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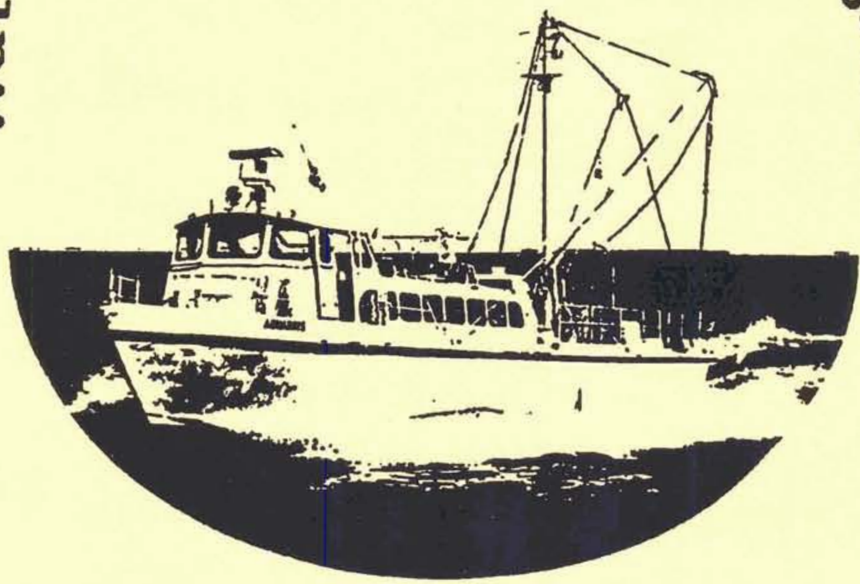
Chesapeake Bay

Water Quality Monitoring Program

ECOSYSTEMS PROCESSES COMPONENT (EPC)



LEVEL ONE REPORT #12

PART 1: Interpretive Report

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MARYLAND DEPARTMENT OF THE ENVIRONMENT

MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT NO. 12

INTERPRETIVE REPORT

(July 1984 - December 1994)

PREPARED FOR:

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PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in Contract **4-C-MDE 94** between the Maryland Department of the Environment (MDE), Chesapeake Bay and Special Projects Program and the University of Maryland System, Center for Environmental and Estuarine Studies (CEES).

This report outlines sampling and data management procedures used by the Ecosystems Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program to collect, analyze and interpret data. The remainder of the examines the long term trends and spatial features of sediment-water fluxes. Section 7 outlines a proposal for new approaches to ecosystem monitoring.

Sediment oxygen and nutrient exchanges (SONE) data for all previous years, August 1984 through December 1991, were submitted as a four volume reference data set with the Level 1, Interpretive Reports. Data volumes I and II containing data for August 1984 through December 1989 were submitted with the Level 1, No. 7 Interpretive Report [UMCEES]CBL Ref. No. 90-062 (Boynton *et al.*, 1990). One set of changes pages has been inserted into Volumes I and II (Boynton, Rohland and Matteson, 1992). Volume III contains SONE data tables for 1990 through 1991 and Volume IV contains VFX data for 1990 through 1992 (Appendix C). The VFX program was terminated on 3rd June, 1992 when the sediment traps were finally retrieved. The VFX data set is now complete. These two volumes were part of Level One, Report No. 9 [UMCEES]CBL Ref. No. 92-042 (Boynton *et al.*, 1992). SONE data for 1992 and 1993 was submitted with the yearly Interpretive Reports (Boynton *et al.*, 1992, 1993b) and data sheets for these years are being prepared before incorporation into these volumes. The SONE data for 1994 is submitted in Part II: Data Tables: Appendix B of with this report. Variable names, used in data tables, together with a description of the units presently used in these programs, and the matching variable used in the public information data base of the Chesapeake Bay Program called CHESSEE are listed in Appendix A: Data Tables, and in the EPC Data Dictionary (Boynton and Rohland, 1990). Entries are arranged alphabetically using the MDE/EPC table names.

A copy of the Ecosystem Processes Component Data Dictionary is available on request from Dr. R. Eskin (Maryland Department of the Environment) or from Dr. F.M. Rohland (Chesapeake Biological Laboratory). Any specific questions concerning changes in file or variable names should be directed to: Dr. F.M. Rohland: Tel. (410) 326-7215.

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No additional data has subsequently been collected.

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ABSTRACT

The 1994 objectives of the Ecosystem Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program are to: (1) characterize the present state of the bay relative to sediment-water nutrient and oxygen exchanges (2) determine the long-term trends that develop in sediment-water exchanges and deposition rates in response to pollution control programs, and (3) integrate the information collected in this program with other elements of the monitoring program.

Measurements of sediment-water nutrient and oxygen exchanges were made six times during 1994 between mid-May and mid-October at two locations in the mainstem bay, at single locations in two tributary rivers (lower Choptank and Potomac Rivers) and at four locations in the Patuxent River.

This program was initiated in July 1984, and the basic data collection scheme has been followed through December 1994 with one major exception. The collection of data to determine the rate of deposition of organic matter to deep waters and sediments at one site (R-64) in the Maryland mainstem bay (referred to as the Vertical Flux [VFX] study of this monitoring program in previous reports) was discontinued after June 3, 1992 due to fiscal constraints of the monitoring program. Data collected during the 1994 monitoring period is evaluated in detail in this report. A discussion of significant ecological trends and interpretation of relationships observed during the ten years of the sediment-water nutrient and oxygen exchanges (SONE) monitoring program are presented.

During the winter-spring period of 1994, all four of the major systems monitored, Susquehanna (Maryland mainstem bay), Potomac, Patuxent and Choptank Rivers, experienced both freshwater flows and nutrient loads which were associated with the spring freshet from the major rivers entering these systems (Susquehanna, Potomac, Patuxent and Choptank Rivers). In all cases the freshet of 1994 was much larger than previous years with the exception of 1993. Flows for the remaining portion of the year closely followed the pattern of previous years and were average.

During the monitoring period temperature ranged from 15.8 - 29.3 C and salinity conditions ranged between 3.1 - 22.3 ppt during 1994. Bottom water salinities were lower than usual in spring due to the strong winter-spring freshet and higher than usual during late summer. At some locations there were very low dissolved oxygen concentrations observed during spring and summer (*e.g.* 0.1 mg l^{-1} at Marsh Point [MRPT] in June, 1994) which is not normally the case and was probably caused by the high river flows of 1994.

Rates of sediment-water fluxes of oxygen (SOC) in the Patuxent River during 1994 ranged from -0.16 g O_2 m^{-2} day^{-1} to -3.02 g O_2 m^{-2} day^{-1} while sediment oxygen consumption (SOC) at all other monitoring stations ranged from near -0.01 g O_2 m^{-2} day^{-1} to -3.27 g O_2 m^{-2} day^{-1}. In part, these low rates were the result of severely depressed oxygen concentrations in bottom waters which occurred earlier than normal in 1994.

Ammonium (NH_4^+) fluxes in the Patuxent River were higher (33% of the observations exceeded one standard error of long-term means) than those recorded in earlier years probably as a response to the large spring river flow (and associated diffuse source nutrient load) which occurred in 1994. Despite important reductions in point source nitrogen (N) and phosphorus (P) loads to this system, it appears that wet years generate enough diffuse source loading to produce high sediment nutrient fluxes. Ammonium (NH_4^+) fluxes were also higher than normal in the lower Potomac River (Ragged Point [RGPT], lower in the

mainstem bay (Point No Point [PNPT]) and in the lower Choptank River (Horn Point [HNPT]). Average or below average mainstem bay (R-64) ammonium (NH_4^+) fluxes possibly resulted from lower than normal deposition in this zone of the bay in 1994 due to the down bay transport of the spring bloom. Fluxes of nitrate plus nitrite (NO_2^- + NO_3^-) were occasionally larger than usual at most stations and with few exceptions were directed into sediments in response to high nitrate concentrations in bottom waters.

During 1994, inorganic phosphate (DIP or PO_4^-) fluxes generally followed the pattern of ammonium (NH_4^+) fluxes with enhancements at most stations. Silicate fluxes ($Si(OH)_4$) tended to be slightly above average at most stations in the Patuxent River but average or slightly below average at the remaining sites.

Selected environmental variables (river flow and bottom water dissolved oxygen concentrations) and key sediment nutrient fluxes (ammonium and phosphate) were examined for the entire monitoring period (1985 - 1994). Strong relationships of flux to river flow were found and the importance of low dissolved oxygen concentrations on sediment phosphorus flux confirmed.

Measurements were made at some additional locations as well as at SONE sites during 1994. Several of these sites were heavily impacted by organic matter and nutrient loads (*e.g.* Inner Harbor of the Patapsco River). Sediment fluxes from these and SONE locations were compared in terms of flux magnitude and the impacts of these fluxes on water quality conditions. Impacts ranged from severe to moderate at this collection of sites.

Three new approaches to monitoring impacts of nutrient and organic matter enrichment were also investigated during 1994. A method of increasing spatial resolution of the SONE program was introduced. This approach involves using sediment chlorophyll-a, sediment Eh (redox potential) and bottom water dissolved oxygen conditions as predictors of flux. These variables would be mapped at fine spatial scales in spring and early summer and flux magnitude calculated based on these conditions. Data would be stored and manipulated using a Geographic Information System (GIS) approach. Field data are presented which indicate the feasibility of the approach. Secondly, a method for measuring total sediment metabolism which is consistent with the needs of a monitoring program has been implemented. Recently developed and reliable technology is used to detect changes in total inorganic carbon flux (TCO_2 flux at a reasonable cost. Data based on TCO_2 fluxes were compared with sediment oxygen consumption (SOC) rates and were found to be appreciably larger, as expected. The technique completely avoids the low dissolved oxygen problems associated with SOC rate measurements. Finally, a series of community metabolism measurements is presented (*i.e.* water column production and respiration rates using the open water diel oxygen technique) made at the lower end of the turbidity maximum zone of the Patuxent River during 1964, a period pre-dating serious enrichment of the river. These data were compared with exactly the same measurements made in 1992. Both the magnitude of production and respiration and the seasonal patterns differed markedly between these periods. It is suggested that implementing such measurements would serve as a sensitive monitoring tool for gauging the recovery of this system.

2. INTRODUCTION

During the past decade much has been learned about the effects of both natural and anthropogenic nutrient inputs (*e.g.*, nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and oxygen conditions in deep waters (Nixon, 1981, 1988; Kemp *et al.*, 1983 ; D'Elia *et al.*, 1983; Malone, 1992; and Kemp and Boynton, 1992). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production are sustained through summer and fall periods by benthic recycling of essential nutrients and (3) deposition of organic matter from surface to deep waters links these processes of production and consumption (Boynton *et al.*, 1982a ; Garber *et al.*, 1989).

2.1 The Role of Sediments and Depositional Processes in Determining Chesapeake Bay Water Quality Conditions

Research conducted in Chesapeake Bay and other estuaries indicates that estuarine sediments can act as both important storages and sources of nutrients as well as sites of intense organic matter and oxygen consumption (Kemp and Boynton, 1984). For example, during summer periods in the Choptank and Patuxent estuaries, 40-70% of the total oxygen utilization was associated with sediments and 25-70% of algal nitrogen demand was supplied from estuarine sediments (Boynton *et al.*, 1982b). Processes of this magnitude have a pronounced effect on estuarine water quality and habitat conditions. Sediments in much of Chesapeake Bay, especially the upper bay and tributary rivers, contain significant amounts of carbon, nitrogen, phosphorus and other compounds (Boynton *et al.*, 1992). A large percentage of this material appears to reach sediments following the termination of the spring bloom and again after the fall bloom. A portion of this material is available to regenerative processes and once transformed into inorganic nutrients again becomes available for algal utilization. Nutrients and other materials deposited or buried in sediments represent the potential "water quality memory" of the bay.

2.2. Conceptual Model of Estuarine Nutrient and Water Quality Processes in Chesapeake Bay

Nutrients and organic matter enter the bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on bay waters. Dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. Much of this particulate material then sinks to the bottom and is potentially available for remineralization. Essential nutrients released during the decomposition of organic matter may then again be utilized by algal communities. A portion of this newly produced organic matter sinks to the bottom, contributing to the development of anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative capacities and the potentially large nutrient storages in bottom sediments ensure a large return flux of nutrients from sediments to the water column and thus sustain continued phytoplankton growth. Continued growth supports deposition of organics to deep waters, creating anoxic conditions typically associated with eutrophication of estuarine systems. To a considerable extent, it is the magnitude of these processes which determines nutrient and oxygen water quality conditions in many zones of the bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings decrease, changes in the magnitude of the processes monitored in this program will serve as a guide in determining the effectiveness of strategies aimed at improving bay water quality and habitat conditions. The schematic diagram in Figure 2-1. summarizes this conceptual eutrophication model where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced nitrogen and phosphorous loads lead to a restoration trajectory. Sediment processes play a prominent role in both trajectories.

Within the context of this model a monitoring study of deposition, sediment oxygen demand and sediment nutrient regeneration has been initiated and has continued since 1984. The working hypothesis is that if nutrient and organic matter loading to the bay decreases then the cycle of deposition to sediments, sediment oxygen demand, release of sediment nutrients and continued high algal production will also decrease. Since benthic processes exert important influences on water quality conditions, changes in these processes will serve as important indications of the effectiveness of nutrient control actions.

2.3 Objectives of the Water Quality Monitoring Program

The objectives of the Ecosystem Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program, which at present only comprises the sediment oxygen and nutrient exchanges (SONE) program as the Vertical Flux (VFX) study was discontinued in mid-1992 due to fiscal constraints, are to:

1) Characterize the present state of the bay (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and oxygen consumption rates.

2) Determine the long-term trends that develop in sediment-water exchanges in response to pollution control programs.

3) Integrate the information collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting Chesapeake Bay water quality and its impact on living resources.

2.4 Status of the Ecosystem Processes Component of the Maryland Chesapeake Bay Water Quality Monitoring Program

The Chesapeake Bay Water Quality Monitoring Program was initiated to provide guidelines for restoration, protection and future use of the mainstem estuary and tributaries and to provide evaluations of implemented management actions directed towards alleviating some critical pollution problems. In order to achieve these goals, the monitoring program design was composed of the three phases outlined above. In addition to the EPC portion, the monitoring program also has components which measure: (1) nutrient and pollutant input rates, (2) chemical and physical properties of the water column, (3) toxicant levels in sediments and organisms, (4) phytoplankton and zooplankton populations and (5) benthic community characteristics. A complete description of the monitoring program is provided in Magnien *et al.* (1987).

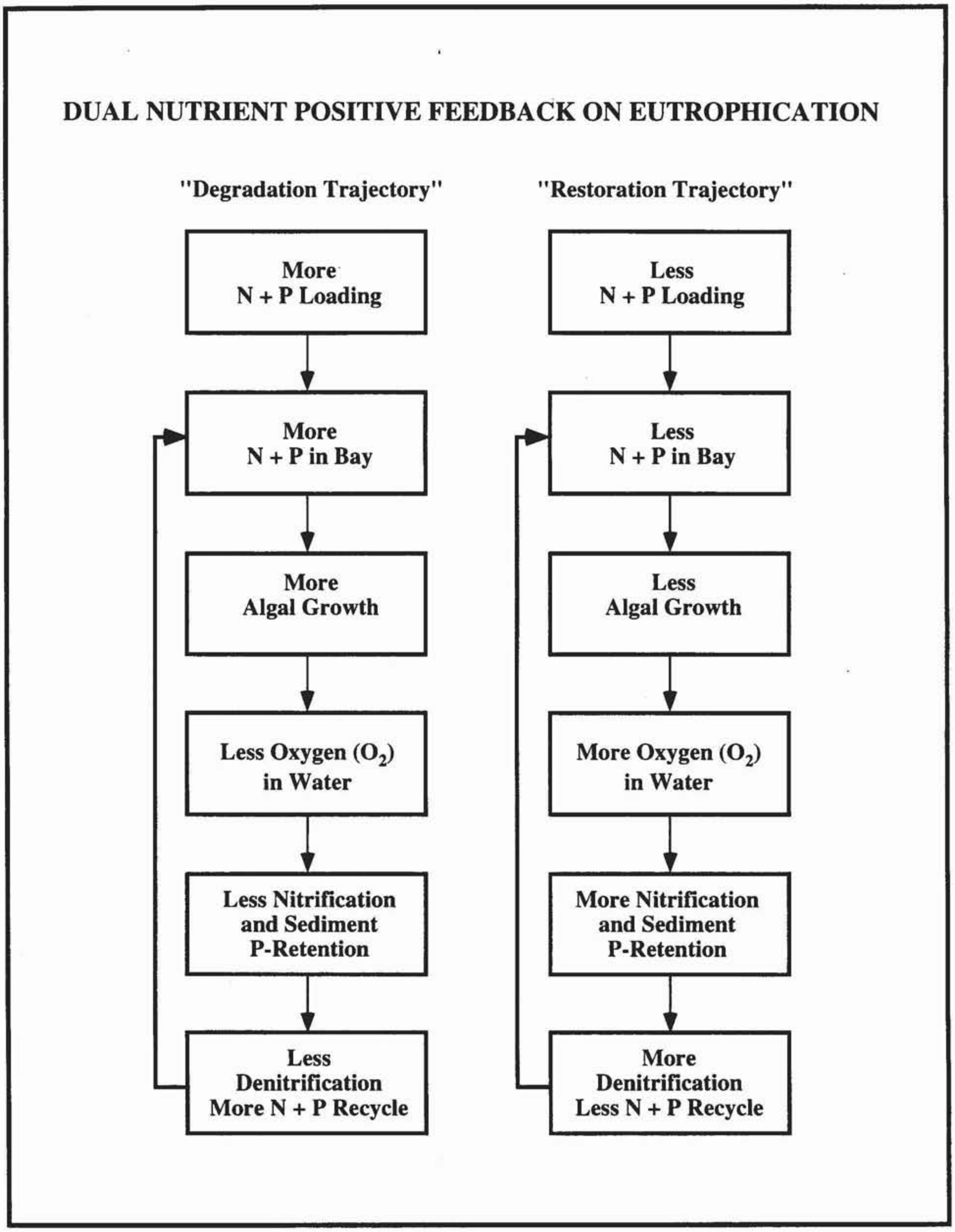

Figure 2-1. Nitrogen (N) and phosphorus (P) loads to the Chesapeake Bay affect coupled sediment nitrification-denitrification and sediment nitrogen and phosphorus cycling. High nitrogen and phosphorus inputs will ultimately result in less nitrogen and phosphorus removal from the benthos, while significant decreases in these inputs will lead to greater removal. (Adapted from Kemp, *pers. comm.*, HPEL)

The first phase of the study was undertaken over a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation, which were keys in the identification of problem areas. The EPC measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and the sediment surface. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of EPC monitoring have been summarized in a series of interpretive reports (Boynton *et al.*, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992b, 1993b and 1994). The results of this characterization effort have largely confirmed the importance of deposition and sediment processes in determining water quality and habitat conditions.

The second phase of the monitoring effort, completed during 1988 through 1990, identified interrelationships and trends in key processes monitored during the initial phase of the program. The EPC was able to identify trends in sediment-water exchanges and deposition rates. Important factors regulating these processes have also been identified and related to water quality conditions (Kemp and Boynton, 1992; Boynton *et al.*, 1991).

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay was reevaluated. In this phase of the process, the monitoring program will be used to assess the appropriateness of targeted nutrient load reductions as well as provide indications of water quality patterns which will result from such management actions.

The preliminary reevaluation report (Progress Report of the Baywide Nutrient Reduction Reevaluation, 1992) included the following conclusions: nonpoint sources of nutrients contributed approximately 77% of the nitrogen and 66% of the phosphorus entering the bay; agricultural sources are dominant followed by forest and urban sources; the "controllable" fraction of nutrient loads is about 47% for nitrogen and 70% for phosphorus; point source reductions are ahead of schedule and diffuse source reductions are close to projected reductions; further efforts are needed to reduce diffuse sources; significant reductions in phosphorus concentrations and slight increases in nitrogen concentrations have been observed in some areas of the bay; areas of low dissolved oxygen have been quantified and living resource water quality goals established; simulation model projections indicate significant reductions in low dissolved oxygen conditions associated with a 40% reduction of controllable nutrient loads.

Sediment Oxygen and Nutrient Exchanges (SONE) program data collected during 1994 are presented in this report. Sediment-water fluxes are examined to determine long term trends and to propose and outline a method which could be used to extend spatial resolution. Finally two new and effective monitoring tools are described which will provide valuable information about the sediment metabolism of this ecosystem, these include the measurement of TCO_2 under both anoxic and oxic conditions and the continuous recording of four previously monitored open water metabolism measurements at Benedict bridge.

3. ACQUISITION AND MANAGEMENT OF SEDIMENT NUTRIENT AND OXYGEN EXCHANGES (SONE) DATA

3.1 Location of Sediment Oxygen and Nutrient Exchanges (SONE) Stations*

During 1994, measurements of sediment-water oxygen and nutrient exchanges (SONE) were made six times at eight locations; two stations in the mainstem bay and at least one station in each of three major tributary rivers (Patuxent, Choptank, and Potomac). These locations shown in Figure 3-1. (specific location details are given in Tables 3-1.1., 3-1.2. and 3-1.3. also EPC Data Dictionary, Boynton and Rohland, 1990; Figure B-6. and Tables B-5.2. and B-5.3.) were selected based on prior knowledge of the general patterns of sediment-water nutrient and oxygen exchanges in Chesapeake Bay.

When the program was initiated in mid 1984 reference was made to several earlier studies (Boynton, Kemp and Osborne, 1980; Boynton, Kemp and Barnes, 1985 and Boynton and Kemp, 1985) which reported the following:

1) Along the mainstem of the Maryland portion of the bay, fluxes were moderate in the upper bay, large in the mid-bay and minimal in the lower bay.

