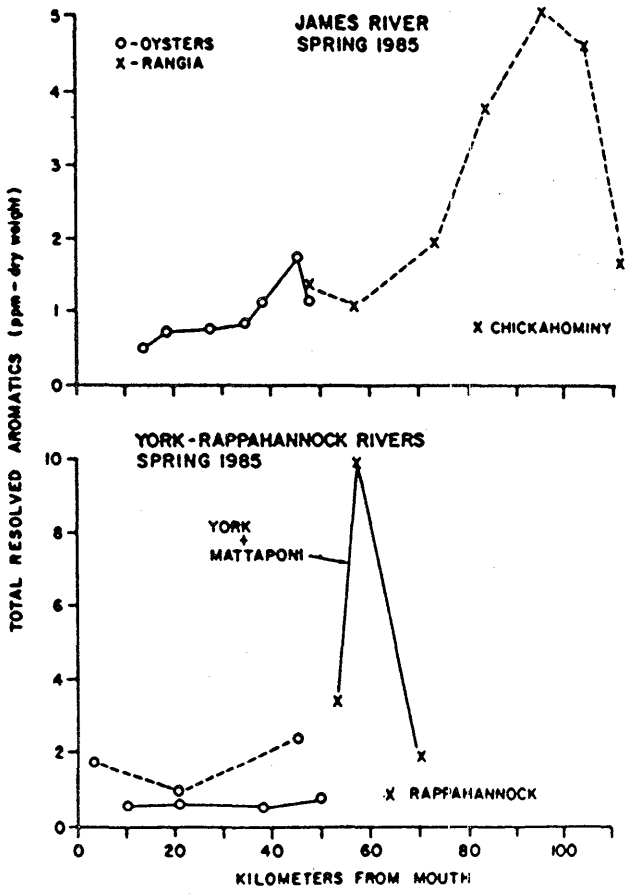

Figure 6

Seasonal differences in residues of total resolved aromatics were observed for both oysters and Rangia (Table 1, Figures 3 and 6). Concentrations were greater in the fall collection period by a factor of 2 to 3 at most stations. This observation is most probably related to the conditioning and spawning cycles of these bivalve species. Oysters spawn during the summer and then build up food reserves of lipids and glycogen during the fall. Rangia are late fall and early winter spawners and were in "peak" condition at the time of the fall 1984 survey. Residues of pesticides, e.g. Kepone, in oysters have been shown to vary with the spawning and conditioning cycle described above [3].

Sediments

The polar fractions from the HPLC fractionation contained no detectable toxic organic compounds (detection limit - 0.1 ppb) and will not be discussed further. The moderately polar fraction containing PAH had compounds from both natural and anthropogenic sources. Some prominent anthropogenic compounds are labelled in Figure 7 (Table 3) and some natural compounds are labelled in Figure 8 (Table 4). Qualitatively, most samples were very similar, differing mainly in the relative contributions of the two classes of compounds. Table 2 summarizes the total PAH concentrations at each station.

The levels of naturally derived PAH, primarily tetramethyloctahydrochrysene isomers and trimethyltetrahydrochyrsene isomers, vary in all three rivers, but are generally quite low at the mouths and higher upstream indicating an upriver source as do the bivalve data. The exact origin of this class of compounds is not known, but it is postulated that they derive from aromatization of terpenoid components of plant resins of the oleane and ursane family [7, and the references therein].

Table 2

Sediment PAH Concentrations
ppm - dry weight

River	Station	Total Resolved	Natural	Anthropogenic
James	1	1.36	0.06	1.30
James	2	1.04	0.12	0.92
James	3	6.22	0.93	5.29
James	4	7.12	1.45	5.67
James	5	13.90	1.26	12.64
James	6	5.69	0.55	5.14
James	7	7.25	1.05	6.20
James	8	5.02	0.57	4.67
James	9	6.36	0.38	5.98
York	1	0.97	0.07	0.90
York	2	1.03	0.09	0.94
York	3	0.98	0.14	0.84
Pamunkey	1	14.22	12.25	1.97
Pamunkey	2	1.75	0.49	1.26
Mattaponi	1	1.19	0.25	0.94
Mattaponi	2	0.57	0.26	0.31
Rappahannock	1	0.09	0.01	0.08
Rappahannock	2	0.62	0.03	0.59
Rappahannock	3	0.94	0.26	0.68
Rappahannock	4	0.67	0.04	0.63
Rappahannock	5	0.82	0.09	0.73
Rappahannock	6	0.89	0.20	0.69
Rappahannock	7	1.28	0.45	0.83
Rappahannock	8	5.11	2.12	2.99
Rappahannock	9	0.32	0.12	0.20

All of the anthropogenic PAH found can be derived from various sources, but are primarily from combustion of organic matter. Any type of combustion (internal combustion engines, home heating, power generation, industry, etc.) produces PAH as a by-product, with different compound distributions depending on the temperature of the combustion rather than the fuel. Aeolian transport, land runoff and river transport are all significant modes of introduction of PAH to aquatic systems with the relative importance of each mode being determined by the particular area. The James River sediments contained the highest levels of anthropogenic PAH of the three, corresponding to the large amount of

commercial and industrial activity on and around the river. With the exception of station 5, the upriver stations all are approximately 5 ppm and the lower river stations approximately 1 ppm. The higher level at station 5 cannot be accounted for. The levels in the York/Mattaponi/Pamunkey system do not differ drastically. Similarly, the Rappahannock is quite constant with the exception of station 1 near the mouth and station 8 which is quite close to a major highway bridge. These data reflect an input from street runoff, and a dilution effect at the mouth.

Table 3

Anthropogenic PAH Labeled in Figure 7

A	Phenanthrene
B	Methyl phenanthrene isomers
C	Fluoranthene
D	Pyrene
E	1,1' binaphthyl (internal standard)
F	Benzo(a)anthracene
G	Chrysene
H	Benzo fluoranthene isomers
I	Benzo(e)pyrene
J	Benzo(a)pyrene
K	Indeno(1,2,3,cd)pyrene
L	Benzo(ghi)perylene

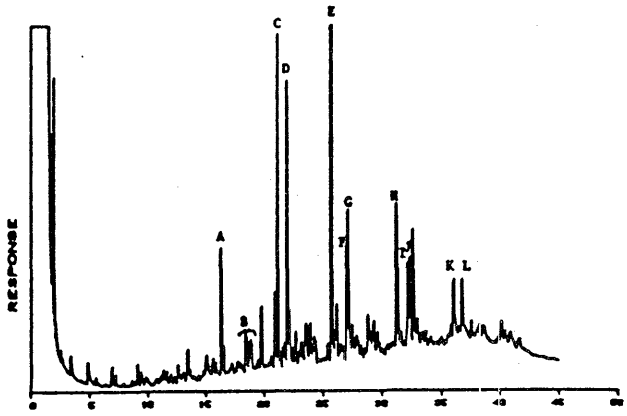

Figure 7

Table 4

Natural PAH Labeled in Figure 8

1	Retene
2	3,3,7,12a tetramethyl 1,2,3,4,4a,11,12,12a octahydrochrysene
3	1 methyl (isopropyl 7,8 cyclopenta)phenanthrene
4	3,4,7 trimethyl 1,2,3,4 tetrahydrochrysene
5	3,3,7 trimethyl 1,2,3,4 tetrahydrochrysene
6	Perylene
7	1,2,9 trimethyl 1,2,3,4 tetrahydropicene
8	2,2,9 trimethyl 1,2,3,4 tetrahydropicene

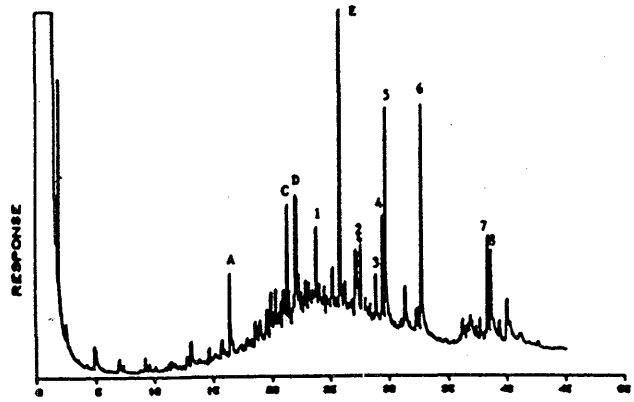

Figure 8

SUMMARY

The results of these surveys indicate that:

(1) both bivalves and sediments are good indicators of inputs, both natural and anthropogenic;

(2) differences in residues between river systems exist;

(3) the UCM appears to reflect anthropogenic inputs and the influence of the turbidity maximum;

(4) residue levels of naturally occurring compounds in bivalves differ between river systems; and,

(5) the high residue levels of resin acid compounds detected in Rangia from the York, Pamunkey and Mattaponi rivers indicate an unnatural input.

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Title: Bioconcentration of PAH from contaminated sediments by bivalve molluscs

Authors: M.E. Bender and M.H. Roberts, Jr.

Background

Bivalve molluscs provide an excellent monitor for the presence of a wide variety of substances in the marine environment; so much so that a national program has been developed known as "Mussel Watch". Bivalves are sedentary species, so any material detected within the meats must result from the presense of that material in the immediate environment. Further, bivalves have relatively high bioaccumulation rates, often resulting in high body burdens even in situations in which there is an undetectable amount of a substance in the water.

Bivalves used for such monitoring in the Virginian portion of the Chesapeake Bay include Crassostrea virginica, Mercenaria mercenaria, and Rangia cuneata. Both C. virginica and M. mercenaria occur throughout the polyhaline and mesohaline reaches of the Bay, but at any given sampling location, only one or the other species may be present. R. cuneata is restricted to the oligohaline regions where the other two species are absent. All three species are essential to any monitoring program within the estuarine system. A central question is therefore whether the equilibrium bioconcentration factor (BCF_e) for selected compounds is the same for the three species under identical conditions of salinity and temperature.

Monitoring programs continue throughout the year despite wide divergence in some environmental parameters, notably temperature. The BCF_e is a function of the uptake (k_1) and clearance (k_2) rates for any specific compound. Temperature is generally a prime regulator of physiological rate functions such as these. Yet to date, little or no direct measurements of temperature effects on these rates or the resultant BCF_e have been made. It is, nevertheless, obviously important to understand the relationship between temperature, uptake rate, clearance rate, and the BCF_e.

Objectives

1. To compare the BCF_e, k_1, and k_2 for a variety of PAHs found in contaminated sediment from the Elizabeth River for three bivalve species, Crassostrea virginica, Mercenaria mercenaria, and Rangia cuneata.

2. To evaluate the relationship between temperature and both uptake and clearance rates for each of the compounds recovered from both bivalve tissues and water samples.

Materials and Methods

C. virginica for the experiments were collected from the Rappahannock River. M. mercenaria were purchased from a commercial source harvesting clams from the lower York River. Both species were held in the laboratory for 2 weeks prior to use in an experiment during which time they were fed

cultured algae to ensure adequate food quantities. Two populations of Rangia were procured. This first, from the Chicahomony River, was suspect since about half the clams were gapers at the time of collection. During the laboratory quarantine period, high mortality was observed, and an experiment was therefore not initiated. The second group was collected from the Rappahannock River from a seemingly healthy population. After a two week quarantine period to allow laboratory acclimation, an experiment was initiated despite a low background mortality rate.

Each bivalve species was tested separately. For each species, four groups were used, one control and one exposure group at each of two temperatures, 15 °C and 25 °C. The exposure group received York River water to which was added contaminated sediments collected from the Elizabeth River at a suspended solids concentration of 10 mg/l. The control group was provided with uncontaminated sediments collected from the York River. Temperatures of the diluent water flows were controlled by thermostatically controlled resistance heaters; the ambient water was generally below 15 °C during all experiments except those with R. cuneata; for these latter experiments, the ambient water was chilled using a simple glass condensor on the inflow line with a chilled exchange medium in the condensor jacket.

The experiments with C. virginica and M. mercenaria were performed at the ambient salinity which typically averages 18-20 °/₀₀. This salinity is considerably above that necessary for Rangia. For the latter species, water of 5 °/₀₀ was prepared continuously by diluting filtered York River water with charcoal filtered domestic tap water. The proportion of each water type was controlled by gravity feed from head tanks.

During the experiments, cultured algae was added as food in an amount calculated to provide optimal growth of C. virginica (Epiphanio and Ewart, 1977). The amount of food provided for hard clams and Rangia may not have been appropriate. No data was available however from which to derive species specific estimates of optimal food concentrations.

Body burdens of each PAH was measured on a pooled group of unexposed animals sampled on day 0 to define the background body burden. Three oysters from each exposure group were removed from each treatment on Day 3, 7, 14, 21, and 28 of the uptake phase. On Day 28, the supply of sediment was stopped for all treatments, and three animals were again removed from each treatment on Day 3, 7, 14, 21, and 28 of the clearance phase. Each animal was analyzed individually for PAH using the gas chromatographic method of Bieri et al. (1986). Water samples were collected weekly from each treatment and analyzed by analogous methods.

The body burden data was analyzed statistically using a pharmacokinetic equilibrium model as implemented by the BIOFAC computer programs developed by Blau and Agin (1978). This model uses a maximum likelihood ratio procedure to estimate the uptake and clearance rates from which are derived the BCF_e, time to 50% clearance, and time to 90% BCF_e along with appropriate 95% confidence limits. A graphical presentation can also be obtained for each test compound. This model was applied to data for a series of specific compounds for which sufficient data were available as well as total PAH.

Water temperature, salinity, dissolved oxygen concentration and pH were measured daily. All water flows were measured and adjusted if necessary on

a daily frequency. Water flows were essentially invariate throughout all experiments.

Results

The experiments with C. virginica and M. mercenaria were successfully completed with no mortalities during either uptake or clearance phases of the experiment other than those due to animal sacrifice. The experiment with Rangia was not satisfactory. When excessive mortalities were observed, after about 14 days in the 25 °C treatments, both control and PAH exposure treatments at this temperature were terminated. Mortality increased late in the experiment in the 15 °C treatments, precluding the clearance phase of the experiment. The sequence of mortality at both temperatures is consistant with a disease epidemic, but no responsible organism was identified. Tissue samples collected from Rangia at both temperatures have been preserved, but to date have not been analyzed for PAH; the amount of useful information which could be gleaned from these samples is minimal.

Temperatures within each experiment were well controlled. During the oyster experiment, the measured temperature in the warm treatment averaged (standard deviation) 24.5 (1.5) °C, while the measured temperature in the cool treatment averaged 14.7 (1.0) °C. The salinity averaged 17.9 (0.9) $^{o}/_{oo}$. Dissolved oxygen concentration in all treatments remained near saturation for each temperature condition with a mean of 90.6 (18.48) % in the warm treatment and 95.8 (14.2) % in the cool treatment. pH remained within a normal range with a mean of 7.7 (0.3). During the clam experiment, the measured temperature in the warm treatment averaged 24.7 (1.5) °C, while in the low temperature treatment it averaged 15.0 (1.0) °C. Salinity averaged 17.3 (1.1) $^{o}/_{oo}$. The percent of oxygen saturation averaged 89.1 (7.9) % at the warm temperature, and 93.0 (6.9) % at the low temperature. pH was slightly higher than in the oyster experiment with a mean of 8.0 (0.1). It must be stressed that while there was at time supersaturation with oxygen (up to 120 % of saturation) in both experiments, no mortalities resulted from "gas bubble" disease.

Oyster shell weight gain, normalized to initial underwater weight, was not significantly affected by temperature or PAH exposure. The only statistically significant factor affecting shell weight gain was time. Though not significant, mean weight gains were greater at 15 °C than at 25 °C. The broad range in underwater weights of the test animals despite selection for total shell length may partly explain the lack of statistically signicant difference. The incremental increase in shell length was also significantly related to time, but not quite significantly affected by treatment ($p=0.052$). PAH exposure did result in reduced shell growth.

Clams exhibited larger growth increments in shell weight at 15 °C than at 25 °C, but neither temperature nor PAH exposure resulted in a statistically significant difference; only time produced a significant effect. Statistically significant differences in shell length increments were found to be related to time and temperature, but not PAH exposure. As with shell weight gain, growth increments were larger at 15 than 25 °C.

Graphically, the time courses of uptake and clearance for total PAH in the oyster and hardshell clam experiments at both temperatures followed a

first order kinetic model (figures not presented). Thus application of the BIOFAC model to these data is appropriate. The uptake and clearance rates, BCF_e and oyster:clam ratio of BCF_e for indivudual compounds and total PAH as calculated by this model are summarized in Table 1.

