# NBP-89-16

# Monitoring of the Providence & Seekonk Rivers for Trace Metals

& Associated Parameters (SPRAY) 70 pp

Doering, Pilson, & Oviatt (URI)

Narragansett Bay Estuary Program

# Monitoring of the Providence and Seekonk Rivers for Trace Metals and Associated Parameters

REPORT # NBP-89-16

FINAL REPORT

to

THE NARRAGANSETT BAY PROJECT

P. H. DOERING, C. A. OVIATT AND M. E. Q. PILSON

Marine Ecosystems Research Center Graduate School of Oceanography University of Rhode Island Narragansett Bay Campus Narragansett, RI 02882-1197

June 1988

Revised November 1988

#### **FOREWORD**

The United States Congress created the National Estuary Program in 1984, citing its concern for the "health and ecological integrity" of the nation's estuaries and estuarine resources. Narragansett Bay was selected for inclusion in the National Estuary Program in 1984 and designated an "estuary of national significance" in 1988. The Narragansett Bay Project (NBP) was established in 1985. Under the joint sponsorship of the U.S. Environmental Protection Agency and the Rhode Island Department of Environmental Management, the NBP's mandate is to direct a five-year program of research and planning focussed on managing Narragansett Bay and its resources for future generations. The NBP will develop a comprehensive management plan by December, 1990, which will recommend actions to improve and protect the Bay and its natural resources.

The NBP has established the following seven priority issues for Narragansett Bay:

\* management of fisheries

\* nutrients and potential for eutrophication

\* impacts of toxic contaminants

- \* health and abundance of living resources
- \* health risk to consumers of contaminated seafood
- \* land-based impacts on water quality

recreational uses

The NBP is taking an ecosystem/watershed approach to address these problems and has funded research that will help to improve our understanding of various aspects of these priority problems. The Project is also working to expand and coordinate existing programs among state agencies, governmental institutions, and academic researchers in order to apply research findings to the practical needs of managing the Bay and improving the environmental quality of its watershed.

This report represents the technical results of an investigation performed for the Narragansett Bay Project. The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under assistance agreement #CX812680 to the Rhode Island Department of Environmental Management. It has been subject to the Agency's and the Narragansett Bay Project's peer and administrative review and has been accepted for publication as a technical report by the Management Committee of the Narragansett Bay Project. The results and conclusions contained herein are those of the author(s), and do not necessarily represent the views or recommendations of the NBP. Final recommendations for management actions will be based upon the results of this and other investigations.

### Executive Summary

The principal goal of the SPRAY Cruises was to determine if the concentrations of inorganic plant nutrients and selected trace metals observed in the Providence and Seekonk Rivers were a function of point source inputs.

Six cruises occupying 10 stations at consecutive high and low tides were conducted approximately every two months. Concentrations of various parameters were measured in samples obtained from within 1.0 meter of the surface and 1.0 meter of the bottom. Vertical profiles of salinity, temperature, potential density and turbidity were also taken. Concentrations of nutrients and trace metals were measured in each of eight point sources (5 rivers, 3 sewage treatment plants) for three days prior to each cruise.

Freshwater input to the system derived mainly from the Blackstone and Pawtuxet Rivers. These two rivers also comprised the major inputs of silicate and nitrite + nitrate. The Field's Point Sewage Treatment Plant was the major source of ammonia. Significant inputs of phosphate came from a number of sources: the Blackstone Valley and Field's Point Sewage Treatment plants and the Blackstone and Pawtuxet Rivers.

The Field's Point Sewage Treatment plant was the major source of both dissolved and particulate copper and nickel. The Blackstone River was the major source of cadmium and together with the Field's Point facility supplied most of the lead to the system.

Only concentrations of copper and nickel frequently exceeded chronic criteria for saltwater aquatic life. In a few instances, lead exceeded chronic levels in the Seekonk River portion of the estuary. Cadmium never exceeded chronic levels.

A box model was employed to predict concentrations of nutrients and metals in the estuary based on inputs and mixing of fresh and salt water. The concentrations of nitrate + nitrite predicted by the model agreed with those actually observed in the estuary. Predicted concentrations of silicate and phosphate in surface water were somewhat less than observed while in bottom water these were greater than observed. Although in general ammonia concentrations observed in surface water agreed with model predictions, the correlation between observed and predicted values was relatively weak. Observed ammonia concentrations in bottom waters were greater than those predicted by the model. Various processes could be invoked to explain differences between observed and predicted concentrations. These included biological uptake, remineralization, resuspension of sediment, and geochemical precipitation.

The results for metals (Cd, Cu, Ni, Pb) were more difficult to interpret. There appeared to be an unidentified source of dissolved copper and nickel in the Sabin Point Reach of the Providence River. Processes such as resuspension of sediment, and phase changes between the dissolved and particulate could be speculatively invoked to explain differences

between observed and predicted concentrations.

Despite deviations of observed concentrations of both nutrients and metals from those predicted by the model, it can be concluded that concentrations in the Providence and Seekonk Rivers are to a large extent controlled by point source inputs. This result implies that reductions in loading from these sources should produce lower concentrations in the estuary. As pointed out by a reviewer, copper and nickel often exceed chronic levels and control of their discharge at the Field's Point Sewage Treatment Plant (the major source of copper and nickel) might alleviate this problem.

Further investigation of nutrients and trace metals in the Providence and Seekonk River might focus on 1) a better definition of the relationship between input and observed concentrations and 2) internal processes (eg. sediment resuspension, benthic remineralization) which may also be important in controlling the concentration of a given constituent in the estuary.

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#### Introduction

The Seekonk and Providence Rivers are located at the head of Narragansett Bay. Although most of Narragansett Bay may be characterized as weakly stratified (Pilson, 1985), the waters of this region are typically highly stratified (Doering et al. 1988). The vertical density structure of the water column varies as a function of salinity. Vertical density profiles are consistent with the concept of two layered estuarine flow with net seaward flow at the surface and net landward flow in bottom waters.

Being surrounded by the Greater Providence Metropolitan area, the Seekonk and Providence Rivers receive effluent from several sewage treatment facilities as well as a number of rivers which themselves carry both industrial and sewage discharge. From a pollution standpoint, this area is arguably the most heavily impacted region of Narragansett Bay. Indeed, a "pollution gridient" extending from the Providence River to the cleaner portions of the lower West Passage has been demonstrated (Oviatt et al., 1984).

In this report we summarize results of a year long water quality survey of the Seekonk and Providence Rivers. We measured inputs of nutrients and metals and their concentration within the system to determine if water quality was a function of allochthonous sources. Sampling events, although spanning a year, were timed to occur when combined sewer overflow was unlikely. An additional goal of the study was to assess the variability in water quality induced by tidal forces.

#### Methods

Sampling:

Six cruises, occurring about every two months (Table 1) occupied 10 Stations (Fig. 1) in the Seekonk (3) and Providence Rivers (7) at both high and low tide. In general stations were sampled within  $\pm$  1.5 hours of slack tide.

Discrete water samples were pumped (bellow or hand) from within 1.0 meter of the surface and 1.0 meter of the bottom through acid rinsed (1% HCl) teflon tubing. Vertical hydrographic profiles of temperature and salinity were obtained either with an Applied Microsystems, Inc. STD-12 (Providence River) or a Beckman Instruments Inductive Salinometer (Seekonk River). The resolution of depth was about 0.5 meters.

Coincidently with each cruise, 5 rivers and 3 sewage freatment plants (Fig. 1) were sampled on the three days preceding each cruise. Rivers were sampled at low tide to minimize saltwater intrusion. Sampling was usually conducted from a bridge or other structure which allowed access to mid-stream. Samples were taken with a plastic bucket suspended from a rope. An inverted funnel prevented contamination of the sample by

11, 1986
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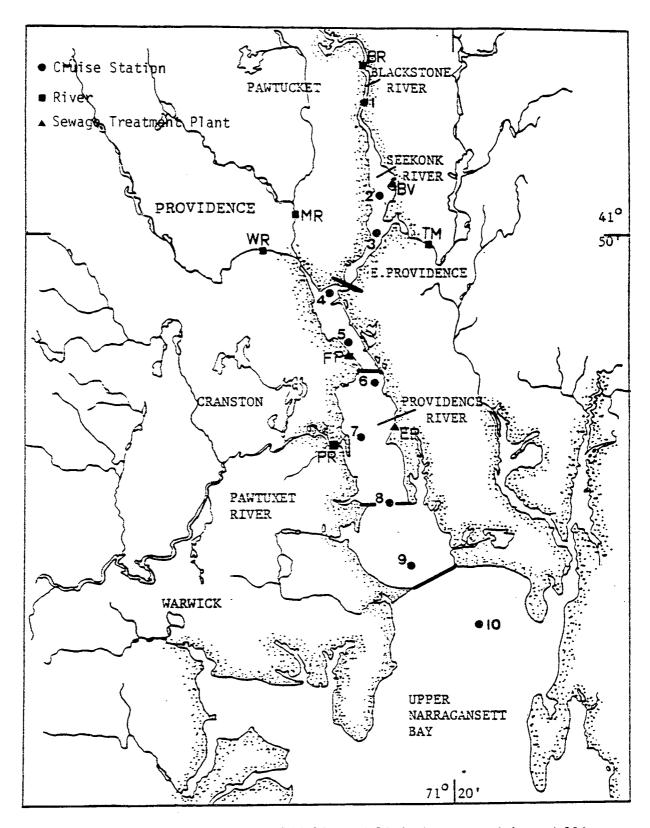


Figure 1: Station Locations. Solid lines delimit boxes used in modelling effort. BR = Blackstone River, BV = Blackstone Valley Sewage Treatment Plant (STP), TM = Ten Mile River, MR = Moshassuck River, WR = Woonasquatucket River, FP = Field's Point STP, EP = East Providence STP, PR = Pawtuxet River

Composite (24 hour) samples of effluent were collected from the three sewage treatment plants by plant operators. These were refrigerated until returned to the laboratory. In general samples were brought to the laboratory within 24 hours of collection.

#### Processing and Analysis:

Samples for dissolved inorganic nutrients (NH $_3$ , NO $_2$  + NO $_3$ , PO $_4$ , SiO $_4$ ) were manually (60 ml plastic syringe) passed through 47 mm diameter, 0.4 micron pore size membrane filters (Nuclepore) into 60 ml polypropylene jars. These were stored on ice until returned to the laboratory where they were frozen until analysis on a Technicon Autoanalyzer (Lambert & Oviatt, 1986). Duplicate samples from Station 1 were refrigerated for silicate analysis to avoid problems caused by freezing low salinity samples (Macdonald et al., 1986).

Particulate carbon and nitrogen samples were passed manually (60 ml plastic syringe) through 13 mm diameter Whatman GF/F glass fiber filters (nominal pore size 0.7 um) which had been combusted at 425°C. Duplicate filters were stored on ice until returned to the laboratory where they were dried (40°C) and stored until analysis. The filtrate was collected and its weight determined in the laboratory. Carbon and nitrogen retained on the filters were determined by elemental analysis on a Carlo Erba Model 1106 Elemental (CHN) Analyzer. The mean coefficient of variation for 218 duplicate analyses was 12% for carbon and 14.5% for nitrogen.

Samples for dissolved and particulate trace metals (Cd, Ni, Cu, Pb) were collected in 500 ml plastic bottles. Particulate samples were filtered on to tared 47 mm, 0.4 um Nuclepore polycarbonate filters using polysulphone filtration units. All plasticware and filters were precleaned in nitric acid.

Filters were dried, reweighed and digested in 5 ml of 2N Ultrex  ${\rm HNO_3}$ . One hour of ultrasonification aided digestion.