2) Fluxes in the transition zone of tributaries were larger than those observed in the downstream higher salinity portions of tributaries.

Based on this information the original series of ten SONE stations were located along the mainstem bay from Still Pond Neck in the upper bay to Point No Point near the mouth of the Potomac River. A pair of stations were established in each of the three tributaries (Potomac, Patuxent, and Choptank Rivers), one in the transition zone and one in the lower estuary. In all cases, station locations were selected to have depths and sediment characteristics representative of the estuarine zone being monitored.

In a few instances (Patuxent stations and Choptank station at Horn Point [HNPT]) SONE stations are not located exactly at the same site as other Maryland Chesapeake Bay Water Quality Monitoring Program stations, although they are close (< 10 km). The prime reason for including these stations was the considerable amount of benthic flux data available from the SONE sites selected in the Patuxent and Choptank Rivers that could be used by the monitoring program. In all cases SONE and MDE stations are in the same estuarine zone. Benthic fluxes are reasonably similar over small spatial scales (10-20 km) within estuarine zones of similar salinity, sediment type and depth; therefore, this program retains a high degree of comparability with other program components (Boynton *et al.*, 1982b).

This basic data collection scheme initiated in July, 1984 has been followed through December 1994. Prior to July 1989, four of the ten SONE stations sampled were located along the salinity gradient in the mainstem bay between Point No Point (north of the mouth of the Potomac River) and Still Pond Neck (20 km south of the Susquehanna River mouth). Two stations were located in each of three tributary rivers (Patuxent River: Buena Vista [BUVA] and St. Leonard Creek [STLC], Choptank River: Windy Hill [WDHL] and Horn Point [HNPT] and Potomac River: Maryland Point [MDPT] and Ragged Point [RGPT]),

* Deposition measurements referred to as the Vertical Flux (VFX) study in previous reports at one site, R-64, were discontinued on June 3, 1992 due to fiscal constraints.

one in the turbidity maximum or salinity transition zone and one in the lower mesohaline region. After July 1, 1989 sampling at all of the upper tributaries (except in the Patuxent River) and sampling at the two upper mainstem stations was discontinued and two stations (Marsh Point [MRPT] and Broomes Island [BRIS]) were added in the Patuxent River (Figure 3-1. and Table 3-1.1.). These modifications were made in response to budget constraints, but also to improve spatial resolution in the Patuxent River which is a focal point of management activities.

Figure 3-1. shows both current and previously sampled monitoring stations of the sediment oxygen and nutrient exchanges (SONE) program. A comprehensive listing of all SONE stations, providing the station code names, associated latitude and longitude, basin and station location description and references to the nearest MDE station are outlined in Tables 3-1.1., 3-1.2. and 3-1.3. and in the Ecosystem Processes Component (EPC) Data Dictionary (Tables B-5.1., B-5.2. and B-5.3.; Boynton and Rohland, 1990). In 1994, two of the eight stations sampled as part of the SONE study are located in the mainstem bay adjacent to Point No Point (north of the mouth of the Potomac River) and Buoy R-64 (south of the Choptank River mouth). Four stations are located in the Patuxent River estuary and one each in the lower mesohaline regions of the Choptank and Potomac Rivers. The salinity characteristics of each station and the four salinity codes are listed in Table 3-2. (also in EPC Data Dictionary, Table B-7.; Boynton and Rohland, 1990).

3.2 Sampling Frequency

The sampling frequency for the sediment oxygen and nutrient exchanges (SONE) program is based on the seasonal patterns of sediment water exchanges observed in previous studies conducted in the Chesapeake Bay region (Kemp and Boynton, 1980; Kemp and Boynton, 1981; Boynton *et al.*, 1982b; and Boynton and Kemp, 1985). These studies indicated four distinct periods over an annual cycle including:

1) A period characterized by the presence of a large macrofaunal community, high concentrations of nitrite in surface waters and the development and deposition of the spring phytoplankton bloom (April - June). Characteristics of sediment water nutrient and oxygen exchanges typically include the following: relatively high sediment oxygen consumption (SOC) rates, nitrate uptake by sediments and low exchange rates of other nutrients.

2) A period during which macrofaunal biomass is low but water temperature and water column metabolic activity high with anoxia prevalent in deeper waters (July - September). Characteristics of sediment water nutrient and oxygen exchanges typically include the following: low sediment oxygen consumption (SOC) and nitrate flux rates, very high releases of ammonium (NH_4^+), phosphate (PO_4^-) and silicate ($Si(OH)_4$).

3) A period in the fall when anoxia is not present and macrofaunal community abundance is low but re-establishing (October - November). Characteristics of sediment water nutrient and oxygen exchanges typically include the following: increased sediment oxygen consumption (SOC) flux rates, intermediate release rates of ammonium (NH_4^+), phosphate (PO_4^-) and silicate ($Si(OH)_4$) and occasional nitrate release.

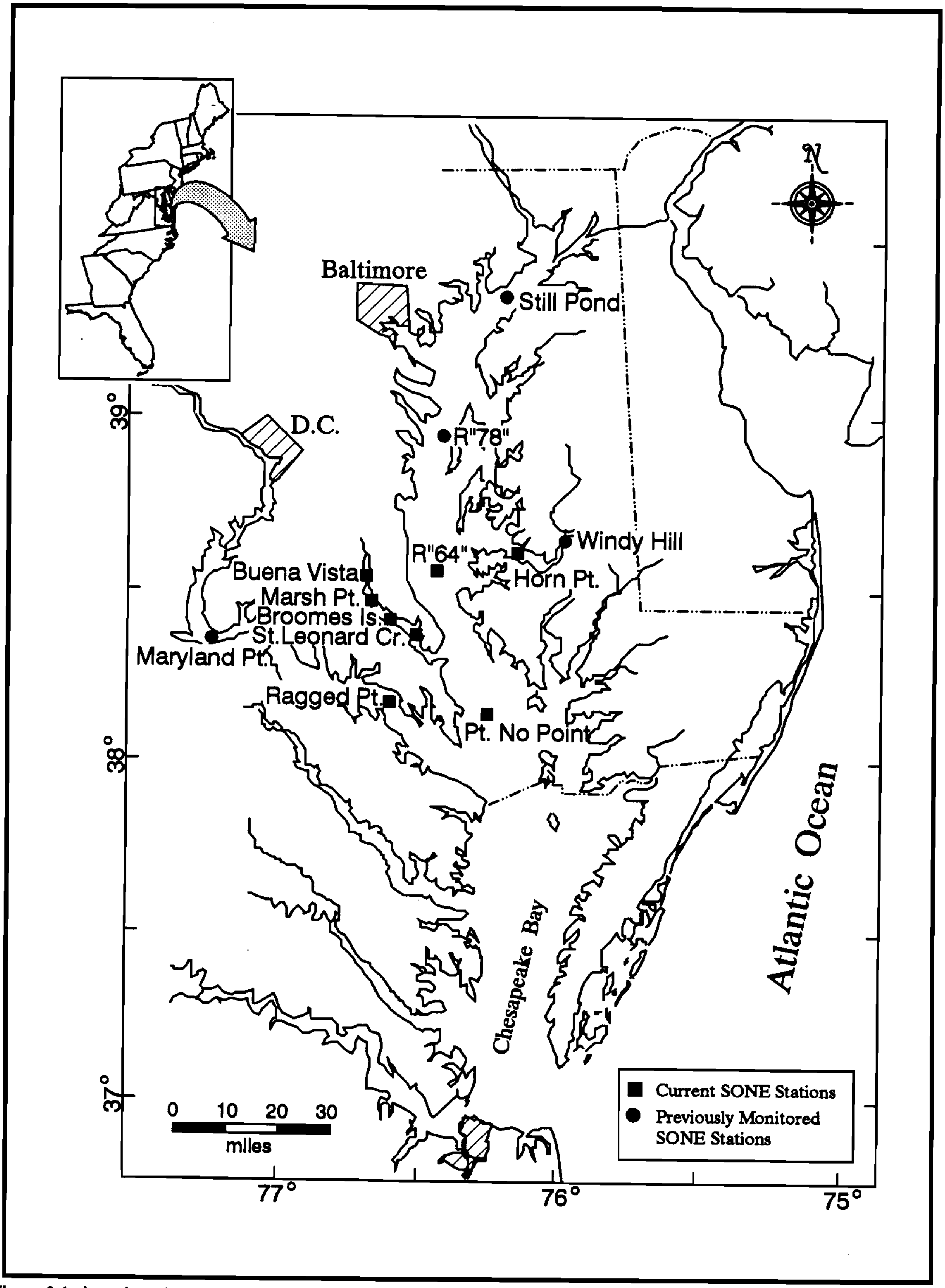

Figure 3-1. Location of Current and Previously sampled Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations in the Maryland portion of Chesapeake Bay (1984 - 1994).

Table 3-1.1. SONE Station Name, ID and Sampling Order

REGION	STATION NAME	STATION CODE NAME	SAMPLING ORDER* A B
Patuxent River	St. Leonard Creek	STLC	1 1
	Broomes Island	BRIS	2
	Marsh Point	MRPT	3
	Buena Vista	BUVA	2 4
Choptank River	Horn Point	HNPT	3 5
Potomac River	Ragged Point	RGPT	5 6
Chesapeake Mainstem	Point No Point	PNPT	7 7
	Buoy R-64	R-64	8 8

NOTES:

A = Stations sampled in SONE 1-20, August 1984 - June 1989. Numerical ranking indicates the order in which the stations appear in the data tables.

B = Stations sampled beginning with SONE 21 and future samples. Numerical ranking indicates the order in which the stations appear in the data tables.

* Prior to July 1, 1989, measurements at SONE stations were made four times per year (April or May, June, August and October or November). During 1990 and 1991, measurements were made five times per year (May, June, July, August and October) and six times in 1992, 1993 and 1994 (May, June, July, August, September and October).

Table 3-1.2. SONE Station Code, Grid Location and Nearest MDE Station

STATION CODE NAME	LATITUDE DEG MIN	LONGITUDE DEG MIN	STATION DEPTH	MDE STATION	BAY SEGMENT
Patuxent River					
STLC	38° 22.88'	76° 30.06'	7.0	XDE2792	LE1
BRIS	38° 23.64'	76° 33.17'	15.0	XDE2792	LE1
MRPT	38° 26.81'	76° 30.06'	5.2	XDE5339	LE1
BUVA	38° 31.12'	76° 39.82'	5.8	XDE9401	RET1
Choptank River					
HNPT	38° 37.18'	76° 08.09'	8.2	MET5.2	ET5
Potomac River					
RGPT	38° 09.86'	76° 35.52'	16.5	XBE9541	LE2
Chesapeake Mainstem					
PNPT	38° 07.99'	76° 15.13'	14.2	MCB5.2	CB5
R-64	38° 33.59'	76° 26.63'	16.8	MCB4.3C	CB4

Table 3-1.3. SONE Station Code and Description

STATION CODE NAME	DESCRIPTION
Patuxent River	
STLC	7.5 nautical miles upstream of Patuxent River mouth. (R km[1] = 12.1)
BRIS	10 nautical miles upstream of Patuxent River mouth. (R km[1] = 16.1)
MRPT	14.5 nautical miles upstream of Patuxent River mouth. (R km[1] = 23.4)
BUVA	0.75 nautical miles north of Route 231 Bridge at Benedict, MD. (R km[1] = 31.5)
Choptank River	
HNPT	4.0 nautical miles downstream of Route 50 Bridge at Cambridge, MD. (R km[1] = 18.6)
Potomac River	
RGPT	1.5 nautical miles WNW of Bouy 51-B. (R km[1] = 29.8)
Chesapeake Mainstem	
PNPT	3.2 nautical miles east of Point No Point. (R km[1] = 129.0)
R-64	300 yards north east of Channel Buoy R-64.* (R km[1] = 177.4)

NOTES:

* Marked buoy number corresponds to numbering system prior to USCG renumbering.

[1] River kilometers (R km) are measured from the mouth of the river or Chesapeake Bay.

Table 3-2. Station Salinity

STATION CODE	SALINITY CODE
Patuxent River	
STLC	M
BRIS	M
MRPT	M
BUVA	O
Choptank River	
HNPT	M
WDHL	O
Potomac River	
RGPT	M
MDPT	O
Chesapeake Mainstem	
PNPT	M
R-64	M
SLPD	O

The Salinity Zone layer codes are as follows:

SALINITY CODE	DESCRIPTION	
F	Freshwater	
O	Oligohaline	0.5 - 5.0 ppt
M	Mesohaline	5.0 - 18.0 ppt
P	Polyhaline	18.0 - 32.0 ppt

4) A winter period (December - March) when fluxes are very low due primarily to low temperature. No samples were collected during the period November through April.

Previous studies also indicate that short-term temporal (day-month) variation in these exchanges is small; however, considerable differences in the magnitude and characteristics of fluxes appear among distinctively different estuarine zones (*i.e.*, tidal fresh *vs.* mesohaline regions). In light of these results, the monitoring design adopted for the SONE study involves six monthly measurements made between May and October, 1994, SONE 47 through SONE 52. A complete listing giving the sampling dates of all SONE cruises (1984 - 1994) together with alpha-numeric cruise identification codes can be found in Table 3-3.

3.3 Field Methods

Details concerning methodologies are described in the Ecosystem Processes Component (EPC) Study Plan (Garber *et al.*, 1987) and fully documented in the EPC Data Dictionary (Boynton and Rohland, 1990). Field activities are reviewed in sections 3.3.1 through 3.3.4.

3.3.1. Water Column Profiles

At each of the eight SONE stations (ten stations prior to July 1989), vertical water column profiles of temperature, salinity and dissolved oxygen are measured at 2 meter intervals from the surface to the bottom immediately after obtaining intact sediment cores for incubation. The turbidity of surface waters is measured using a Secchi disc.

3.3.2 Water Column Nutrients

Near-surface (approximately 0.5 meters) and near-bottom (approximately 1 meter) water samples are also collected using a high volume submersible pump system. Samples are filtered, where appropriate, using 0.7 μm GF/F filter pads, and immediately frozen. Samples are analyzed by Nutrient Analytical Services Laboratory (NASL) for the following dissolved nutrients and particulate materials: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), dissolved inorganic phosphorus corrected for salinity (DIP or PO_4^-), silicious acid ($Si(OH)_4$), particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations and seston content.

Measurements of total dissolved nitrogen (TDN: $NH_4^+ + NO_2^- + NO_3^-$ + DON), and total dissolved phosphorus (TDP: DIP + DOP) were discontinued at the end of the 1987 calendar year due to reduction in finances related to the grant supplied by the funding agency. Near-surface samples were discontinued in July 1991 (SONE 31) as these measurements are not of particular importance in the interpretation of flux data. This was also necessary due to further budget reductions.

3.3.3 Sediment Profiles

At each SONE station an intact sediment core is used to measure the redox potential, (Eh, mV) of sediments at 1 cm intervals to about 10 cm. Additionally, surficial sediments are sampled to a depth of 1 cm (2 mm since 9 August 1989) for particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), and total and active chlorophyll-a concentrations.

Table 3-3. SONE Cruise Identifier

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 01	AUG 1984	27 AUG	30 AUG	Aquarius
SONE 02	OCT 1984	15 OCT	18 OCT	Aquarius
SONE 03	MAY 1985	06 MAY	09 MAY	Aquarius
SONE 04	JUN 1985	24 JUN	27 JUN	Aquarius
SONE 05	AUG 1985	19 AUG	22 AUG	Aquarius
SONE 06	OCT 1985	14 OCT	17 OCT	Aquarius
SONE 07	MAY 1986	03 MAY	08 MAY	Aquarius
SONE 08	JUN 1986	23 JUN	26 JUN	Aquarius
SONE 09	AUG 1986	18 AUG	22 AUG	Orion
SONE 10	NOV 1986	10 NOV	13 NOV	Aquarius
SONE 11	APR 1987	20 APR	23 APR	Aquarius
SONE 12	JUN 1987	10 JUN	15 JUN	Aquarius
SONE 13	AUG 1987	17 AUG	20 AUG	Aquarius
SONE 14	NOV 1987	09 NOV	16 NOV	Aquarius
SONE 15	APR 1988	17 APR	22 APR	Aquarius
SONE 16	JUN 1988	01 JUN	07 JUN	Aquarius
SONE 17	AUG 1988	15 AUG	21 AUG	Aquarius
SONE 18	NOV 1988	01 NOV	09 NOV	Aquarius
SONE 19	APR 1989	04 APR	10 APR	Aquarius
SONE 20	JUN 1989	12 JUN	16 JUN	Aquarius
SONE 21	JUL 1989	12 JUL	14 JUL	Aquarius
SONE 22	AUG 1989	14 AUG	16 AUG	Aquarius
SONE 23	OCT 1989	16 OCT	18 OCT	Aquarius
SONE 24	MAY 1990	1 MAY	3 MAY	Orion
		8 MAY	8 MAY	Aquarius
SONE 25	JUN 1990	11 JUN	14 JUN	Aquarius
SONE 26	JUL 1990	16 JUL	19 JUL	Aquarius
SONE 27	AUG 1990	17 AUG	22 AUG	Aquarius
SONE 28	OCT 1990	15 OCT	18 OCT	Aquarius
SONE 29	MAY 1991	6 MAY	9 MAY	Aquarius
SONE 30	JUN 1991	10 JUN	13 JUN	Aquarius
SONE 31	JUL 1991	22 JUL*	25 JUN	Aquarius
SONE 32	AUG 1991	15 AUG	15 AUG	Aquarius
		19 AUG*	22 AUG	
SONE 33	SEP 1991	16 SEP	18 SEP	Aquarius
SONE 34	OCT 1991	14 OCT (14, 15, 18 OCT)	18 OCT	Aquarius

NOTES:

* Data was also collected for the Pooles Island Dredge Survey (PIDS) Program at:
GCNT in Jul and Aug 1991

Table 3-3. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 35	MAY 1992	18 MAY	21 MAY	Aquarius
SONE 36	JUN 1992*	15 JUN	18 JUN	Aquarius
SONE 37	JUL 1992*	13 JUL	17 JUL	Orion
SONE 38	AUG 1992*	10 AUG	14 AUG	Aquarius
SONE 39	SEP 1992	08 SEP	10 SEP	Aquarius
SONE 40	OCT 1992	05 OCT	08 OCT	Aquarius
SONE 41	MAY 1993	17 MAY	20 MAY	Aquarius
SONE 42	JUN 1993*	10 JUN	11 JUN	Orion
		14 JUN	15 JUN	
SONE 43	JUL 1993*	19 JUL	22 JUL	Orion
SONE 44	AUG 1993*	16 AUG	20 AUG	Aquarius
SONE 45	SEP 1993	13 SEP	16 SEP	Aquarius
SONE 46	OCT 1993	11 OCT	15 OCT	Aquarius
SONE 47	MAY 1994	16 MAY	18 MAY	Aquarius
		20 MAY	21 MAY	
SONE 48	JUN 1994*	13 JUN	17 JUN	Orion
		20 JUN		
SONE 49	JUL 1994*	11 JUL		Orion
		13 JUL	15 JUL	
SONE 50	AUG 1994*	8 AUG	11 AUG	Orion
		15 AUG		
SONE 51	SEP 1994	12 SEP	14 SEP	Orion
SONE 52	OCT 1994	11 OCT	12 OCT	Orion
		17 OCT	18 OCT	

NOTES:

* Data was also collected for the Pooles Island Dredge Survey (PIDS) Program at:
GCNT in Jun, Jul and Aug 1992, PLIS in Jul and Aug 1992, GC-1 in Aug 1992, GC-2 in Aug 1992
for the Pooles Island Reconfiguration Assessment (PIRAS) Study at:
PLIS in Jun, Jul and Aug 1993, GWST in Jun 1993, GTST in Jun and Jul 1993, GW-1 in Aug 1993
and for the G-West Berm Monitoring Study at:
PLIS in Jun, Jul and Aug 1994, GW-2 in Jun, Jul and Aug 1994

3.3.4 Sediment Cores

Intact sediment cores are obtained at each SONE station using a modified Bouma box corer. After deployment and retrieval of the box corer, the metal box is removed to reveal the Plexiglas liner containing the sediment core. The core is visually inspected for disturbance. A satisfactory core is placed in a darkened incubator maintained at ambient temperature prior to further processing.

Three intact cores are used to estimate net exchanges of oxygen and dissolved nutrients between sediments and overlying waters (Figure 3-2.). Prior to beginning flux measurements, the overlying water in the core is replaced by fresh bottom water to ensure that water quality conditions in the core closely approximate *in situ* conditions. Gentle circulation of water, with no induction of sediment resuspension, is maintained in the cores during the measurement period via the stirring devices attached to the oxygen (O_2) probes. The cores are placed in a darkened water bath to maintain ambient temperature. Oxygen concentrations are recorded and overlying water samples (35 ml) are extracted from each core every 30 to 60 minutes (depending on the rate of oxygen uptake) over a 2 to 5 hour incubation period. During the incubation period, five overlying water samples are extracted from each core. As a nutrient sample is extracted from a core, an equal amount of ambient bottom water is added. An opaque Plexiglas liner filled with bottom water, incubated and sampled as described above, serves as a blank. Overlying water samples are filtered and immediately frozen for later analysis for ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate (NO_2^- + NO_3^-), dissolved inorganic phosphorous (DIP or PO_4^-) and silicious acid ($Si(OH)_4$) concentrations. Oxygen and nutrient fluxes are estimated by calculating the mean rate of change in concentration over the incubation period and converting the volumetric rate to a flux using the volume:area ratio of each core.