For both species, the equilibrium body burden calculated as the ration of uptake rate to clearance rate was slightly higher at the low temperature than the high. This was observed previously for bivalves exposed to individual PAHs in the laboratory (Neff and Anderson 1981).

Oysters accumulated about 3 times more total PAH than did hardshell clams at 15 °C, and about 3.7 times more total PAH at 15 °C. This apparent difference in relative uptake by the two species as a function of temperature is probably not significant, since the ranges in BCF_e are rather broad. The species difference per se, however, is large and clearly significant. For most individual compounds, the oyster:clam ratio ranged between 1 and 5, meaning that oysters accumulated as much or more of specific compounds than did clams.

For each bivalve species, the BCF_e for the various PAH compounds were in some cases unaffected by temperature, in others either increased or decreased as a function of temperature. One must keep in mind, however, that the BCF_e is a secondarily derived datum; the BCF_e is calculated from two primary derived data, the uptake (k_1) and clearance k_2) rates, each with an associated error term. The resultant error term for the BCF_e is a function of the sum of error terms for the primary derived data. Therefore, the differences in BCF_e must be interpreted with caution.

An important question relates to whether the changes in BCF_e for specific compounds in each species at the two temperatures result from temperature effects on either the k_1, the k_2, or both rates. For oysters and clams, the clearance rates (k_2) for total PAH and various specific compounds were not affected by temperature. Clams exhibited uniformly higher k_2 values than oysters, which at least partly explains the observed differences in BCF_e. The k_1 values also seem unaffected by temperature for either species. For many compounds, clams had a slightly higher k_1 than oysters, but rarely did the uptake rates differ by a factor of 2 or more. Therefore the between species differences in BCF_e result from differences in k_2.

The equilibrium model as implemented by BIOFAC quite adequately models much of the data for individual compounds, and all of the total PAH data. For some specific compounds, the model did not produce reasonable estimates of the primary and and therefore also the secondary derived data. The deficiency in fit is generally observed or at least most obvious for the clearance phase of the experiment. Some of these cases result from an inadequate number of valid data points and are excluded from Table 1. The remaining cases result from the presence of one or more data points which deviate drastically from the general trend, causing the model to converge on a less than appropriate value of k_2 (clearance rate). A larger data set would reduce the weight of these points in driving the model, but at significanly increased cost for the experiments.

Summary Conclusions and Interpretation

1. Oysters bioaccumulate about 3 times as much total PAH as do hard clams. The BCF_e values are affected relatively little by temperature, with a larger thermal effect for clams than oysters.

2. The relative bioaccumulation of specific PAHs by the bivalve species varies extensively, but for most compounds, oysters accumulate 1-5 times as much as do clams.

3. The difference in BCF_e values between bivalve species and temperatures results primarily from differences in clearance rate, with clams having a significantly higher clearance rate than oysters. Differences in uptake rate were relatively unaffected by temperature or bivalve species for most identified compounds in the contaminated sediment.

4. The implications of these results are important to a monitoring program.

   a. The observed amounts of total PAH in hard shell clams used in field monitoring studies should be inflated by a factor of three (3) for comparison to those observed amounts in oysters regardless of the time of year (i.e. temperature in the field).

   b. One can consider the concentrations found in feral bivalves to be good estimates of the BCF_e since the time to reach this concentration is short, generally less than 90 days; except in the vicinity of a recent spill, one can reasonably assume that if the bivalves have been at a given location for this period, they will have reached equilibrium with the environment.

5. Additional research needs to be accomplished to extend these results to include Rangia which must serve as the bivalve of choice for monitoring in low salinity areas the the Chesapeake Bay system.

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Table 1. Summary of uptake and clearance rates, bioconcentration factor, and BCF ratio for oysters/clams.

Compound	Mol. Wt.	Temp (°C)	Crassostrea virginica k_1	k_2	BCF_e	Mercenaria mercenaria k_1	k_2	BCF_e	BCF_{ost}/BCF_{clam}
Benzo(a)anthracene	228	15	1848	0.042	44155	3164	0.133	23755	1.858
Benzo(a)fluorene	216	15	818	0.056	14728	1833	0.201	9136	1.612
Benzo(b)fluorene	216	15	2677	0.066	40608	2362	0.195	12114	3.352
Benzo(a)pyrene	252	15	853	0.041	20572	567	0.135	4198	4.900
Benzo(e)pyrene	252	15	920	0.026	35439	2568	0.172	14946	2.371
Benzo(ghi)fluoranthene	226	15	2843	0.052	55027	4167	0.140	29708	1.852
Benzofluoranthene	252	15	702	0.028	33689	1680	0.122	13816	2.438
Chrysene	228	15	1195	0.039	30902	1324	0.145	9126	3.386
Fluoranthene	202	15	1793	0.098	18212	3436	(0.447)	7684	2.370
Methylphenanthrene	192	15	1239	0.121	10267	1286	(0.735)	1749	5.870
Methylpyrene	216	15	3569	0.050	71853	2642	0.158	16735	4.293
Perylene	252	15	728	0.073	10011	2290	0.191	11981	0.835
Phenanthrene	178	15	1360	0.401	3394	122	0.143	857	3.960
Pyrene	202	15	1276	0.094	13544	4303	(0.550)	7827	1.730
Total PAH		15	1111	0.060	18580	952	0.158	6034	3.079
Benzo(a)anthracene	228	25	1310	0.045	28846	2842	0.172	16516	1.746
Benzo(a)fluorene	216	25	508	0.066	8796	994	0.167	5943	1.480
Benzo(b)fluorene	216	25	1410	0.072	19666	1190	0.162	7332	2.682
Benzo(a)pyrene	252	25	639	0.032	19673	361	0.087	4143	4.748
Benzo(e)pyrene	252	25	790	0.023	33731	2366	0.148	15980	2.110
Benzo(ghi)fluoranthene	226	25	1465	0.056	26206	3384	0.145	23306	1.124
Benzofluoranthene	252	25	794	0.009	84217	1857	0.180	10331	8.151
Chrysene	228	25	1187	0.046	26019	1190	0.162	7335	3.547
Fluoranthene	202	25	821	0.118	6965	1477	0.213	6934	1.004
Methylphenanthrene	192	25	529	0.103	5151	187	0.115	1628	3.164
Methylpyrene	216	25	2365	0.066	36074	2002	0.148	13571	2.658
Perylene	252	25	817	0.075	10861	1133	0.161	7059	1.538
Phenanthrene	178	25	330	0.206	1604	224	0.114	1974	0.812
Pyrene	202	25	921	0.104	8857	1587	0.194	8172	1.083
Total PAH		25	798	0.053	15190	556	0.137	4072	3.730

FINAL REPORT

Organotin Concentrations in the Southern Chesapeake Bay

to

Virginia State Water Control Board

by

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ABSTRACT

A monitoring program designed to determine the concentrations of tributyltin in waters surrounding marinas in the southern Chesapeake Bay started in January, 1986. In addition, water samples were analyzed from the Elizabeth River to ascertain the tributyltin concentrations in this highly industrialized estuary. The data show that tributyltin concentrations vary considerably over both space and time. Concentrations, an order of magnitude apart, were found at the same location within the same week and levels a factor of two different were found in samples collected from different locations at the same marina, at the same time.

INTRODUCTION

For the past decade, the use of antifouling paints containing tributyltin (TBT) has increased. Recent scientific studies show that TBT can leach from paint films and accumulate in natural waters. Concentrations approaching effect levels for sensitive organisms have been found (Bryan et al., 1986; Maguire et al., 1982; Thain and Waldock, 1986; Valkirs et al., 1985).

The ever-increasing number of recreational and commercial vessels moored in the Chesapeake Bay and the U.S. Navy's proposed fleetwide use of TBT paints necessitated that a TBT monitoring program be instigated here. Aqueous samples collected in the vicinity of marinas and in larger, more open waters of the southern Chesapeake Bay have been analyzed. This manuscript reports the findings of this effort to date, with emphasis on temporal and spacial trends.

METHODS AND PROCEDURES

I. Sampling locations

Sarah Creek, a tributary to the York River, contains several recreational marinas as well as areas which are more rural (Figure 1). Three sampling locations were chosen in this system. One (station A) is near the mouth of the creek and is the site of a 288 slip marina. Station B is approximately one kilometer upstream and is a private berthing facility for a condominium complex. The third location (station C) is on a rural segment of the creek with only occasional boat traffic. Outside of Sarah Creek in the York River, a fourth station was established at the end of the Virginia Institute of Marine Science pier (station D). Starting in January, 1986, biweekly samples have been collected, always on high slack tides. In May, 1986, five additional marinas, in other areas of the southern Chesapeake Bay, were sampled to determine if concentrations found in Sarah Creek were similar to those found elsewhere.

The Elizabeth River flows into Hampton Roads at the mouth of the James River (Figure 1). It is highly industrialized with numerous commercial shipping facilities, including shipyards. In addition, it is the site of the largest naval complex on the East coast. This system was sampled in September and November, 1985 and May, 1986.

II. Sampling Procedure

The sampling apparatus consisted of an aluminum frame to which a 4 liter amber glass solvent bottle was attached. The frame was at the end of a 4 meter length of 2.5 centimeter aluminum pipe. A teflon conical plug, which fits the bottle opening, was attached to a 0.5 cm aluminum rod. This rod was guided by screw eyes attached to the pipe so that the plug could be

inserted or removed from the bottle by raising or lowering the rod. Surface water samples were collected from a depth of approximately 15 cm below the surface using this apparatus. The bottle was lowered below the surface with the plug inserted. At the prescribed depth the plug was removed and the bottle was allowed to fill. After plugging the bottle, it was retrieved and the contents discarded as a rinse. The procedure was repeated for the collection of a sample. After collection, samples were acidified to pH 2 with HCl and stored in the dark at 5°C until analysis.

III. Sample Stability

Experiments were designed and undertaken to determine the stability of TBT in stored samples. One consisted of extractions and analyses over a 13 week period, of a single natural water sample. Six water samples, collected within a five minute period from Sarah Creek, were mixed by pouring from one bottle to another in an attempt to create one homogeneous sample in six containers. These were acidified and five were stored in the dark at 5°C for the prescribed times indicated in Table 1. One was extracted and analyzed immediately. In the other experiment, repetitive analyses of stored, refrigerated, derivatized extracts (see below) over a 10 week interval were conducted.

IV. Analytical Procedure

The method used to quantify organotins has been described by Unger et al. (1986). It involves liquid-liquid extraction with hexane-tropolone to remove the organotins, followed by Grignard derivatization to form hexyl adducts. After cleaning by column chromatography, the derivatized organotins are quantified by capillary gas chromatography with flame photometric detection using tripentyltin as an internal standard. In

selected samples the presence of TBT is verified by mass spectrometry. Actual minimum detection for environmental samples is approximately 1 ngL^{-1} as TBT^{+}.

RESULTS AND DISCUSSION

The results from the sample stability experiments are presented in Table 1. The data derived from analyses of stored water samples show remarkable stability of the TBT at low ngL^{-1} levels. No degradation or loss is apparent over a 13 week period which implies that even longer storage times may be expected under the same conditions.

The data also show that extracted and derivatized TBT is stable over a ten week period when stored in the dark at 5°C. The relative standard deviation of the analyses over time is approximately that of replicate analyses performed on the same day indicating no loss of the analyte.

The results of the Sarah Creek monitoring are given in Table 2. Station A shows the highest variability with concentrations varying as much as a factor of ten within the same week. As noted previously, all the samples were collected on high slack tides. Station B appears much more stable relative to TBT concentrations but is still subject to spikes. The difference in the magnitude of variability may be due to station A being near the mouth of the estuary, where there is a tidal influx of "clean" York River water into Sarah Creek, thus diluting the TBT concentrations more so than upstream.

Station C is from a relatively rural part of Sarah Creek and the low TBT concentrations found here reflect this. Even lower concentrations were found at station D in the York River.

Data from the five other marinas indicate that the Sarah Creek TBT values are not anomalous (Table 3). More important, however, may be the observation that whole water TBT concentrations in samples from a given marina, collected at the same time, may differ by a factor of five.

Data reported here suggest that in areas of high boat densities, spacial differences of more than a factor of two may be expected at any one time; while at any one location, temporal differences of an order of magnitude may be observed over a three to four day period. Such variabilities must be given serious consideration in the design of TBT monitoring programs and in the interpretation of results from such programs.

Samples analyzed from the Elizabeth River show an increase in TBT concentrations in the upstream direction (Figure 2). Highest levels were found in samples collected nearest two shipyards, one commercial and one naval. Samples collected in September, 1985 were two to three times higher in TBT than those collected afterwards. This may be explained by the presence in September of a newly painted tour ship at the commercial shipyard and an aircraft carrier with TBT antifouling paint berthed at the Naval yard. At the time of the other samplings, neither situation existed. The concentration trends were, however, similar during all samplings. This suggests that TBT contaminated bottom sediments and/or chronic TBT inputs from the shipyards may be responsible for part of the organotin load in the river water.

Some microbes have the ability to degrade TBT to dibutyltin and eventually to monobutyltin (U.S. Naval Sea Systems Command, 1985). One would therefore expect the ratio of dibutyltin to tributyltin to increase as water temperatures rise, since microbial activities are usually inhibited by

colder temperatures. Figure 3 shows such a trend for samples collected at station B in Sarah Creek. A trend at station A is not so pronounced. This may be due to a changing input of TBT from the relatively numerous vessels entering and leaving the marina. Or, it may be due to the more rapid flushing of this area, thus removing organotins before much microbial degradation occurs.

Recent research indicates that TBT concentrations below 100 ngL^{-1} can adversely affect some aquatic species (Bryan et al., 1986; Thain and Waldock, 1986). This paper shows that such levels can exist in marinas in the southern Chesapeake Bay.

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Table 1

Tributyltin Stability in Stored Water and Extracts
(Concentrations as TBT^{+} in ngL^{-1})

Sample	Weeks 0	1	2	3	4	5	6	7	10	13	$\bar{x}$±sd
Stored water	16	13 13	18	17	18	--	--	--	--	16	17±2
Extract 1	10	9.3	8.6	10* 9.3	9.5	9.0	8.5	9.5 9.0	--	--	9.5±0.4
Extract 2	22	--	21	19	20 20 18 20 19	--	20	--	--	--	20±1
Extract 3	47	46	47	44	45	45	--	49 46	48* 46	--	48±1

*More than one value on the same week indicates replicate injections on the same day.

Table 2

Tributyltin in Whole Water from Sarah Creek
(Concentrations as TBT^{+}, ngL^{-1})

Date	A	B	C	D
1/13/86	15	14	--	--
1/16/86	27	16	--	--
1/20/86	39	23	7	N.D.*
1/24/86	5	18	9	2
1/27/86	22	16	10	2
1/30/86	11	15	7	1
2/3/86	47	14	5	2
2/6/86	5	12	9	1
2/10/86	16	9	8	1
2/13/86	7	12	6	N.D.
2/17/86	9	13	5	3
2/21/86	10	17	7	N.D.
2/24/86	9	20	8	2
2/27/86	5	9	7	N.D.
3/3/86	23	10	6	1
3/7/86	13	17	7	N.D.
3/11/86	23	17	9	1
3/13/86	6	14	8	N.D.
3/17/86	14	13	7	2
3/20/86	13	20	7	N.D.
3/24/86	6	16	8	2
3/27/86	28	17	10	2
3/31/86	32	18	15	4
4/3/86	11	22	11	1
4/8/86	11	18	9	2
4/10/86	6	15	10	3
4/14/86	9	19	9	2
4/17/86	22	20	20	2
4/22/86	16	18	10	N.D.
4/24/86	14	20	13	8
4/28/86	26	19	9	2
5/1/86	26	14	7	3
5/6/86	22	98	7	2
5/9/86	7	22	7	N.D.
5/13/86	11	23	12	N.D.