Filtrates were acidified to a pH of 2.3 with Ultrex HNO<sub>3</sub>. Samples from the estuary (Providence and Seekonk Rivers) were concentrated by coprecipitation with Ammonium Pyrrolidine Dithicocarbomate (APDC) and Cobalt Chloride (CoCl<sub>2</sub>) (Boyle and Edmund, 1975). Sewage effluent filtrates were concentrated (10x) by evaporation (60°C) and redissolution in 10 ml 2N HNO<sub>3</sub>. River filtrates were not concentrated.

Soluble and particulate trace metal samples from the Providence and Seekonk Rivers were analyzed by Graphite Furnace Atomic Adsorption Spectrophotometry using a Perkin-Elmer Zeeman/5000 AAS. Riverine samples were analyzed on a Perkin-Elmer 603 Atomic Adsorption Spectrophotometer equipped with a Model 400 Graphite Furnace and Deuterium Arc Background Correction. Sewage treatment plant samples were analyzed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Leeman Labs Plasma-Spec I.

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Discrete salinity samples were stored in 60 ml plastic bottles. Duplicate samples were analyzed on an Autosal Model 8400 Inductive Salinometer. The mean coefficient of variation of 222 duplicate analyses was 0.84%

#### The Model:

Concentrations of dissolved inorganic nutrients, particulate carbon and nitrogen and dissolved and particulate metals (Cd, Cu, Ni, Pb) were predicted using a two layer box model (Kester, 1988). The model assumes 1) steady state conditions 2) instantaneous and complete mixing in each box and 3) that net flow is seaward in surface boxes and landward in bottom boxes. Vertical exchange in both directions between layers also occurs. Freshwater inputs are to the surface layer. Calculation of water transport ( $m^3/\sec$ ) between layers within a box requires knowing the salinity of each layer in each box and the freshwater input to each box. Both volume and salt are assumed to be conservative. Calculation of the steady state concentration of a given constituent in a particular layer of a box requires a knowledge of the water flows in and out of the layer and concentrations of inputs from freshwater and adjacent layers.

Predicted concentrations are thus a function of the mixing of fresh and saltwater in the water column. Chemical reactions or inputs from bottom sediments are not considered. Agreement between observed and predicted concentrations suggests that observed concentrations are a function of inputs, both from freshwater sources and adjacent boxes. If predicted concentrations exceed the observed, then a constituent is being removed from the system by some process (Kester, 1988). If predicted concentrations are less than observed than an unknown source (e.g. bottom sediments, chemical reaction, biological production) is indicated (Kester, 1988).

Another useful characteristic of this model is that if the volume of each layer in each box is known, then the residence time (volume/transport in or out) of water in each layer of a box can be calculated (Kester, 1988).

#### Application of the Model:

The Providence and Seekonk Rivers were divided into 4 boxes (Fig. 1, Table 2) according to Chinman and Nixon (1985). At least two sampling stations were included in each box. Station 10 served as a saltwater endmember.

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Each box was partitioned into a surface and bottom layer using the hydrographic profiles. The depth of the surface layer was taken as the average depth to the top of the halocline. Total area and volume for each box at mean low water are given in Chinman and Nixon (1985). After adjustment for tidal height, the volume of water in each layer of each box could be determined.

Table 2. Characteristics of the boxes used in model calculations. Volume and depth data are from Chinman and Nixon (1985). For sampling station locations and freshwater inputs see Fig. 1.

===							
Вс	×	Area (Km²)	Mean Depth (m)	Sampling Stations	Preshwater Inputs		
===			333222222222	*********			
1.	Seekonk River	2.80	1.29	1,2,3	BR, BV, TM		
2.	Fox Pt. Reach	3.00	7.03	4,5	WR, MR, FP		
3.	Sabin Pt. Reach	8.54	3.39	6,7	PR, EP		
4.	Nayatt Pt. Reach	9.79	3.58	8,9			
					*******		

Salinity in each layer was taken as the mean of discrete samples in each box. Observed concentrations of various constituents were estimated similarly. Freshwater input was determined from river flow data furnished by the U.S. Geological Survey and sewage treatment plant discharge records. Freshwater input was taken as the mean of the three days preceding each cruise. The river discharge data represent flows measured at gauging stations. Since the locations of these stations are often some distance from Narragansett Bay (e.g. the Blackstone River is gauged in Woonsocket, R.I.), the actual discharge may be different. The long term average gauged flow of the Blackstone is probably about 77% (see Oviatt et al. 1984) of the actual average discharge. River flow data could be corrected by applying the ratio of gauged drainage area: total drainage area (Pilson, 1985) but we have not yet done this. Such considerations do not apply to sewage treatment plants as these are located on the shores of Narragansett Bay.

Concentrations of the various constituents in each box were calculated for each cruise at both high and low tide, yielding a total of 96 predictions, equally divided between surface and bottom layers. The agreement between observed and predicted concentrations was determined by regressing the predicted (y) on the observed (x). Surface and bottom layers were considered separately. A slope equal to 1.0 suggests no difference. A slope greater than 1.0 indicates that predicted concentrations were greater than observed. Conversely a slope less than 1.0 indicates that observed concentrations were greater than predicted. The R-square of the regression represents an indication of the degree to which the model explains observation.

#### Results

#### Freshwater Input:

By far the most important source of freshwater in the Seekonk and Providence Rivers is the Blackstone River which enters at the head of the estuary (Fig. 2). The Pawtuxet River was next in importance. Thus, the two primary sources of freshwater in the system are widely separated in space being at the head and lower end of the estuary.

The six cruises encompassed a range of freshwater input to the system, spanning nearly an order of magnitude (Fig. 2). The cruises were apportioned equally between higher flow conditions (Dec., Mar., Apr.) and low flow conditions (Oct., June, Aug.). By way of comparison to the ranges of flow encountered during a given year, the following is illustrative. The highest mean monthly flows in the Blackstone River occurred during Dec., March and April. These were 55, 38, and 103 m³/sec respectively. The mean disharges for the three days preceding the SPRAY cruises were: Dec. 35 m³/sec, Mar. 56 m³/sec and April 67 m³/sec.

Surface salinity (Fig. 3) generally was inversely related to the seasonal pattern of freshwater influx, being relatively low in Dec, Mar, and Apr, and relatively high when freshwater flow was low (Oct., June, Aug.).

#### Nutrient Loading:

Both dissolved silicate and the oxidized forms of nitrogen ( $^{NO}_2$  +  $^{NO}_3$ ) entered the system through the Blackstone and Pawtuxet Rivers (Fig. 4). The discharge from the remaining rivers and sewage treatment plants was relatively unimpressive except, perhaps, the input of  $^{NO}_2$  +  $^{NO}_3$  from the Ten Mile River. Nevertheless, silicate and  $^{NO}_2$  +  $^{NO}_3$  enter the system primarily at its head and lower end.

By contrast, the Field's Point Sewage Treatment Plant was the largest source of ammonia (Fig. 4). The Blackstone River, Pawtuxet River and the Blackstone Valley Plant also appeared significant but each discharged at less than half the rate of the Field's Point Plant.

The annual pattern of silicate and nitrate + nitrite loading (Fig. 5) generally follows the pattern of freshwater influx which is driven by the Blackstone and Pawtuxet Rivers. Since the latter represent the major sources of these constituents such a correspondence is expected. The annual pattern of ammonia and phosphate loading did not follow any discernable pattern (Fig. 5).

Major inputs of particulate carbon and nitrogen came from the Blackstone and Pawtuxet Rivers and the Blackstone Valley and Field's Point Sewage Treatment Plants (Fig. 6). The seasonal inputs of both particulate carbon and nitrogen appeared loosely coupled to freshwater influx, but the correspondence was clearly not as good as that observed for dissolved silicate.

#### Metal Loading:

Cadmium, both particulate and dissolved, entered the system from the Blackstone River (Fig. 7, Fig. 8). Nickel and copper entered mainly from the Field's Point Sewage Treatment Plant. Both the Blackstone River and the Field's Point Plant were the most significant sources of lead (Fig. 7 and Fig. 8).

The seasonal pattern of loading for cadmium and lead generally followed freshwater input although somewhat loosely (Fig. 9 and Fig. 10). Copper and nickel input showed no discernable seasonal pattern.

The partitioning of the metals between dissolved and particulate phases is given in Table 3. Cadmium and nickel were primarily dissolved, about-80 and 90% respectively. Copper was somewhat more evenly distributed being 65% dissolved and 35% particulate. Lead entered primarily on particles (61%) but a significant fraction (39%) entered in the dissolved phase.

From the preceding qualitative description, several general statements can be made. First there are three major sources of nutrients and metals: the Blackstone and Pawtuxet Rivers and the Field's Point Sewage Treatment Plant. This holds for all constituents examined excepting phosphate and perhaps dissolved lead. If the major source is riverine,

Table 3. Average percent of total metal input entering in the dissolved and particulate phases.

	Dissolved	Particulate				
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Cadmium	76	23				
Nickel	92	8				
Copper	65	35				
Lead	39	61				

then the seasonal loading pattern corresponds to that of freshwater influx (e.g., silicate, cadmium). As sewage treatment facilities become important these correspondences become less obvious (e.g., particulate carbon and nitrogen). When sewage treatment facilities are the major source, no aparent pattern in discharge can be discerned (e.g. copper, nickel, ammonia).

#### Spatial Distribution:

Surface salinity generally increased from Station 1 at the head of the system to Station 10 in upper Narragansett Bay (Fig. 11). On average however, there was no change in salinity between Stations 2 and 3 in the Seekonk River. The salinity of bottom water was always higher than in surface water and increased precipitously between Station 3 in the Seekonk River and Station 5 above Field's Point. Below Field's Point bottom water salinity did not change appreciably although Stations 7, 8, and 9 exhibited slightly lower salinity than Station 6. This may reflect the influence of the Pawtuxet River on the lower portion of the Seekonk-Providence River Estuary.

The mean concentrations of dissolved inorganic nutrients were always higher in surface waters than in bottom waters (Figs. 12 - 15). Although concentrations were always lower at Station 10 than at Station 1, the shapes of the curves suggest that concentrations are influenced by various point sources. The Blackstone Valley Sewage Treatment Plant, located between Stations 1 and 2 and the Field's Point Plant, between Stations 5 and 6 appears to affect ammonia concentrations (Fig. 13). Phosphate concentration in the Seekonk River is clearly elevated by the Blackstone Valley facility (Fig. 15).

The concentration of particulate carbon (Fig. 16) in surface waters declined from Station 1 to Station 4 in the upper Providence River. Concentrations in the upper Providence River (Sta. 4-6) were less than those in the lower estuary (Sta. 7-10). This pattern may result from higher biological productivity in the less turbid waters of the lower Providence River. Bottom water concentrations appear affected by the Ten Mile River (between Stations 2 and 3) and the Field's Point Plant (between Stations 5 and 6). The pattern for particulate nitrogen is similar except the influence of the Ten Mile River is not apparent (Fig. 17).

নতামক কৰাল মিজত আনদ ক্ৰমায়তে এই মতে এই ৪ কেন্টোক ক্ৰ'নিম্মান ক্ৰমিটাৰ্ম্বাধীক্ৰ নিৰ্মাণ ক্ৰিটাৰ্মিটাৰ কৰিছে

The concentrations of dissolved metals were always greater in surface waters than in bottom waters, while the concentrations of particulate phases are generally similar (Figs. 18 - 25). In the Seekonk River, however, particulate cadmium, copper and lead were more concentrated in bottom waters than in surface waters. The same is true on average for nickel but differences are slight. Resuspension of bottom sediments in this shallow region may account for this pattern.

Again, the shapes of the curves suggest that concentrations of some metals are affected by particular point sources. The Field's Point Plant appears to affect concentrations of dissolved nickel and copper in surface waters and particulate cadmium, nickel, copper, and lead in bottom waters. There appears to be a significant input of dissolved lead between Stations

7 and 8; probably the Pawtuxet River. It is interesting to note that most particle bound constituents exhibit a peak in bottom water concentration at Station 6, below Field's Point. Perhaps, on average this is a region of relatively high sediment resuspension.