It should be noted that at low oxygen concentrations (< 2 mg l^{-1}) sediment oxygen consumption (SOC) rate measurements underestimate actual sediment metabolism because much of the decomposition of organic matter is supported through anaerobic pathways (primarily sulfate reduction). Additionally sediment oxygen consumption (SOC) rates made under low dissolved oxygen (DO) conditions do not capture the eventual oxygen demand that is exerted by the reoxidation of reduced compounds (primarily H_2S) formed during anaerobic periods. Prior to 1989, between five and seven of the sediment oxygen and nutrient exchanges (SONE) stations rarely if ever experienced low bottom water dissolved oxygen (DO) concentrations. Since 1989, SONE stations have been modified and only three of eight stations rarely experience low oxygen concentrations. Hypoxic conditions are common at the remaining stations and influence sediment oxygen consumption (SOC) rates. This represents a methodological limitation which is more serious given the current configuration of stations in the study. A method for measuring total sediment metabolism (dissolved inorganic carbon flux) is being developed (but is at present not yet ready for use in the monitoring program) which is independent of oxygen conditions. During 1993 and 1994, a series of preliminary measurements of sulfate reduction ($SO_4^=$) were made. It appears that this method may be useful for measuring anaerobic metabolism.

3.3.5 Methodology for Measurement of Sulfate Reduction Rates

The method developed for the Ecosystem Processes Component (EPC) Monitoring Program measures sulfate reduction, the dominant form of anaerobic metabolism in Chesapeake Bay. It is reasonably inexpensive and the minicores needed for further laboratory analysis are collected in the field during the normal SONE cruise. The method is based on the time dependent disappearance of sulfate from pore waters of an intact sediment minicore incubated under anoxic conditions at ambient temperature for the period

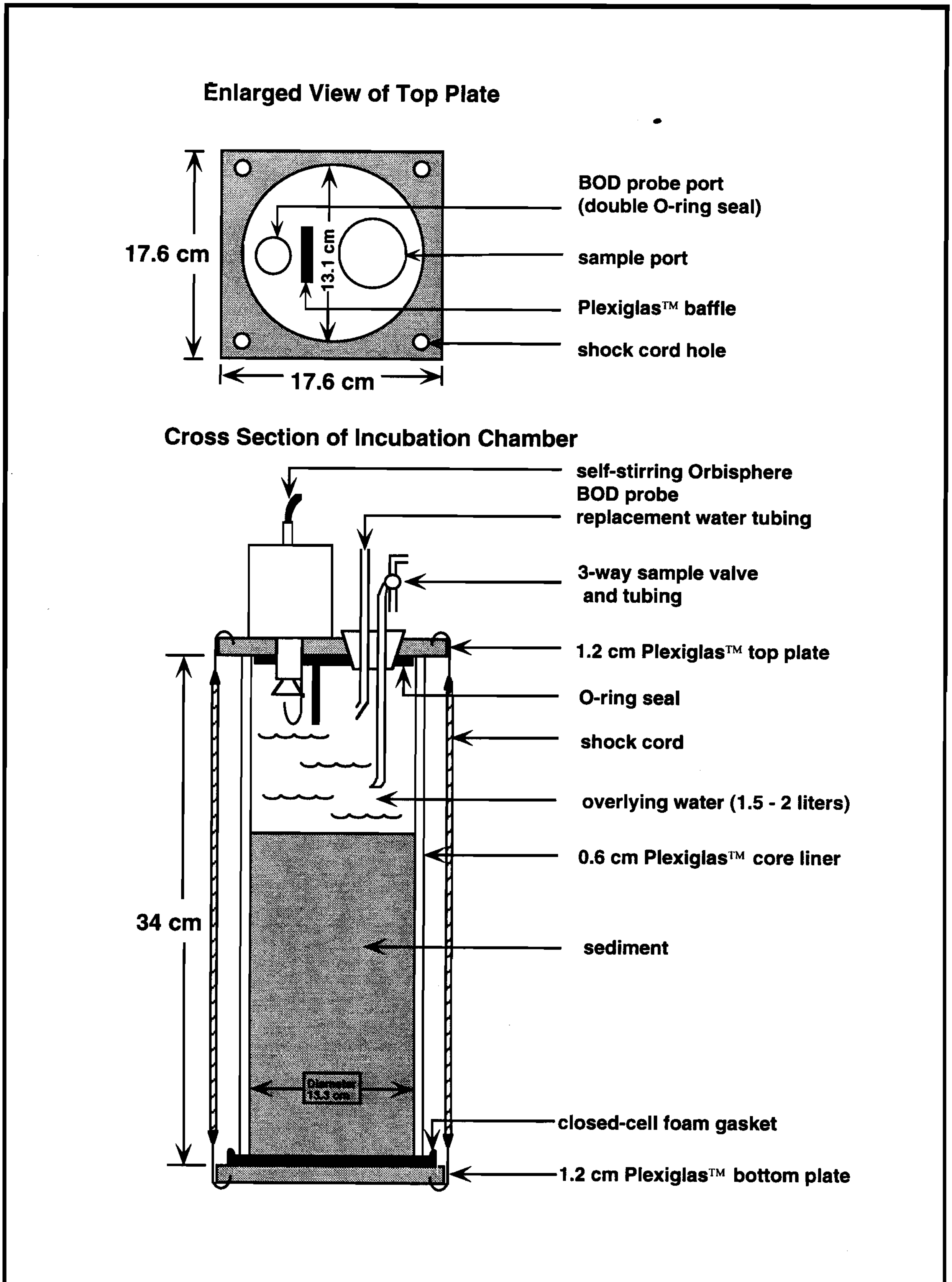

Figure 3-2. Schematic Diagram of the Incubation Chamber

of one month.

3.3.5.1 Sample Collection

At each SONE station, two or three undisturbed sediment cores (13.5 cm diameter; 20 cm depth) were obtained using a modified Bouma box corer. The cores were shaded to maintain ambient temperature. Using a Van Veen grab, a labeled five gallon incubation container was filled with bottom sediment. Sediment temperature was recorded, then the container covered and shaded. Bottom water was collected in a 2 liter Nalgene jug, covered and shaded.

At least thirteen minicore tubes, each color coded to match the box core from which it was taken (to assess any intercore variation) were pushed into the box cores to a depth exceeding 10 cm. Minicore tube measurements: 2.5 cm diameter acrylic tubing, wall thickness of 0.16 cm and length of 20 cm. Number five (#5) stoppers were inserted into the top of each minicore tube. While applying pressure to the top stopper so that no sediment was lost from the bottom and resuspension of the sediment surface was prevented, each minicore was gently pulled out of the box core. The #5 stopper was then gently lifted until sediment slowly fell from the bottom of the tube leaving a measured 10 cm sediment column. A number four (#4) stopper was then inserted into the bottom of the core without introducing any air. While this bottom stopper was slowly pushed up, displacing most of the surface water, another #4 stopper was twisted into the top of the minicore with no introduction of air. The minicore was kept in an upright position at all times.

Next, the remaining surface water was removed. If the sediment in the minicore tube was highly sloped, most but not all of the surface water was removed to insure that the surficial sediment remained undisturbed. To remove the surface water the minicore was loosely placed in a clamp attached to a ring stand. Five ml of bottom water was pulled into a 20 ml syringe through a Beckton - Dickinson #21G1.5 needle. Using the syringe plunger to push a stream of water through the needle, the needle was inserted into but not through the top #4 stopper. A plastic rod induced a gentle upward pressure on the bottom stopper while the needle was pushed through the upper stopper until just the tip protruded into the surface water of the minicore. Continued gentle upward pressure on the bottom stopper, while holding down the upper stopper and syringe, forced the remaining surface water in the minicore up into the syringe. Finally, while maintaining a gentle pressure on the rod, the needle was carefully removed from the top stopper.

Each minicore was placed upright into a container of circulating bottom water and shaded until all the minicores were processed. Any remaining air space between the ends of each tube and the #4 stoppers was packed with bottom sediment to prevent possible atmospheric intrusion and subsequent oxidation of analyzed sediment. The minicores were then completely submerged in a upright position in the incubation container filled with *in situ* bottom sediment. This container was covered and shaded until the end of the day's field operations.

3.3.5.2 Laboratory Incubation and Processing

At the conclusion of each day's cruise, the minicore incubation containers (one for each station) were transferred to a temperature controlled room at the laboratory. In preparation for the initial time zero core processing, three minicores were randomly pulled from the incubation container. The station, location, date, time and tube color were recorded. All the mud on the exterior of the three minicores was washed off and the minicore dried. A glove bag connected to nitrogen gas was set up to limit atmospheric oxidation. The three minicores, three preweighed and labeled 50 ml centrifuge tubes, three clean scrapes, a plastic rod and a box of Kim wipes were placed into the glove bag while it was being flushed with nitrogen. The centrifuge tubes were uncapped and flushed with nitrogen to remove oxygen. Then the glove bag was sealed and the nitrogen flow slowed. Using the plastic rod, the bottom stopper was carefully pushed up until the top stopper was almost out of the minicore. The top stopper was carefully pulled out so that no mud or pore water was lost. The top stopper was scraped to remove any clinging sediment. Then the entire minicore was pushed into one of the labeled centrifuge tubes, the bottom stopper scraped and the tube tightly capped. After all three tubes were completely processed, the nitrogen flow was turned off, and the tubes removed from the bag. The outside of each tube was carefully rinsed, to remove all mud (especially around the rim of the cap), then dried, shaking out the water trapped underneath the cap.

The tubes, paired by weight, were centrifuged in an IEC model MP-4 centrifuge at 4000 rpm for 10 minutes. The wet weight of each tube was recorded. A 20 ml syringe and a #3BD cannula was used to pull all of the supernatant from the tube. A Gelman filtration apparatus (GF/F 2.5 cm diameter) was attached to the syringe. Approximately 5 to 10 ml of filtered water was used to rinse two labeled Auto Analysis (AA) vials and caps. The remaining supernatant was filtered into the vials and frozen (<- 20 C) for later analysis.

The centrifuge tubes containing the sediment were placed in a drying oven (45-50 C) for approximately 2-3 weeks. Once dry, the tubes were placed in a desiccator overnight to cool before weighing. The dry weight of each centrifuge tube was recorded

Following this initial sampling, three random minicores were removed at ten day intervals and processed, using the procedure outlined above. Station locations, dates and times recorded. Each station depending upon the day of the initial sampling had its own 30 day schedule.

3.3.5.3 Sulfate Analysis

Sulfate (SO_4) concentrations were analyzed using the Dionex Ion Chromatograph connected to an auto sampler. Detection limit is approximately 0.3 ppm.

After the frozen AA vials thawed, they were shaken to homogenize the sample. Each sample, after sitting for a few minutes (to settle out precipitates of humics and some elemental sulfur) was diluted 1:100 or 1:40 with deionized water to a final volume of 5 ml.

Data for 1994 were obtained using standards of 0.0, 0.5, 5.0, 10.0, and 20.0 ppm for the standard curve for all cruises. Standards were run after every ten samples throughout the analysis.

3.3.5.4 Porosity Analysis

Porosity is the percent of pore water in 1 cubic centimeter (cm^3) of the minicore. Porosity was calculated as the volume of water over the volume of sediment in the minicore using the following equation:

$$P = (W-D)/[(W-D) + \{(D - T)/K\}]$$

where P = porosity (%),
W = wet weight of sample (g),

D = dry weight of sample(g),
T = tube weight(g), and
K = bulk density for silt/clay sediments (2.5 g cm^{-3}).

3.3.5.5 Flux Calculations

Depletion rate of sulfate (SO_4) was estimated from sulfate (SO_4) concentrations in the pore water of the minicores using the following equation:

$$F = (d[SO_4]/dt) \times V \times P \times K \times 1/M$$

where F = sulfate flux (mM SO_4 m^{-2} day^{-1}),
d[SO_4]/dt = rate of change of sulfate concentrations over time (mg l^{-1} day^{-1}),
V = sediment volume (0.0507 liters in each minicore),
P = porosity, and
K = 1972; conversion of surface area of minicore (5.07 cm^2) to a meter square
M = 96; converts weight measurement of SO_4 (mg l^{-1}) to molar units.

3.4. Chemical Analyses

Detailed reference material pertaining to all chemical analyses used is to be found in the EPC Data Dictionary (Boynton and Rohland, 1990). In brief, methods for the determinations of dissolved and particulate nutrients: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate (NO_2^- + NO_3^-), and dissolved inorganic phosphorus (DIP or PO_4^-) are measured using the automated method of EPA (1979); silicious acid ($Si(OH)_4$) is determined using the Technicon Industrial System (1977) method; particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using a model 240B Perkin-Elmer Elemental Analyzer; particulate phosphorus (PP) concentration is obtained by acid digestion of muffled-dry samples (Aspila *et al.*, 1976); methods of Strickland and Parsons (1972) and Shoaf and Lium (1976) are followed for chlorophyll-a analysis; biogenic silica is measured using the method of Paasche (1973); total suspended solids (seston) are determined by the gravimetric technique of EPA (1979).

3.5. Analytical methods Quality Assurance/Quality Control (QA/QC)

The Nutrient Analytical Services Laboratory (NASL) at the Chesapeake Biological Laboratory provides nutrient analyses to university, State and federal agencies. As part of the laboratory's QA/QC program, NASL participates in cross calibration exercises with other institutions and agencies whenever possible. Some examples include:

- Particulate carbon and nitrogen cross calibration with Woods Hole Oceanographic Institution and Horn Point Environmental Laboratory.

- International Council for the Exploration of the Sea (ICES) inorganic nutrient round-robin communication. This will result in an international inter-comparison report to be issued in the near future.

- Comparisons of dissolved nutrients analyses conducted at Horn Point Environmental Laboratory, Bigelow Laboratory, the University of Delaware and the University of New Hampshire.

- Cross calibration exercises with Virginia Institute of Marine Science (VIMS) and Old Dominion University (ODU). The most recent inter-comparison (March 1990) confirmed all parameters routinely analyzed by these laboratories as part of the Chesapeake Bay Monitoring Program. Samples from various salinities and nutrient regimes were analyzed under this exercise.

- Environmental Protection Agency (EPA) unknown audits for various nutrients have been conducted.

- EPA audits of known nutrients were analyzed using samples in different salinity water while looking for possible matrix effects.

NASL has analyzed National Institute of Standards and Technology (NIST) and National Research Board of Canada reference materials, primarily estuarine sediment, as a check for their particulate and sediment carbon, nitrogen and phosphorus methods.

As part of the Chesapeake Bay Mainstem Monitoring Program, the laboratory analyzes approximately ten percent of the total sample load for QA/QC checks. These samples include laboratory duplicates and spike analyses.

Specific EPC procedures include inorganic nutrients (ammonium [NH_4^+], nitrite [NO_2^-], nitrite plus nitrate [NO_2^- + NO_3^-], dissolved inorganic phosphorus [DIP or PO_4^-] and silicious acid [$Si(OH)_4$]) for which a standard curve usually comprising five concentrations encompassing the expected range for that particular sample set, are analyzed at the beginning of each new run. A standard which is treated as a sample, is analyzed at least every 20 samples. Baseline corrections are determined either manually or automatically, depending on the instrument providing the analysis. Data needed to calculate concentrations are recorded along with the sample concentration in laboratory notebooks, a carbon copy of which is provided to the EPC group. This procedure is also carried out for other parameters performed by the laboratory in support for the EPC effort. Precision and limits of detection for the variables measured by the EPC program are provided in the EPC Data Dictionary (Boynton and Rohland, 1990).

3.6. Data Management

Hard copy data table listings of every variable measured during SONE and VFX monitoring programs for August 1984 through December 1991, were submitted in four volumes. Volumes I and II were appended to Level 1, No 7 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 90-062 (Boynton *et al.*, 1990) and Volumes III and IV were appended to Level 1, No 9 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 92-042 (Boynton *et al.*, 1992). Data tables for 1992 and 1993 are in preparation and will be added to these volumes.

Appendix B of this report contains SONE data tables listings of variables measured during 1994. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor which indicates the number of the SONE cruise (EPC Data Dictionary; Boynton and Rohland, 1990).

3.6.1. SONE Data Sets

The data collected at each SONE station are organized into six data sets:

WATER COLUMN PROFILES (Filename: **H2OPRFxx,** Table B-1) contain temperature, salinity and dissolved oxygen data measured at two meter intervals.

WATER COLUMN NUTRIENTS (Filename: **H2ONUTxx,** Table B-2) report surface and bottom water dissolved nutrient concentrations.

SEDIMENT PROFILES (Filename: **SEDPRFxx,** Table B-3) include redox potential and selected sediment measurements of particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations.

CORE PROFILES (Filename: **CORPRFxx,** Table B-4) lists percentage water, particulates and pore water nutrient measurements at SONE stations. Data are available **only** for SONE Cruise Numbers 2, 6 and 10.

CORE DATA (Filename: **CORDATxx,** Table B-5) lists dissolved oxygen and nutrient measurements in SONE sediment-water flux chambers.

SEDIMENT-WATER FLUX (Filename: **SWFLUXxx,** Table B-6) is a summary table providing oxygen and nutrient flux data.

3.6.2 Incorporation of Error Codes in Data Tables

In order to eliminate blank spaces in the data tables a one or two letter alpha code (Table 3-5.) is used to describe the problems associated with questionable parameter values. Valid entries from the Sediment Data Management Plan (EPA, 1989) are used and where necessary additional codes which are related to the sediment oxygen and nutrient exchanges (SONE) program have been added.

3.6.3 Data Tables Quality Assurance/Quality Control (QA/QC)

Data recorded by instruments in the field are entered directly onto specially prepared data sheets. Data from samples analyzed by Nutrient Analytical Services Laboratory (NASL) are returned in written format. Data are keyed into Lotus using the standard format developed during the continuing effort begun in August 1989 to standardize all EPC data files. Hard copies of the files are manually checked for errors. Data files are corrected, a second printout produced which is re-verified by a different staff member.

3.6.4 Statistical Analysis System (SAS) Files

Lotus files are stripped of headings and converted to ASCII files. The 1994 data files, one file for each data set, are to be added to the Statistical Analysis System (SAS) database now resident on the VAX 8650. Additional information regarding the format of the data and details of variable labels, file structure and data and sampling anomalies are to submitted as a data dictionary file to fulfill the requirements of the EPA Chesapeake Bay Liaison Office (EPA/CBLO).

A complete set of SAS data files for 1994 was submitted to MDE in March, 1995. SAS reference files for each data set containing detailed station and variable information as well as other pertinent information related to missing data will be submitted to MDE during 1995 to complete the existing Water Quality database.

The final step in this processes involves rigorous data checking prior to requesting the formal sign off of each data set.

Table 3-5. Analysis Problem Codes

ANALYSIS PROBLEM CODE	DESCRIPTION
A	Laboratory accident
B	Interference
C	Mechanical/materials failure
D	Insufficient sample
N	Sample lost
P	Lost results
R	Sample contaminated
S	Sample container broken during analysis
V	Sample results rejected due to QA/QC criteria
W	Duplicate results for all parameters
X	Sample not preserved properly
AA	Sample thawed when received
BB	Torn filter paper
CC	Pad unfolded in foil pouch
EE	Foil pouch very wet when received from field, therefore poor replication between pads. mean reported.
FF	Poor replication between pads; mean reported
HH	Sample not taken
JJ	Amount filtered not recorded (calculation could not be done)
LL	Mislabeled
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
PP	Assumed sample volume (pouch volume differs from data sheet volume; pouch volume used)
QQ	Although value exceeds a theoretically equivalent or greater value (e.g., PO4F>TDP), the excess is within precision of analytical techniques and therefore not statistically significant
RR	No sample received
SS	Sample contaminated in field
TF	Dissolved oxygen probe failure
TS	Dissolved oxygen probe not stabilized
TT	Instrument failure on board research vessel
UU	Analysis discontinued
WW	Station was not sampled due to bad weather conditions, research vessel mechanical failure, VFX array lost or failure of state highway bridges to open or close
XX	Sampling for this variable was not included in the monitoring program at this time or was not monitored during a specific cruise
YY	Data not recorded.

4. PATTERNS OF RIVER FLOW

4.1. Overview

One of the continuing objectives of the Ecosystem Processes Component (EPC) Program is to explore monitoring program data, as well as other data sources, for relationships between nutrient loading (*e.g.*, point, non-point and atmospheric sources) and responses of sediment and deposition processes. Sediment oxygen consumption (SOC) and sediment nutrient exchanges have been shown to have strong influences on water quality conditions (Boynton *et al.*, 1990) and are ultimately regulated by rates of external nutrient supplies. Freshwater input to the bay and tributary rivers is an important external forcing on bay ecology, largely determining salinity patterns, buoyancy and other features. Moreover, both the magnitude and timing of freshwater flow events have been shown to influence bay water quality (Boicourt, 1992). River flow has been shown to be a good first approximation of nutrient loading rates for many areas of Chesapeake Bay and in this report river flow has again been used as an indication of nutrient loading rates.

4.1 River Flow Characteristics in 1994

In earlier reports (*e.g.* Boynton *et al.*, 1989) it was proposed that the magnitude of sediment-water exchanges of oxygen and nutrients were ultimately related to nutrient loading rates. Diffuse source nutrient input is the dominant term in nutrient budgets of most areas of the bay. Therefore, it is useful to consider patterns of river flow, which is a good surrogate variable for diffuse source loading.

4.1.1 Average Annual River Flows

Annual average river flows for the period 1978 through 1994 are shown in Figure 4-1.1. The seventeen year average (1978 - 1994) flow to each system during this period is indicated by horizontal lines on this figure (James *et al.*, 1990; James, *pers. comm.*, 1994). The seventeen year average in the Susquehanna River was 39,763 cubic feet per second (cfs), in the Potomac River 12,327 cubic feet per second, in the Patuxent River 363 cubic feet per second and in the Choptank River 133 cubic feet per second. Despite the fact that these basins are distinctly different, and in some cases separated in space by large distances, there are strong similarities in inter-annual flows among systems.