*N.D. = nondetectable at 1 ngL^{-1}

Table 3

Tributyltin in Whole Water Collected on May 12, 1986 from Marinas in the Southern Chesapeake Bay (concentrations as TBT^{+}, ngL^{-1})

Marina	Location	Tributyltin
Bluewater Yacht Yard	Sunset Creek, VA	53
Hampton Roads Marina #1	Hampton Creek, VA	21
Hampton Roads Marina #2		100
Harbor View Marina #1	Warwick River, VA	10
Harbor View Marina #2		16
Poquoson Marina #1	Bennett Creek, VA	36
Poquoson Marina #2		43
Wormley Creek Marina #1	Wormley Creek, VA	23
Wormley Creek Marina #2		14

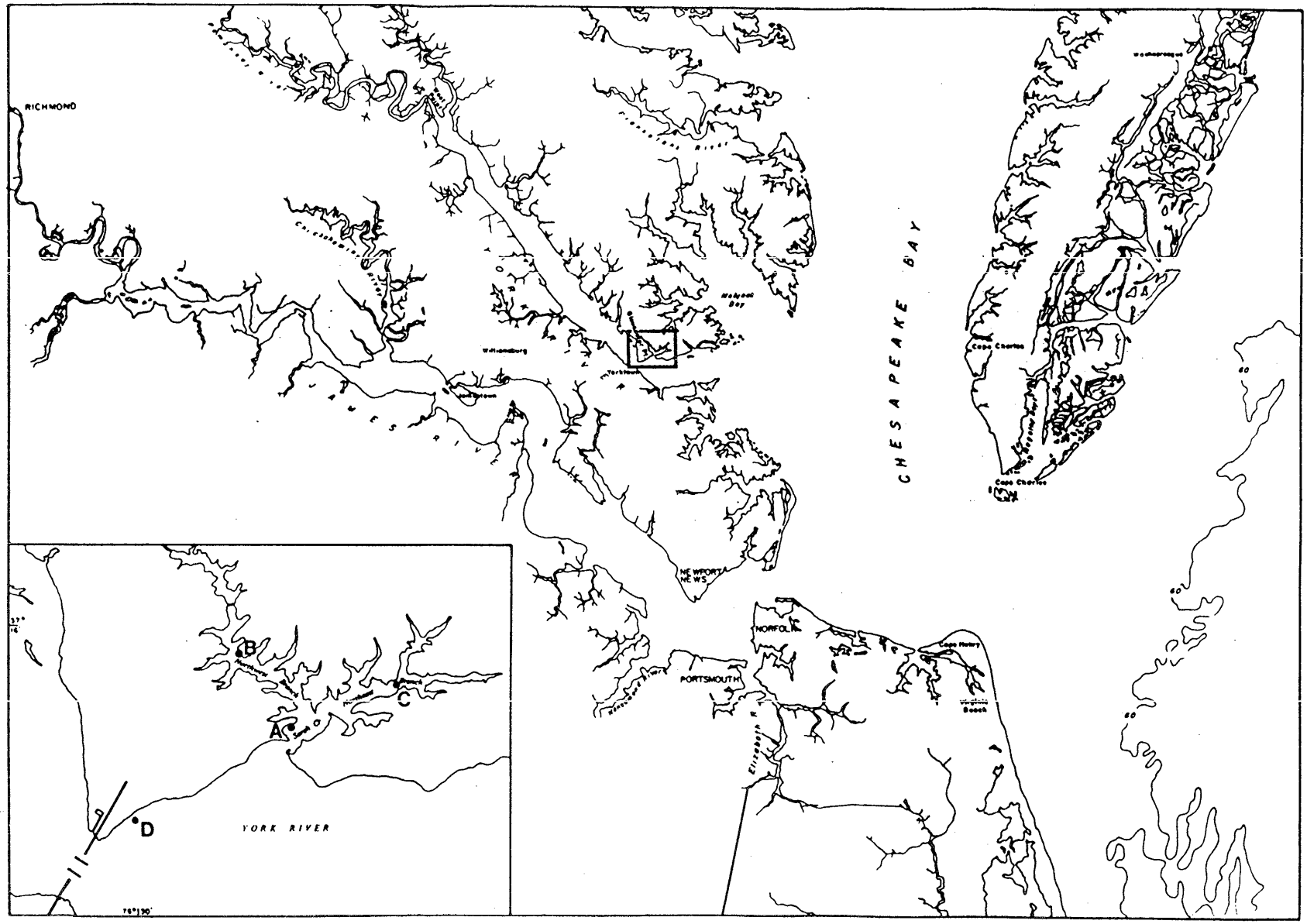
RICHMOND
CHESAPEAKE BAY
NEWPORT NEWS
NORFOLK
PORTSMOUTH
A
B
C
D
YORK RIVER

Figure 1

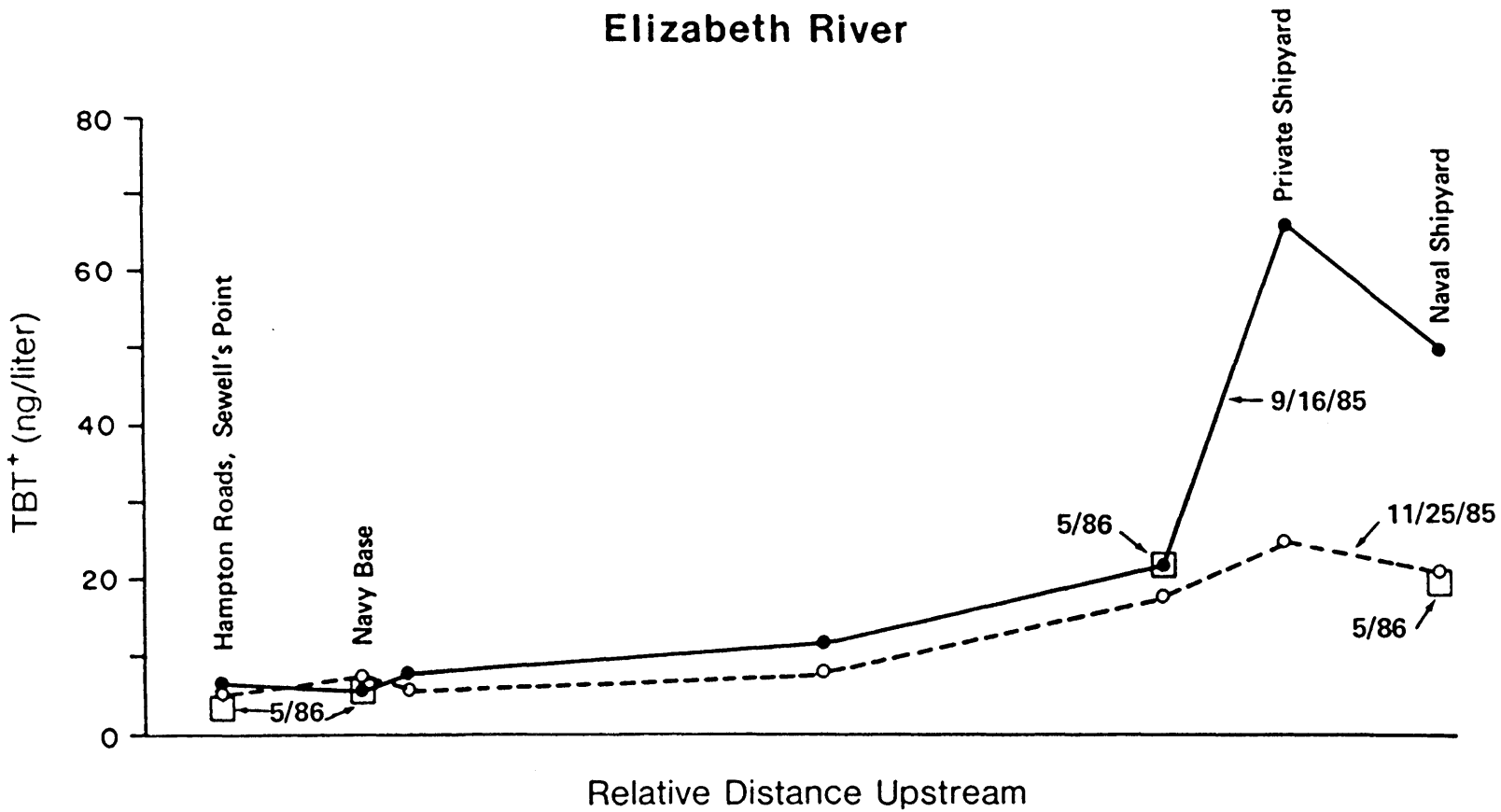
Elizabeth River
80
60
40
20
0
TBT+ (ng/liter)
Hampton Roads, Sewell's Point
Navy Base
Private Shipyard
Naval Shipyard
9/16/85
11/25/85
5/86
5/86
5/86
Relative Distance Upstream

Figure 2

Dibutyltin/Tributyltin & Temperature

Station B

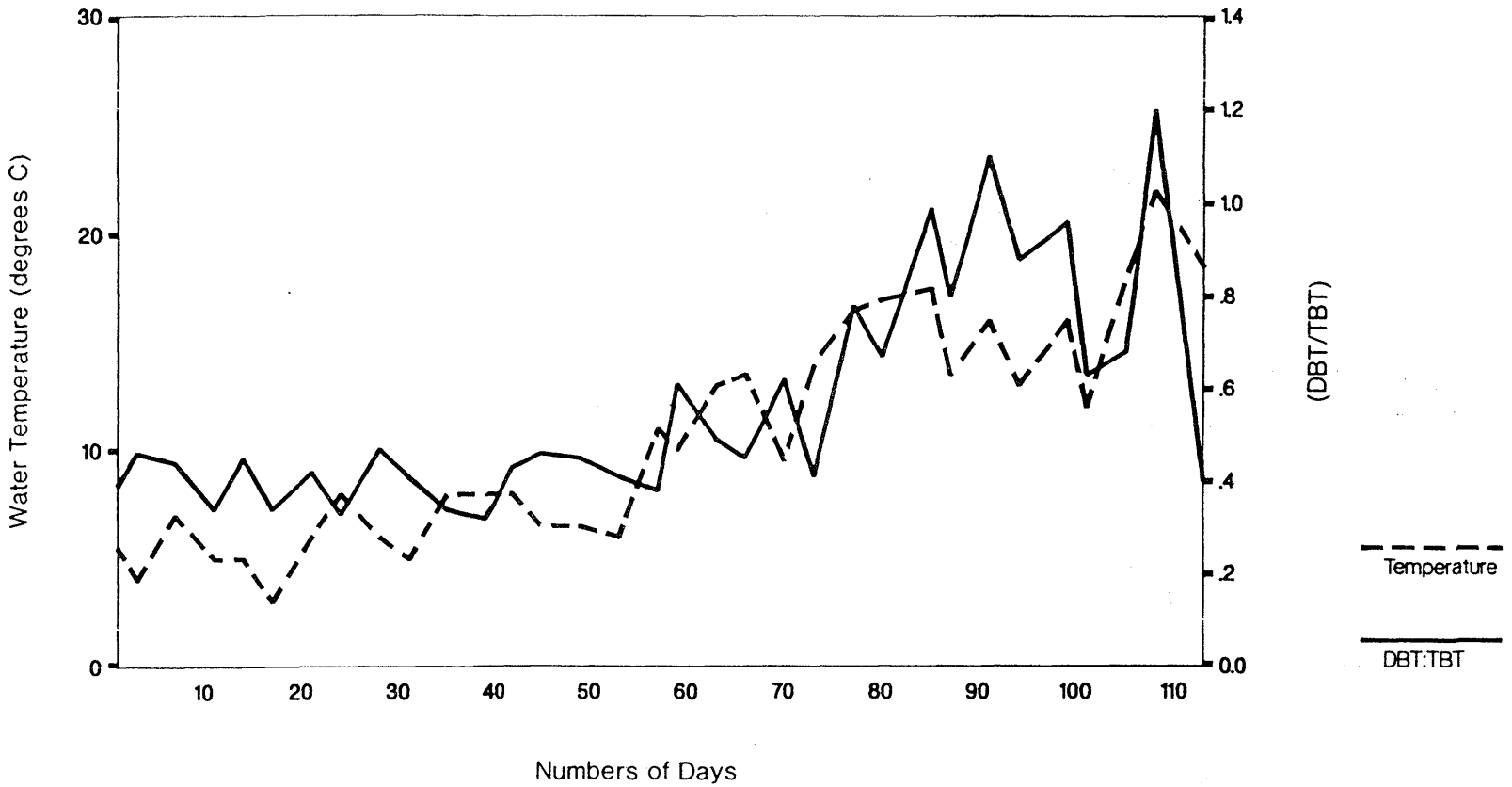

Figure 3

Acute toxicity of tributyltin chloride to embryos and larvae of two bivalve molluscs, *Crassostrea virginica* and *Mercenaria mercenaria*

A final report

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ABSTRACT

The acute toxicity of tributyltin chloride to embryos and larvae of two bivalve mollusc species was determined in a series of static replacement experiments. The test species were the commercially important hard clam, Mercenaria mercenaria, and the eastern oyster, Crassostrea virginica. Embryos of both species were slightly more sensitive than straight-hinge larvae. The 48-hr LC_{50} was 1.13 ug/l for clam embryos and 1.30 ug/l for oyster embryos, and the 48-hr LC_{50} was 1.65 ug/l for clam larvae and 3.96 ug/l for oyster larvae. Delayed development and some morphological anomalies were observed in embryo tests at doses slightly below the 48-hr LC_{50}.

INTRODUCTION

Tributyltin (TBT) was introduced in the marketplace as an ingredient in antifouling paints in the early 1960s. It has proven highly effective in the control of macrofouling invertebrates on boat hulls immersed in estuarine and marine waters, and, as a result, has gradually come to dominate some segments of the market for this type of product (Evans and Karpel, 1985). There has also been some consideration of TBT-based coatings in the cooling systems of electric power generating plants (Burton, 1980), leading to a study to evaluate the utility of this application of TBT undertaken by the Electric Power Research Institute (Hillman et al. 1985). In both applications, TBT is leached into estuarine water from antifoulant coated surfaces. While TBT degrades to form dibutyltin (DBT), monobutyltin (MBT), and ultimately elemental tin, it does persist for significant periods of time in natural waters (Maguire and Huneault, 1981), raising concern regarding effects on non-target species.

French researchers were the first to relate a biological effect to the presence of TBT. Pacific oysters (Crassostrea gigas) in the Baie d'Arcachon exhibited abnormal shell growth which was concluded to result from exposure to TBT leaching from antifoulant coatings on boats in marinas (Alzieu et al., 1980, 1982). Similar abnormalities observed in the shells of Pacific oysters along the coast of England had been attributed to high sediment concentrations (Key et al., 1976). In a laboratory study to distinguish the effects of TBT and sediment on oysters, Waldock and Thain (1983) demonstrated that the effect was due to TBT, not suspended solids. There is presently no evidence of this shell thickening effect in the American oyster, Crassostrea virginica.

TBT has since been reported to be acutely toxic at extremely low concentrations for many marine organisms, with 96-hr LC_{50} ranging from 0.5 ug TBTO/l for a mysid shrimp to 20-60 ug TBTO/l for a mussel (US Navy, 1983). About half the larvae of the mussel (Mytilus edulis) exposed

(beginning 7 days after fertilization) to 0.1 ug TBTO/1 were dead after 15 days, and all those exposed to 10 ug/1 were dead after 5 days (Beaumont and Budd, 1984). In this study, the number and range of dosages tested was not sufficient to calculate a valid LC_{50}. His and Robert (1980; Robert and His, 1981) observed an acute toxic reaction of oyster (Crassostrea gigas) larvae at TBT acetate concentrations as low as 1 ug/1, but did not calculate an LC_{50}. Their data suggest a 48-hr $LC_{50} > 5$ ug/1, a 96-hr LC_{50} of about 4 ug/1, and a 216-hr LC_{50} of about 1 ug/1. Thain (1983) reported a 48 hr LC_{50} for Crassostrea gigas of 1.6 ug/1 (age of larvae unspecified). In sharp contrast, Becerra-Huencho (1984) estimated the 96-hr LC_{50} for TBTO to clam larvae (Mercenaria mercenaria) to be 0.006 ug Sn/1 (0.015 ug TBTO/1), by far the lowest acute concentration yet reported.

The objectives of the present study were to verify the result of Becerra-Huencho (1984) for M. mercenaria larvae, to extend the observations to fertilized clam embryos and to determine the acute toxicity of tributyltin oxide (TBTO) to embryos and larvae of the native oyster, Crassostrea virginica.

MATERIALS AND METHODS

The test methodology is described in considerable detail since it deviates substantively from the method described in ASTM (1980) and differs in significant detail from all the varied methods used in prior TBT studies with bivalve larvae. Lack of reliability in results using the ASTM standard method and alternative methods necessitated development of a more reliable procedure.