The partitioning of the four metals between the dissolved and particulate phases is summarized in Table 4. As compared to the inputs, the distribution of cadmium and nickel shifted towards the dissolved phase while copper and lead shifted towards the particulate phase.

The chronic exposure criteria for saltwater marine life adopted by the State of Rhode Island are 8.3 ug/l for total (dissolved + particulate) nickel, 2.9 ug/l for total copper, 5.6 ug/l for total lead and 9.3 ug/l for total cadmium. Cadmium never exceeded chronic levels during the SPRAY Cruises. Copper exceeded chronic criteria in 66% of the measurements and these occurred mostly (70%) in surface waters (Table 4A). Nickel exceeded chronic criteria in 29% of the measurements. Such occurrences were almost entirely limited (95%) to surface waters. Lead exceeded chronic levels in only 3% of the measurements, these being equally distributed between surface and bottom water. Water quality criteria were more frequently exceeded in the Seekonk River (Stations 1-3) then in the Providence River (Stations 4-9) but the differences were not large (Table 4A).

#### Tidal Influence:

The effect of tide on the concentrations of metals in the estuary was examined using the paired t-test. Values were paired by cruise, station and depth. The results are summarized in Table 5. In general concentrations tended to be higher at low tide than at high tide. Few differences were statistically significant (dissolved cadmium, dissolved copper). Observed tidal effects tended to be an order of magnitude less than the mean concentration of a particular metal. Thus, tidal fluctuations induced about a 10% change in concentration.

### Model Results

#### Transports and Replacement Time:

Mean non-tidal transport coefficients for the three high river flow and three low river flow cruises are given in Figure 26. As expected net seaward flow in the surface layer is greater when river discharge is high. The influx of seawater at the mouth of the estuary is also somewhat greater, but the difference is not large (about 40  $\rm m^3/sec$  as compared to 78  $\rm m^3/sec$  increase in freshwater discharge).

Although there are few data, the results are of some interest. First, the up-estuary transport of seawater in the bottom layer is greatly reduced at the entrance to the Seekonk River. This might be expected given the constricted physiography of the area. Nevertheless, most of the saline bottom water mixes across the halocline and moves back down estuary in the Fox Point Reach. This interpretation is supported by 1) the precipitous

Table 4. Average percentage of total metal concentration in the dissolved and particulate phases in the Providence and Seekonk Rivers.

·	Dissolved	Particulate			
	x ====================================				
Cadmium	85	15			
Nickel	94	6			
Copper	59	41			
Lead	19	81			

Table 4A. Total number of metal analyses in the Providence and Seekonk Rivers compared with those in which concentrations (dissolved + particulate) exceeded State of Rhode Island chronic criteria for saltwater aquatic life.

Number	Exceeding	Chronic
	Critaria	

				Average/Station		
	Measurements	Total	Surface	Bottom	Seekonk	Providence
Nickel	219	64	61	3	8.7	4.5
Copper	223	148	103	45	19.0	14.8
Lead	221	7	4	3	2.3	0.0
	~ ·	,	*	3	2.3	0.0
Cadmium	0	0	0	0	-	-

Table 5: Mean differences between high and low tide concentrations of metals in the Providence and Seekonk Rivers.

=========			
<u>Metal</u>	Phase	Difference (ug/Kg)	<u>p</u>
		*************	
Cadmium	dissolved	-0.033	0.017*
	particulate	-0.009	0.246
Nickel	dissolved particulate	-0.374 -0.044	0.062 0.132
Copper	dissolved particulate	-0.339 -0.100	0.004 <sup>*</sup> 0.697
Lead	dissolved particulate	0.002 0.001	0.934 0.993

<sup>\*</sup> statistically significant difference

increase in surface water salinity between Stations 3 in the Seekonk and 4 in the Fox Point Reach (Fig. 11), and 2) the agreement between horizontal transport into the bottom of Box 2 and vertical transport to the surface (Fig. 26).

Under high river flow conditions there is little or no downward vertical transport of water across the halocline in Box 3. This may be due to the influence of the Pawtuxet River. Lastly, under low flow conditions, the downward vertical transport of water in Box 4 exceeds upward transport. Thus surface water is mixed down and transported up-estuary. The mean salinity of this water was  $27.31 \, ^{\circ}/^{\circ} \cdot ^{\circ}$  Taking Station 10 bottom water as an endmember (sal =  $30.50 \, ^{\circ}/^{\circ} \cdot ^{\circ}$ ) then about 10% of this flow was freshwater. It can be calculated that at a minimum, about 2 m³/sec or 13% of the freshwater inflow is entrained in the estuary during low river flow conditions. Such a mechanism would reduce transport of pollutants to lower Narragansett Bay.

It is often useful to consider the time for water to be replaced in a system. In some sense, such data place bounds on the rates at which other processes must proceed in order to produce a measurable effect (Hinga, pers. comm.). Replacement times under high and low flow conditions are summarized in Table 6. Under low flow conditions the surface layer of a given box is replaced every day or two. The maximum residence time for a parcel of water in the system would be about 5.5 days. Under high flow conditions this would drop to about 2 days.

Bottom waters tended to have longer replacement times than surface waters and in general decreased down estuary. Freshwater input had little effect on replacement of bottom water in the lower estuary (Boxes 3 and 4) while increased river input affected Boxes 1 and 2 differently. As might be expected, replacement times in the Seekonk decreased dramatically with increased river flow. In Box 2, however, replacement time increased with increasing river flow, perhaps due to a shallower halocline and increased bottom water volume. The maximum residence time of a parcel of bottom water in the system may be around 11 days during high river discharge and about 14 days under low flow conditions.

### Nutrient Concentrations:

The agreement between concentrations predicted by the model and those observed in the estuary was very good (Table 7). For all dissolved constituents, regressions of predicted on observed had zero intercepts. Silicate and phosphate showed some loss in surface waters (slopes greater than one), probably due to precipitation (phosphate) and biological utilization (phosphate and silicate). Silicate, phosphate, and ammonia all showed some enrichment in bottom waters (slopes less than one), possibly due to remineralization in the water column or by the benthos. Nitrate + nitrite concentrations in both surface and bottom waters were predicted adequately by the model (slopes equal to one). Although the slope of the regression for ammonia in surface waters was not different from one, the variability was quite large as signified by the low R<sup>2</sup>. This poor agreement may have been caused by biological utilization.

Table 6: Model Results. Mean (+SD) replacement times (days) of water in modelled sections of the Seekonk and Providence Rivers under high river flow (Cruises 2, 3, 4) and low river flow (Cruises 1, 5, 6) conditions (n=6 in each case).

Вох		High Flow	Low Flow
		*****************	
1 - Seekonk River	Surface Bottom	$\begin{array}{c} 0.5 \pm 0.2 \\ 3.5 \pm 3.2 \end{array}$	1.8 <u>+</u> 1.1 8.1 <u>+</u> 4.1
2 - Fox Pt. Reach	Surface Bottom	0.3 <u>+</u> 0.05 3.7 <u>+</u> 0.9	1.0 <u>+</u> 0.5 2.1 <u>+</u> 1.3
3 - Sabin Pt. Reach	Surface Bottom	0.5 ± 0.3 2.2 ± 1.0	1.4 ± 0.5 2.1 ± 1.3
4 - Nayatt Pt. Reach	Surface Bottom	0.6 ± 0.2 1.4 ± 0.5	$\begin{array}{c} 1.3 \pm 0.3 \\ 1.2 \pm 0.5 \end{array}$

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Table 7: Model Results for Nutrients. Regressions of concentrations predicted by the model on observed concentrations. n=48 in each case. Reported errors are the 95% confidence interval.

			********	
Nutrient	Depth	Slope	Intercept	<u>R</u> 2
	******		**********	
Silicate	Surface Bottom	$\begin{array}{c} 1.13 \pm 0.09 \\ 0.92 \pm 0.05 \end{array}$	$-1.88 \pm 4.40$ $0.94 \pm 1.36$	0.937 0.967
Phosphate	Surface Bottom	$\begin{array}{c} 1.31 \pm 0.18 \\ 0.83 \pm 0.07 \end{array}$	-0.58 <u>+</u> 0.85 0.10 <u>+</u> 0.27	0.819
Ammonia	Surface Bottom	1.05 <u>+</u> 0.34 0.78 <u>+</u> 0.07	5.12 <u>+</u> 11.82 0.85 <u>+</u> 1.66	0.448 0.906
<sup>NO</sup> <sub>2</sub> + NO <sub>3</sub>	Surface Bottom	$\begin{array}{c} 0.95 + 0.06 \\ 1.04 + 0.07 \end{array}$	1.81 + 2.12 0.18 + 0.82	0.959 0.954
Particulate Carbon	Surface Bottom	1.12 + 0.36 0.10 + 0.12	$\begin{array}{c} 0.07 \pm 0.34 \\ 0.55 \pm 0.12 \end{array}$	0.455 0.058
Particulate				
Nitrogen	Surface Bottom	$\begin{array}{c} 1.00 \pm 0.35 \\ 0.13 \pm 0.14 \end{array}$	$\begin{array}{c} 0.022 + 0.05 \\ 0.87 + 0.02 \end{array}$	0.417 0.066

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The results for particulate carbon and nitrogen in surface waters are similar to those for ammonia. Although the slopes are not different from one, variability is high. In bottom waters the model failed to predict the concentrations of particulate carbon and nitrogen. The poor agreement may be a function of resuspension.

#### Metal Concentrations:

The results for metals were not as straightforward as those for nutrients. Regressions of predicted or observed concentration were in general much more variable, and it was sometimes necessary to perform regressions for each tide or for individual boxes in order to make sense of the data (Table 8).

Of the four metals examined, the results for cadmium were the most satisfactory. Intercepts of all regressions were not statistically different from zero and the errors about the slopes were relatively small. Observed concentrations of dissolved cadmium in surface waters were less than predicted, while those for the particulate phase were greater. This inverse correspondence suggests conversion of dissolved to particulate cadmium.

In bottom waters, the model explained concentrations of dissolved cadmium but could not fully account for concentrations of particulate cadmium. Again resuspension of particulate matter may account for this discrepancy.

For lead, the regressions for high tide are more variable than for low tide. Conclusions based on statistical significance are thus equivocal. Nevertheless, the results indicate a phase change from dissolved to particulate in surface waters. In bottom waters, both dissolved and particulate phases appear in excess of predicted levels.

The results for both copper and nickel were quite poor when the full data set was considered. Individual regressions for each box, as shown for copper, were substantially better as judged by the higher R<sup>2</sup>'s. There appears to be an unrecognized source of both dissolved copper and nickel in the Sabin Point Reach, Box 3 in the model. Dissolved copper exhibits significant losses from the bottom water in Box 3 and from the surface water in Box 4. The significant excess of particulate copper in the bottom water of Box 3 suggests conversion from dissolved to particulate as a mechanism. Thus, these seems to be a large source of dissolved copper in the Sabin Point Reach which is lost to particulate matter, much of which settles quickly to bottom water. More dissolved copper appears to be lost in Box 4, the Nayatt Point Reach but this is not reflected in the data for particulate copper.

The results for nickel also indicate a source to surface waters in Box 3, but the data are insufficient to determine its fate.

Table 8: Model Results for Metals. Regressions of concentrations predicted by the model on observed concentrations. Reported errors are the 95% confidence interval.

HT = High Tide, LT = Low Tide.