Flows in all systems were above the seventeen year average in 1978 and 1979, below this average from 1980 to 1982, higher than this average during 1983 and 1984, generally lower than the seventeen year average from 1985 through 1988 (except in the Susquehanna River in 1986) and above this average in 1989 (except in the Potomac River). Flows during 1990 were higher than the seventeen year average in the Susquehanna (39,763 cfs) and Patuxent Rivers and lower than this average in the Potomac and Choptank Rivers. In 1991 and 1992 annual average flows were lower than the seventeen year average in all systems. Flows in three rivers were well above average in 1993 in the Susquehanna, Potomac and Patuxent Rivers while flows were below average in the Choptank River.

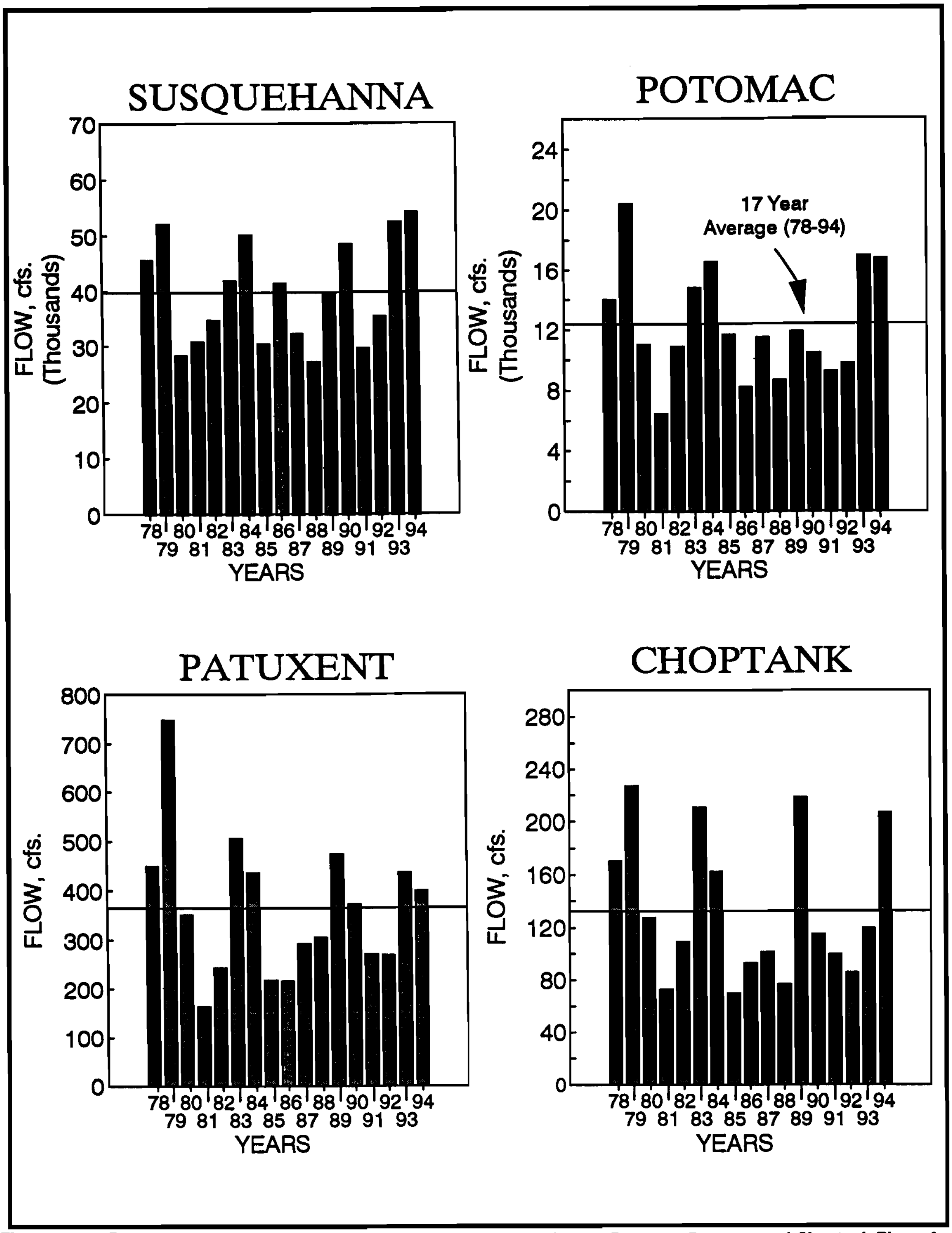

Figure 4-1.1. Bar graphs of average annual river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for the period 1978 through 1994 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers. comm.*, 1994). Flows were measured at Conowingo, MD; Washington, D.C.; Bowie, MD and Greensboro, MD for the four systems, respectively.

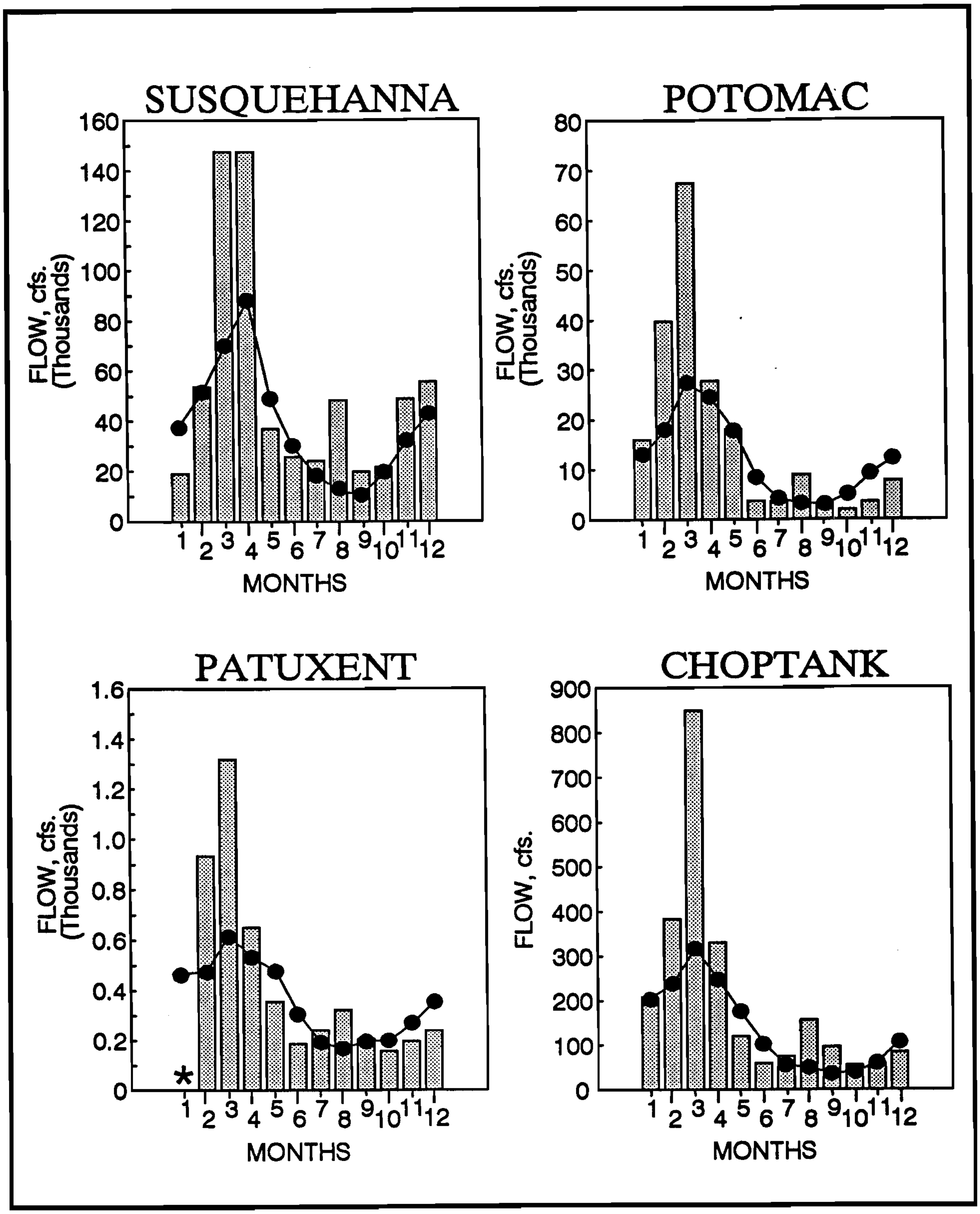

Figure 4-1.2. Bar graphs of average 1994 monthly river flows from the Susquehanna, Potomac, Patuxent and Choptank Rivers. The dot and line plots represent the long-term average flow for the period 1978 through 1994 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers comm.*, 1994). Flows were measured at Conowingo, MD; Washington, D.C.; Bowie, MD and Greensboro, MD for the four systems, respectively.

* *No measurement was recorded in January, 1994 for the Patuxent River.*

Flows in all systems were well above average in 1994, in the Susquehanna River 54,248 cfs, in the Potomac River 16,774 cfs, in the Patuxent River 400 cfs and in the Choptank River 207 cfs. In general, river flows have either been near or below the seventeen year average value during the Ecosystem Processes Component monitoring period except for three years (1989, 1993 and 1994). As a result of this, water column stratification might be expected to be less intense than usual and diffuse source nutrient loads to be lower than normal in most years. The very high flows in 1994 are associated a large spring freshet indicating an above normal year regarding freshwater and diffuse source nutrient inputs.

4.1.2 Average Monthly River Flows

One of the more obvious characteristics of estuarine systems is the time and space variability associated with many variables as is the case for river flow (and diffuse source nutrient loading). Monthly average river flows for all of the main Maryland tributary rivers are shown as a series of bar graphs (Figure 4-1.2.). In this figure the vertical bars represent average monthly flows for 1994 while the bold dots represent average monthly flows calculated over longer time periods (1978 - 1993). The data provided by the United States Geological Survey (U.S.G.S.) office are complete for 1994 with the exception of the Patuxent River where data was not available for January 1994.

In 1994 flows in all rivers generally followed the seventeen year average with the exception of March and April, 1994 when peak flows were recorded in one or both of these two months in all four rivers. The Susquehanna had a flow rate of 147,800 cfs with very high flows persisting during the month of April, 1994. The Potomac had a flow rate of 67,420 cfs, the Patuxent 1318 cfs and the Choptank 849 cfs (Figure 4-1.2.). A secondary peak is evident in all rivers in August, 1994 when the Susquehanna had a flow rate of 48,580 cfs, the Potomac 8.826 cfs, the Patuxent 322 cfs and the Choptank 157 cfs (Figure 4-1.2.). This was followed by decreasing flows as was the trend in 1993 and other years. There is a very slight upward trend towards the end of 1994, in October, November and December. This was the second consecutive wet spring experienced in the bay region. The flows in December tended also to be larger than average in the Susquehanna River (55,640 cfs).

These data are presented to emphasize the need for careful consideration of temporal relationships between variables such as river flow or nutrient loading and ecosystem processes such as deposition and sediment-water nutrient and oxygen exchanges. In cases where a rapid response is expected (weeks to months) examination of intra-annual data will be necessary. In those cases where effects of inputs such as river flow or nutrient loading are expected to appear over longer periods of time (months to years) consideration of inter-annual data will be necessary. It is becoming apparent that both time scales are important features governing relationships between nutrient loading rates and sediment-water nutrient and oxygen exchange rates in Chesapeake Bay.

5. CHARACTERISTICS OF SEDIMENT-WATER OXYGEN AND NUTRIENT EXCHANGES

5.1. Overview

Monthly average sediment-water fluxes are summarized in the form of bar graphs (Figures 5-1.1. through 5-1.5.) for five variables: sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate ($NO_2^- + NO_3^-$), phosphate (PO_4^-), and silicate ($Si(OH)_4$). Data collected over a period of ten calendar years, 1985 through 1994, were used in the preparation of these graphics. Each bar represents the average mean flux value for a particular month calculated for the nine calendar year period 1985 through 1993, while the error bar indicates the standard deviation from this mean. Outlier values identified in statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded from the calculation of average fluxes and standard deviations. In those cases where the standard error of a monthly mean is large, this almost always indicated that there was considerable inter-annual difference in monthly fluxes rather than that the variability among replicates from any particular measurement was high. *It is important to note that positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.*

Data collected during 1994 (SONE 47 [May 1994] through SONE 52 [October 1994]; mean flux value of three replicates) are shown as bold dots superimposed on the bar (Figures 5-1.1. through 5-1.5.). The order of the eight stations in these figures reflects their spatial position in the Chesapeake Bay. The four stations on the left side of the figures are located in the Patuxent River from the lower estuary (St. Leonard Creek [STLC]) to the middle regions of the estuary (Broomes Island [BRIS] and Marsh Point [MRPT]) to the turbidity maximum zone (Buena Vista [BUVA]). The right half of the figure shows one station in the lower Choptank River (Horn Point [HNPT]), one in the lower Potomac River (Ragged Point [RGPT]) and two stations in the mainstem bay (Point No Point [PNPT] and R-64 [R-64]).

5.2 Sediment Oxygen Consumption (SOC)

Mean monthly sediment oxygen consumption (SOC) for 1994, ranged from -0.16 g O_2 m^{-2} day^{-1} in June, 1994 at Marsh Point (MRPT) to -3.02 g O_2 m^{-2} day^{-1} in May, 1994 at Buena Vista (BUVA) in the Patuxent River, from -1.70 g O_2 m^{-2} day^{-1} in May and August to -3.27 g O_2 m^{-2} day^{-1} in June in the Choptank River (Horn Point [HNPT]), from -0.04 g O_2 m^{-2} day^{-1} in July, 1994 through -1.44 g O_2 m^{-2} day^{-1} in September, 1994 in the Potomac River (Ragged Point [RGPT]) and from -0.01 g O_2 m^{-2} day^{-1} in July at Point No Point (PNPT) through -1.10 g O_2 m^{-2} day^{-1} in May, 1994 at Point No Point (PNPT) in the mainstem of the bay (Figure 5-1.1.; Tables B6-47. - B6-52.). Values were generally larger in magnitude in the Patuxent and Choptank Rivers than at other sites. *Note that: larger negative sediment oxygen consumption (SOC) flux indicate larger rates of oxygen loss to sediments.*

At most stations the 1994 data closely followed the seasonal pattern, evident in previous years, with peaks or increased rates of sediment oxygen consumption (SOC) in the springtime (May and June), depressed values in the summer (August) and increased rates in the fall (October). The largest fluxes were recorded in May and June, with a secondary peak recorded in October. However, summer and fall rates of SOC were considerably enhanced at St. Leonard Creek (STLC) and Horn Point (HNPT). Bottom water dissolved oxygen levels remained high at these sites during 1994 and were probably responsible for the enhanced rates.

Fluxes at hypoxic stations (where hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters) were depressed in July and occasionally in August, 1994 as was the case in all previous years with the exception of July 1992 when aerobic sediment metabolism persisted longer than in previous years because of higher dissolved oxygen (DO) concentrations in these bottom waters. In both 1991 and 1992, river flow to all sites was quite low (Figure 4-1.2.) and as a result diffuse source nutrient loads were probably lower than normal as was organic matter enrichment of bottom waters and sediments.

5.3 Ammonium (NH_4^+) Fluxes

Average monthly ammonium (NH_4^+) fluxes in 1994, ranged from 65 μMN m^{-2} hr^{-1} in October, 1994 at St. Leonard Creek (STLC) to 492 μMN m^{-2} hr^{-1} in July, 1994 at St. Leonard Creek (STLC) in the Patuxent River, from 57 μMN m^{-2} hr^{-1} in May, 1994 to 355 μMN m^{-2} hr^{-1} in July, 1994 in the Choptank River (Horn Point [HNPT]), from 100 μMN m^{-2} hr^{-1} in September, 1994 to 479 μMN m^{-2} hr^{-1} in June, 1994 in the Potomac River (Ragged Point [RGPT]) and from 112 μMN m^{-2} hr^{-1} in May, 1994 at Point No Point (PNPT) through 312 μMN m^{-2} hr^{-1} in September, 1994 in Point No Point (PNPT) in the mainstem of the bay (Figure 5-1.2.; Tables B6-47. - B6-52.).

At two stations in the Patuxent River (Broomes Island [BRIS] and St. Leonard Creek [STLC]) the highest values on record were observed during summer 1994, again reflecting the especially high loading rates of spring 1994. The values recorded in 1994 generally followed temporal trends exhibited in previous years, although the magnitude of fluxes was exceptionally high at St. Leonard Creek while values at R-64 were lower than previous year sin most summer months. In all of these systems there were especially high freshwater flows during March and April and due to these flows, nutrients could support a large spring algal bloom. It is expected that sediments would respond with larger than normal ammonium releases during the warm season following a large loading event. The magnitude of ammonium (NH_4^+) fluxes was below mean values for most months of 1994 (as it was in 1993) at R-64 in the mainstem bay while fluxes at a station downstream of R-64 (Point No Point [PNPT]) were higher than normal (Figure 5-2.1.b.). It has been proposed that in years of high river input the deposition of spring bloom occurs further downstream than usual (Boynton *et al.*, 1993a). As a result, nutrient fluxes at R-64 were lower than normal and fluxes at Point No Point (PNPT) were higher than normal. The flow pattern of 1994 may not only influence the magnitude of inputs but also affect the characteristics of sediment processes and the location at which these occur in the bay.

5.4 Nitrite + Nitrate (NO_2^- + NO_3^-) Fluxes

Average nitrite plus nitrate (NO_2^- + NO_3^-) fluxes for 1994, ranged from -267 μMN m^{-2} hr^{-1} in May at Marsh Point (MRPT) to 32 μMN m^{-2} hr^{-1} in October, 1994 at St. Leonard Creek (STLC) in the Patuxent River, from -206 μMN m^{-2} hr^{-1} in May, 1994 to 67 μMN m^{-2} hr^{-1} in October, 1994 in the Choptank River (Horn Point [HNPT]), from -178 μMN m^{-2} hr^{-1} in June, 1994 to 14 μMN m^{-2} hr^{-1} in August, 1994 in the Potomac River (Ragged Point [RGPT]) and from -275 μMN m^{-2} hr^{-1} in June, 1994 (R-64) through 14 μMN m^{-2} hr^{-1} in October, 1994 (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-1.3.; Tables B6-47. - B6-52.). *Note that positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.*

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Figure 5-1.1. Mean monthly (April to November) sediment oxygen consumption (SOC) rates at eight SONE stations located in the Maryland portion of Chesapeake Bay.

- Monthly means and standard deviations were calculated using flux data for a specific month at each station from 1985 - 1993.
- Station locations are shown in Figure 3-1.
- In general there was one set of triplicate flux values available for each month for 1985 through 1994. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1993.
- September values for all stations only include three years data, 1991 through 1993.
- The bold solid dots indicate average monthly fluxes recorded in 1994; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.
- * = Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT).
  ** = Very hypoxic stations are Ragged Point (RGPT), Point No Point (PNPT) and R-64.

Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

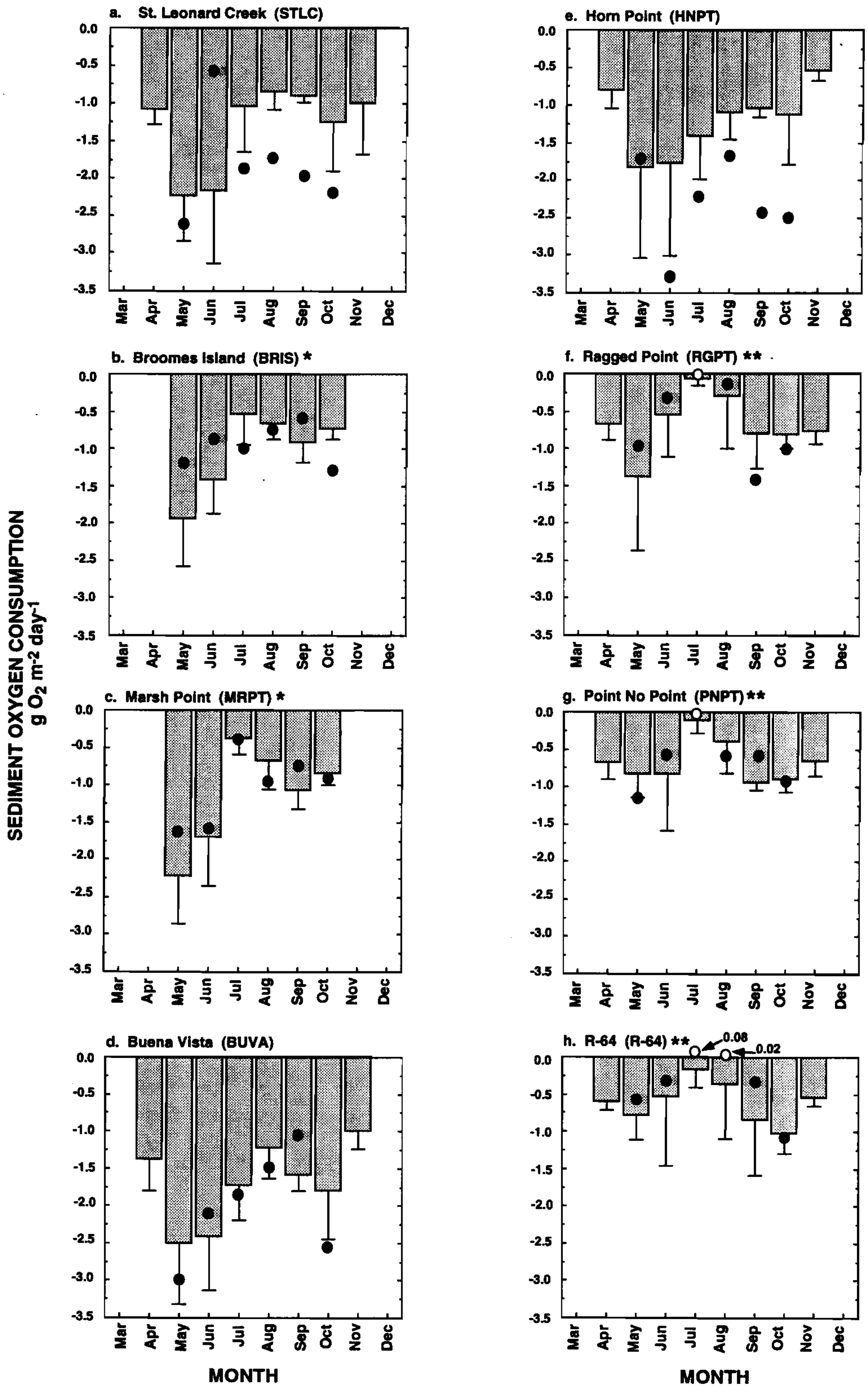

Figure 5-1.1. Mean monthly (April to November) sediment oxygen consumption (SOC) rates at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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Figure 5-1.2. Mean monthly (April to November) ammonium (NH_4^+) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

- Monthly means and standard deviations were calculated using data available for a specific month at each station from 1985 - 1993.
- Station locations are shown in Figure 3-1.
- In general there was one set of triplicate flux values available for each month for 1985 through 1994. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1993.
- September values for all stations only include three years data, 1991 through 1993.
- The bold solid dots indicate average monthly fluxes recorded in 1994; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water.