Broodstock clams used for this study were obtained from two sources; one group was purchased from Biosphere, Inc. and held in flowing water at the Institute for four months and a second group was collected locally from the York River, VA. Oysters broodstocks used were native oysters collected variously from the James and Rappahannock Rivers. Broodstocks of both species were conditioned by maintaining them in heated flowing York River water (24-26 ^{o}C supplemented with cultured algae (Tetraselmis suecica or Dunaliella tertiolecta) until they developed ripe gametes after which they were maintained at 19-20 ^{o}C until spawned. One test with oyster embryos was performed with broodstocks held under similar temperature conditions but in static water.

Embryos and larvae were obtained by inducing the broodstock clams or oysters to release gametes by the thermal shock method and introduction of small amounts of sperm (Loosanoff and Davis, 1963). Eggs from a single female were collected and fertilized with sperm from one or more males. For embryo tests, the fertilized gametes were maintained at the spawning temperature (28 ^{o}C) until the zygotes reached the 4-16 cell stage at which time an accurate count of fertilized embryos could be made. For larval tests, embryos were diluted to about 50/ml and held at the spawning temperature for 24 hours by which time the embryos had hatched and developed to the straight-hinge stage. In clam larval tests, about 35% of the larvae remained in the trochophore stage, and are thought not to have developed

further under any treatment during the test.

Tests with both developmental stages of oyster and clam larvae were performed using a static replacement procedure. For each test a logarithmic concentration series (0.056 to 1.8 ug/l or 0.180 to 5.6 ug/l) was used. In all but one experiment, glacial acetic acid was used as a carrier for the tributyltin chloride. The amount of carrier was in all cases 16 ul/l. A carrier control was included in the experimental design as well as a diluent water control. The pH was reduced approximately 0.6 pH units in all cases by the glacial acetic acid, with a final pH of 7.1 or greater. Sufficient amounts of each test solution were prepared to provide a sample for chemical analysis.

The embryo tests were initiated with a known number of 4- to 16-cell stage embryos, larval tests with a known number of straight-hinge larvae. For each treatment, an appropriate volume was removed from the stock culture to provide an embryo density of about 40/ml or a larval density of about 10/ml. The sample for each treatment was placed in a graduated cylinder in 100 ml of water and three replicate 1 ml samples were counted to establish the initial larval concentration. For embryo tests, only fertilized eggs were counted. For larval tests, trochophores and straight-hinge larvae were counted and recorded separately. The larvae were then introduced into the test medium and exposed at room temperature for 24 hours. At that time, the test medium in each vessel was passed through a 35 um screen to collect the larvae which were then resuspended in 100 ml of water, counted as described above, and returned to freshly prepared medium. A sample of used medium from two test concentrations was set aside for chemical analysis. This procedure was repeated after the second 24 hour exposure. For the larval tests, cultured algae was added to the test medium to yield approximately 10^4cells/ml using a mixture of Pavlova lutheri and Isochrysis galbana since the straight-hinge is a feeding stage.

York River water was used as diluent for all experiments reported here. The water was filtered to 1 um and extracted by passage through an activated carbon filter. The purpose of carbon filtration was two-fold: to remove any TBT which is known to be present at times in the water delivered to the laboratory (Huggett, personal communication), and to remove any bacterial or algal toxins which were thought to be present in the water (Brown, 1983). Measured TBT concentration in control water samples was < 10 ug/l (as TBTCl).

Each day during the experiments, water temperature, salinity, dissolved oxygen concentration and pH were determined. On day 0, water samples were collected from the diluent control plus four test concentrations and acidified. On day 1 three samples were collected from the new diluent control and two freshly prepared test concentrations and two samples from day-old test concentrations. At the end of most tests, samples were obtained from the 24 hour old control and 4 test concentrations. All samples were analyzed for TBT by the method of Unger et al. (1986). The time required for analyses prevented analysis of additional samples. The measured concentrations were regressed against the applied concentrations calculated from stock TBT concentrations. Since these regressions were

linear, the exposure doses were taken to be the concentration calculated from the regression for each applied concentration. These values were then used to calculate LC_{50}s.

For each treatment, the count data were averaged for each day and the number per milliliter calculated. From these values, the percent survival for each treatment was calculated for each day of the test. Since control mortality was significant, the mortality resulting from TBT at each dose was calculated as

$$\% \text{ response} = \frac{\% \text{ survival}_{T,d}}{\% \text{ survival}_{C,d}}$$

where $\text{survival}_{T,d}$ = survival in treatment T on day d and $\text{survival}_{C,d}$ = survival in the control treatment on the same day. This formula is mathematically equivalent to the Abbott's formula correction recommended by Finney (1971). The LC_{50} was estimated by plotting $\text{sine}^{-1}(\%\text{ response})^{1/2}$ against calculated exposure dose. The response range was generally so narrow that the best estimate was derived by nonlinear interpolation (Stephan, 1977).

The degree of oxygen saturation in the water was calculated from the measured temperature, salinity and dissolved oxygen concentration based on the data of Weiss (1970). All physicochemical parameters are expressed in terms of mean and standard deviation.

RESULTS AND DISCUSSION

Within each test, the temperature was extremely uniform, varying less than 1°C. For all experiments, mean temperatures ranged from 20 to 24 °C. The salinity was uniform within any test, with only slight inter-experiment differences. The salinities within an experiment varied less than 1 $^{o}/_{oo}$. For all experiments, salinity ranged from 18 to 22 $^{o}/_{oo}$ depending on conditions in the estuary at the time of the test. Initial oxygen concentrations were in all cases approximately equal to 100% of saturation. In later experiments, the oxygen concentration was also determined on the used culture medium; in these cases, the oxygen concentration was at saturation in the diluent control and progressively depressed with increasing doses of TBT. Oxygen saturation was never below 66%.

The maximum exposure concentration was insufficient to produce a 24 hour LC50 in embryo tests with either species; therefore the 24-hr LC50 exceeded 1.8 ug/l (Table 1). The 48-hr LC50 for clam embryos (based on numbers reaching the straight-hinge stage) was 1.13 ug/l and that for oyster embryos was 1.30 ug/l (0.71 ug/l with acetone carrier). In these tests, the control survival rate was 73% for clams and 38% for oysters after 24 hours

and 52% for clans and 28% for oysters after 48 hours. There was no marked difference between the survivorship in diluent control and solvent control treatments.

Clam embryos exhibited a delay in development at doses of TBT somewhat below the measured 48-hr LC50. At 0.77 ug/1, the formation of straight-hinge larvae was recognizably delayed, although the experimental design does not allow one to calculate a delay time. Despite the delay, most resultant larvae were normal in appearance. Some larvae failed to develop to the straight-hinge stage in all conditions including the diluent control; many trochophores which failed to develop into normal straight-hinge larvae did deposit some shell material which could, in some orientations, be observed. It was not possible to enumerate accurately these larvae separate from trochophores with no shell development.

Oyster embryos, in addition to some slight delay in development at higher doses, also exhibited some abnormal development. In this species, all surviving larvae did develop into straight-hinge larvae during the test. At TBT concentrations of 0.77 ug/1 and above, some larvae developed shells which were quite flattened rather than concave resulting in an inability of the larva to maintain the normal body conformation with all but the velum within the shell cavity. It was not found possible to enumerate the abnormal animals separately from the normal straight-hinge larvae, since in some positions one could not readily evaluate the configuration of the shell. At the highest doses, the meats of still motile larvae often consisted of portions of the mantle, the heart, and the velum, leaving a large "vacuolated" space within the shell.

Anomalous development has been reported previously. His and Robert (1980) reported that after exposure to 5 ug/1 TBT for 24 hours, 100% of the larvae of C. gigas were "trochophore monstrueuses". It is not clear precisely what this means anatomically, but obviously no larvae reached the straight-hinge stage. At 10 ug/1, trochophores were rarely observed to develop. In the present study, all embryos developed into straight-hinge fertilized larvae without observed formation of extremely anomalous trochophores, but in no case were embryos exposed to concentrations as high as 5 ug/1 TBT. Robert and His (1981) subsequently reported that straight-hinge larvae produced at 1 ug/1 were often markedly reduced in size. Subjectively, at least, any such effect in the present study was not recognized.

Clam and oyster larvae were found to be slightly more tolerant of TBT than the embryo stages. The 24-hr LC50 exceeded 5.6 ug/1 in both cases. The 48-hr LC50 was 1.65 ug/1 for clams and 3.96 ug/1 for oyster larvae. There was no obvious flattening of the valves of oyster larvae which already had well formed valves at the start of the experiment. There were some subtle changes in shell morphology observed at the two highest doses including a notching of the valves opposite the hinge line.

Clearly there was no significant difference in LC50 for clam and oyster

embryos or larvae within this study. The LC50 in each case was within the range of values reported for many other invertebrate species. The data also seem to compare favorably within an order of magnitude with nearly all results reported for other bivalve embryos and larvae (Table 2). The only exceptional data seems to be that of Becerra-Huencho (1984) who reported a markedly lower 96 hr LC50 for M. mercenaria than the present study or any other study with bivalve larvae despite the fact that he was testing a slightly older larval stage. In the larval experiments reported herein, the exposure period extended 72 to 96 hours, but the data were not used to calculate a 72- or 96-hr LC50. After 48 hour, there was obvious and significant bacterial growth, especially in the treatments receiving glacial acetic acid, and survival declined in all dosed treatments. There was no way to determine the extent to which the mortality resulted from TBT versus bacteria. Whether the experimental results of Becerra-Huencho (1984) reflect an impact of bacterial contamination or some other intervening factor cannot be determined. Although bacterial contamination is to be expected in a 96 hour exposure without replacement of medium, the technique used by Becerra-Huencho (1984), there was no evidence of such an effect in the data for other compounds tested.

One must be somewhat cautious in making these between species comparisons because of differences in methodology or uncertainties about certain experimental details in some experiments. Nevertheless, it seems fair to conclude that larvae of the 5 species of bivalve molluscs which have been tested are similar in sensitivity to TBT and that tolerance increases slightly with increasing larval age. This trend is not unique to this taxon or this compound, but is a general observation.

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Table 1. Toxicity of tributyltin to embryos and larvae of the eastern oyster, Crassostrea virginica, and the hard clam, Mercenaria mercenaria.

Species	Life Stage	LC50 (in ug/1 TBTCl) 24 hr	48 hr	
Crassostrea virginica	Embryo	>1.38	1.30 (0.78-1.38)	GAA carrier
			0.71 (0.53-1.20)	Acetone carrier
	Larva	>4.21	3.96 (2.42-4.21)	
Mercenaria mercenaria	Embryo	>1.31	1.13 (0.72-1.31)	
	Larva	>4.21	1.65*	

* 95% confidence limits cannot be specified in this case.

Table 2 Comparison of TBT toxicity to bivalve molluscan larvae.

Species	Stage	Comment	Source
Crassostrea virginica	embryo	48-hr LC50 = 1.30 ug/l	this study
	S-h larva	48-hr LC50 = 3.96 ug/l	this study
Crassostrea gigas	embryo	24-hr LC50 < 5 ug/l (nc)*	His & Robert, 1980
	embryo	{incomplete formation of S-h larva at 1 ug/l at 24 hr; mortality after 48 hr}	Robert & His, 1981
	S-h larva	48-hr LC50 < 5 ug/l (nc)	His & Robert, 1980
	S-h larva	~50% dead: (nc) at 5 ug/l after 192-240 hr at 3 ug/l after 123-144 hr at 1 ug/l after 96-120 hr	Robert & His, 1981
	S-h larva(?)	48-hr LC50 = 1.61 ug/l	Thain, 1983
Mercenaria mercenaria	embryo	48-hr LC50 = 1.13 ug/l	this study
	S-h larva	48-hr LC50 = 1.65 ug/l	this study
	post S-h larva	96-hr LC50 = 0.015 ug/l**	Becerra-Huencho, 1984
Mytilus edulis	S-h larva(?)	48-hr LC50 = 2.3 ug/l	Thain, 1983
	7-day larva	360-hr LC50 ~ 0.1 ug/l (nc) 240-hr 0.1 < LC50 < 1.0 ug/l 120-hr 1.0 < LC50 < 10.0 ug/l	Beaumont & Budd, 1984
Mytilus galloprovincialis	embryo	48-hr 1.0 < LC50 < 3 ug/l (nc) 96-hr LC50 = 1.0 ug/l	Robert & His, 1981
	S-h larva	120-hr LC50 = 5 ug/l (nc)	Robert & His, 1981

* nc = values derived by subjective examination of data presented; calculation not possible for various reasons.

** Expressed as TBTO; reported originally as 0.006 ug/l as Sn.

EFFECTS OF SHIPPING ON SEDIMENT RESUSPENSION IN THE ELIZABETH RIVER, NORFOLK, VIRGINIA

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CONTENTS

EXECUTIVE SUMMARY

This study aims to determine if shipping activity disturbs contaminated sediments on the floor of the Elizabeth River. Little is known about how cohesive sediments react to, or interact with, ship motions, i.e. wake waves and propeller wash, thereby increasing turbidity and dispersing chemicals away from their pollution source.

Bed disturbance was examined throughout the Elizabeth with a side-scan sonar system. Sediment resuspension and haline stratification were observed before, during or after ship movement, from measurements of suspended sediment concentration, transparency and salinity, supplemented by current velocity.

Ship disturbance of the bed is displayed in sonar records by linear bedforms, scour holes, anchor and keel drag marks. The sonar records reveal that more than 70 percent of the estuary floor is disturbed by dredging or ship activity. The most pronounced bed disturbance by ships occurs in the 40-foot channel of Southern Branch near Portsmouth.

The distribution of suspended sediment concentrations reveals that normal or background, concentrations are relatively low and uniform with time and location (i.e. 8-12 mg/l). Since natural resuspension by tidal currents is limited, disturbance by ship movement produces pronounced perturbations. Ship berthing, backing and turning movements of a naval support ship and a naval aircraft carrier the "America", produced the greatest enrichment of suspended sediment. Concentrations increased throughout most of the water column and locally reached 90 times the background level. Ship passage through the channel irregularly enriched bottom water from 3 to 20 fold but the extent of enrichment is limited and patchy.

The overall effect of repeated bed disturbance and sediment resuspension is to reinforce landward transport of suspended sediment through the lower layer. By stirring the bed, ship movement prevents deposition in the channel axis and enhances deposition in less energetic zones on lower sides of the channel and in berths and pier slips.

To reduce the effect of ship disturbance on the bed, management strategies should aim to increase clearance, reduce shoaling and stabilize the bed. These findings fill a gap in knowledge of contaminant transport in the Elizabeth River where little is known about the impact of shipping activity on the disturbance and fate of contaminated sediment.

EFFECTS OF SHIPPING ON SEDIMENT RESUSPENSION IN THE ELIZABETH RIVER, NORFOLK, VIRGINIA

1. Problem and Purpose

Sediments of the Elizabeth River are enriched with potentially toxic trace metals and polynuclear aromatic hydrocarbons (PAHs). The PAHs exceed thousands of ppm, reportedly the highest concentrations of any estuary in the world. When large ships pass through a channel with limited bottom clearance above the channel floor, it may be expected that the bed will be disturbed. Since the time-dependent interaction of ship movement and cohesive sediment resuspension cannot be predicted from theoretical analyses or experimental models, field observations are the main source of information.

The purpose of this study is to determine the effects of ship movement on the resuspension and transport of contaminated bottom sediment. The key questions addressed are: (1) Does ship movement disturb the bed and resuspend contaminated bottom sediments? (2) If sediments are resuspended by shipping, what are the effects on water quality? (3) Where does the resuspended sediment go and deposit?

2. Status of Information

Although shipping is active throughout many harbors and channels of the world, very little data exist on the effects of ship movement on bottom sediments and water quality. Most research on ship motion deals with reducing resistance forces to improve speed and maneuverability. Research on cohesive sediments mainly addresses the critical conditions for initiation of erosion in laboratory flumes. Very little information exists on how cohesive sediments react to, or interact with, motions generated by ship movement. A literature survey however, uncovered some notions of the

important parameters involved and the potential effects that may be expected.

Liou and Herbich (1976) provide a mathematical model showing that ship draft in relation to channel depth, or "clearance", is a key factor for initiating sediment resuspension.

On evidence from laboratory studies (Wilson, 1973) and from field observations (Sly, 1969), it may be suggested that large vessels having a bottom clearance of 1-2 m will significantly disturb bottom sediments to a depth approaching one-half a meter over a path 2-3 times the vessel width.