	-3230223		**********	*************	******
	Depth		Slope	Intercept	$\frac{R}{R}^2$
22332222222		********	***********	*************	********
Cadmium Dissolved	Surface Bottom	•	$\begin{array}{c} 1.32 \pm 0.16 \\ 0.93 \pm 0.08 \end{array}$	-0.05 <u>+</u> 0.06 0.004 <u>+</u> 0.01	0.857 0.925
Particulate	Surface Bottom		$\begin{array}{c} 0.69 \pm 0.18 \\ 0.77 \pm 0.12 \end{array}$	$\begin{array}{c} 0.04 \pm 0.02 \\ 0.00 \pm 0.008 \end{array}$	0.545 0.791
Lead Dissolved	Surface		1.58 <u>+</u> 0.60 1.62 <u>+</u> 0.27	0.018+ 0.21 -0.033+ 0.10	0.589 0.877
	Bottom		$\begin{array}{c} 0.39 \pm 0.41 \\ 0.48 \pm 0.25 \end{array}$	$\begin{array}{c} 0.12 \pm 0.10 \\ 0.08 \pm 0.08 \end{array}$	0.153 0.419
Particulate	Surface		$\begin{array}{c} 0.72 \pm 0.23 \\ 0.53 \pm 0.19 \end{array}$	$\begin{array}{c} 0.63 \pm 0.37 \\ 0.91 \pm 0.37 \end{array}$	0.664 0.615
	Bottom	· ·	$\begin{array}{c} 0.38 \pm 0.37 \\ 0.70 \pm 0.17 \end{array}$	$\begin{array}{c} 0.51 \pm 0.47 \\ 0.10 \pm 0.29 \end{array}$	0.171 0.764
Nickel Dissolved	Surface	(n=48)	0.61 <u>+</u> 0.38	4.13 <u>+</u> 3.62	0.189
	Box 3*		$0.43 \pm 0.28$	1.67 <u>+</u> 3.19	0.534
	Bottom	(n=48)	0.80 + 0.11	0.59 <u>+</u> 0.45	0.826
Particulate	Surface Bottom		0.63 <u>+</u> 0.44 0.59 <u>+</u> 0.32	$0.43 \pm 0.19 \\ 0.09 \pm 0.06$	0.153 0.322

<sup>\*</sup>slopes of regressions for other boxes not different from one

Table 8: Model Results for Metals. Regressions of concentrations predicted by the model on observed concentrations. Reported errors are the 95% confidence interval.

HT = High Tide, LT = Low Tide.

Continued

######################################	Depth		Slope	<u>Intercept</u>	<u>R</u> <sup>2</sup>
Copper Dissolved		(n=48)	0.68 + 0.34	<del>-</del>	0.264
	Box 1 Box 2 Box 3 Box 4		-	4.27 + 3.01 0.56 + 1.23	0.644 0.484 0.745 0.604
	Bottom Box 1 Box 2 Box 3 Box 4	(n=48)	$ 1.04 \pm 0.25  1.06 \pm 0.48  2.33 \pm 1.04  1.92 \pm 0.27  1.22 \pm 0.40 $	-0.34 <u>+</u> 1.13 -1.06 <u>+</u> 1.25	0.597 0.706 0.715 0.963 0.812
Copper Particulate	Surface	(n=48)	0.65 <u>+</u> 0.40	1.86 <u>+</u> 0.36	0.184
	Box 3*	(n=47)	0.54 <u>+</u> 0.19 0.31 <u>+</u> 0.22	$0.44 \pm 0.48$ $0.20 \pm 0.53$	0.432

<sup>\*</sup> slopes of regressions for other boxes not different from one

#### Discussion

There are several issues which deserve discussion. First, is the notion that concentrations of various constituents are a function of inputs. If so, would abatement of input improve water quality in the system? Lastly, it might be worthwhile to consider what sort of information might clarify our understanding of the Seekonk-Providence River estuary.

The model used to predict dissolved inorganic nutrient concentrations is based on a conservative mixing where both salt and water volume are conserved (Kester, 1988). The model considers predicted concentrations in a given box to be a function of mixing in the water column, and to be controlled by input from freshwater and adjacent boxes.

In general, a significant proportion of the concentration of a given nutrient could be explained on the basis of conservative water column mixing. For example, when the slope of a predicted vs. observed regression was 0.7 it can be inferred that about 70% of the observed concentration was due to conservative mixing processes, and about 30% might result from other processes. Similarily, if the slope of such a regression were 1.25 then about 80% of the observed concentration is likely to result from conservative mixing and about 20% from other processes.

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In general between 76 and 100% of observed nutrient concentrations in surface waters appear to result from conservative mixing processes. Additional processes tend to reduce observed concentrations to levels below those predicted on the basis of inputs alone. In bottom waters, 78 to 100% of the observed concentration is attributable to conservative mixing. Processes in bottom waters caused observed concentrations to exceed the predicted. Nevertheless, dissolved nutrient concentrations, in large measure, are controlled by conservative mixing processes in the Seekonk-Providence River Estuary.

Of the metals examined only the behavior of dissolved cadmium reasonably conformed to this conservative mixing model. Essentially 100% of the bottom water concentration and about 76% of the surface water conentration were attributable to mixing. Dissolved nickel concentrations in bottom waters could also (80%) be largely explained by the model. The high R<sup>2</sup>'s of the regression indicate the dominant influence of mixing on the concentrations of these constituents. For other metal species, only between 40 and 70% of the observed concentrations could be construed to result from mixing. The low R<sup>2</sup>'s of the regressions suggest that other processes cause concentrations to deviate significantly from those predicted by conservative mixing.

There are several potential explanations for the discrepant behavior of metals. Metals which behaved reasonably (cadmium, nickel) were mostly dissolved. The poor prediction of dissolved nickel in surface waters may be due to unrecognized sources. Concentrations of particle reactive metals (e.g. copper, lead) as well as particulate phases of other metals

and nutrients (nitrogen and carbon) were not predicted very well. In bottom water, resuspension of sediments could well account for this inability to predict. In surface waters, settling of particles and phase changes from dissolved to particulate could be involved. It is possible that correcting gauged river flows might improve the predictions of the model. Rivers were major sources for cadmium and lead. Of the metals examined, these were best explained by the model. By contrast nickel and copper came mainly from sewage treatment plants. Correcting river flow would not appear to directly improve predictions by better estimating input. In terms of the model increased freshwater input would change transport coefficients (Fig. 26) and this might improve predictive capability.

Given that mixing exerts a significant control over nutrient and, at least some, metal concentrations in the estuary, what can we expect upon abatement of input? This question is of concern, not only locally, but for estuaries in general, and is a matter of considerable debate (Nixon, 1987). The controversy centers on whether the flux of material (nutrients, metals) stored in the sediment will elevate water column concentrations long after allochthonous input ceases. Thus, much attention has focused on the magnitude of retention of nutrients and metals in estuaries (D'Elia et al., 1983; Nixon et al., 1986; Nixon, 1987).

For nutrients, our analysis suggests that, at present, bottom waters are enriched only by some 10 - 30% by processes other than conservative mixing. Assuming that the major active process is remineralization and that this remineralization is primarily benthic, then benthic flux provides a small contribution to current nutrient concentrations. This result is in accord with a number of mesocosms experiments which suggest that when allochthonous input is high, as in the Providence River (Oviatt et al., 1986), benthic processes contribute little to observed water column concentrations and dynamics (Oviatt et al., 1982; Oviatt et al., 1984; Kelly et al., 1985).

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We did not measure the magnitude of nutrient storage in sediments of the Seekonk-Providence River Estuary. However, experiments with the MERL mesocosms suggest that if inputs are lowered, water column concentrations would also decrease (Oviatt et al., 1984). In these experiments, the impact of heavily polluted sediments from the Providence River on a relatively clean overlying water column were observed for about 19 months. Although concentrations were elevated for 5 months relative to clean sediments, thereafter the polluted system was much more similar to the clean sediment treatment than to in situ conditions in the Providence River. The MERL water column flushes in about 27 days. Our analysis indicates that the replacement time of water in the Providence River is substantially less than this. Thus, one might expect both a more rapid response to input abatement and a reduced impact of sediments on the water column relative to that observed in the mesocosms.

For metals, the relatively soluble species (nickel, cadmium) might behave much like nutrients. Particle reactive metals (e.g. copper, lead) might behave differently as these are more likely to reach the sediments. Hunt and Smith (1983) noted remobilization of copper from the polluted sediments of the Providence River, upon cessation of allochthonous input to

the water column. Water column conentrations of total copper remained higher (1.5 ug/l) in mesocosms with polluted sediments relative to those with clean sediments (0.9 ug/l), but less than in situ conditions (2.3 ug/l). The concentration difference between polluted and clean meosocoms was presumably caused by benthic flux of dissolved copper, measured to be about 145 ug/m²/d. It can be calculated assuming no water exchange that such a flux would raise water column concentrations by about 0.9 ug/l in 30 days. This is about an order of magnitude less than observed concentrations of dissolved copper in the bottom waters of the Seekonk-Providence River (Fig. 22).

#### Recommendations

#### Future Research:

With respect to nutrients, the modelling effort was quite satisfying. Except for ammonia in surface waters, it is clear that concentrations of dissolved inorganic nutrients are maintained by river and sewage treatment plant discharge. More detailed measurements of salinity and nutrient concentration are unlikely to further the understanding of nutrient dynamics in the area. A more frequent sampling program similar to the one conducted here, providing better seasonal coverage, would however allow reliable estimation of nutrient retention and/or export to lower Narragansett Bay. Such a study should include sampling at equal time intervals and measurement of input from the major combined sewer overflows.

In addition measurement of several processes, which could be included in subsequent models, would improve predictive capability. These processes are 1) ammonia utilization by phytoplankton 2) benthic input of all dissolved nutrients and 3) water column remineralization rates, especially in bottom waters. Study of the biogeochemical behavior of phosphorus in surface waters would also be valuable. Note that observed phosphate was depleted relative to predicted values and it is important to distinguish between biological utilization and geochemical precipitation (e.g. with iron).

The attempt to predict metal concentrations met with mixed success. Clearly, identification of potential sources of nickel and copper in the Sabin Point Reach would improve predictive ability. Again, knowledge of benthic inputs of both dissolved and particulate (resuspended) forms would be useful. Settling velocities of particulate matter might improve the predictions for both particulate metals and nutrients. The chemistry of trace metals is complex. Perhaps a more complete knowledge of the chemistry of these elements in the Seekonk-Providence River Estuary would be at least as instructive as additional salinity and concentration data. Trace metals are associated with a variety of materials (e.g. other ions, clay, particulate and dissolved organic matter). It is certainly worthwhile to consider the possibility that division of the total metal pool into dissolved and particulate fractions was inadequate to reliably predict observed concentrations or to predict what the effect of input abatement might be. Put simply, some forms of a particular metal may

behave conservatively, some may not and this might well have caused the poor correspondence between observed and modelled concentrations.

## Retrospective Comments on the Present Study

One hopes that experience renders hindsight clearer than foresight and it is with this concept in mind that the following are offered.

Combining an effort to resolve tidal variability with one to resolve that caused by allochthonous input significantly diminished the amount of data which could be brought to bear on the latter. Because of the way in which inputs to the system were measured, each cruise produced two sets of concentration data to be explained by a single estimate of input. The estimate of input had a decidedly low tide character (5 rivers measured at low tide only) and it is interesting to note that low tide estimates of lead concentration were better than high tide predictions. Inputs could have been measured twice as often (high and low tide) but given the available people the work load would have been prohibitive.

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As a first cut at answering the tide question, inputs need not be measured, only the concentrations and salinity in the estuary itself. If observed differences could not be explained by changing salinity, then tidal variation in river and treatment plant dishcarge would be worth investigation.

Although we have not examined tidal variability with great rigor, it is clear from the high  $\mathbb{R}^2$  of the predicted versus observed regressions for nutrients that the tidal component of variation can not have been large. For metals, although some differences were found, no consistent pattern emerged and actual calculated differences were small.