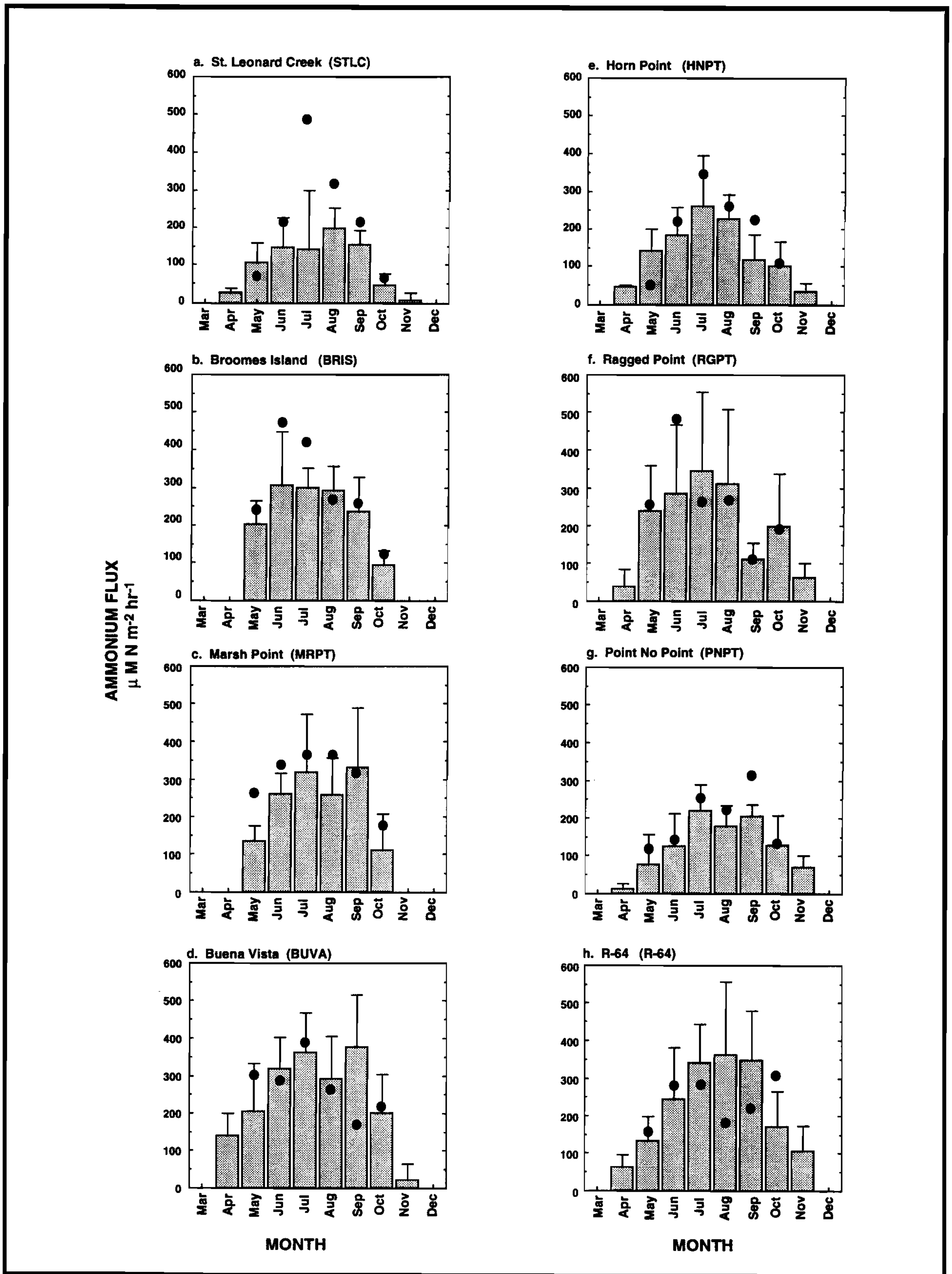

Figure 5-1.2. Mean monthly (April to November) ammonium (NH_4^+) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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Figure 5-1.3. Mean monthly (April to November) nitrite plus nitrate ($NO_2^- + NO_3^-$) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1993.
- Station locations are shown in Figure 3-1.
- In general there was one set of triplicate flux values available for each month for 1985 through 1994. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1993.
- September values for all stations only include three years data, 1991 through 1993.
- The bold solid dots indicate average monthly fluxes recorded in 1994; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.

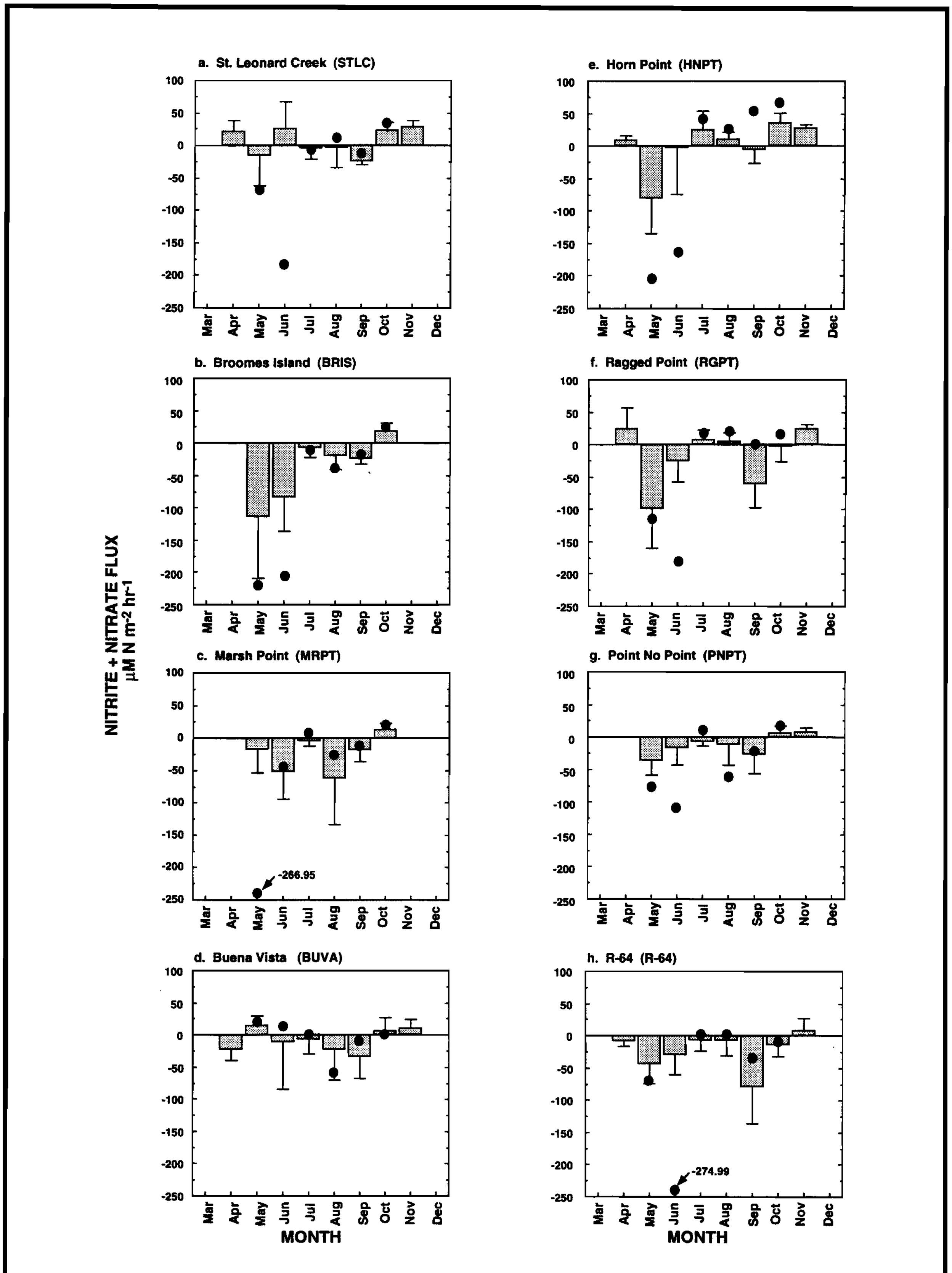

Figure 5-1.3. Mean monthly (April to November) nitrite plus nitrate (NO_2^- + NO_3^-) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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Figure 5-1.4. Mean monthly (April to November) phosphorus (PO_4^- or DIP) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1993.
- Station locations are shown in Figure 3-1.
- In general there was one set of triplicate flux values available for each month for 1985 through 1994. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1993.
- September values for all stations only include three years data, 1991 through 1993.
- The bold solid dots indicate average monthly fluxes recorded in 1994; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.

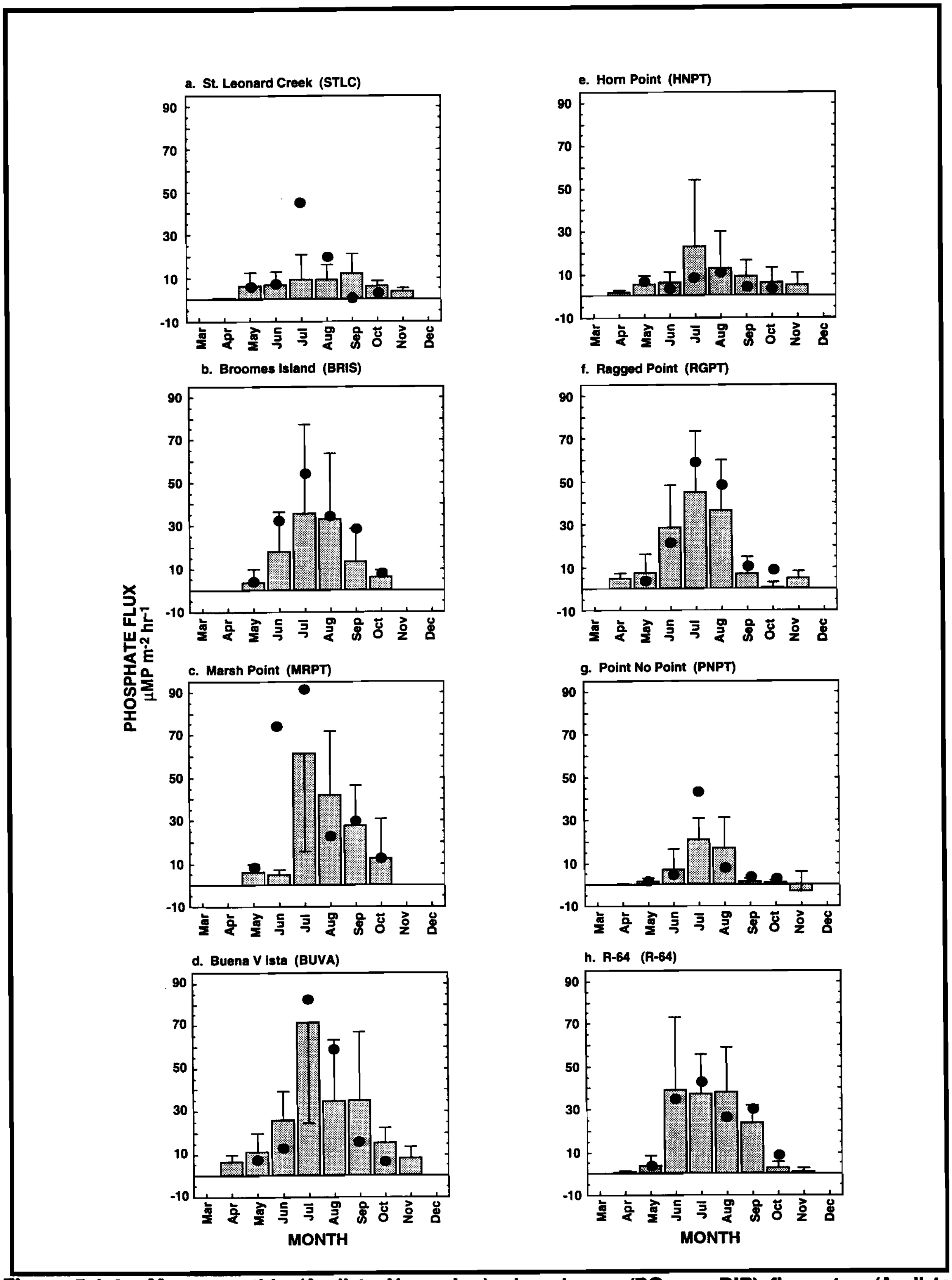

Figure 5-1.4. Mean monthly (April to November) phosphorus (PO_4^- or DIP) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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Figure 5-1.5. Mean monthly (April to November) silicate ($Si(OH)_4$) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1993.
- Station locations are shown in Figure 3-1.
- In general there was one set of triplicate flux values available for each month for 1985 through 1994. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1993.
- September values for all stations only include three years data, 1991 through 1993.
- The bold solid dots indicate average monthly fluxes recorded in 1994; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.

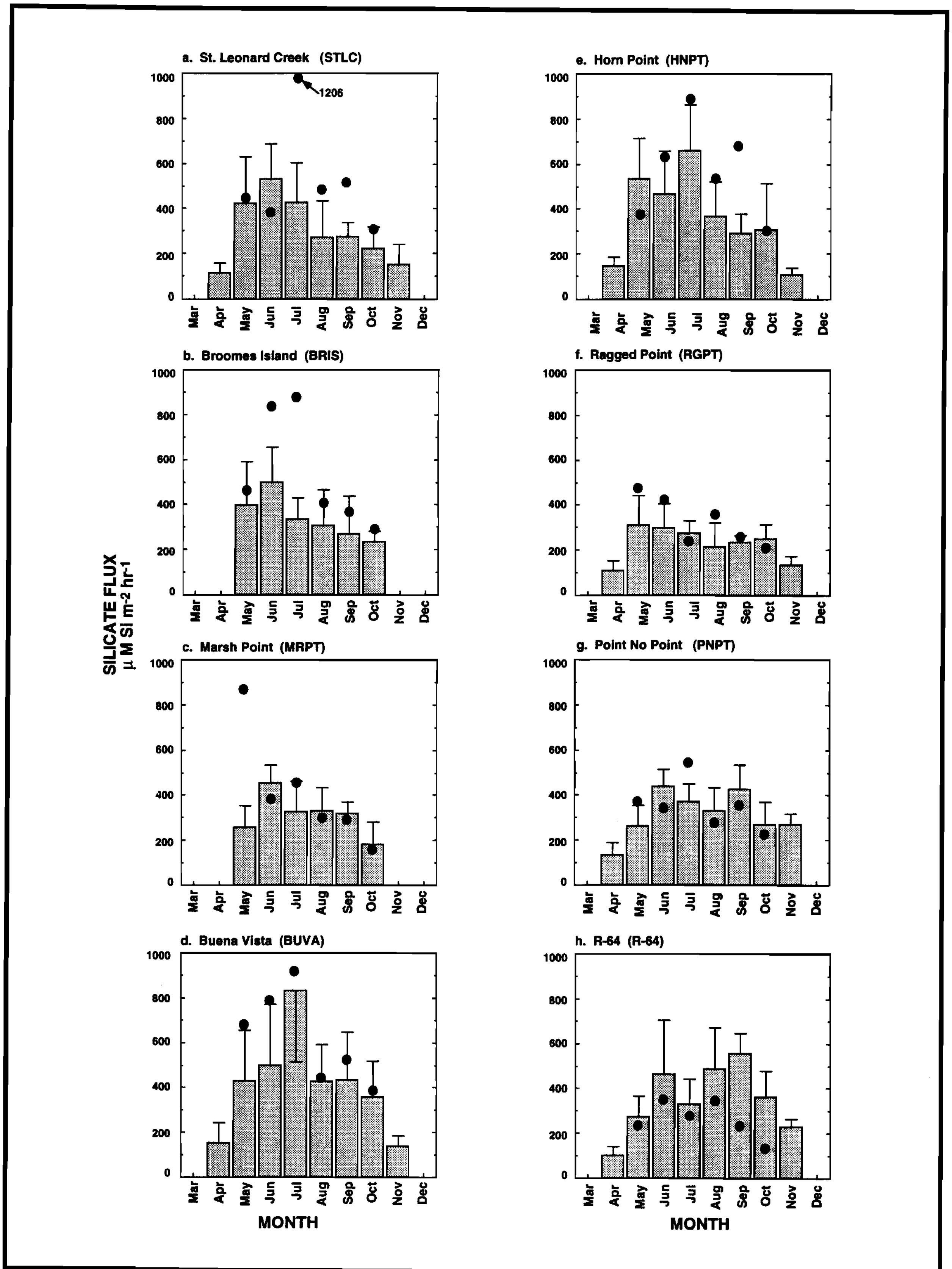

Figure 5-1.5. Mean monthly (April to November) silicate ($Si(OH)_4$) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

In general flux values in May and June 1994 were larger than previous years. This is consistent with the fact that nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes into sediments are strongly influenced by nitrate concentrations in overlying waters. In years of above normal flow high water column nitrate concentrations are typical and are responsible for these patterns.

With a few exceptions (*e.g.*, Broomes Island [BRIS] in May and June, 1991; R-64 in September, 1991), nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes in either direction (into or out of sediments) were small compared to ammonium (NH_4^+) fluxes and even these maximum nitrate fluxes were small compared to maximum ammonium fluxes. Most of this nitrate may subsequently be denitrified but there is no direct evidence for this based on monitoring program data (Jenkins and Kemp, 1984).

One of the main uses of nitrate flux data in the monitoring program is as an indicator of sediment quality. In this context good sediment quality means that sediments that have not been routinely exposed to hypoxic or anoxic conditions or, have not been loaded with organic material to an extent wherein anoxic conditions develop. In cases where hypoxic conditions have not occurred regularly, nitrification of ammonium can occur and nitrate plus nitrite ($NO_2^- + NO_3^-$) can escape from sediments and is recorded as a flux from sediments to overlying waters. In situations were bottom waters and sediments are hypoxic or anoxic nitrification is effectively blocked and nitrate is not produced in sediments and hence none escapes from sediments to overlying waters. Positive nitrate plus nitrite ($NO_2^- + NO_3^-$) fluxes therefore indicate oxidized surficial sediment conditions, an indication of good sediment quality. During 1994 there were few positive nitrate fluxes observed and those which were tended to be small. While this was not an indication of good sediment quality it was consistent with heavily loaded sediments resulting from heavy spring diffuse source loads.

5.5 Dissolved Inorganic Phosphorus (PO_4^- or DIP) Fluxes

Average monthly dissolved inorganic phosphorus (DIP) fluxes in 1994 ranged from zero (0.0) in September, 1994 at St. Leonard Creek (STLC) to 91.2 μMP m^{-2} hr^{-1} in July, 1994 at Marsh Point (MRPT) in the Patuxent River, from 2.4 μMP m^{-2} hr^{-1} in June, 1994 to 11.4 μMP m^{-2} hr^{-1} in August in the Choptank River (Horn Point [HNPT]), from 2.8 μMP m^{-2} hr^{-1} in May, 1994 to 58.1 μMP m^{-2} hr^{-1} in July in the Potomac River (Ragged Point [RGPT]) and from 1.0 μMP m^{-2} hr^{-1} in May, 1994 (Point No Point [PNPT]) to 43.4 μMP m^{-2} hr^{-1} in July, 1994 (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-1.4.; Tables B6-47. - B6-52.). Large phosphate fluxes were recorded at each of the four stations in the Patuxent River in July, 1994, 46.4 μMP m^{-2} hr^{-1} at St. Leonard Creek (STLC), 54.3 μMP m^{-2} hr^{-1} at Broomes Island (BRIS), 91.2 μMP m^{-2} hr^{-1} at Marsh Point (MRPT) and 82.4 μMP m^{-2} hr^{-1} at Buena Vista (BUVA) which were among the highest on record.

With the exception of the station in the upper Patuxent River (Buena Vista, [BUVA]), all large dissolved inorganic phosphorus (PO_4^-) fluxes were associated with hypoxic or anoxic conditions in overlying waters. It has been suggested that the high dissolved inorganic phosphorus (PO_4^-) fluxes observed at Buena Vista (BUVA) were caused, at least in part, by the burrowing and irrigation activities of the large benthic macrofaunal community present at this location rather than iron-sulphur (Fe-S) reactions which are probably responsible for high fluxes elsewhere under low dissolved oxygen conditions (Krom and Berner, 1980).

Data collected during 1994 generally followed well established temporal trends with some very high fluxes measured during the summer months (June, July and August).