Stortz and Sydor (1980) in a study of Duluth-Superior Harbor, found suspended sediment concentrations in ship plumes ranging 10 to 50 mg/l or five times the normal concentration. However, less than one percent of the sediment flows out of the harbor.

Lee (1983) and Bhowmik et al. (1982) in a study of the Illinois River, found that barge movement created bank erosion and resuspended channel sediments that caused sedimentation in backwaters and side channels.

The effects of shipping on sediment movement are also reported in Newark Bay by Suszkowski (1978), in the Houston Ship Channel (Hart, 1969), in the Coos River, Oregon (Slotta et al., 1973), in the Clair-Detroit River (Sly, 1977) and in the Tay Estuary, Scotland (Buller and McManus, 1976). This information provides some insights into what effects <u>can</u> happen particularly on sandy beds, but it is of limited use for predicting what <u>does</u> happen on a contaminated mud bed in the Elizabeth River.

3. Dynamic Model

Experimental tests (Wilson, 1973; Bhowmik et al., 1982) show that the passage of ships produces energy dissipation in three zones: (1) the hull zone, (2) the propeller zone and (3) the wake zone (Fig. 1). As a vessel moves through the water, flow around the chines of the hull sets up relatively small vortices that induce disturbance patterns on the bed (Fig. 1A). In restricted channels there is also an increase of current velocity relative to mean velocity, beneath the ship (Fig. 1A). Reportedly (Lee, 1983), the acceleration of flow depends on the proximity of the ship bottom to the sediment bed and is due to pressure differences created by the water surface profile along sides of the hull (Fig. 1A).

In the propeller zone the most significant disturbance is a localized turbulence caused by rapidly fluctuating velocities and pressures off the propeller blades. The bed is scoured beneath the propeller and a certain amount of sediment is either suspended or moved along the bed (Fig. 1A). The sediment remains in suspension until turbulence decays sufficiently for the material to settle out. In addition to local turbulence, the propeller generates a turbulent jet in the wake zone. Bed disturbance takes place where the jet expands sufficiently to contact the bed. Sediment movement is a function of the shear stress of the jet, the propeller diameter, the bottom clearance and rigidity of the sediment. The motion is complicated by orbital velocity of superimposed wake waves.

The system of wakes generated by ship movement consists of: (1) bow wave, (2) local hull side waves, (3) transverse stern waves, (4) diverging stern waves (Fig. 1B). The effect of wake waves is complicated by narrowing and shoaling of channels, by the interaction of

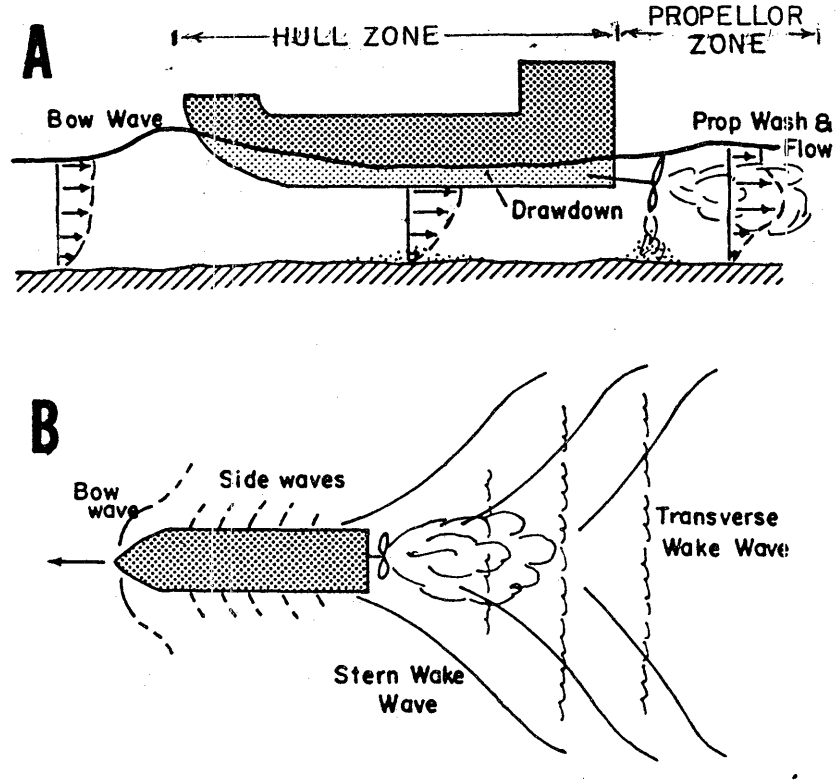

Figure 1. Schematic diagram of wake waves and current velocity generated by hypothetical ship movement in a channel.

different waves as phasing of bow and stern waves, and by accelerations associated with drawdown of the ship (a drop of water level during ship passage, Fig. 1A). Consequently, sediment at a particular location on the channel floor may be affected by many different types of complex time-varying fluid motions. Therefore, this study examined the overall end-product of disturbance to ship movement rather than the response to specific ship motions.

4. Approach and Scope

The approach to this study follows several lines of research inquiry: (1) to examine the bed disturbance recorded by side-scan sonar and X-ray radiographs of box cores, (2) to observe the concentrations of suspended sediment, current velocity and certain water quality parameters before, during or after ship passage, (3) to evaluate the role of shipping in resuspension of bottom sediments.

Field observations and side-scan sonar tracking focused on the Southern Branch of the Elizabeth and for comparison, embraced central and entrance reaches of the main channel extending to Sewells Point (Fig. 2). Channels of the Eastern and Western Branches of the Elizabeth were also covered by sonar tracks. Water quality and bottom sediment samples were collected at 10 stations located at about 4 km intervals along the main channel. These were located to sample reaches of varying shipping activity and gradients of turbidity and salinity (Fig. 2). Additionally, an anchor station was occupied for one tidal cycle near Portsmouth in the Southern Branch (Fig. 2). Field observations were concentrated between March and June, 1985. This included a period of northeast storm, a period after a heavy northwest wind and eight ship events. Most longitudinal "background"

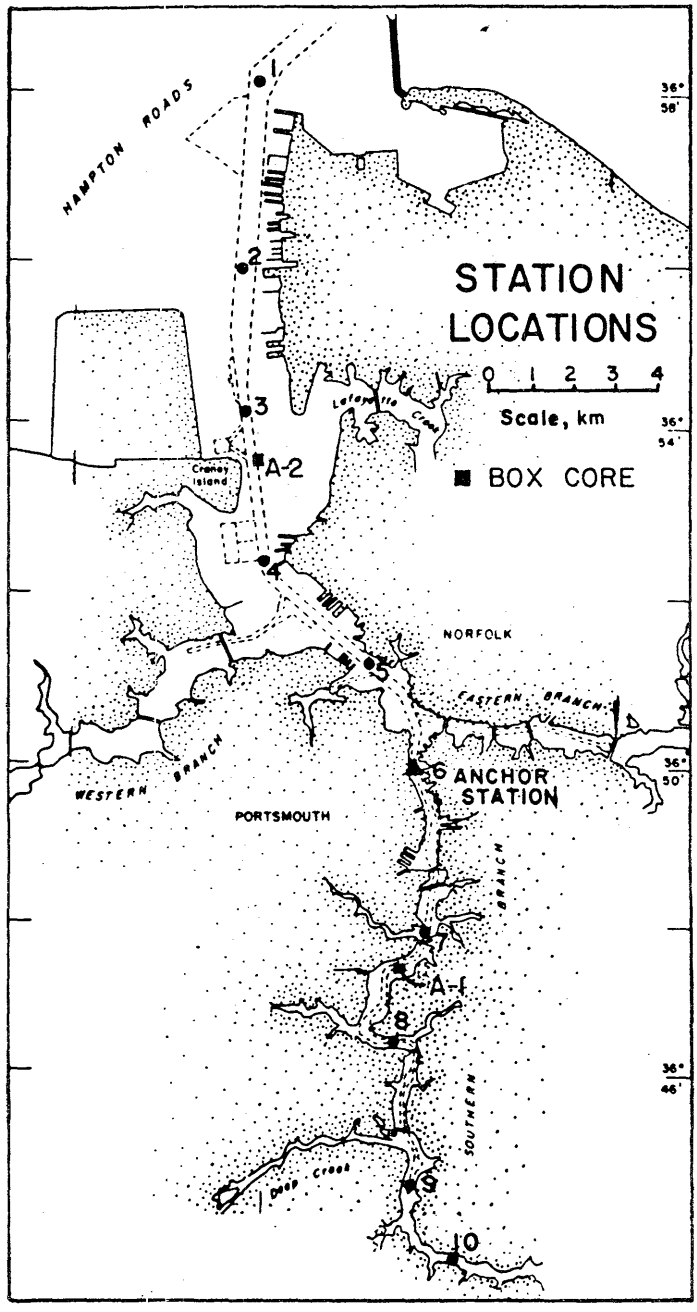

Figure 2. Station locations occupied in the Elizabeth River system, March to May, 1985.

sections were surveyed during slack water (± hour) and one was surveyed during maximum tidal current. The X-ray radiographs were obtained from a prior investigation (Schaffner and Diaz, 1982).

5. Field and Laboratory Procedures

The floor of the Elizabeth River was examined with an EG&G side-scan sonar seafloor mapping system equipped with a SMS 960 recorder and Model 272 tow fish having a frequency of 105 kHz and swath range of 200 m. Spatial resolution is such that features of about 50 cm size can be detected.

Suspended solids of fresh samples from the water column were collected with a Kemmener water bottle. Near-bottom water that typically has high vertical gradients of solids, was sampled with a horizontal oriented van Dorn water bottle mounted on top of a weighted pipe. Height of sampling above the bed was measured from the mudline observed on the pipe (usually in the range of 30 to 70 cm), whereas successively greater heights above the bed (e.g. +1.0 and +2.0 m) were measured on a shipboard meter wheel. Water samples were processed in the laboratory within 12 hours after recovery by vacuum filtration using Millipore filters of 0.80 pore size. Procedural details of the gravimetric analysis follow Strickland and Parsons (1972), except for minor modifications included in the set of procedures described in Appendix A of the 1985 CSA Annual Report on this study. Organic content of the filtered suspended solids was analyzed by weight loss after combustion at 350^{0} C for 8 hours generally following procedures of Manheim et al., 1970.

Settling Velocity of fresh bottom sediment from four stations (Fig. 2) returned to the laboratory, was analyzed by methods of Owen (1976). A portion of natural mud, without dispersant or seiving, was allowed to settle

in a 1-meter high tube and withdrawn from the bottom at various time intervals. From the weight of sediment collected on Milipore filters of 0.80 size, cumulative frequency curves were drawn and median settling velocities determined.

Transparency of the water was measured in situ to the nearest 0.1 m with a black and white Secchi disk, 40 cm in diameter.

Salinity of water samples returned to the laboratory was measured in an induction salinometer, Beckman RS-7B.

Current speed was measured with a cross-vane drogue tethered by rope to a surface float. The time required to travel a distance of 30 m as measured on a rope trailed from an anchored boat, was taken as the current speed.

Current direction was measured by a hand-held pelorus sighted from the boat to the current drogue float. Accuracy of current speed measurements is estimated at about $\pm$ 4 cm per sec while that of current direction is about $\pm$ 10 degrees.

Bed sediment was obtained with a stainless steel Smith-MacIntyre grab. The near-surface portion, usually fluid mud, was recovered with a plastic spoon.

Suspended sediments for metal analysis were obtained with a plastic van Dorn water bottle and temporarily stored in polypropylene bottles. All bottles were pre-rinsed with a 5 percent solution of hydrochloric acid prior to each cast. Bottom sediments were recovered from the inner part of a stainless steel Smith-MacIntyre grab which was coated with a Crown 6065, TEF coating compound. Subportions were stored in plastic bags and frozen for future analysis.

Stations were located by ranging and dead-reckoning on buoys and landmarks. Side-scan sonar tracks were positioned by Loran C and fixes were recorded on paper tape.

6. Results

a. Bed Disturbance. The side-scan sonar records reveal various types of bed morphology indicative of bed disturbance. The major morphological features are: (1) dredge marks, (2) lineations, (3) scour holes, (4) anchor and keel drag marks, and (5) scarps, slumps and gullies.

The dredge marks consist of small ridges and troughs oriented transverse to the channel axis. Dredging records of the Corps of Engineers confirm their origin. They are caused by repeated cross channel sweeps of a suction cutter head on a drag arm. The relief ranges about 30 to 80 cm with crests of firm mud (light-toned) and troughs of soft mud (dark-toned) in various stages of backfilling (Appendix B, sonar record 1). The dredge marks are most prominent in the entrance reach between stations 3 and 4. They also occur off Sewells Point and in the Southern Branch near station 9 (Fig. 3).

The lineations are longitudinal bedforms consisting of undulating mud ridges and troughs with heights of 25 to 90 cm (Appendix B, sonar record 2; Appendix C). These features are most prominent at the junction of Southern and Eastern Branch as well as in the 40-foot channel of Southern Branch between stations 6 and 7 (Fig. 3). They also occur locally off Lambert Point and in the vicinity of station 5. Typically the lineations occur on the sides of the channels where sedimentation is faster than in the channel axis. These are also zones of occasional maintenance dredging. Dredging between stations 4 and 7 took place last in 1978. The lineations are likely

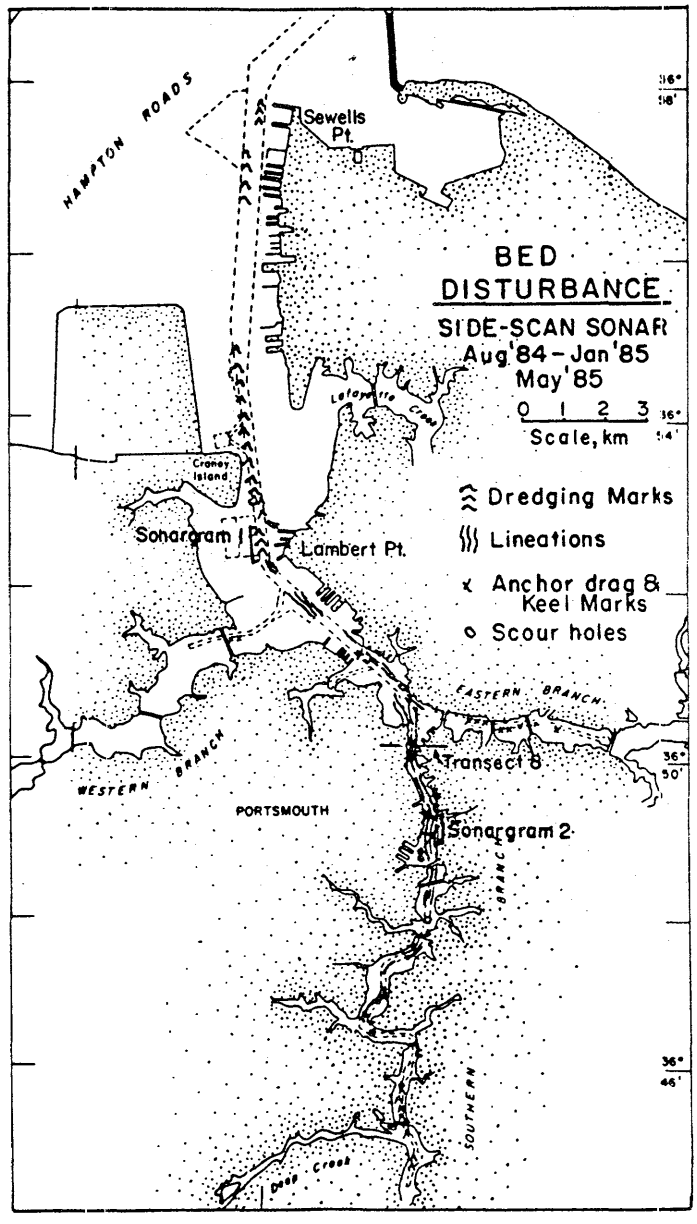

Figure 3. Distribution of bed disturbance features displayed on side scan sonograms; location of fathogram presented in Appendix C.

created by ship movement, either wake waves interacting with channel walls, or helical flow induced by propeller jet flow. The interrelationship between flow and sediment movement in the lineations, however, is uncertain. It seems possible that accumulated sediment in these features is swept by recurring episodic prop wash that redistributes part of the sediment into ridges and abrades small longitudinal troughs. The troughs likely fill during intervals between shipping events.