The data set with which we must resolve the input question is about half as powerful as it might have been. Instead of 12 different levels of input we have 6. Instead of 48 totally independent predicted concentrations of a constituent in each layer of the model we really have 24, with the status of the remaining 24 rather confused. From our analysis, it is clear that different processes affect metal concentrations in different regions of the estuary (see Table 8). Our ability to resolve these processes would have been greatly enhanced by a doubling of independent estimates.

In short, much effort was expended in quantifying an apparently unascendent source of variation (tidal) at the expense of a clearly dominant source (input).

On a more positive note, this study has certainly taught us much about the Seekonk-Providence River Estuary and will undoubtedly further our understanding of Narragansett Bay in general.

#### Acknowledgements

We thank Dr. Dana Kester for graciously allowing us to use his model. Doug Cullen, Kate Schweitzer, and Wayne Warren kindly provided data for metal concentrations. Steve Kelly competently took and analyzed inorganic nutrient samples. Laura Weber analyzed samples for particulate carbon and nitrogen. Laura Weber and Wayne Warren collected salinity data. The U.S. Geological Survey provided discharge data for rivers. The Narragansett Bay Project supplied sewage effluent discharge data. We also thank the numerous individuals who helped gather the data: M. Gustafson, J. Allan and R. Tombarri of the R/V Lauri Lee, E. Klos, E. Requintina, C. Brown, N. Craig, and V. Banzon of MERL, G. Hoffman, and R. Lapan of the EPA Narragansett Lab.

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Figures 2 - 39

Point Source Key

BR= Blackstone River

BV= Blackstone Valley Sewage Treatment Plant

TM= Ten Mile River

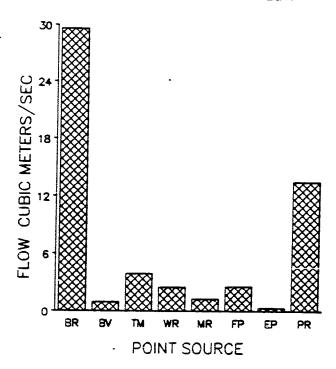
WR= Woonasquatucket

MR= Moshassuck River

FP= Field's Point Sewage Treatment Plant

EP= East Providence Sewage Treatment Plant

PR= Pawtuxet River



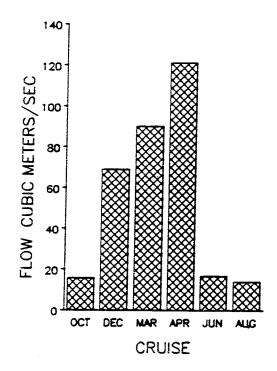
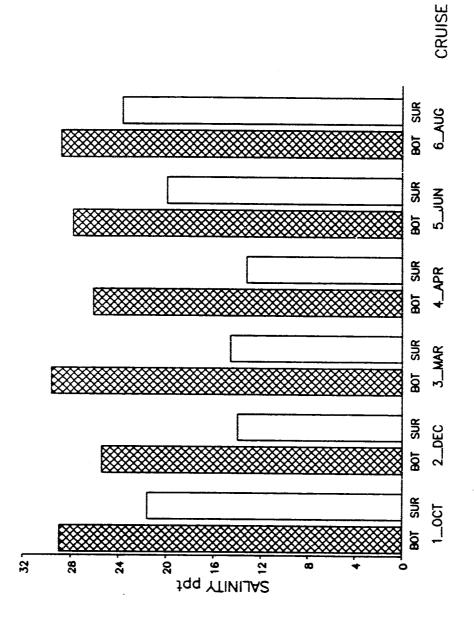
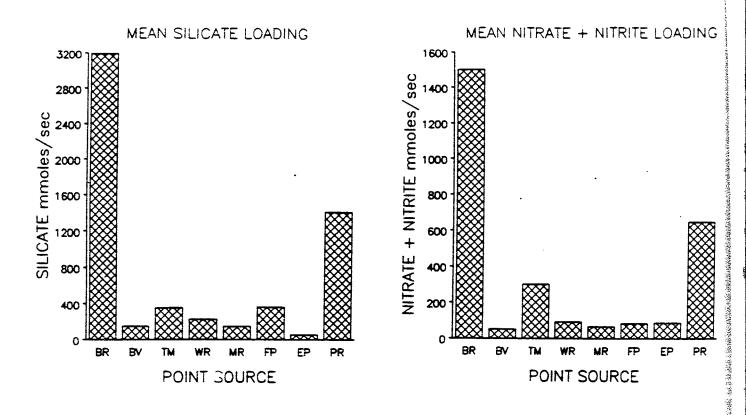


Figure 2: Freshwater to the Seekonk-Providence River estuary. Top panel:
Mean point source input for the six cruises. Bottom panel:
Total freshwater input for each cruise. Point sources as in
Figure 1.



Average surface and bottom water salinities observed in the Seekonk-Providence River Estuary during each cruise. Figure 3:



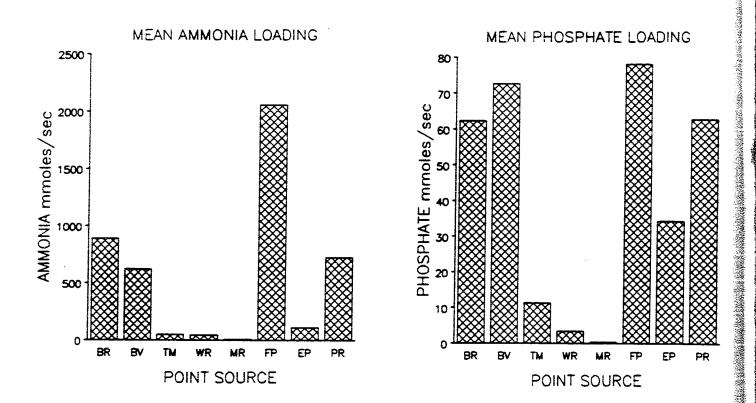
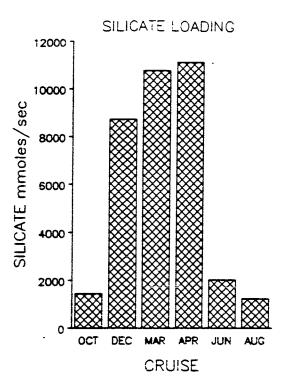
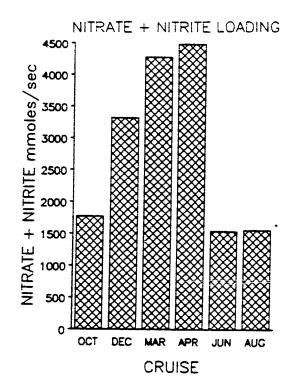


Figure 4: Mean discharge of nutrients by point sources observed during the study.





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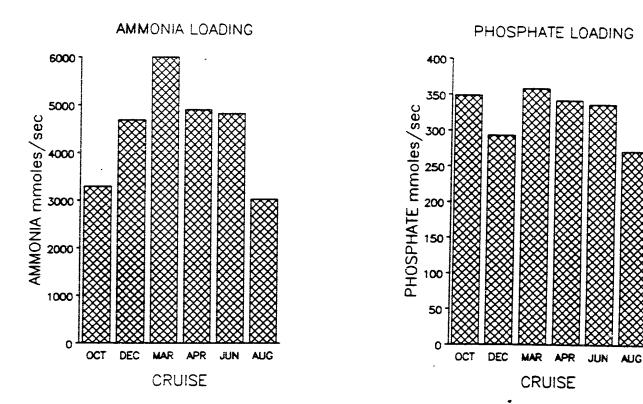
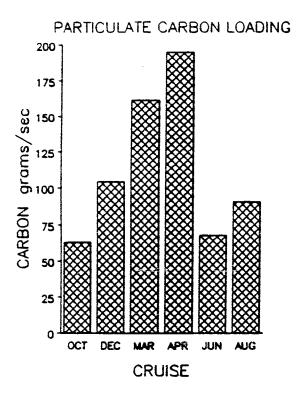
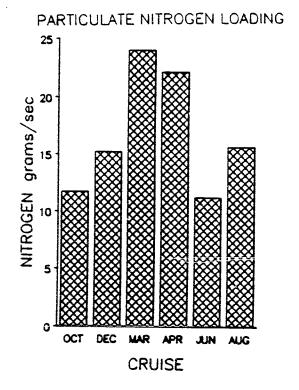
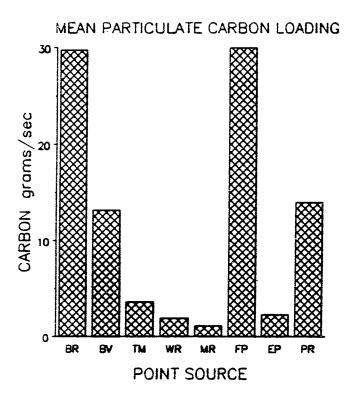


Figure 5: Total nutrient input for each cruise by all point sources.







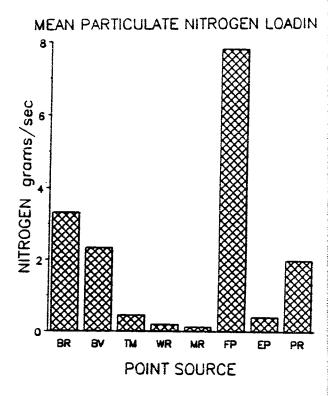
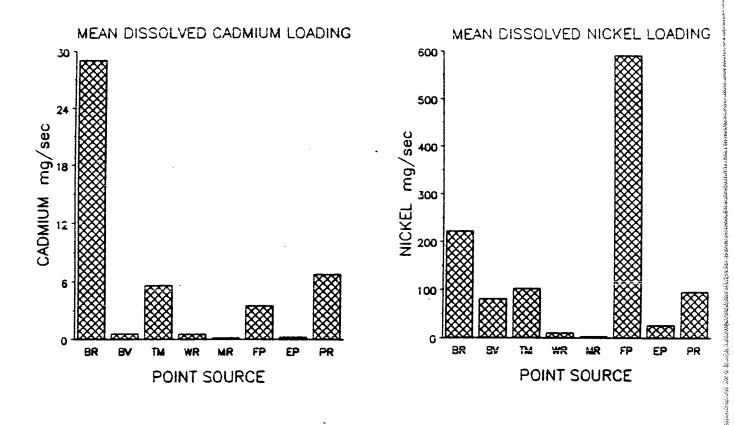
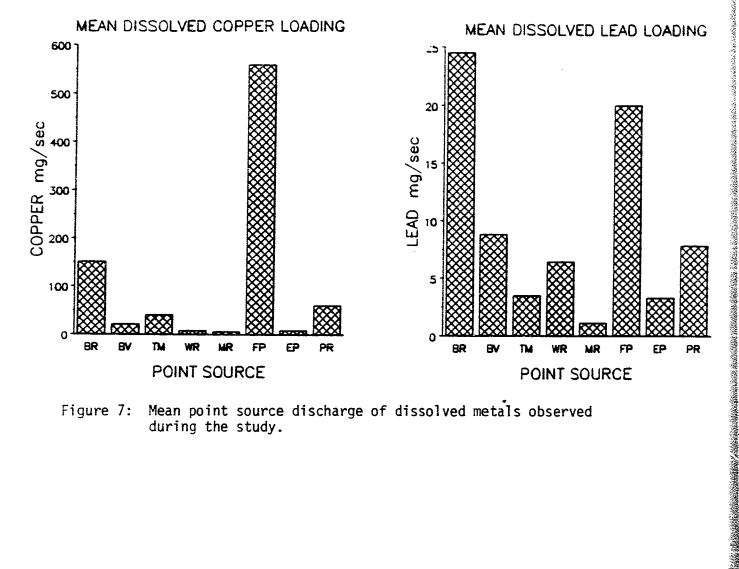
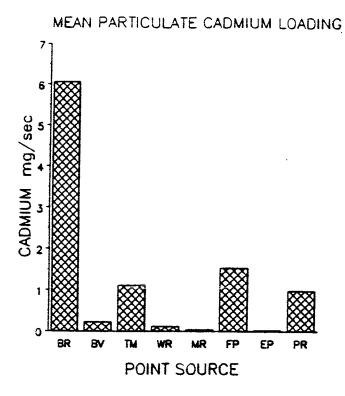


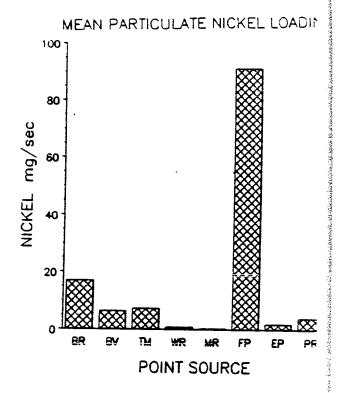
Figure 6: Mean discharge of particulate carbon and nitrogen by each point source and total discharge by all point sources for each cruise.