5.6 Dissolved Silicate ($Si(OH)_4$) Fluxes

Average monthly silicate fluxes in 1994 ranged from 168 μM Si m^{-2} hr^{-1} in October, 1994 at Marsh Point (MRPT) to 1206 μM Si m^{-2} hr^{-1} in July, 1994 at St. Leonard Creek (STLC) in the Patuxent River, from 292 μM Si m^{-2} hr^{-1} in October, 1994 to 884 μM Si m^{-2} hr^{-1} in July, 1994 in the Choptank River (Horn Point [HNPT]), from 209 μM Si m^{-2} hr^{-1} in October, 1994 to 475 μM Si m^{-2} hr^{-1} in May, 1994 in the Potomac River (Ragged Point [RGPT]) and from 122 μM Si m^{-2} hr^{-1} in October, 1994 (R-64) to 540 μM Si m^{-2} hr^{-1} in July, 1994 (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-1.5.; Tables B6-47. - B6-52.).

Silicate fluxes followed the general pattern of previous years although large fluxes were reported in May, June and July, 1994 in the Patuxent River. Larger values were also recorded in the Choptank (Horn Point [HNPT]) and Potomac Rivers (Ragged Point [RGPT]). Values at R-64, in the mainstem of the bay, were generally lower in 1994, as in 1993, which is consistent with the lower deposition rates indicated at this station in high rather than in lower flow years.

5.7 Sulfate Reduction Fluxes

A second set of sulfate reduction rate measurements (Figure 5-1.6) were taken at seven of the eight sediment oxygen and nutrient exchanges (SONE) stations during 1994. No measurements were taken at Point No Point (PNPT) because previous efforts to obtain rates at this station failed probably because of the hard clay sediments which underlie the shallow (2 - 3 cm) surface silt layer.

Sulfate reduction rates in 1994 ranged from 4.4 mM SO_4 m^{-2} day^{-1} in October at Buena Vista (BUVA) to 33.8 mM SO_4 m^{-2} day^{-1} in May at Marsh Point (MRPT) in the Patuxent River. During the period May through October average sulfate reduction rates were 17.5 mM SO_4 m^{-2} day^{-1} at St. Leonard Creek [STLC], 18.1 mM SO_4 m^{-2} day^{-1} at Broomes Island [BRIS], 16.65 mM SO_4 m^{-2} day^{-1} at Marsh Point [MRPT] and 6.08 mM SO_4 m^{-2} day^{-1} at Buena Vista [BUVA]. The pattern emerging for the Patuxent River is one in which rates were greatest in the central regions of the river and lower in upper and lower river. Qualitatively, this pattern reflects oxygen conditions in the Patuxent River where oxygen concentrations were generally highest at the upper river station (Buena Vista [BUVA]), lower at the lower river site (St Leonard Creek [STLC]) and lowest at the two central river sites (Broomes Island [BRIS] and Marsh Point [MRPT]).

At the other SONE sites sulfate reduction rates in 1994 ranged between 7.6 mM SO_4 m^{-2} day^{-1} and 36.2 mM SO_4 m^{-2} day^{-1}. Sulfate reduction rates in the lower Choptank River were comparable to those in the central region of the Patuxent River and the average rate for May through October, 1994 was slightly lower (14.3 mM SO_4 m^{-2} day^{-1}) than the rates at Broomes Island (BRIS) and Marsh Point (MRPT) in the Patuxent River. At the lower Potomac River site (Ragged Point [RGPT]) sulfate reduction rates were very high ranging from 12.6 mM SO_4 m^{-2} day^{-1} to 33.6 mM SO_4 m^{-2} day^{-1} and averaging 21.0 mM SO_4 m^{-2} day^{-1} for May through October, 1994. In the mainstem bay (R-64) sulfate reduction rates were very high ranging from 13.4 mM SO_4 m^{-2} day^{-1} to 36.3 mM SO_4 m^{-2} day^{-1} and averaged 19.0 mM SO_4 m^{-2} day^{-1} for May through October, 1994. The lowest sulfate reduction rates were observed at the upper river station in the Patuxent River, Buena Vista (BUVA), where values for all five months were exceptionally low.

5.7.1 Factors regulating Sulfate Reduction Fluxes

There was a factor of 2.5 between the lowest and highest average sulfate reduction rates measured at eight SONE stations during 1993 and a factor of 3.45 in 1994. Sulfate reduction rates were lowest at Point No Point (PNPT) and highest at Ragged Point (RGPT) in 1993 while they were lowest at Buena Vista (BUVA) and highest at Ragged Point in 1994 (Figure 5-1.6.). The differences among SONE stations in average sulfate reduction rates were of the same magnitude as those observed for other sediment-water fluxes and suggests that this is the sort of responsive variable that is worth monitoring.

Sulfate reduction rates at three of the four stations in the Patuxent River (the exception being Buena Vista [BUVA]) and the station in the lower Choptank River (Horn Point [HNPT]) were of the same magnitude and both rivers were subjected to a very strong nutrient pulse during the spring of 1994 as was the case in 1993. Sulfate reduction rates in the lower Potomac River were the highest recorded at any SONE station. The Potomac River was also exposed to a very strong spring nutrient pulse in 1994 as in 1993. In general, areal nutrient loading rates to the Potomac River are higher than at other SONE station as are chlorophyll-a concentrations and other sediment-water exchanges. The highest rates of sulfate reduction were measured at this site and these rates can be attributed to abundant organic matter supply rates to sediments and the often intense and common hypoxic-anoxic conditions which occur at Ragged Point (RGPT). In the case of the upper river station in the Patuxent (Buena Vista [BUVA]) the lower rates may be related to very well mixed sediments, relatively high oxidation-reduction (Eh) conditions, lower sulfate concentrations and high oxygen concentrations in overlying waters, all of which would tend to limit sulfate reduction rates. The surprising data were from R-64 in the mainstem bay where nutrient loading rates, chlorophyll-a stocks and other indicators of organic loading rates are typically high and bottom water dissolved oxygen conditions depressed, which would suggest that sulfate reduction rates should be high. However, this was not the case during 1993 and similar modest values were observed in 1994 with the exception of one very high value in July (Figure 5-1.6.). This section of the bay was also exposed to a very strong freshet during the spring of 1993, but the freshet occurred later in this system (April) than in the other river systems (March through April). It is possible that a smaller bloom developed in this sector of the bay because of the late freshet (Figure 4-1.1.) as was the case in 1989 or that the large freshet transported the spring bloom farther down bay than in more normal years. In an earlier report (Boynton *et al.*, 1993a) a sediment map of chlorophyll-a developed from data collected during May, 1993 was presented. Major chlorophyll-a concentrations were generally found south of the Potomac River mouth. Under more average flow conditions major chlorophyll-a concentrations are found north of the Potomac River mouth, generally between the bridge at Annapolis, Maryland and the mouth of the Patuxent River. The set of conditions described above would serve to limit organic matter deposition to sediments and hence limit sulfate reduction rates. In fact, Smith (*pers. comm.*) found abnormally low organic matter deposition rates at station R-64 during spring of 1993 (no deposition rate measurements were made in 1994). While these observations are speculative at this time, they appear reasonable because they are consistent with the processes operative in sediments of eutrophicated systems. It is expected that continued monitoring will result in progressively more interpretable patterns of sulfate reduction which will be useful in gauging the influence of nutrient reduction activities.

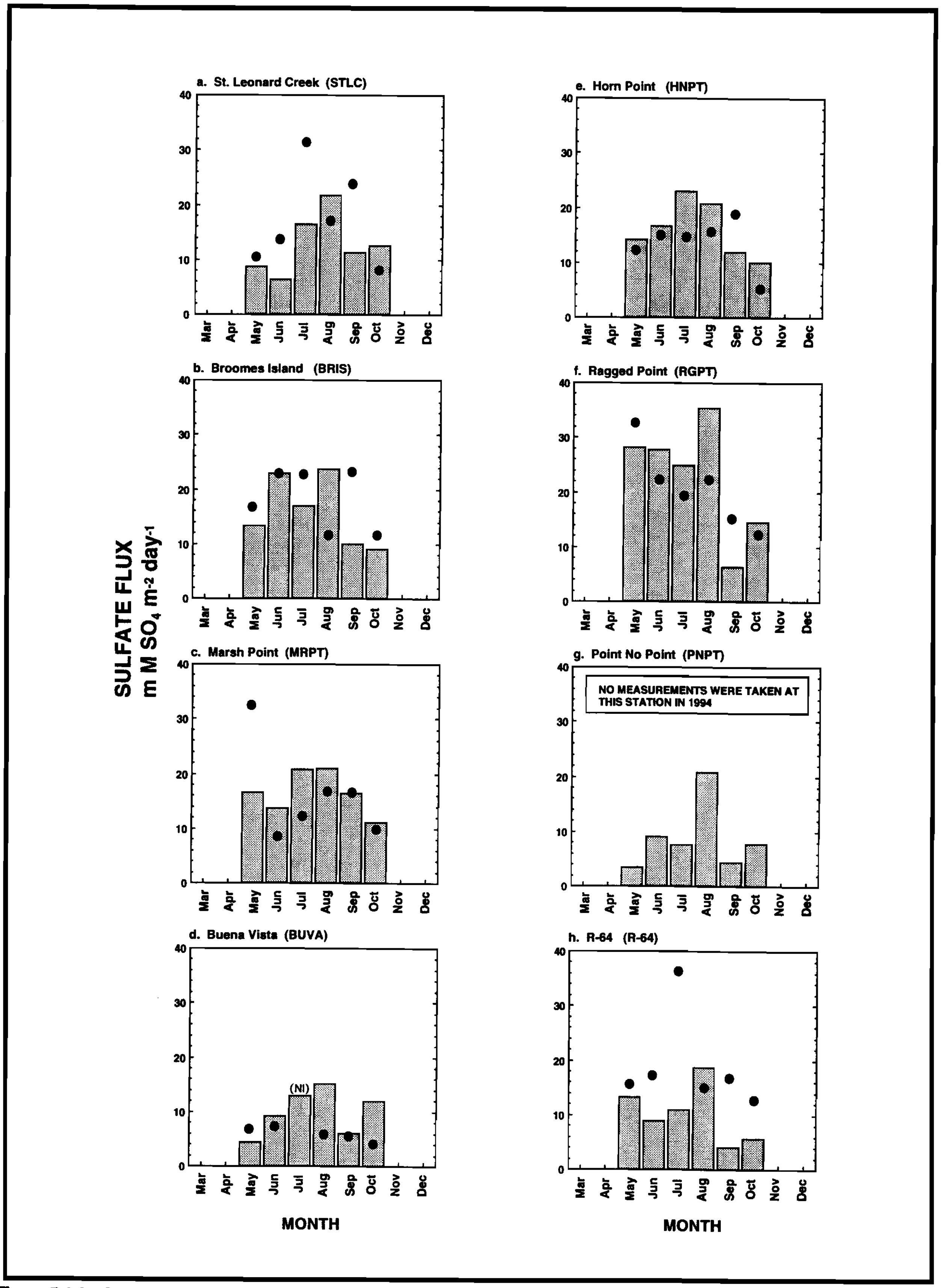

Figure 5-1.6. Average (mean of triplicate minicores) sulfate reduction rates at eight SONE stations for the months of May through October, 1993 and 1994. Bars represent 1993 values while 1994 data are superimposed as bold solid dots.

5.8 Sediment-water Fluxes and *in situ* Environmental Conditions

5.8.1 Overview and Approach

In this section the observed magnitude of sediment-water exchanges is examined for relationships to *in situ* environmental conditions as a step towards building better understanding of factors regulating these fluxes. In earlier reports (Boynton *et al.*, 1987) results of extensive correlation analyses were reported and in more recent reports a series of regression analyses were presented (Boynton *et al.*, 1994). To date a number of significant correlations have been found between specific sediment-water fluxes (*e.g.*, inorganic dissolved phosphorus [PO_4^-] fluxes) and environmental variables (*e.g.*, bottom water dissolved oxygen levels, or sediment characteristics). The predictive power of these relationships (r^2 values) has increased over the years as more observations have been added and as more has been learned about the mechanistic relationship between sediment fluxes and environmental conditions.

5.8.2 Bottom Water and Sediment Conditions

A series of bar graphs summarize temperature (C), salinity (ppt) and dissolved oxygen (DO) in bottom water (Figures 5-2.1. - 5-2.3.) and chlorophyll-a (mg m^{-2}) and Eh (mV) values (corrected to the hydrogen electrode) in sediments (Figures 5-2.4. and 5-2.5.) averaged over nine years (1985 - 1993). The data from 1994 are superimposed as bold dots.

5.8.2.1 Temperature

Bottom water temperature conditions in the Patuxent River during 1994 ranged from 16.3 C at Broomes Island (BRIS) in May, 1994 to 29.3 at Buena Vista BUVA) in July, 1994. In the Choptank River bottom water temperatures at Horn Point (HNPT) ranged from 15.8 C in May, 1994 to 29.2 C in July, 1994. While in the Potomac River bottom water temperatures at Ragged Point (RGPT) ranged from 15.9 C in May, 1994 to 26.1 C in August, 1994. In the mainstem of the bay bottom water temperature conditions during 1994 ranged from 15.8 C at R-64 in May, 1994 to 26.2 at Point No Point (PNPT) in August, 1994 (Figure 5-2.1.; Tables B1-47. - B1-52.).

Temperature conditions followed the pattern observed in previous years but there was little indication of a temperature response to the large freshet of 1994 and little reason to believe that interannual temperature differences (*e.g.* 1994 versus average of previous years) had any large influence on 1994 fluxes.

5.8.2.2 Salinity

Bottom water salinity conditions during 1994 ranged from 3.1 ppt in May, 1994 at Buena Vista (BUVA) to 13.0 ppt in October, 1994 at Broomes Island (BRIS) in the Patuxent River, from 7.2 ppt in June, 1994 to 10.2 ppt in October, 1994 at Horn Point [HNPT] in the Choptank River, from 10.6 ppt In May, 1994 to 15.1 ppt in October, 1995 at Ragged Point (RGPT) in the Potomac River and from 10.0 ppt in May, 1994 at Point No Point (PNPT) to 22.3 ppt in October, 1994 at R-64 in the mainstem of the bay (Figure 5-2.2.; Tables B1-47. - B1-52.).

The influence of the strong 1994 freshet can be seen as depressed salinity conditions, especially in spring, at all SONE sites. The enhanced salinities occurring later in the summer in deep waters is probably the result of enhanced gravitational circulation induced by the spring freshet (Boicourt, 1992).

5.8.2.3 Dissolved Oxygen

Bottom water dissolved oxygen conditions during 1994 ranged from 0.16 mg l^{-1} in June, 1994 at Marsh Point (MRPT) to 8.80 mg l^{-1} in May, 1994 at St. Leonard Creek (STLC) in the Patuxent River, from 3.69 mg l^{-1} In May, 1994 to 7.41 mg l^{-1} in October, 1994 at Horn Point(HNPT) in the Choptank River, from 0.09 mg l^{-1} in July, 1994 to 5.86 mg l^{-1} in October, 1994 at Ragged Point (RGPT) in the Potomac River and from 0.10 mg l^{-1} in August, 1995 at R-64 to 7.50 mg l^{-1} in October, 1994 at Point No Point (PNPT) in the mainstem of the bay (Figure 5-2.3.; Tables B1-47. - B1-52.).

During 1994 river flows to three portions of the Maryland bay monitored in the Chesapeake Bay Program were higher than the long term seventeen year average (Figure 4-1.1.). The conceptual model used to guide the Ecosystem Processes Component (EPC) Program indicates that nutrient loading (associated with river flow) stimulates phytoplankton production which leads to deposition of organic matter to deep waters and sediments. As this material decomposes, oxygen is consumed and nutrients are released from sediments, stimulating further phytoplanktonic production of organic matter and continued low dissolved oxygen conditions. In addition high river flows increased the degree of stratification resulting in lower aeration rates of bottom water. These events are ultimately tied to nutrient loading rates and hence reduction in loading rates is of key importance in improving water and sediment quality conditions.

This scenario is the basis for testing the hypothesis that during 1994 dissolved oxygen (DO) concentrations in deep waters were expected to be depressed. In the Patuxent River dissolved oxygen (DO) concentrations were lower than average in 1994 on several occasions but reached very low levels only at Marsh Point (a deep station) in June. Oxygen concentrations at St. Leonard Creek (STLC) were well above average in the months of July and August. The fact that oxygen levels in deep waters were temporarily depressed despite record river flow suggests that point and diffuse source nutrient reductions are improving water quality conditions. At the mainstem bay stations and in the lower Potomac River dissolved oxygen (DO) conditions in bottom waters were very depressed, presumably in response to the large freshet.

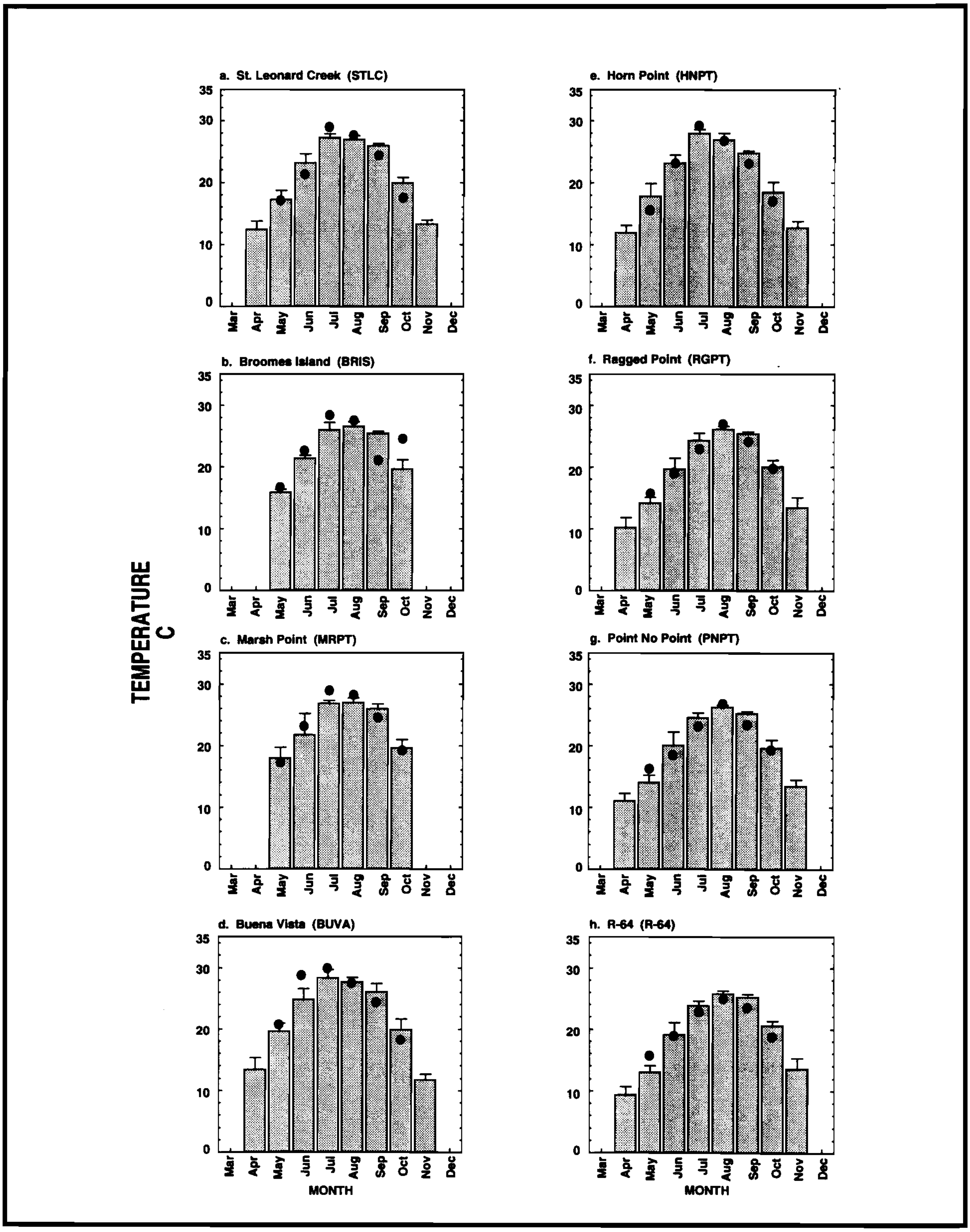

Figure 5-2.1 Monthly (April to November) bottom water temperature measurements at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1994. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