Scour holes are irregular depressions, 30-60 cm deep and about 5 to 20 meters across. They occur locally in the Southern Branch channel, i.e. off the Portsmouth Naval Shipyard, off BP, Texaco and Alcoa terminals (station 7) and off Swann Oil-Atlantic cement pier (station 8) (Fig. 3). These features are likely produced by ships with low clearance turning, backing and berthing.

Anchor marks and keel marks are linear or slightly sinuous grooves about 30 to 60 cm deep and 30 to 150 m long. They are prominent in Eastern Branch, off NORSHIP in Southern Branch and near the West Norfolk bridge in Western Branch (Fig. 3). The keel marks occur in zones of barge activity and are likely produced by grounding of barges or small craft.

Miscellaneous features of the microtopography include: (1) a scarp at the head of the 45-foot entrance channel off Lambert Point, (2) local slumps and gullies on the channel side wall slope off Craney Island Point. This suggests active erosion of the slope and mass transport of erodable material into the main shipping channel.

A graphic comparison between side-scan imagery taken in August, 1983 and 21 months later in May, 1985 revealed that the pattern of ridge crests and trough axes remained essentially stable in Southern Branch, i.e. between

stations 6 and 7 (Fig. 2). However, in the vicinity of the Jordan Bridge new lineations appear in the 1985 imagery along sides of the channel and toward the channel axis. It seems the size of the lineation "field" has grown channelward and landward while the central lineations remain stable.

In summary, the sonar records reveal that more than 70 percent of the Elizabeth River is disturbed by dredging or ship movement. Only portions of Western Branch and inner parts of Eastern Branch are relatively undisturbed. Disturbance is most pronounced in the zone between Lambert Point and Craney Island, a zone of frequent dredging. Disturbance is also pronounced in the 40-foot channel of Southern Branch near Portsmouth, a zone of frequent ship movement where the channel size is relatively small for large deep draft ships.

X-ray radiographs of 2 cm-thick slabs approximately 30 to 40 cm deep in bottom sediments display tonal variations representing changes in structure and layering of the mud. Appendix photo A-1 from Southern Branch exhibits normal regular layering and laminae (n) at 22 to 27 cm depth but wavy bedding (w) at 8 to 11 cm depth suggesting deposition under dynamic conditions associated with occasional ship movement. The base layer 28 to 32 cm depth consists of a chaotic mass (c) of broken shell and pebbles also indicative of disturbance. Photo A-2 displays mud with laminated fragments (f) in a matrix of mud with shell and burrows (b) near the surface (0 to 10 cm depth). This suggests intense disturbance associated with dredging or ship movement.

b. Suspended Sediment Variations. The distribution of suspended sediment concentrations with depth and location is displayed in longitudinal sections (Fig. 4) for March 2-4, and March 19 (for slack water) and May 3,

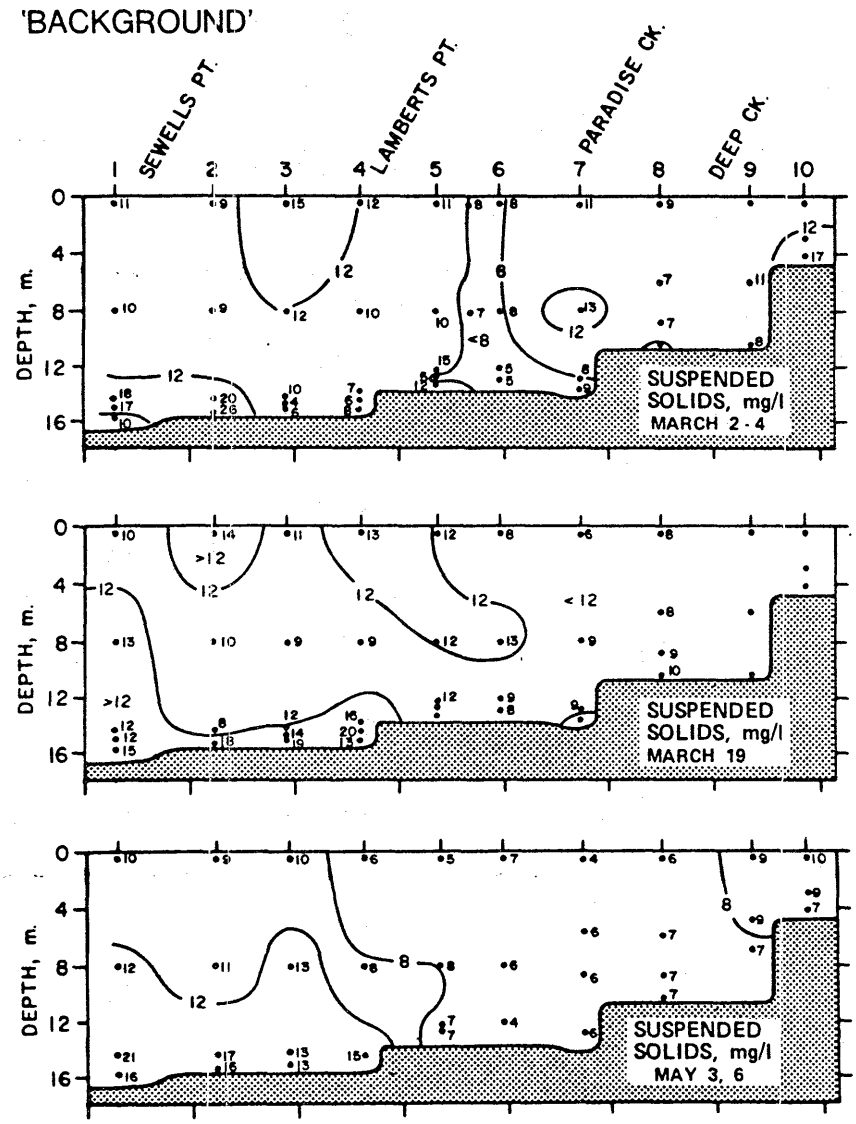

Figure 4. Longitudinal sections of "background" suspended sediment concentrations, March 2-4, March 19 and May 3, 6, 1985.

6, 1985 (at maximum ebb current). These data provide "background" distributions for relatively quiescent conditions of limited ship activity. In general the concentrations vary within narrow limits between 4 and 12 mg/l. Longitudinal and vertical gradients are very flat compared to similar gradients observed in the James River and Hampton Roads. Near-bottom samples from the entrance reach between stations 1 and 4 have values greater than 12 mg/l. On March 19 these are likely the product of intense wind stirring of Elizabeth River source waters in the Chesapeake Bay and Hampton Roads. On May 3, 6 the elevated concentrations are likely produced by sediment resuspension of source waters in Chesapeake Bay by a northeast storm. There is little difference between concentrations observed at slack water May 6 and those observed three hours later during maximum ebb current at spring tide. This suggests resuspension of bed sediment by tidal currents is limited. Such a trend is confirmed by hourly sampling of suspended sediment at an anchor station in Southern Branch (station 6) (Fig. 5). Although tidal currents vary in speed from nearly zero to 20 cm/sec, the suspended sediment concentrations vary within narrow limits even near the bottom.

The distribution of percent organic matter (Fig. 6) for March 2, 1985, exhibits relatively uniform values throughout most of the river except for near-bottom stations 1 thru 5 which have values less than 20 percent.

The range of suspended sediment concentrations for "background" and for corresponding ship events is given in Table 1. Figures 7A, 7B, and 7C and Figure 8 shows the distribution of values and zone of enriched concentrations. Of note, concentrations reached 334 mg/l at mid-depth during backing of a large Navy tanker (Fig. 7A) but during its seaward

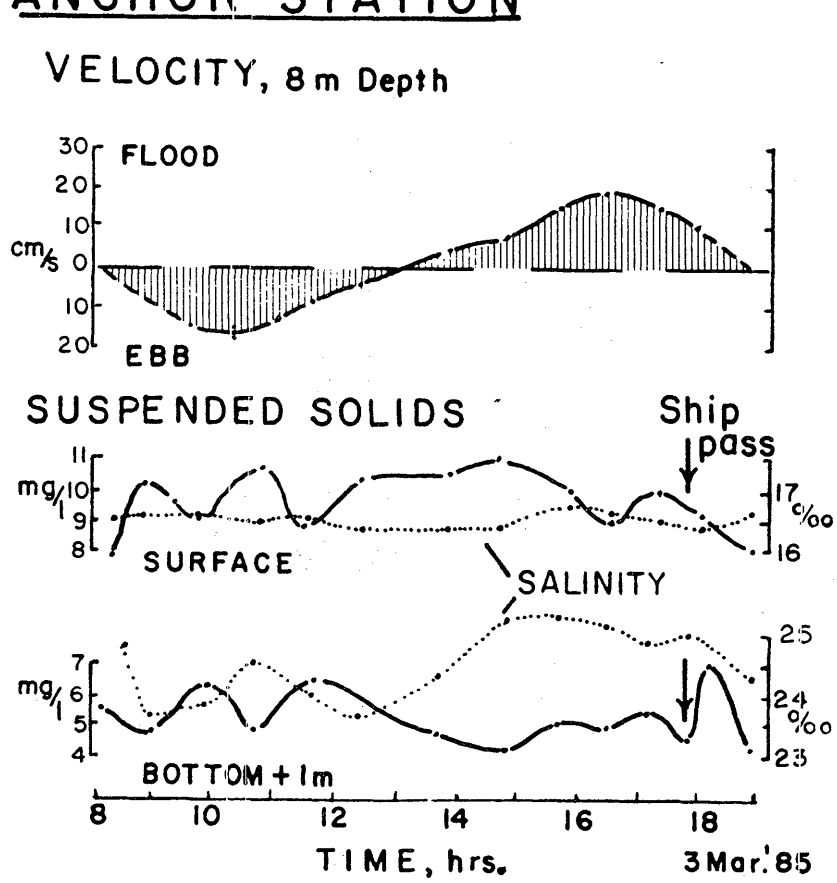

Figure 5. Temporal trends of current velocity, salinity and suspended sediment concentrations at station 6 in Southern Branch. Concentrations vary within narrow limits and lack sediment resuspension near the bed.

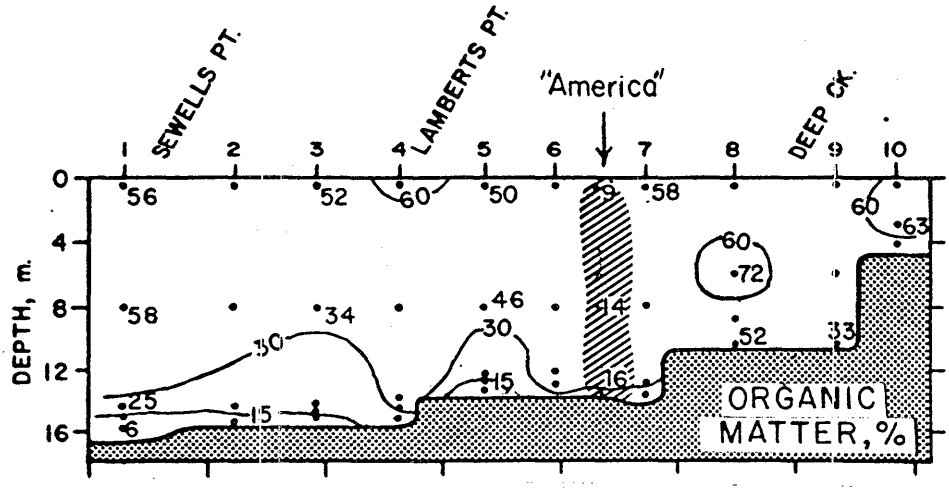

Figure 6. Distribution of percent organic matter (LOI) representing "background" values from the survey of March 2, 1985.

passage, concentrations are close to background level. Other events produced concentrations higher than background mainly in near-bottom water (Fig. 7A).

Backing of the naval aircraft carrier "America", May 13th, produced suspended sediment concentrations in near-bottom water reaching 758 mg/l (Fig. 7B), a value 90 times the background level. However, during seaward passage of the carrier, spot values reached 25 to 70 mg/l, a 3 to 10-fold increase over background concentrations. When values of percent organic matter are compared with background concentrations of March 2, it is evident that percentage values are diminished. This likely reflects mixing of bottom sediment with low values, into the water column.

Passage of the cargo ship "Zeynep K" revealed no change in suspended sediment concentrations but during berthing and backing, spot values reached 39 mg/l in near-bottom water (Fig. 7C). Little change in suspended sediment concentrations was observed during passage of the cargo ship "Beauty E" except for local increases near the bottom (Fig. 8).

In brief, the distributions of suspended sediment show that "background" concentrations are low and relatively uniform with time and location. Therefore, bed disturbance by ship movement produces pronounced zones of enrichment in overlying water. Ship backing, berthing and turning movements produced the greatest enrichment with concentrations locally reaching 90 times background level. Ship passage through the channel irregularly enriched bottom water 3 to 20 fold in limited reaches of the channel.

c. Salinity. The longitudinal distribution of salinity at different tide ranges, i.e. neap (March 2-4), mean (March 19) and spring (May 3, 6) is

Date	Ship/Type	Ship Length, m	Ship Tonnage	Ship Draft, m	Ship Event, Course	"Background" Concen, mg/l	"Event" Concen, mg/l	Increased Concen.
3/ 3/85	"Regent Mayflower" Bulk Carrier	189	24,597	10.8	Inbound	5-10	7-9	None
3/19/85	"Yellowstone" Naval Tender	196	20,500	6.9	Recently Docked	12-20	49	Yes
3/19/85	"Detroit" Naval Combat Support	242	51,700	12.0	Backing	8-18	53, 110, 334	Yes
3/19/85	"Detroit" Naval Combat Support	242	51,700	12.0	Outbound	8-18	8-18	None
3/19/85	Naval Sub	-	-		Inbound, tow(?)	8-16	46, 220	Yes
5/13/85	"America" Naval A/C Carrier	319	79,724	11.3	Backing	4- 7	38 - 758	Yes
5/13/85	"America" Naval A/C Carrier	319	79,724	11.3	Outbound	3-15	3 - 70	Yes
5/13/85	"Zeynep-k" Bulk Carrier	175	16,628	9.9	Outbound	4- 8	4 - 11	None
5/13/85	"Zeynep-k" Bulk Carrier	175	16,628	9.9	Backing	4- 7	4 - 39	Yes
5/14/85	"Limassol" Bulk Carrier	313	-	7.0	Inbound	4- 8	13	Yes
5/14/85	"Limassol" Bulk Carrier	313	-	7.0	Berthing	4- 6	8	None

SHIPPING 'EFFECTS'

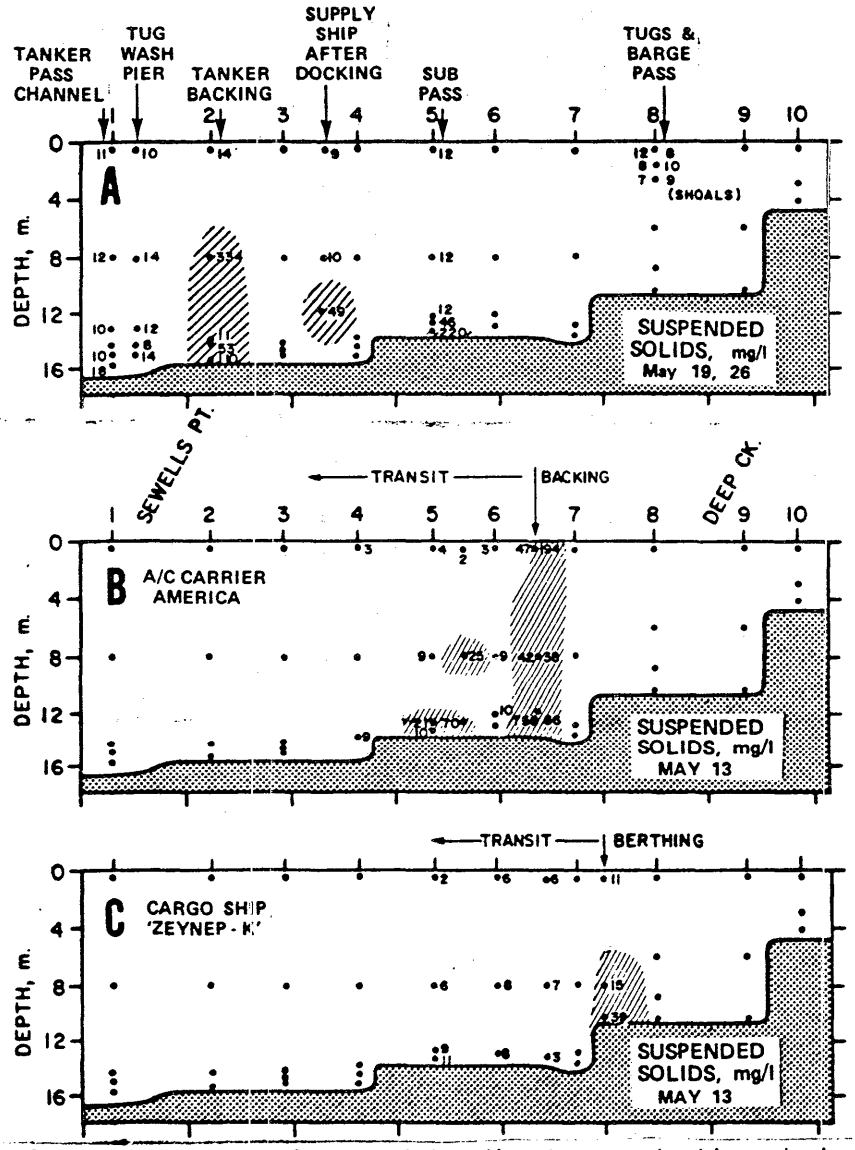

Figure 7. Distribution of suspended sediment concentrations during various shipping events, (A) March 19, (B) May 13, (C) May, 13, 1985. Zones of enrichment are shaded.