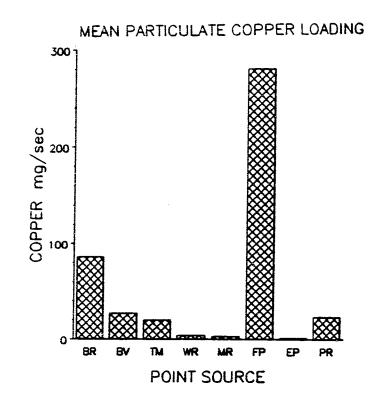




Mean point source discharge of dissolved metals observed Figure 7: during the study.







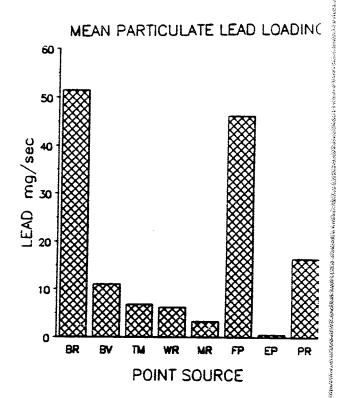
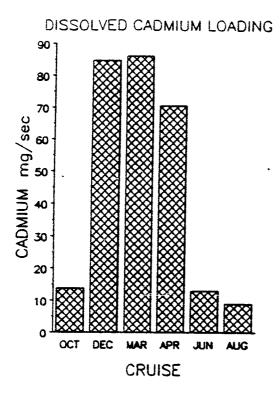
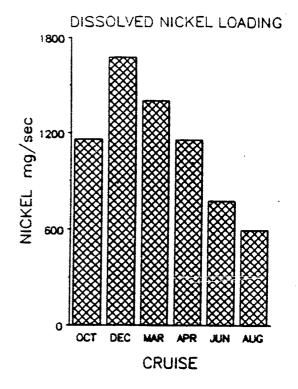
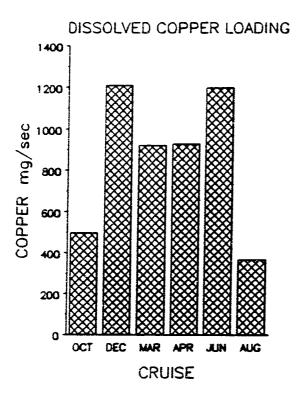


Figure 8: Mean point source dishcarge of particulate metals observed during the study.







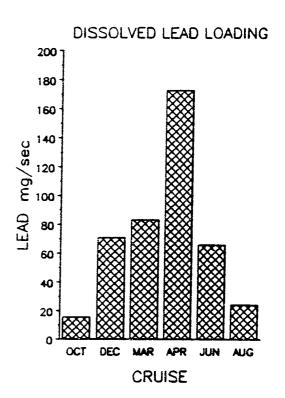
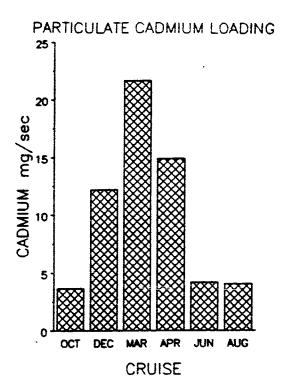
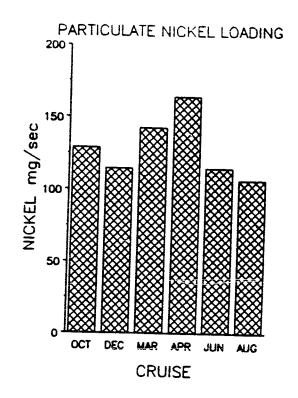
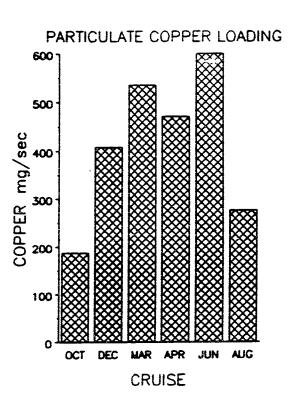
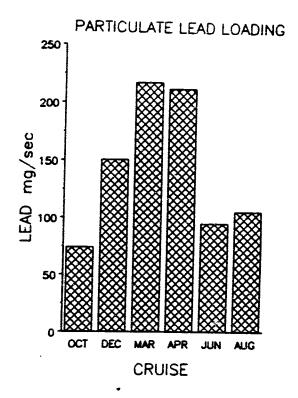


Figure 9: Dissolved metal discharge into the estuary by all point sources observed during each cruise.





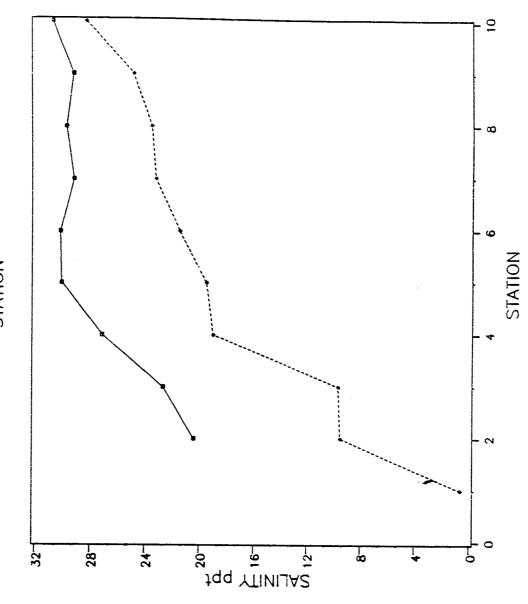




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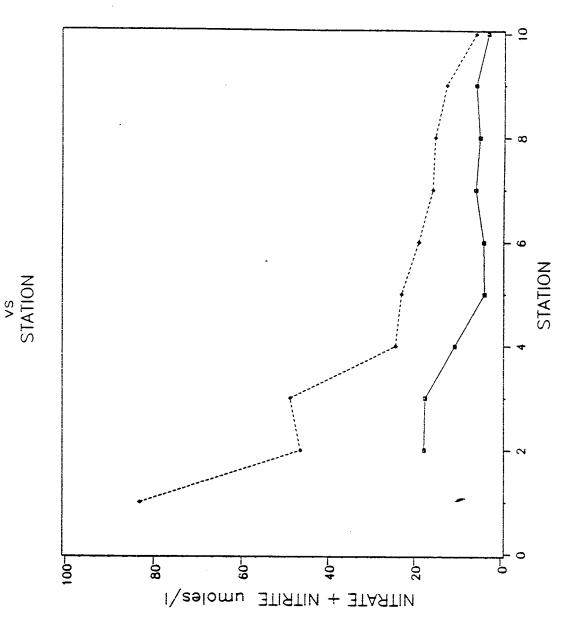
Figure 10: Particulate metal dishcarge into the estuary by all point sources observed during each cruise.

#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM SALINITY vs STATION



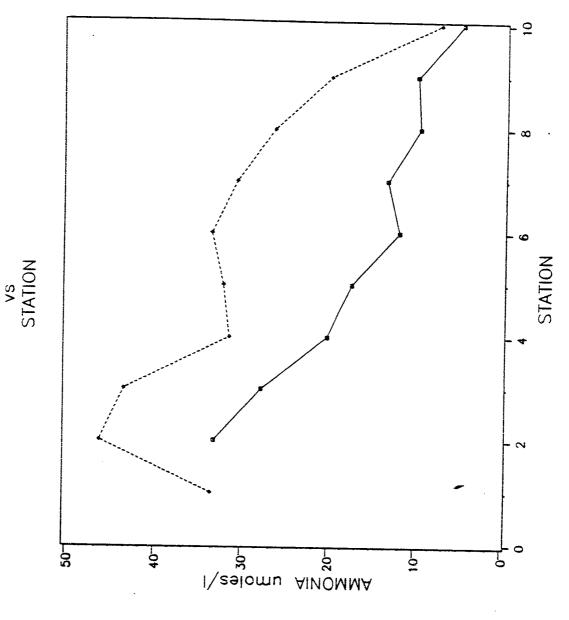
Average surface of a bottom salinity observed at each station during the six cruises. Dotted line = surface. Solid line = bottom. Figure 11:

### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM NITRATE + NITRITE



Average Nitrate - Nitrite concentration observed at each station during the six cruises. Key as in Figure 11. Figure 12:

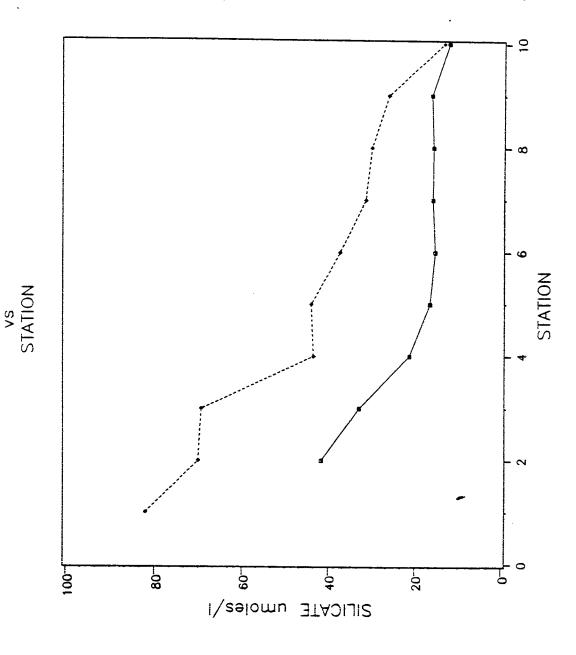
#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM AMMONIA VS



Average annonia concentration observed at each station during the six cruises. Key as in Figure 11. Figure 13:

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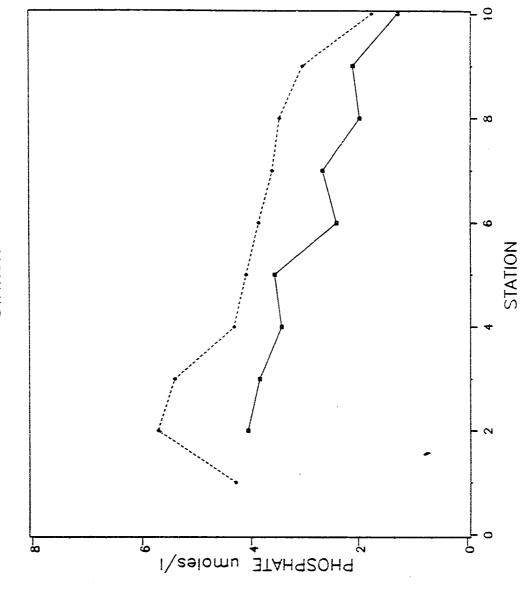
#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM SILICATE vs



Average silicate concentration observed at each station during the six cruises. Key as in Figure 11. Figure 14:

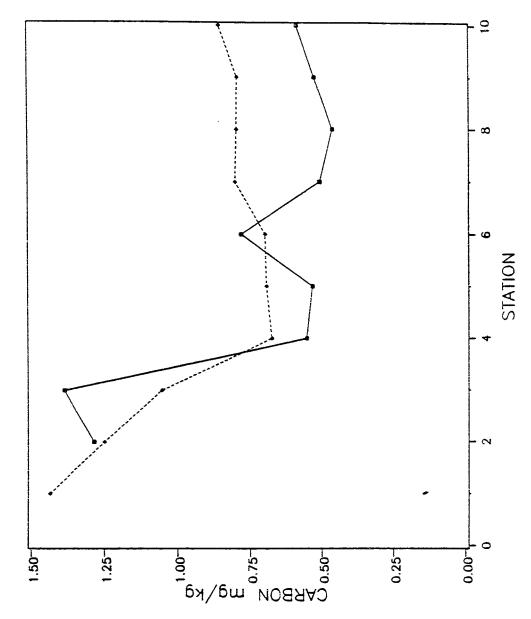
MARINE SENTINGENERAL PROPERTY OF THE PROPERTY

#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PHOSPHATE vs STATION



Average phosphate concentration observed at each station during the six cruises. Key as in Figure 11. Figure 15:

# SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PARTICULATE CARBON vs STATION



Average particulate carbon concentration observed at each station during the six cruises. Key as in Figure 11. Figure 16:

# SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PARTICULATE NITROGEN vs STATION

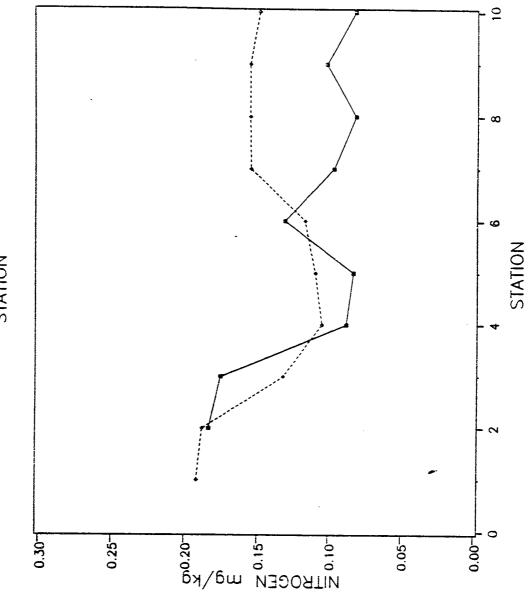
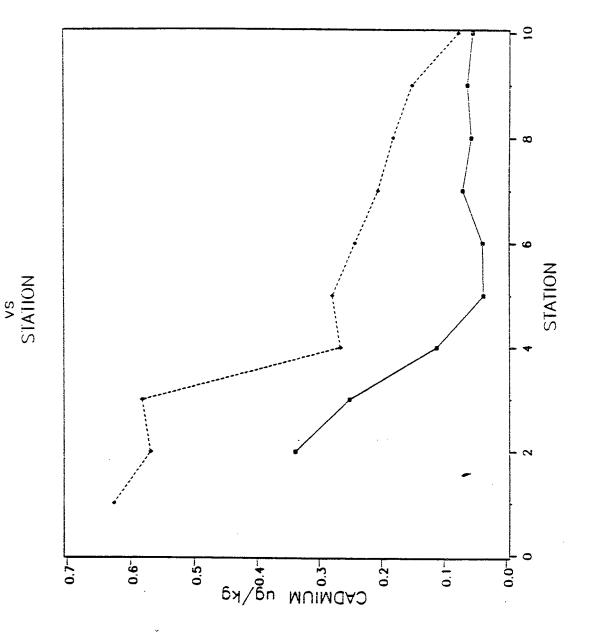


Figure 17: Average particulate nitrogen concentration observed at each station during the six cruises. Key as in Figure 11.

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#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM DISSOLVED CADMIUM vs



Average dissolved cadmium concentration observed at each station during the six cruises. Key as in Figure 11. Figure 18:

# SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PARTICULATE CADMIUM vs STATION

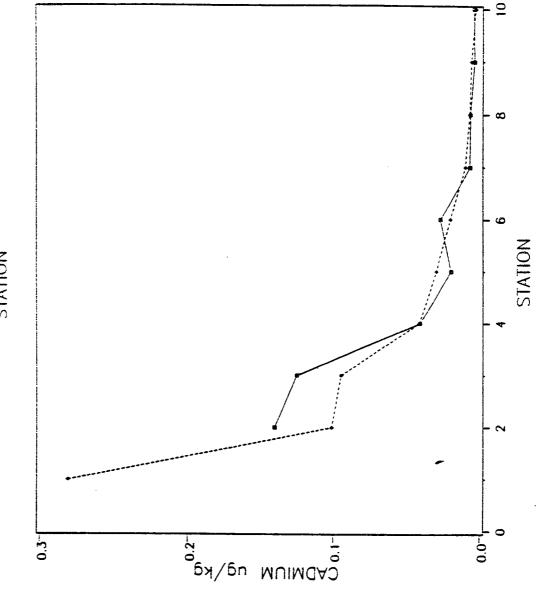
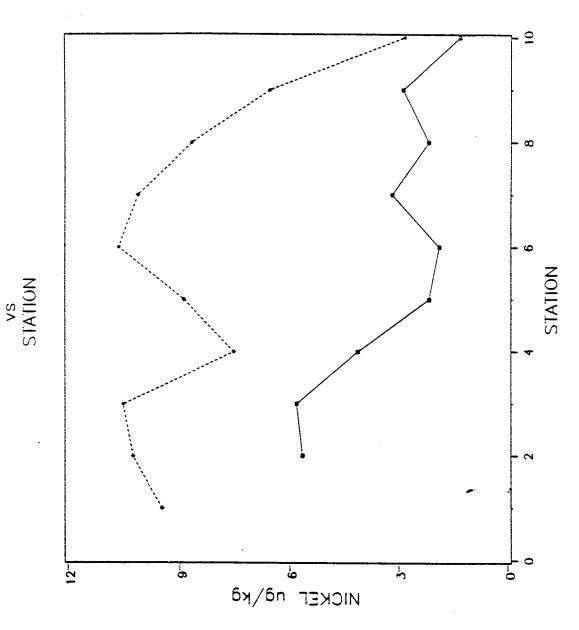


Figure 19: Average particulate cadmium. Explanation as in Figure 18.

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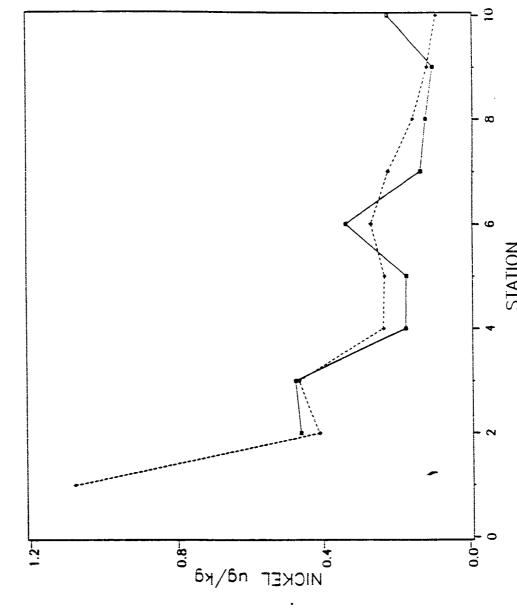
#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM DISSOLVED NICKEL vs



Average dissolved nickel concentration observed at each station during the six cruises. Key as in Figure 11. Figure 20:

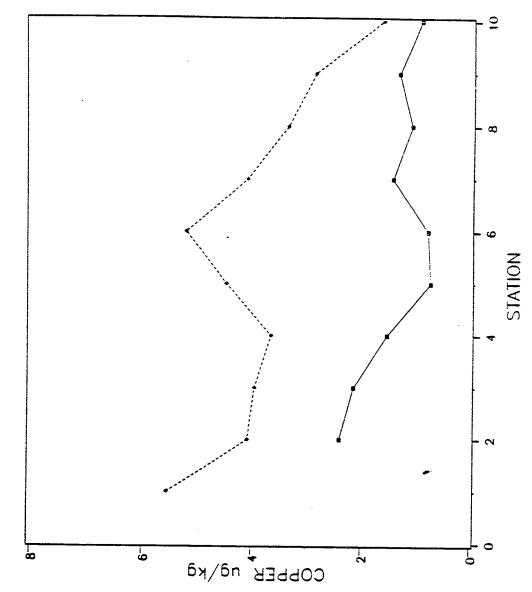
NORTH COLUMN CONTROL OF THE PROPERTY OF THE PR

# SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PARTICULATE NICKEL vs STATION



STATION Figure 21: Average particulate nickel. Explanation as in Figure 20.

## SPRAY CRUISES AVERAGE SURFACE AND BOTTOM DISSOLVED COPPER vs STATION



Average dissolved copper concentration observed at each station during the six cruises. Key as in Figure 11. Figure 22:

# SPRAY CRUISES AVERAGE SURFACE AND BOTIOM PARTICULATE COPPER vs STATION

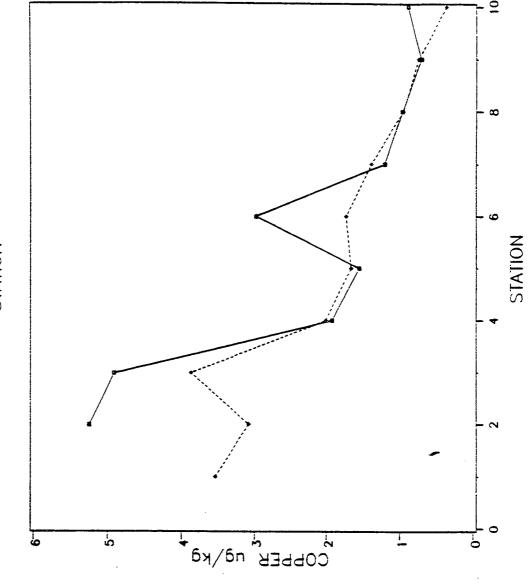


Figure 23: Average particulate copper. Explanation as in Figure 22.

#### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM DISSOLVED LEAD vs STATION

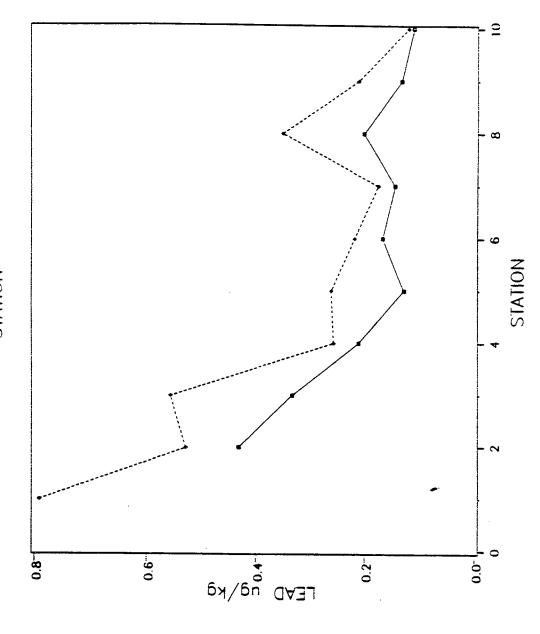


Figure 24: Average dissolved lead concentration observed at each station during the six cruises. Key as in Figure 11.