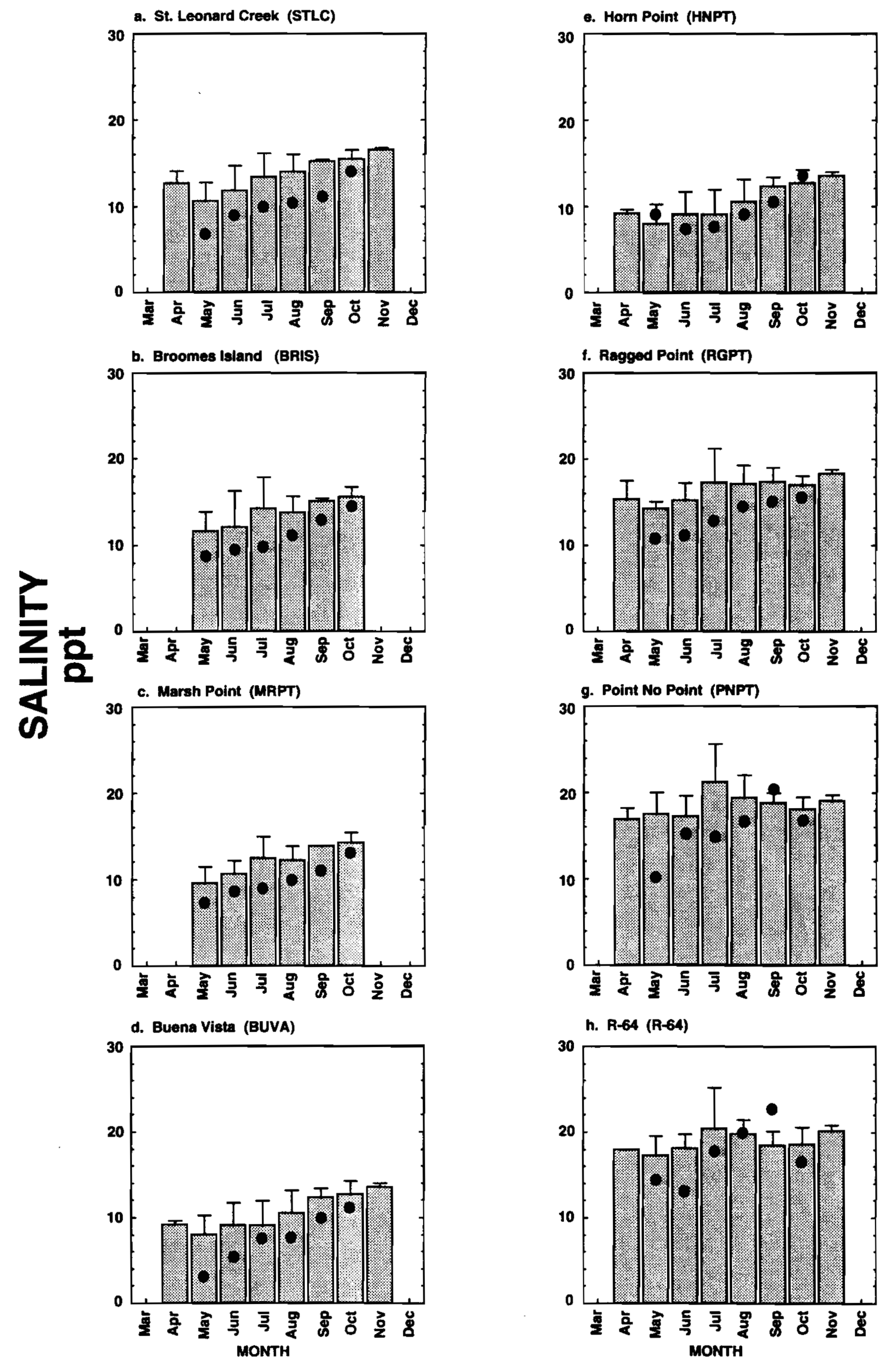

Figure 5-2.2 Monthly (April to November) bottom water salinity at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1994. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

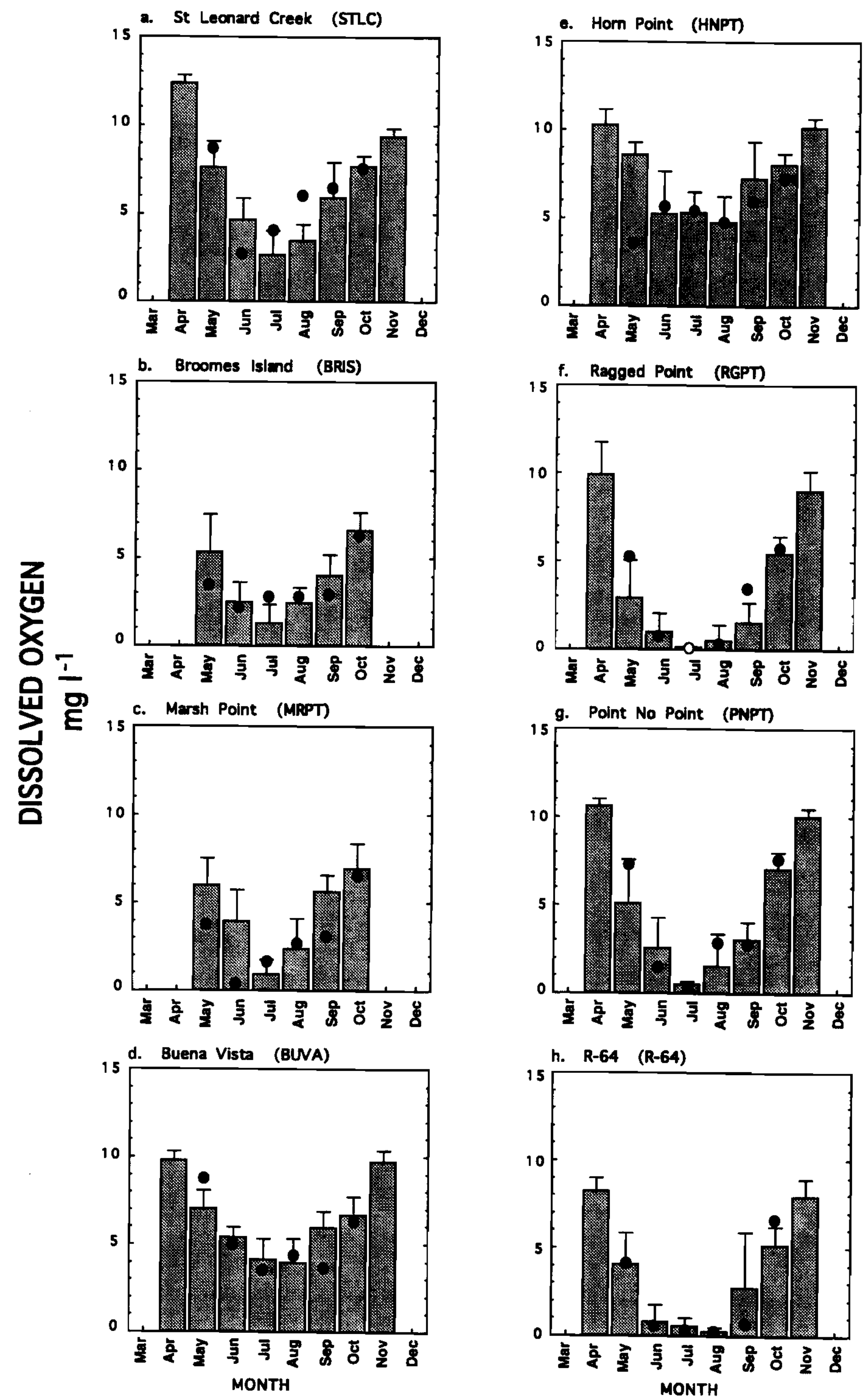

Figure 5-2.3 Monthly (April to November) bottom water dissolved oxygen (DO) concentrations at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1994. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

5.8.2.4 Total Chlorophyll-a

Surficial sediment total chlorophyll-a mass during 1994 ranged from 23.7 mg m^{-2} in September, 1994 at Broomes Island (BRIS) to 117.6 mg m^{-2} in July, 1994 at Broomes Island (BRIS) in the Patuxent River, from 40.1 mg m^{-2} in September, 1994 to 60.8 mg m^{-2} in June, 1994 in the Choptank River (Horn Point [HNPT]), from 35.0 mg m^{-2} in September, 1994 to 115.7 mg m^{-2} in May, 1994 in the Potomac River (Ragged Point [RGPT]) and from 39.1 mg m^{-2} in August, 1994 (R-64) to 109.7 mg m^{-2} in June, 1994 (R-64) in the mainstem of the bay (Figure 5-2.4.; Tables B3-47. - B3-52.).

The main characteristics of sediment chlorophyll-a concentrations mass were that they were at or above the long term averages, especially in the Patuxent River during the first two sampling periods of 1994. This is consistent with the conceptual model wherein high nutrient loads associated with a large freshet stimulate the creation of a larger than normal spring bloom which in turn deposits larger than normal amounts of labile organic material (*e.g.* phytoplanktonic debris) at the sediment surface where it is available for decomposition. There is a striking correspondence between sediment chlorophyll-a mass and the general magnitude of sediment-water nutrient exchanges and sediment anaerobic respiration.

5.8.2.5 Sediment Eh

Sediment Eh (corrected to the hydrogen electrode) values measured at the sediment-water interface (sediment depth = 0 cm) at all sediment oxygen and nutrient exchanges (SONE) stations are shown as a series of bar graphs in Figure 5-2.5. The 1994 values ranged from 118 mV in July at Marsh Point (MRPT) to 392 mV in May, 1994 at St. Leonard Creek (STLC) in the Patuxent River, from 328 mV in August, 1994 to 383 mV in May, 1994 in the Choptank River (Horn Point [HNPT]), from 183 mV in July, 1994 to 350 mV in May, 1994 in the Potomac River (Ragged Point [RGPT]) and from -40 mV in October, 1994 (R-64) to 356 mV (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-2.5.; Tables B3-47. - B3-52.).

The 1994 values generally followed those of previous years although values recorded at Point No Point (PNPT) were higher than the long term nine year (1985 - 1993) average. In the Patuxent River values were elevated (or less negative) at most stations during July, 1994. These more positive Eh values result from the aerobic nature of sediments and the consequent reduction in the amount of chemically reduced compounds (*e.g.*, solid phase sulfur) accumulating in sediments.

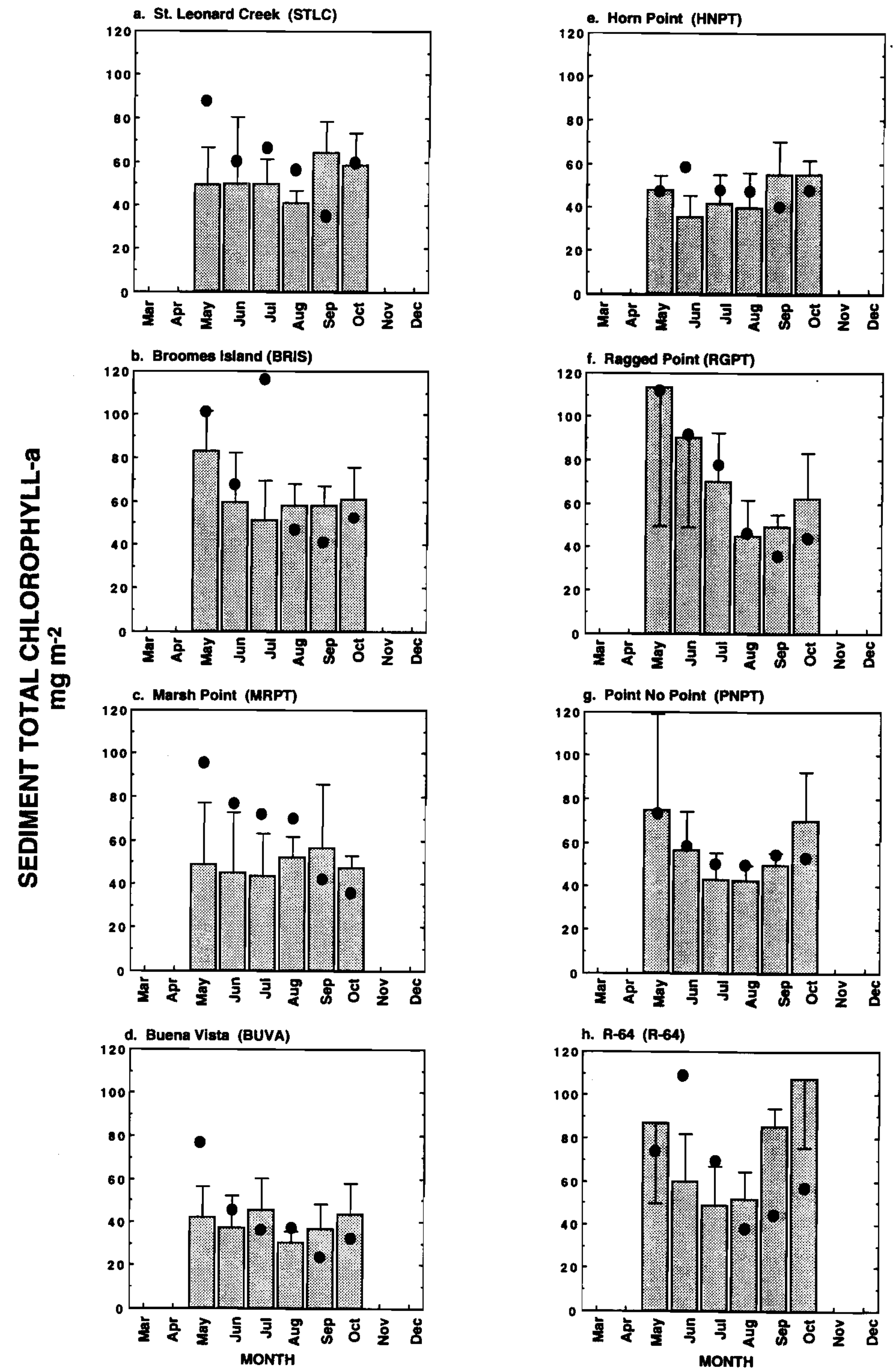

Figure 5-2.4 Monthly (April to November) sediment total chlorophyll-a concentrations at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1994. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

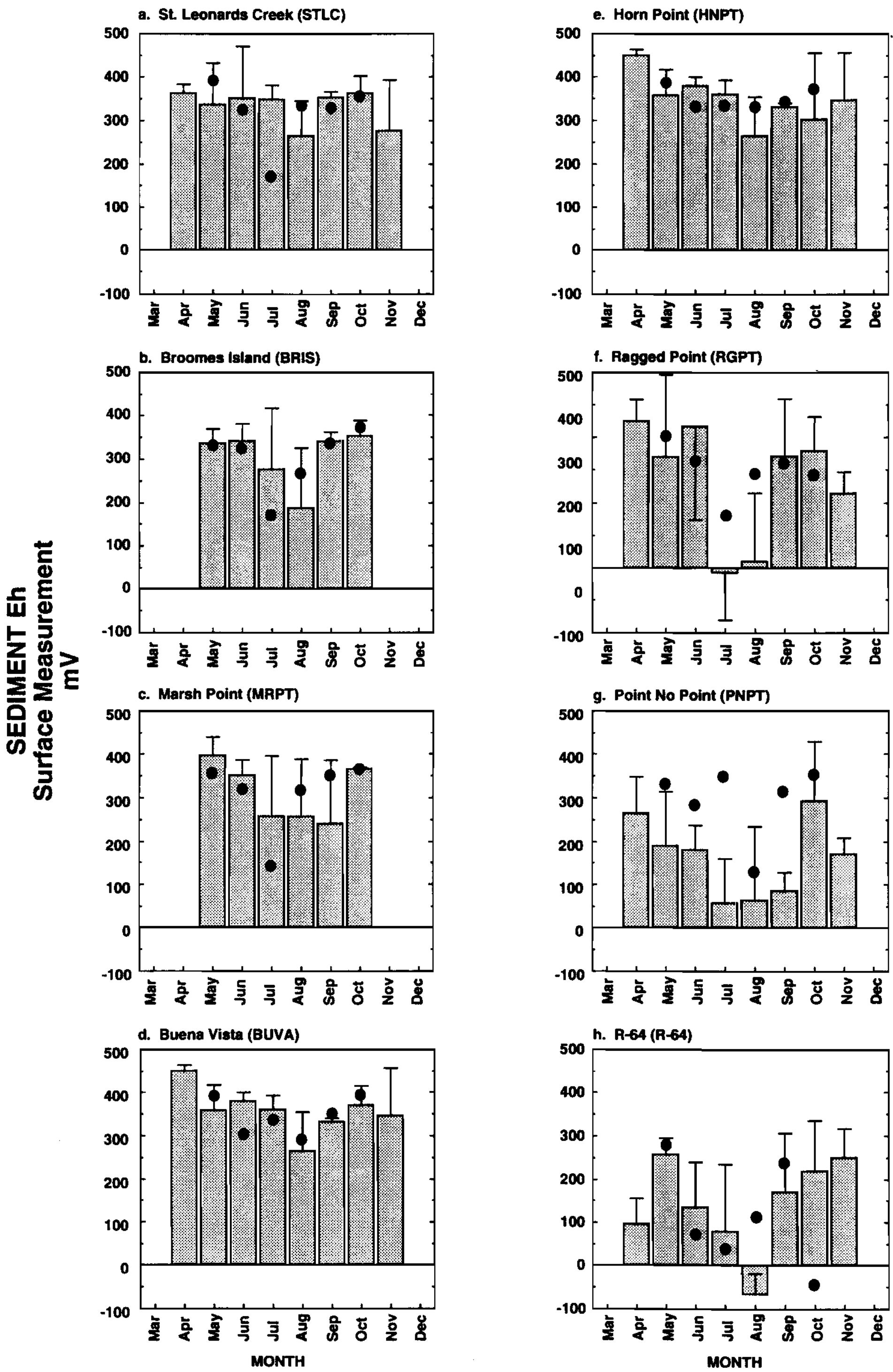

Figure 5-2.5 Monthly (April to November) surficial (sediment-water interface, sediment depth = 0 cm) sediment Eh values (corrected for the hydrogen electrode) at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1994. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

5.8.2.6 Sediment Characteristics

Surface sediment concentrations of particulate carbon (PC), nitrogen (PN) and phosphorus (PP) varied at SONE stations as follows:

(1) Particulate carbon (PC) ranged from 2.46 percent dry weight in August, 1994 at Buena Vista (BUVA) to 4.98 percent dry weight in May, 1994 at Broomes Island (BRIS), from 1.83 percent dry weight in October, 1994 to 2.23 percent dry weight in June, 1994 in the Choptank River (Horn Point, [HNPT]), from 3.38 percent dry weight in September, 1994 to 4.40 percent dry weight in May, 1994 in the Potomac River (Ragged Point [RGPT]) and from 3.21 percent dry weight in August, 1994 (R-64) to 4.84 in May, 1994 (Point No Point [PNPT]) in the mainstem bay (Figure 5-2.6.; Tables B3-47. and B3-52.).

(2) Particulate nitrogen (PN) ranged from 0.28 percent dry weight in August, 1994 at Buena Vista (BUVA) to 0.66 percent dry weight in May, 1994 at Broomes Island (BRIS), from 0.25 percent dry weight in October, 1994 to 0.29 percent dry weight in May, 1994 in the Choptank River (Horn Point, [HNPT]), from 0.46 percent dry weight in September, 1994 to 0.60 percent dry weight in May, 1994 in the Potomac River (Ragged Point [RGPT]) and from 0.41 percent dry weight in August, 1994 (R-64) to 0.61 in September, 1994 (Point No Point [PNPT]) in the mainstem bay (Figure 5-2.7.; Tables B3-47. and B3-52.).

(3) Particulate phosphorus (PP) ranged from 0.15 percent dry weight in August, 1994 at Marsh Point (MRPT) to 0.07 percent dry weight in July, 1994 at St. Leonard Creek (STLC), from 0.04 percent dry weight in July, 1994 to 0.07 percent dry weight in May, 1994 in the Choptank River (Horn Point, [HNPT]), from 0.06 percent dry weight in August, 1994 to 0.17 percent dry weight in September, 1994 in the Potomac River (Ragged Point [RGPT]) and from 0.05 percent dry weight in August, 1994 (R-64) to 0.13 in May, 1994 (R-64) in the mainstem bay (Figure 5-2.8.; Tables B3-47. and B3-52.).