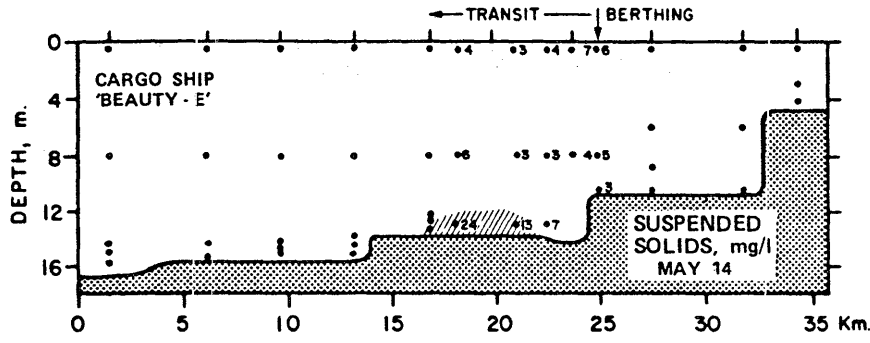

Figure 8. Distribution of suspended sediment concentrations during berthing and passage of the cargo ship "Beauty-E", May 14, 1985.

shown in Figure 9. These sections represent "background" concentrations for the observation period, which includes the local activity of barges and small craft. Since freshwater inflow from the estuary head is very small, less than 1.5 m^3 per sec on the average, and because variations in discharge of the James varied within narrow limits during the period, from a monthly average of 192 m^3 per sec in mid-February, 1985 to 113 m^3 per sec in mid-May, 1985, tidal mixing is a dominant factor affecting the observed salinity variations.

A marked change in stratification takes place from neap to spring tide. During neap tide range, e.g. March 2-4, the system is partly-stratified; surface-bottom differences at station 4, reach 11 $^{o}/oo$ (Fig. 9). By contrast during spring tide range, e.g. May 3-6, the system is well-mixed; surface-bottom differences at station 4 are only 0.06 $^{o}/oo$. Because the water is so well-mixed at spring tide, the effects of ship movement on haline mixing are difficult to detect.

Backing and turning of the aircraft carrier "America", May 13, a time of mean tide range, temporarily mixed the water column for about 10 minutes (Fig. 10). However, stratification "recovered" at the site within about 20 minutes after turning. Passage of the carrier, as well as cargo ships, May 13, 14, produced no significant perturbation in haline stratification.

Salinity at a fixed anchor station over a tidal cycle varied within narrow limits, i.e. 0.4 $^{o}/oo$ in surface water and 1.7 $^{o}/oo$ in bottom water (Fig. 5). Stratification was relatively stable over a tidal cycle and passage of a large cargo ship produced no significant perturbation.

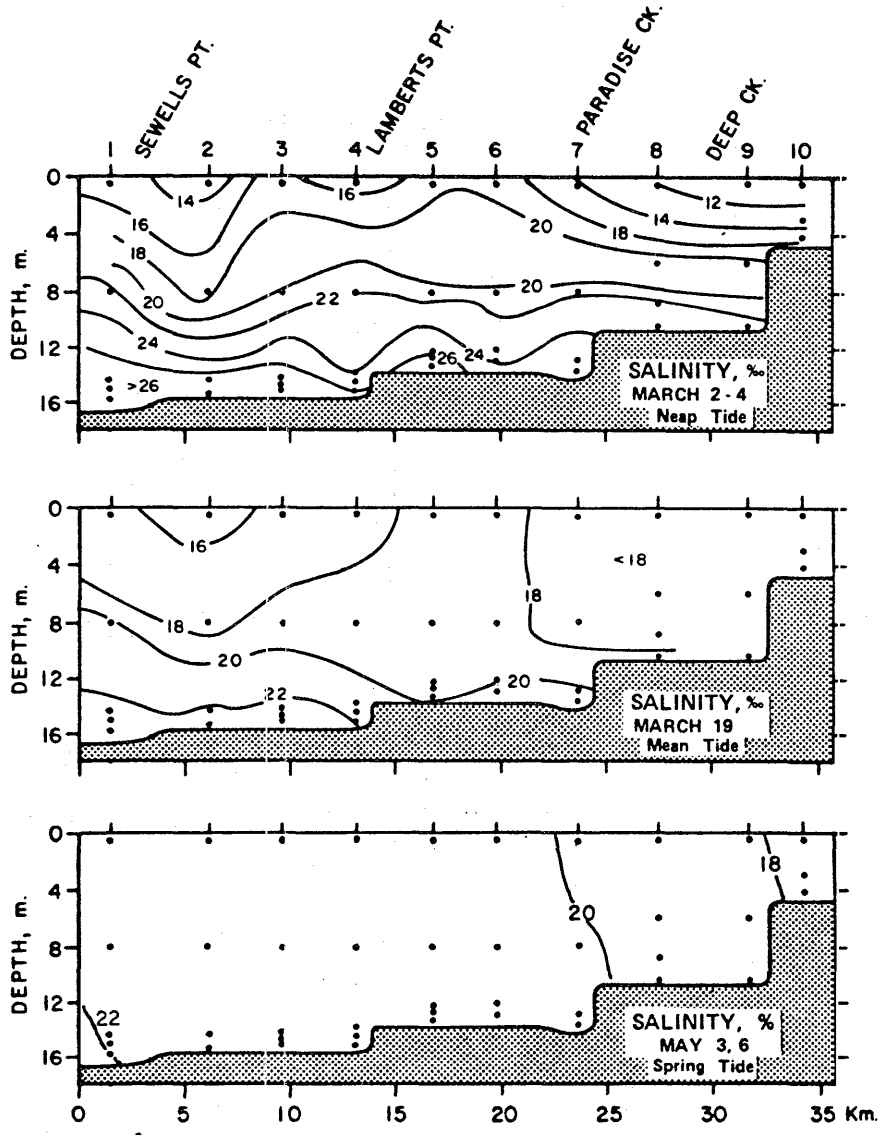

Figure 9. Distribution of background salinity concentrations, March 2-4 and March 19, May 3, 6, 1985.

In brief, the natural biweekly variations of salinity and stratification associated with neap-spring tide are more prominent than the temporary and localized perturbations produced by ship movement.

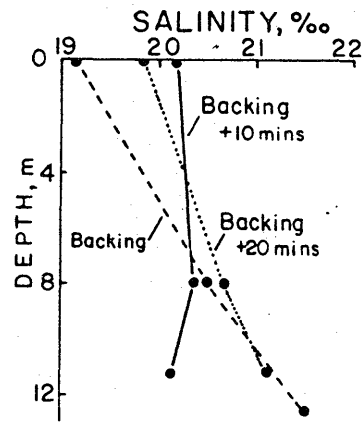

Figure 10. Vertical distribution of salinity concentrations comparing "background" gradients and gradients during backing and turning of the aircraft carrier "America".

d. Settling Velocity. The results of settling tests are shown as settling velocity grading curves in Figure 11. The mud consisted of the top 1/4 cm of watery bottom sediment and was introduced into a one-meter high column of still-water at various concentrations (0.5 to 1.1 g/L). Median settling rates range from 0.11 mm/sec for mud from the entrance reach (station 2) to about 0.01 to 0.001 mm/sec for mud from Southern Branch (stations 7 and 8). These data mean that once sediment, which is very fine-grained and organic-rich, is stirred up from the bottom and allowed to settle in still water, 50 percent of the sediment takes longer than one day to reach the bed from mid-depth in the entrance reach. In contrast, sediment from Southern Branch takes longer than six days. These values give an order of magnitude only.

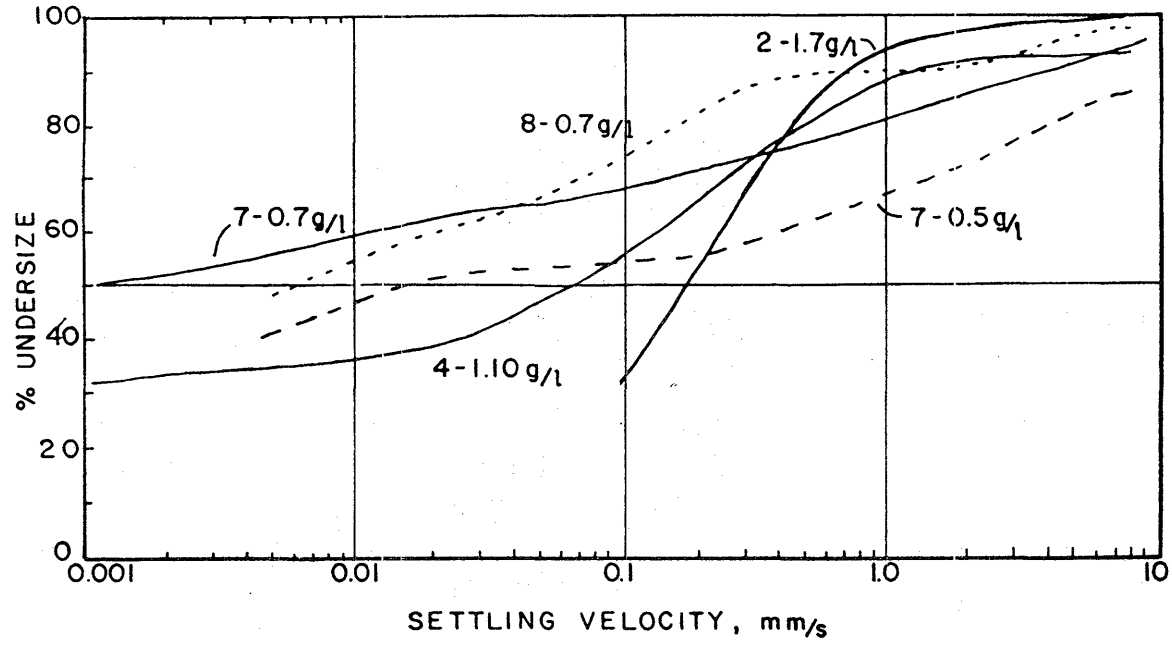

Figure 11. Settling velocity grading curves for selected stations and concentrations.

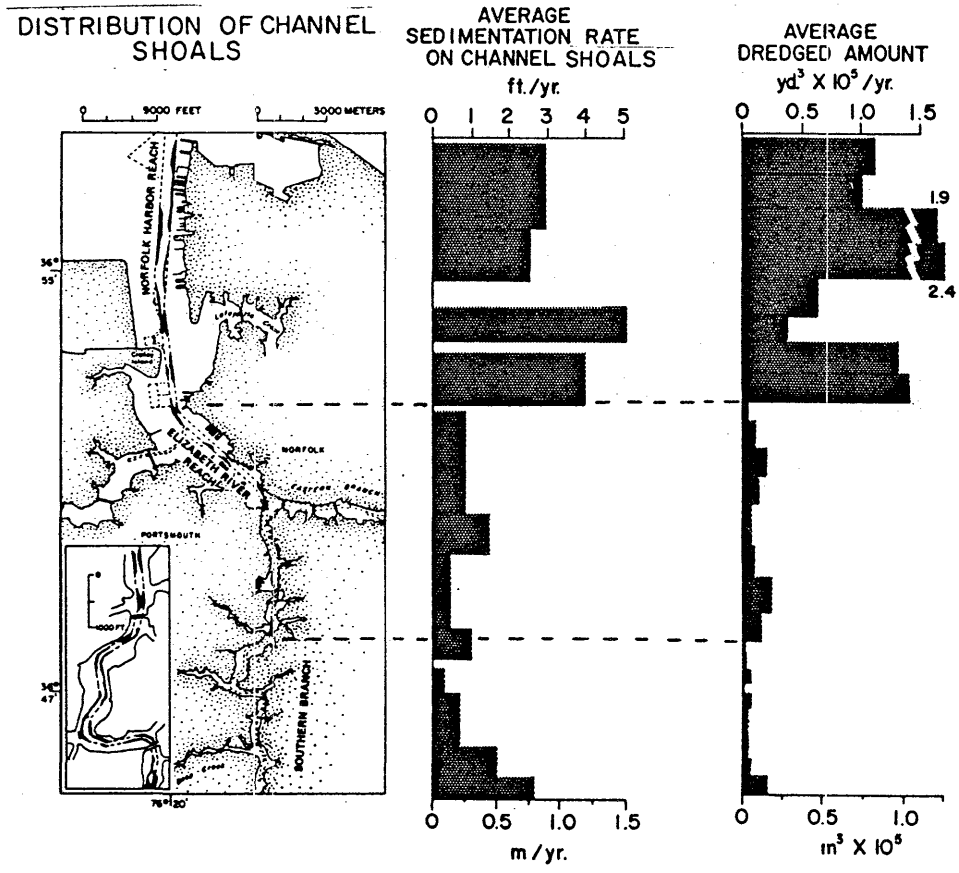

Figure 12. Distribution of shoals in the Elizabeth River shipping channels (left panel), average sedimentation rate on the shoals (middle panel) and average amount of sediment dredged from the shoals. Based on Corps of Engineers bathymetric surveys and dredging records between 1972 and 1981.

7. Summary Discussion

The sonar records reveal widespread disturbance of the estuary floor by ship movement. Linear bedforms are the most prominent features while scour depressions indicate local but intense erosion. These features suggest massive amounts of sediment can be reworked and redistributed. It is evident therefore, ship movement is a significant source of energy for redistributing cohesive sediments on the bed especially in Southern Branch. However, the frequency of effective disturbance and the magnitude of sediment transport induced by ships is unknown.

The sonar records also show the channel axis generally is a zone of non-deposition or local scour. Natural current velocities in central parts of the channel are too slow, less than 25 cm per sec at maximum tidal current, to erode the bed. Therefore, ship movement along the channel axis must keep sediment in suspension so that it is deposited elsewhere. The linear bedforms displayed on the sonar records indicate that lower sides of the channel floor are mainly zones of deposition and reworking. Deposition in lateral zones is confirmed by Corps of Engineers bathymetric surveys and dredging records (Fig. 12). Additionally, substantial amounts of sediment are dredged from berths and pier slips cut into the shore and sides of the main shipping channel. The immediate source of this sediment is the main channel but its ultimate source is likely Hampton Roads and Chesapeake Bay. Sediment can be transported landward via the inflowing density flow through the lower layer. Inflowing sediment, however, is not carried in directly from Hampton Roads. For the most part, the sediment is likely resuspended, retransported and redeposited many times by shipping activity before it finally accumulates.

The distribution of suspended sediment reveals that background concentrations are relatively low and uniform with time and location. A slight enrichment of near-bottom water occurs in the entrance reach (stations 1-2) and this is enhanced and extended landward during storms or strong winds. Since tidal resuspension from the bed is limited, disturbance by ship movement produces pronounced perturbations. The sediment remains in suspension as long as it resists settling. The intensity of resuspension also depends on the frequency of large ship excursions, particularly ships with low clearance. An estimated 224 entered Southern Branch during the year May 1984 to May 1985. However, the two events, i.e. backing of the aircraft carrier and the naval tanker, demonstrate that ship movement can produce a significant enrichment of suspended sediment concentrations in overlying water. These concentrations are more than 7 times those produced by dredging activity in the Elizabeth as observed over a year by Johnson et al. (1980). Figure 13 summarizes and compares the range of suspended sediment concentrations observed in the Elizabeth River.