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### SPRAY CRUISES AVERAGE SURFACE AND BOTTOM PARTICULATE LEAD vs STATION

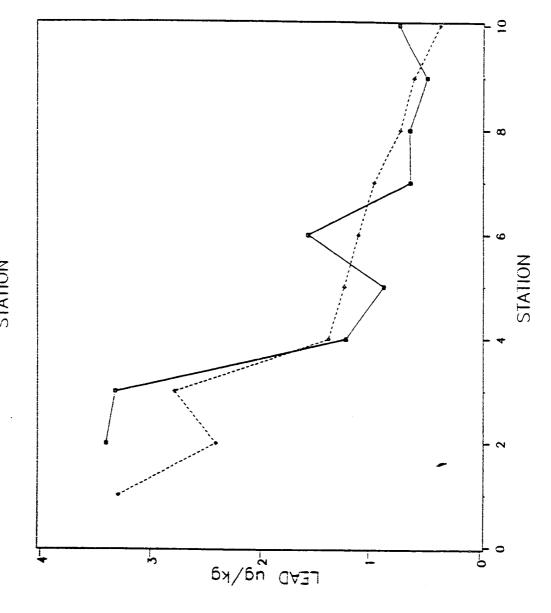
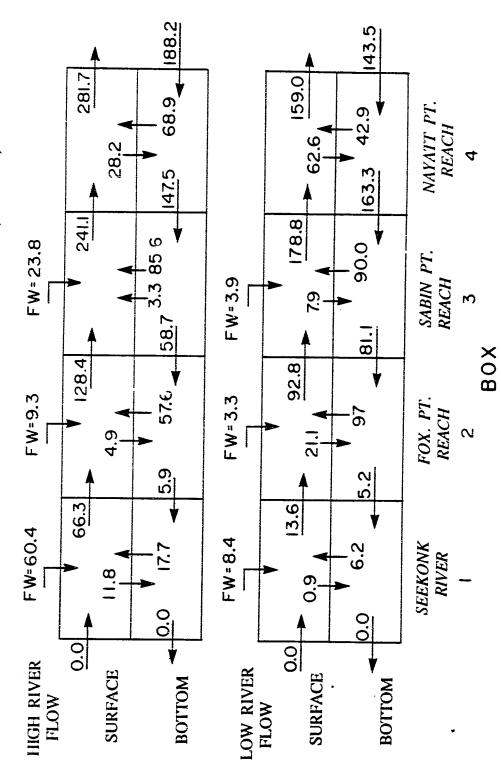


Figure 25: Average particulate lead. Explanation as in Figure 24.

#### SEEKONK AND PROVIDENCE RIVER BOX MODEL TRANSPORT COEFFICIENTS (m<sup>3</sup>/sec)



Box model results. Water transport coefficients  $(m^3/\sec)$  calculated from the model. FW= freshwater. Values are means for two river flow conditions encountered during the study: high river flow (Cruises 2, 3, 4) and low river flow (Cruises 1, 5, 6). Figure 26:

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# BOX MODEL RESULTS PREDICTED AND OBSERVED SILICATE CONCENTRATIONS IN SURFACE WATERS

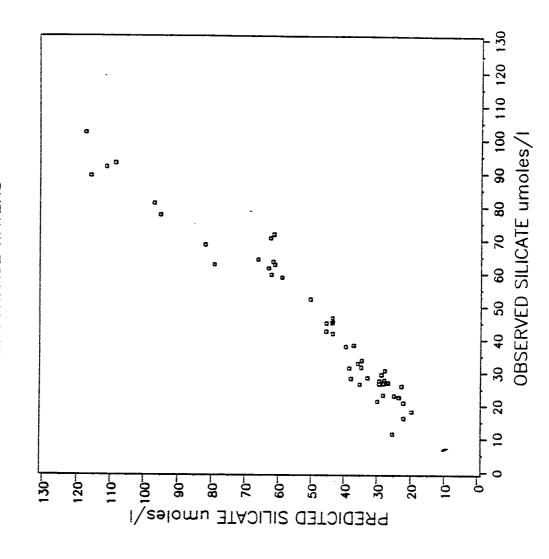
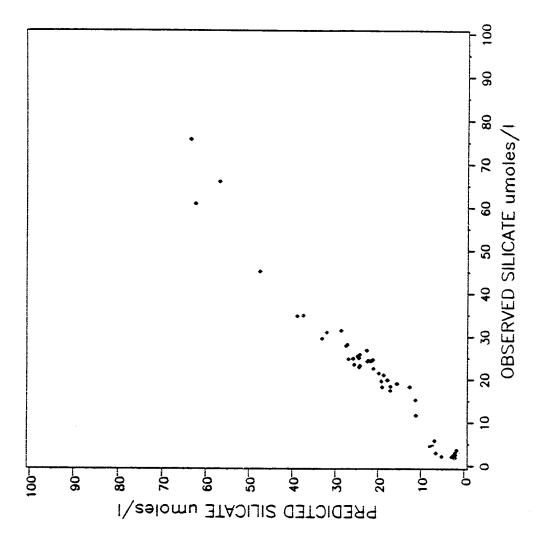


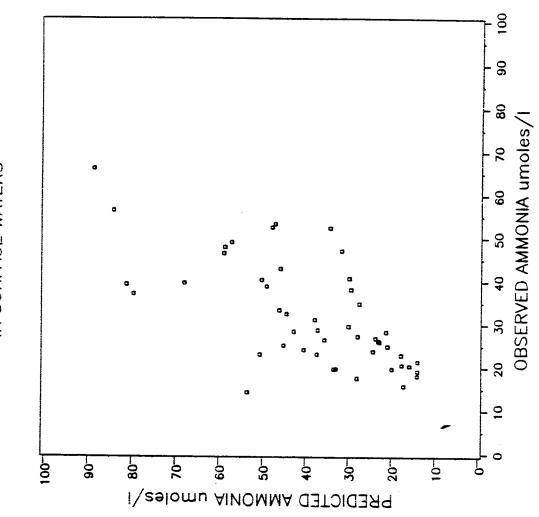
Figure 27: Box model results. Modelled concentrations of silicate (predicted) vs. those observed in surface waters in each of four boxes during six cruises.

BOX MODEL RESULTS
PREDICTED AND OBSERVED SILICATE CONCENTRATIONS
IN BOTTOM WATERS



Predicted vs. observed silicate in bottom waters. Box model results. Predict See Figure 27 for details. Figure 28:

BOX MODEL RESULTS PREDICTED AND OBSERVED AMMONIA CONCENTRATIONS IN SURFACE WATERS



See Figure 27 for details. Figure 29: Box model results for dissolved ammonia in surface waters.

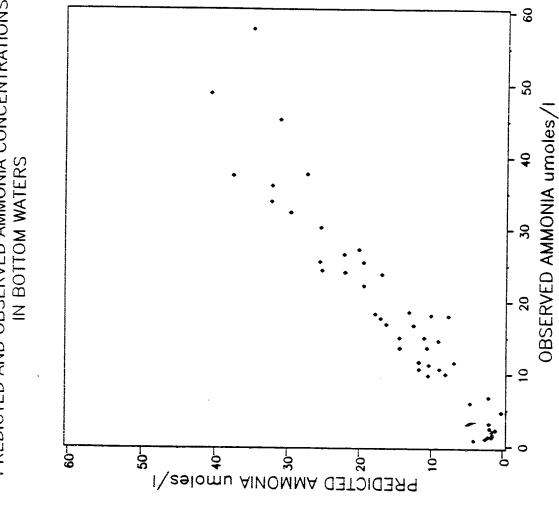


Figure 30: Box model results for dissolved ammonia in b4ttom waters. See Figure 27 for details.

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#### BOX MODEL RESULTS PREDICTED AND OBSERVED DISSOLVED CADMIUM CONCENTRATIONS IN SURFACE WATERS

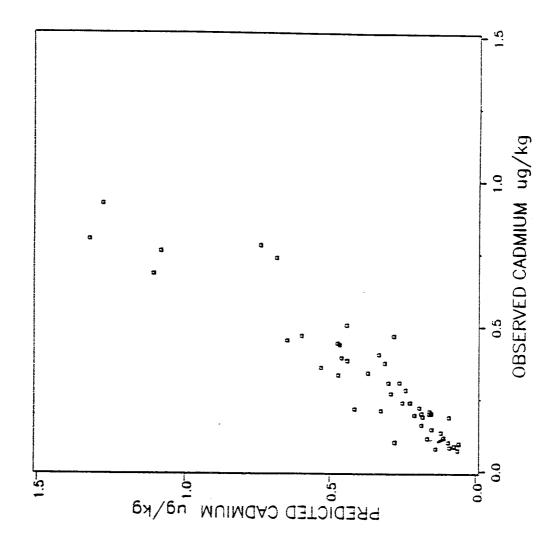


Figure 31: Box model results for dissolved cadmium in surface waters.

BOX MODEL RESULTS
PREDICTED AND OBSERVED DISSOLVED CAUMIUM
CONCENTRATIONS IN BOTTOM WATERS

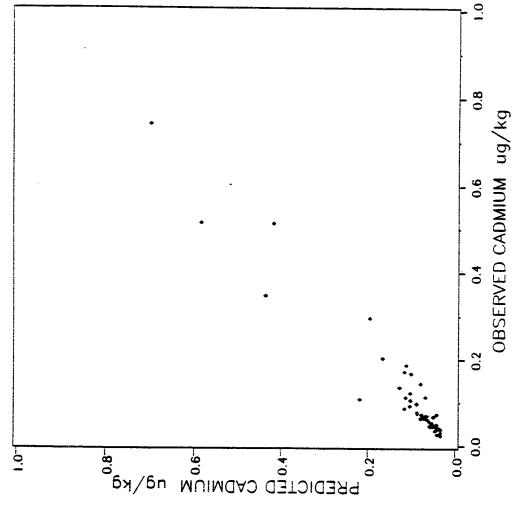


Figure 32: Box model results for dissolved cadmium in bottom waters,

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### BOX MODEL RESULTS PREDICTED AND OBSERVED PARTICULATE CADMIUM CONCENTRATIONS IN SURFACE WATERS

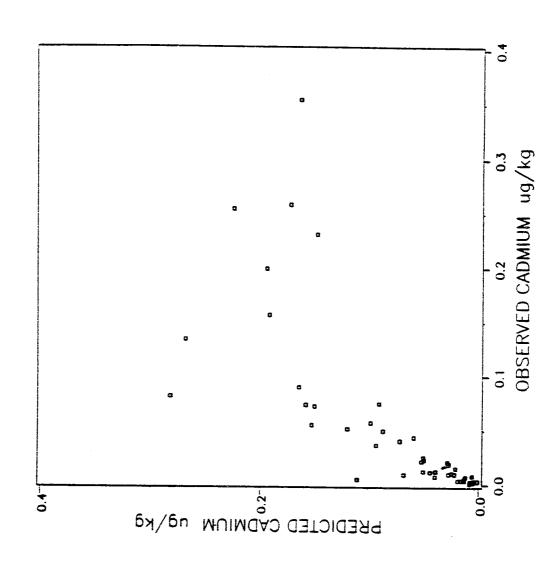


Figure 33: Box model results for particulate cadmium in surface waters.

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### BOX MODEL RESULTS PREDICTED AND OBSERVED PARTICULATE CADMIUM CONCENTRATIONS IN BOTTOM WATERS

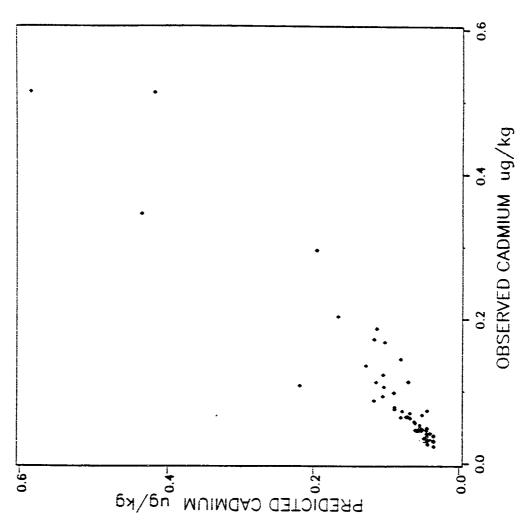


Figure 34: Box model results for particulate cadmium in bottom waters.