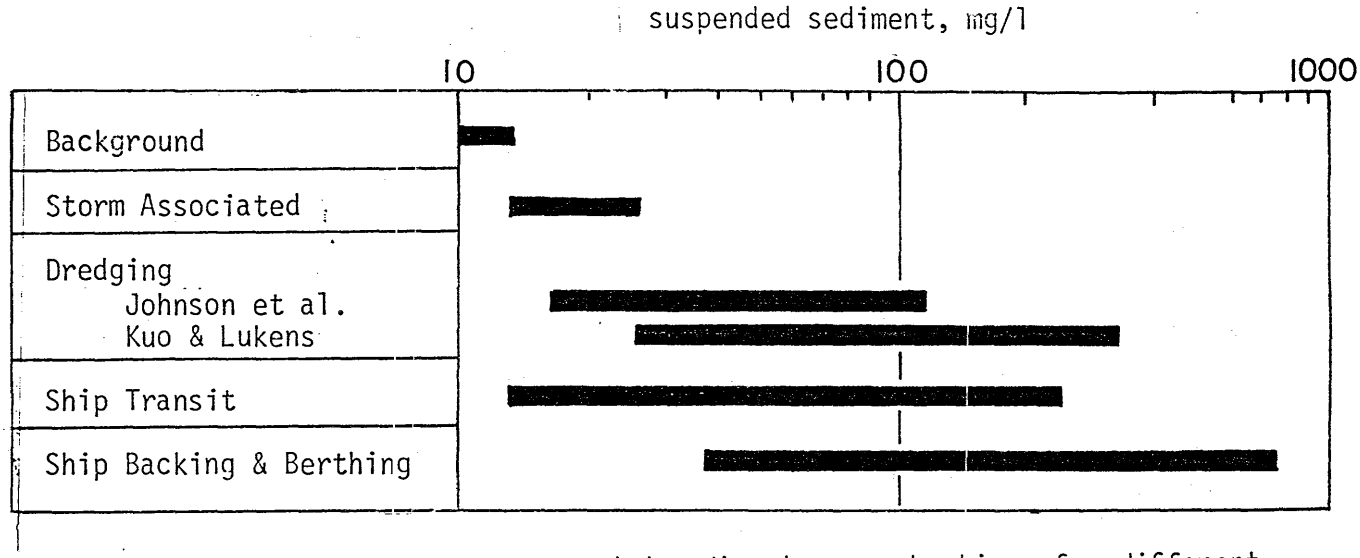

Figure 13. Comparison of suspended sediment concentrations for different types of conditions in the Elizabeth River.

8. Management Strategies

Since the results show that shipping disturbs and resuspends sediment, ship movement is one mechanism that can disperse contaminants from their source and redistribute them within the estuary. It can mix contaminated sediment from different sources and deter deposition and burial. By increasing the residence time of particles in suspension, the interaction time between dissolved chemicals and particles increases, thus allowing sequestering or release of chemicals into the water. Additionally, repeated resuspension can lead to fractionation of the sediment whereby aggregates and relatively dense particles reside near the bottom or on the bed. In contrast, very fine-grained dispersed particles, and light material like organic detritus, can reside in suspension for long periods and thus be carried landward or seaward through the upper and lower estuarine layers. Enrichment of the water with contaminated sediment exposes plankton, fish and filter feeders to chemical pollution.

Since one of the aims of the CSA program is to provide a scientific basis for managing the River, several preliminary strategies are offered to protect the River and maintain it in its best achievable condition.

a. Manage to reduce shoaling in contaminated reaches.

Inasmuch as clearance between the bed and ship hull or propeller, determines the magnitude of bed disturbance, any measure that will increase clearance will reduce sediment resuspension. Shoaling reduces water depth and tends to decrease clearance. Shoaling can be reduced by reducing source inputs of sediment to the inner contaminated reaches. For example, by inducing sedimentation in the entrance reach, which is the main sediment

source and artery of inward transport, so that suspended sediment does not reach the inner contaminated reaches.

Clearance can also be increased by providing greater channel depths or by limiting deep draft ships to zones of the channel having adequate clearance.

b. Manage to stabilize the bed.

Resuspension can be minimized by any measure that will stabilize the bed and retard erosion. This can be accomplished by allowing bed sediments to consolidate and dewater naturally over time, thus increasing their rigidity. Overdeepening and less frequent maintenance dredging provide more time for sediments to consolidate and can reduce the probability of short-term bed disturbance.

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Appendix A-1. X-ray radiographs of 2 cm-thick mud "slab" showing normal regular layering and laminae (n) and wavy bedding (w), and broken shell and pebbles (c). From Southern Branch.

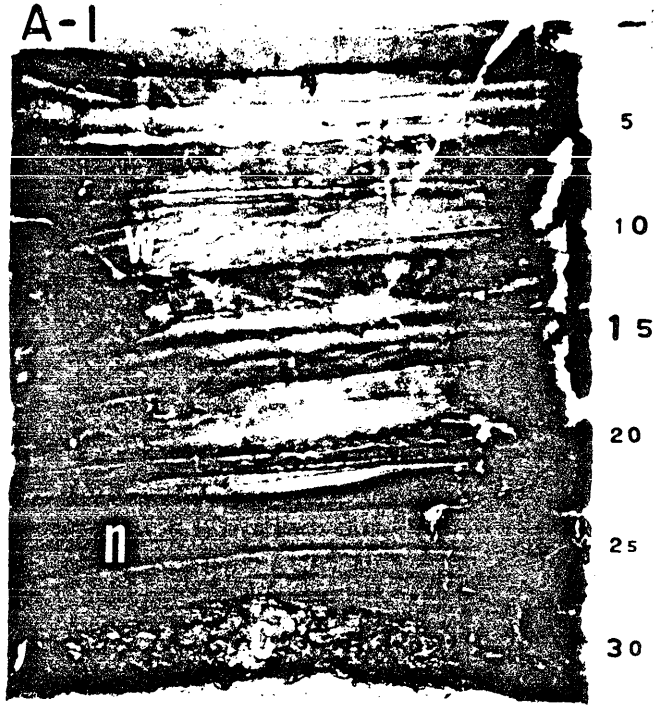
Appendix A-2. Radiograph of 2-cm thick "slab" displaying fragments of laminated mud (f) in matrix of mud with shell and burrows (b). From core near Lambert Point.

Appendix B-1. Side-scan sonargraph of dredge marks and anchor drag marks in the 45-foot Norfolk Harbor Channel.

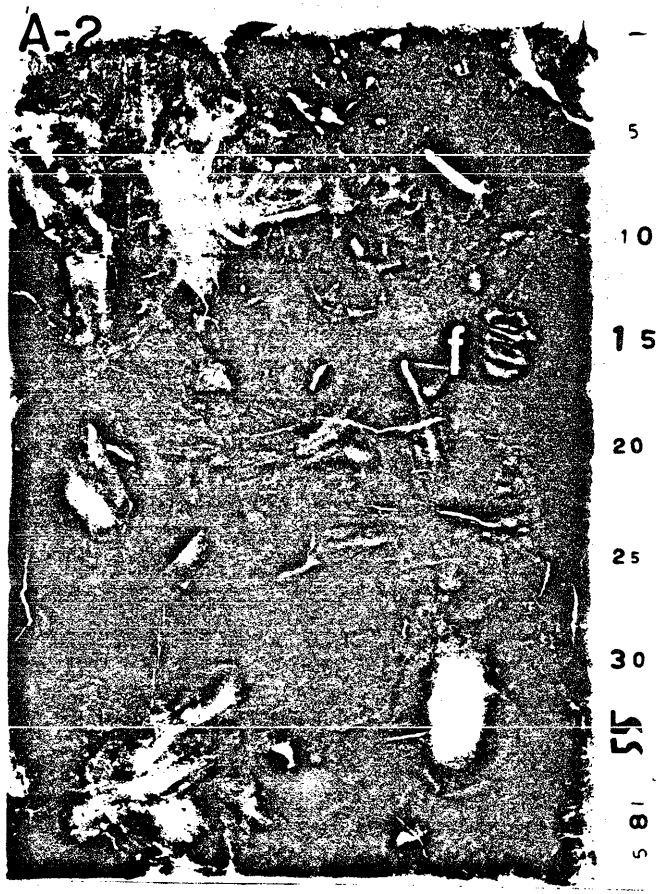
Appendix B-2. Side-scan sonargraph of mud lineations in Southern Branch between the Norfolk Naval Shipyard and Berkley, 40-foot channel.

Appendix C. Fathogram of mud lineations across the entrance to Southern Branch, 40-foot channel.

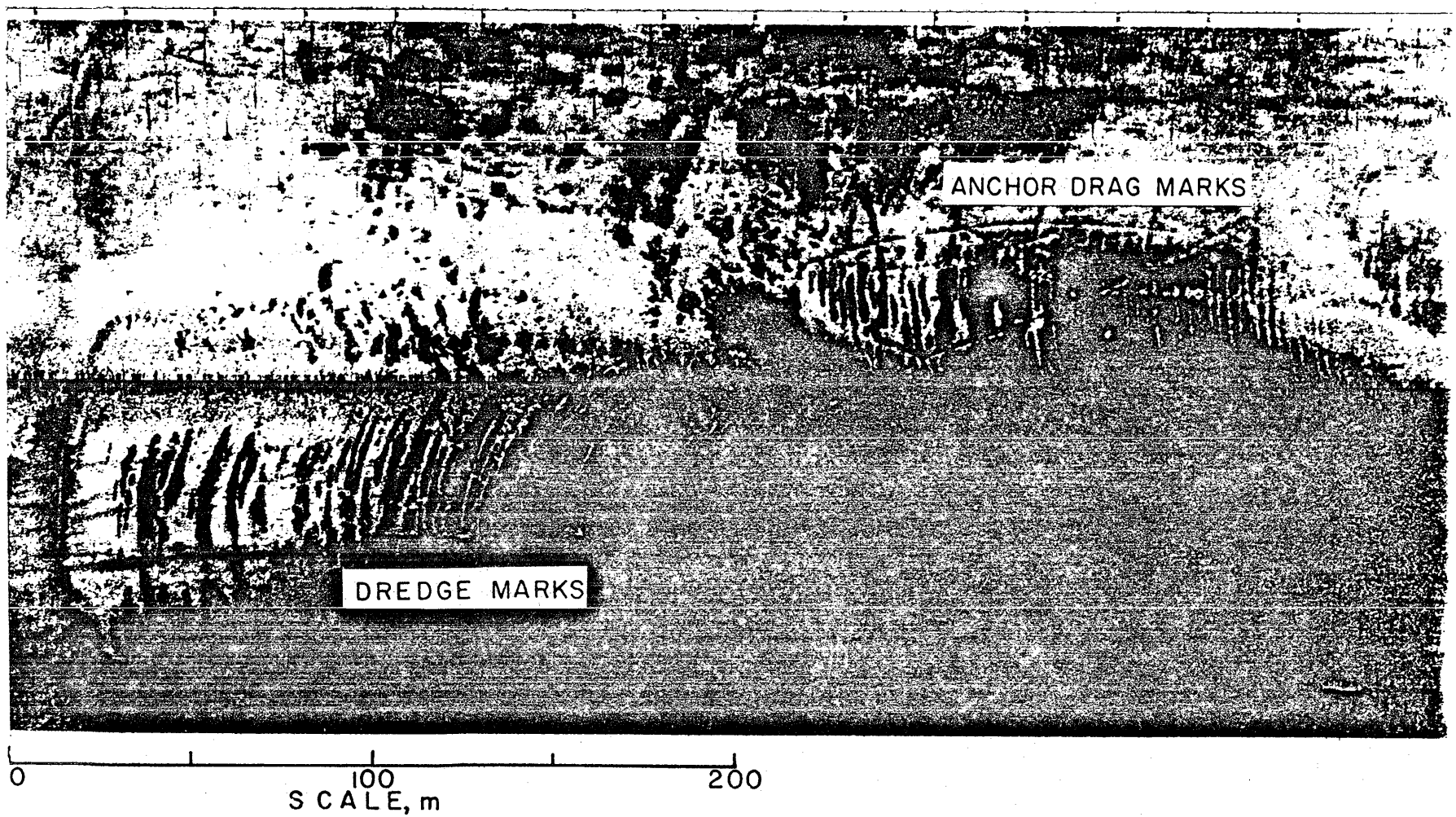
APPENDIX A



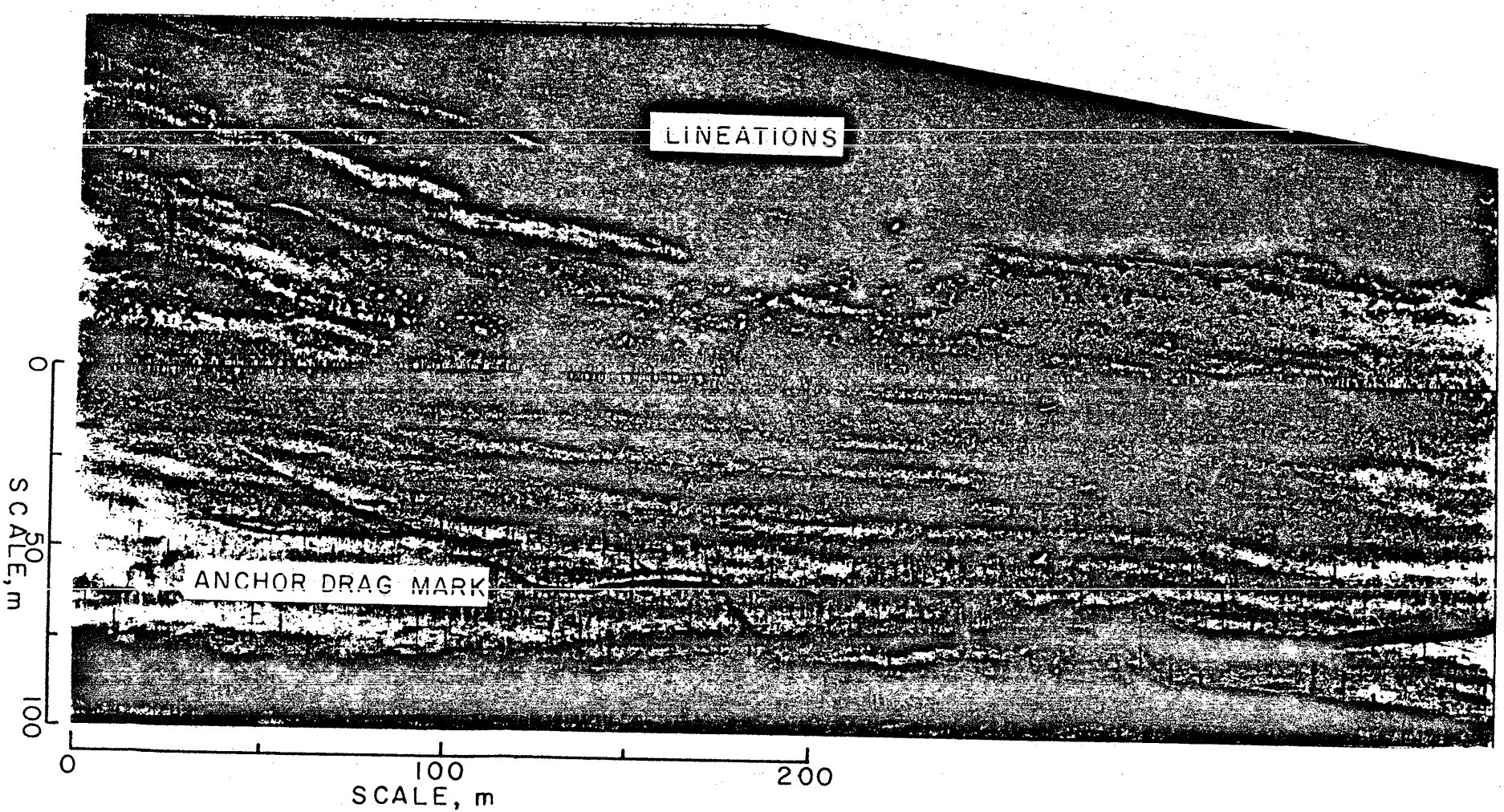
X-RAY RADIOGRAPHS



APPENDIX B, Sonar record 1



APPENDIX B, Sonar record 2



APPENDIX C, Transect 8