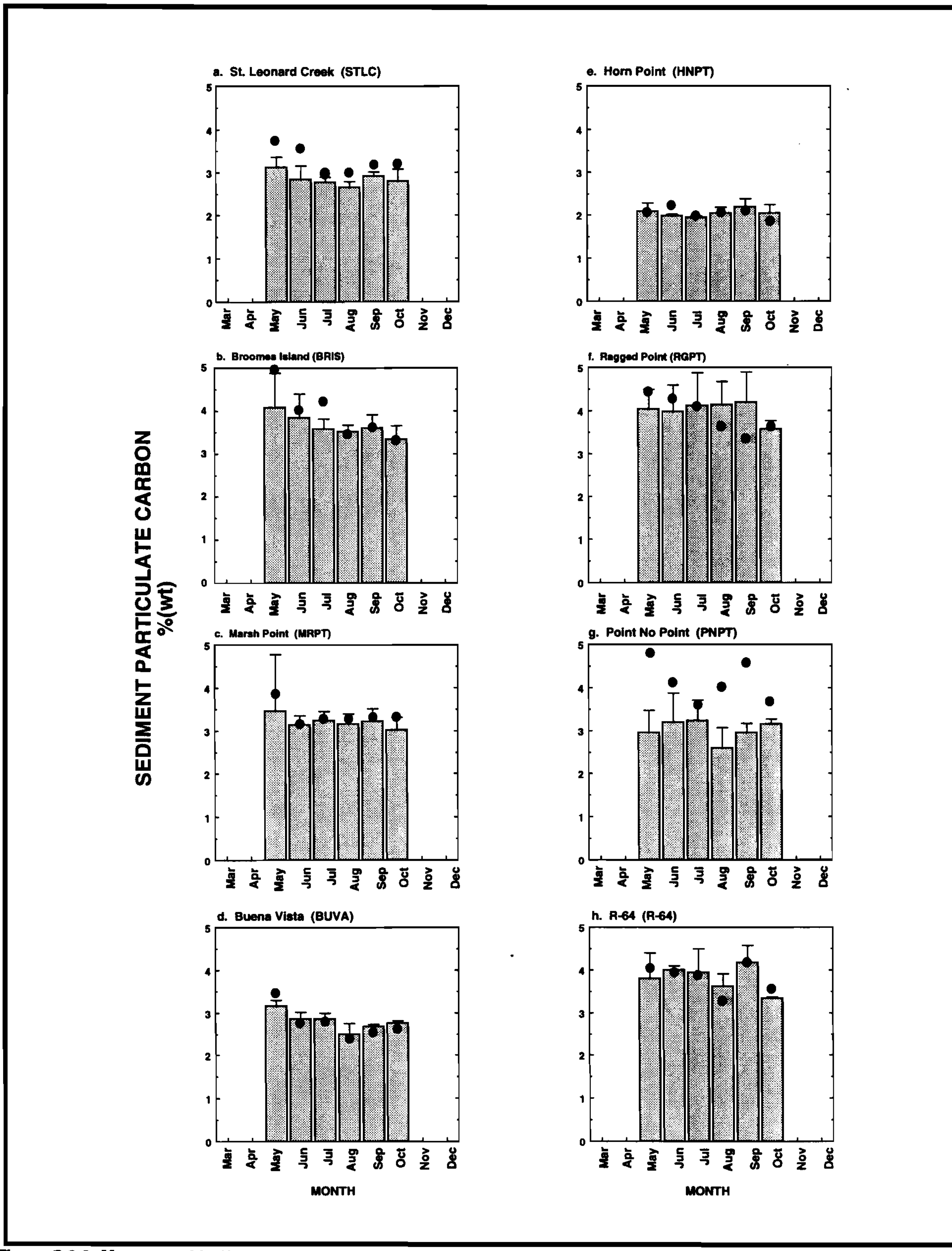

Figure 5-2.6 Mean monthly (April to November) sediment particulate carbon (PC) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1993 for a specific month at each station during which period a standard method was used. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

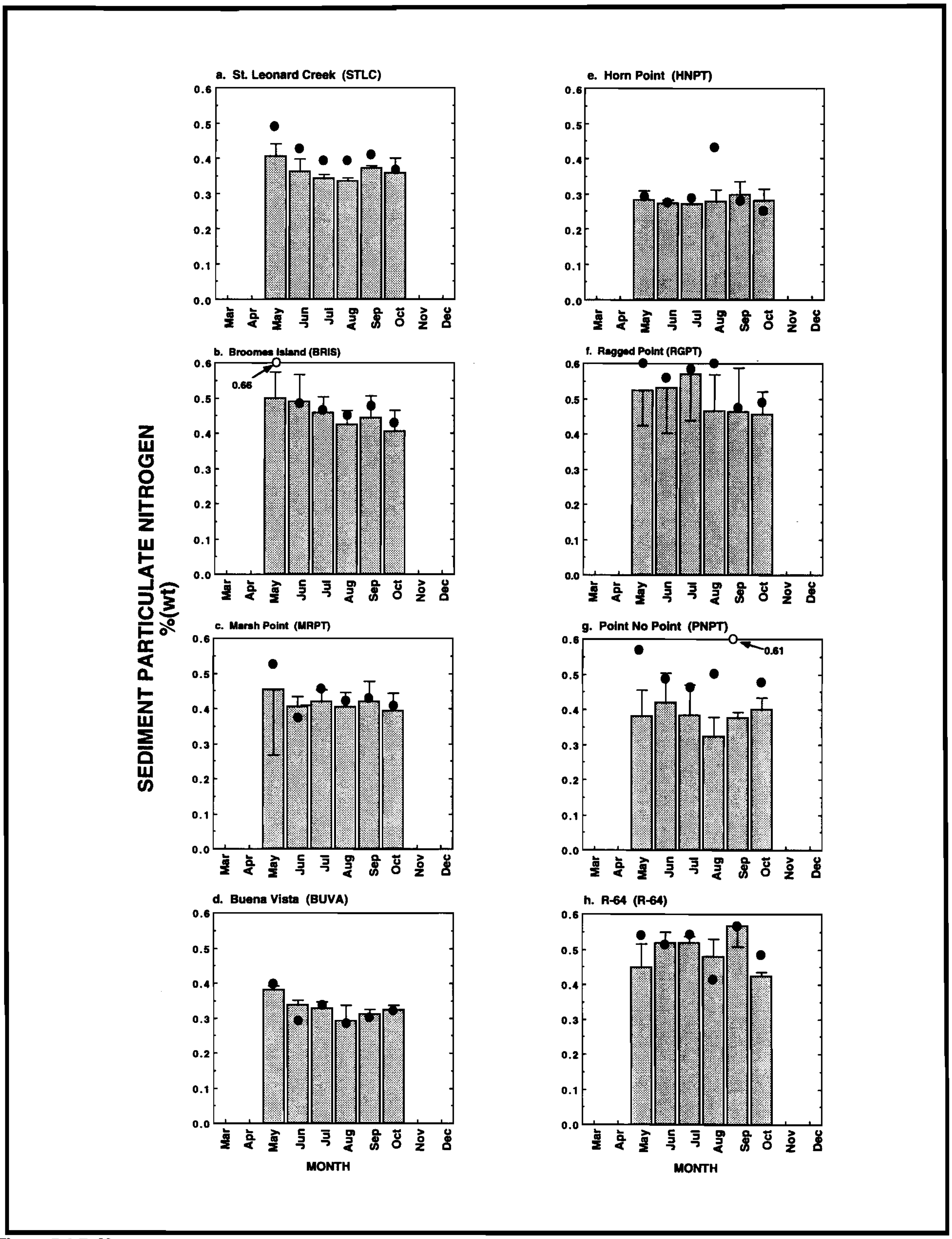

Figure 5-2.7 Mean monthly (April to November) sediment particulate nitrogen (PN) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1993 for a specific month at each station during which period a standard method was used. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

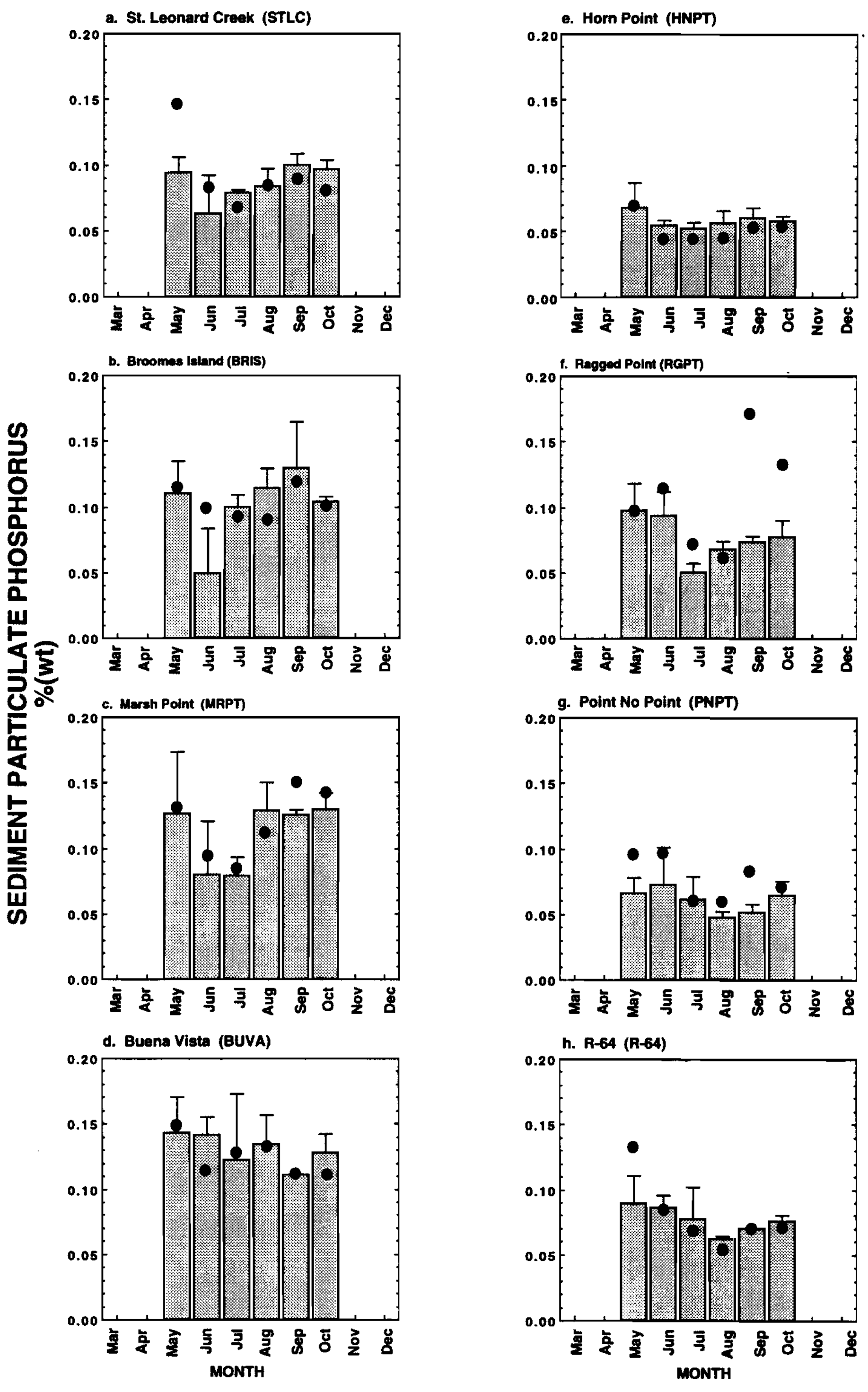

Figure 5-2.8 Mean monthly (April to November) sediment particulate phosphorus (PP) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1993 for a specific month at each station during which period a standardized method was used. The bold dots indicate average monthly values for 1994. Station locations are shown in Figure 3-1.

6. EXAMINATION OF SEDIMENT-WATER FLUXES FOR LONG TERM TRENDS AND SPATIAL FEATURES

6.1 Time Series Examinations of Flux Data

The development of management actions to implement the 40% nutrient load reduction strategy has been the major thrust of the Chesapeake Bay Program during its third phase beginning in 1991. Prior to this, the Chesapeake Bay Water Quality Monitoring Program developed a data base containing information related to water quality conditions throughout the bay system. These data were used to describe conditions in the bay system and identify areas of poor water quality. The Ecosystem Processes Component (EPC) Program has been a part of this effort since 1984 and ten complete years (1985 - 1994) of monitoring data have been accumulated. A part of the Ecosystem Processes Component (EPC) Program was also designed to examine the sediment flux data base in order to determine long-term trends in sediment-water nutrient and oxygen exchanges. In previous Interpretive Reports (Boynton *et al.*, 1993b, 1994) results of statistical testing for trends were presented and discussed. As an addition to this, a time series of important environmental variables, river flow, bottom water dissolved oxygen concentrations and key sediment-water fluxes (ammonium and phosphate fluxes) are presented in graphical format (Figure 6-1.1. - 6.1.6.). These figures include monthly average data covering the complete ten year monitoring period (1985 - 1994) collected at six SONE stations including St. Leonard Creek [STLC, Figure 6-1.1] and Broomes Island [BRIS, Figure 6-1.2] in the Patuxent River, Horn Point [HNPT, Figure 6-1.3] in the Choptank River, Ragged Point [RGPT, Figure 6-1.4] in the Potomac River, and Point No Point [PNPT, Figure 6-1.5] and R-64 (R-64, Figure 6-1.6) in the Maryland mainstem bay. The specific purposes of these figures are to show temporal trends and to provide a basis for discussion relating important environmental conditions to the characteristics of sediment fluxes.

At all SONE stations there have been years with low average river flow and years with high average river flow during the monitoring period. These correspond to periods of relatively low and periods of high diffuse source nutrient loading rates, respectively. For example, in the Patuxent River, flows (loads) were high in 1984 (438 cfs) and then low until 1989 when large flows (475 cfs) again occurred. The years 1990 - 1992 were low flow years; 1993 and 1994 were high flow years, among the highest on record (438 and 440 cfs respectively). Corresponding to these periods of high and low flow were years of high and low ammonium fluxes. These patterns are particularly strong at St Leonard Creek (STLC, Figure 6-2.1) and Ragged Point (RGPT; Figure 6-2.2.). It is useful to note that such flux-loads were strongest during the 1990-1994 period when SONE measurements were of a higher frequency (six per year). At other sites patterns were not as consistent but years of large flow were associated with large fluxes. Some of the exceptions to the load-flux relationships are instructive in and of themselves. For example, fluxes were very high and sustained in the lower Potomac River (Ragged Point [RGPT]) during 1990 but river flow (loads) were relatively small (Figure 6-2.2.). One explanation is that there may have been an intrusion of phytoplanktonic debris into the Potomac River from the bay during this period thereby suppling the organic matter needed to fuel large sediment fluxes. A similar phenomenon (but with very low dissolved oxygen conditions) was seen in the Patuxent River estuary during 1987 (Hagy, *pers. comm.*). In the mainstem bay the load-flux relationship appears more complex than at other sites and seems to indicate spatial shifts in deposition related to river flow. It appears that during years of low to moderate flow, spring blooms are proportional to flow and so is the magnitude of deposition in the vicinity of SONE station R-64. Under these conditions the load-flux relationships appear to be robust (Boynton *et al.*, 1994). However, during years of

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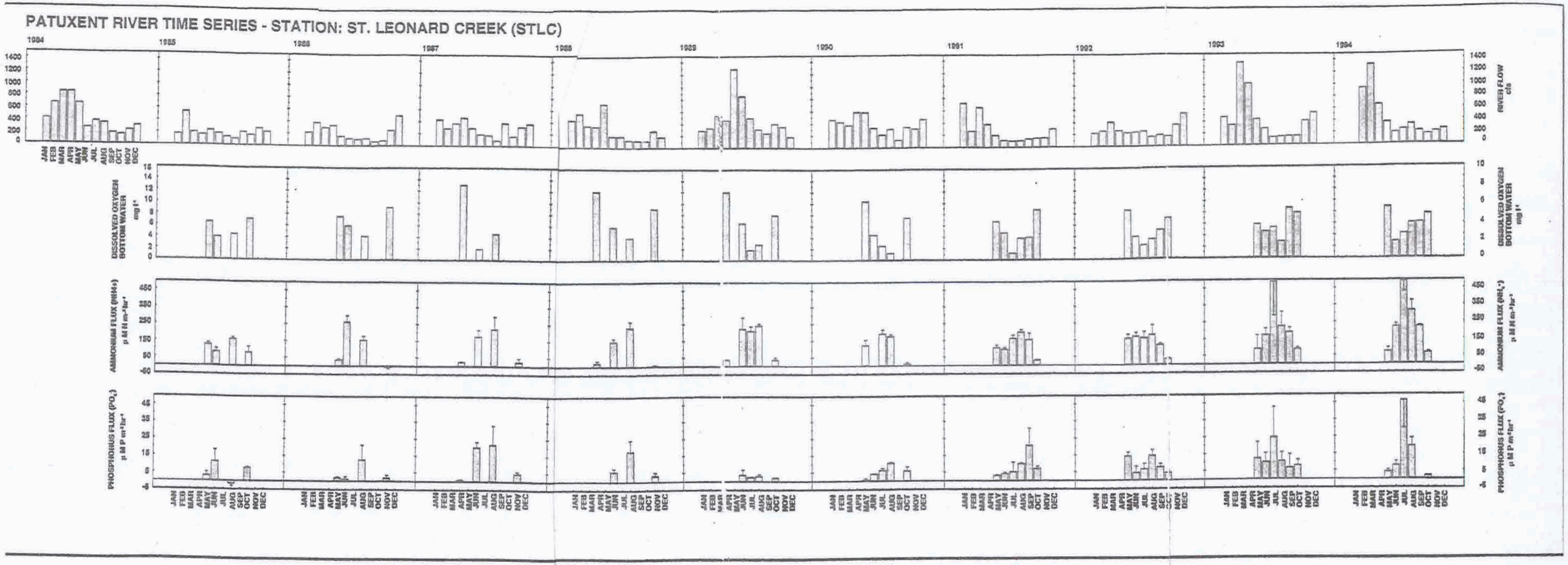
Figure 6-1.1. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Patuxent River at SONE station, St. Leonard Creek (STLC).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in four months, May, June, August and October from 1985 through 1988, in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus (PO_4^-) monthly mean flux values and standard deviations are calculated using one set of triplicate flux measurements available for a specific month at each station from 1985 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.



...ne series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and ...ables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Patuxent River at SONE station, St. ...TLC).

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Figure 6-1.2. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Patuxent River at SONE station, Broomes Island (BRIS).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus (PO_4^-) monthly mean flux values and standard deviations are calculated using one set of triplicate flux measurements available for a specific month at each station from 1989 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.

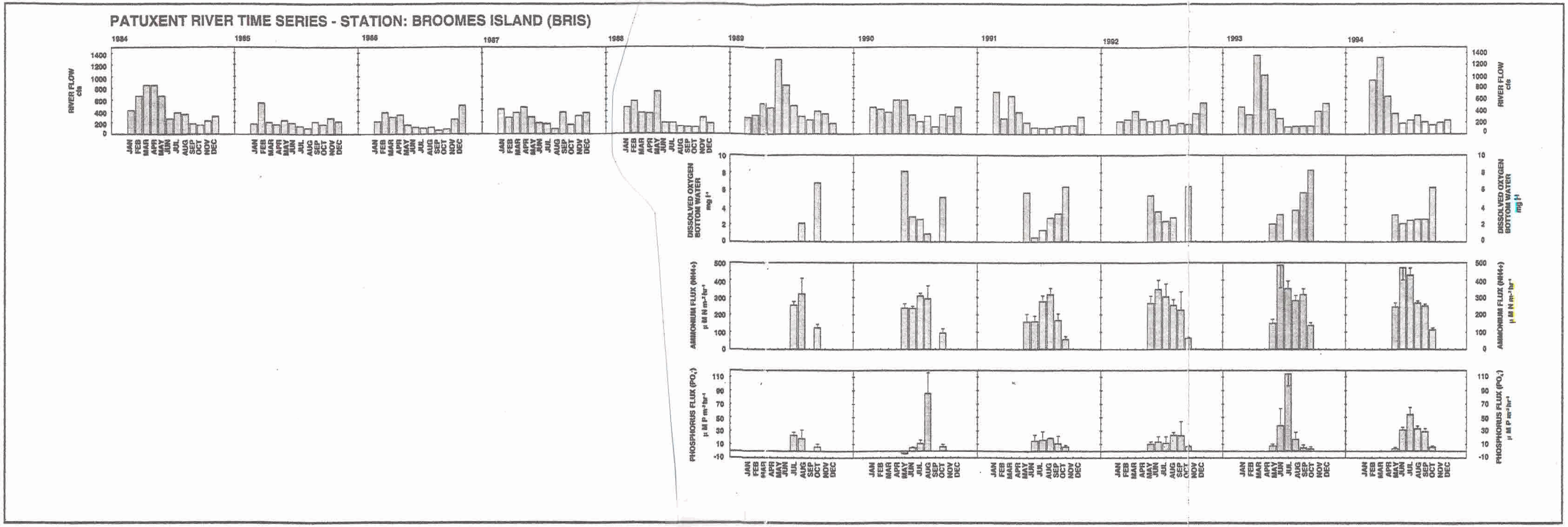

Figure 6-1.2. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Patuxent River at SONE station, Broomes Island (BRIS).

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Figure 6-1.3. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Choptank River at SONE station, Horn Point (HNPT).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in four months, May, June, August and October from 1985 through 1988, in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus(PO_4^-) monthly mean flux values and standard deviations are calculated using one set of triplicate flux measurements available for a specific month at each station from 1985 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.

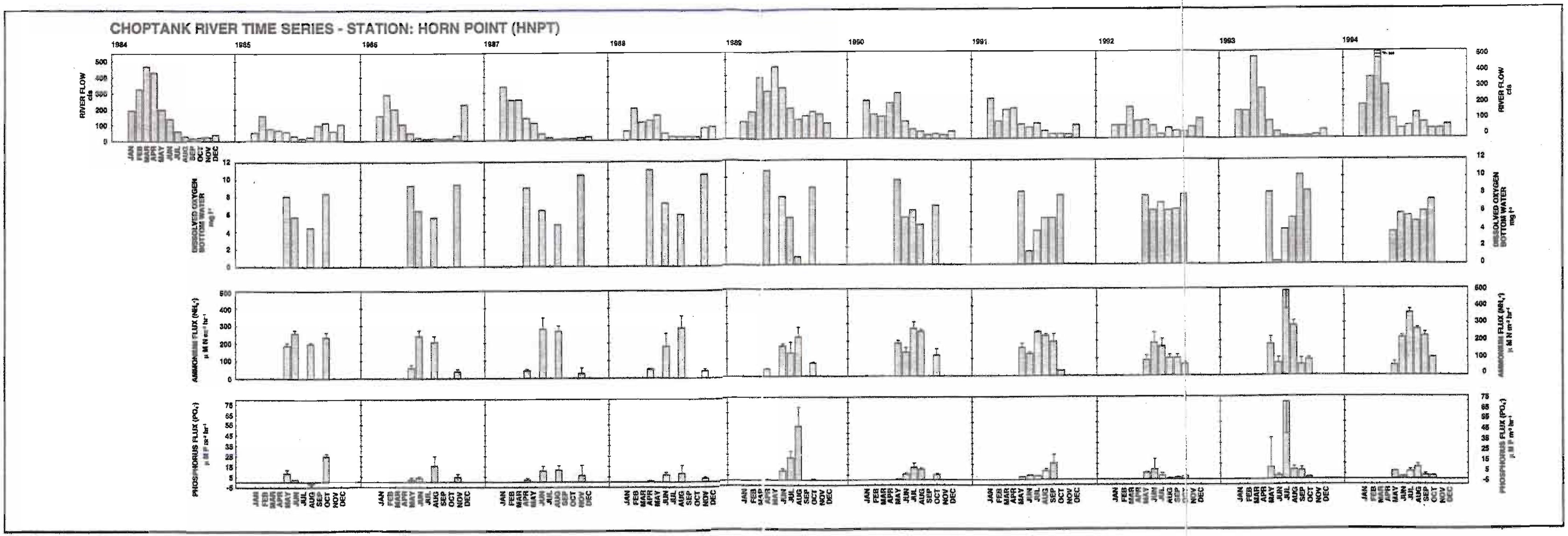

Figure 6-1.3. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Choptank River at SONE station, Horn Point (HNPT).

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Figure 6-1.4. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Potomac River at SONE station, Ragged Point (RGPT).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in four months, May, June, August and October from 1985 through 1988, in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus (PO_4^-) monthly mean flux values and standard deviations are calculated using one set of triplicate flux measurements available for a specific month at each station from 1985 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.

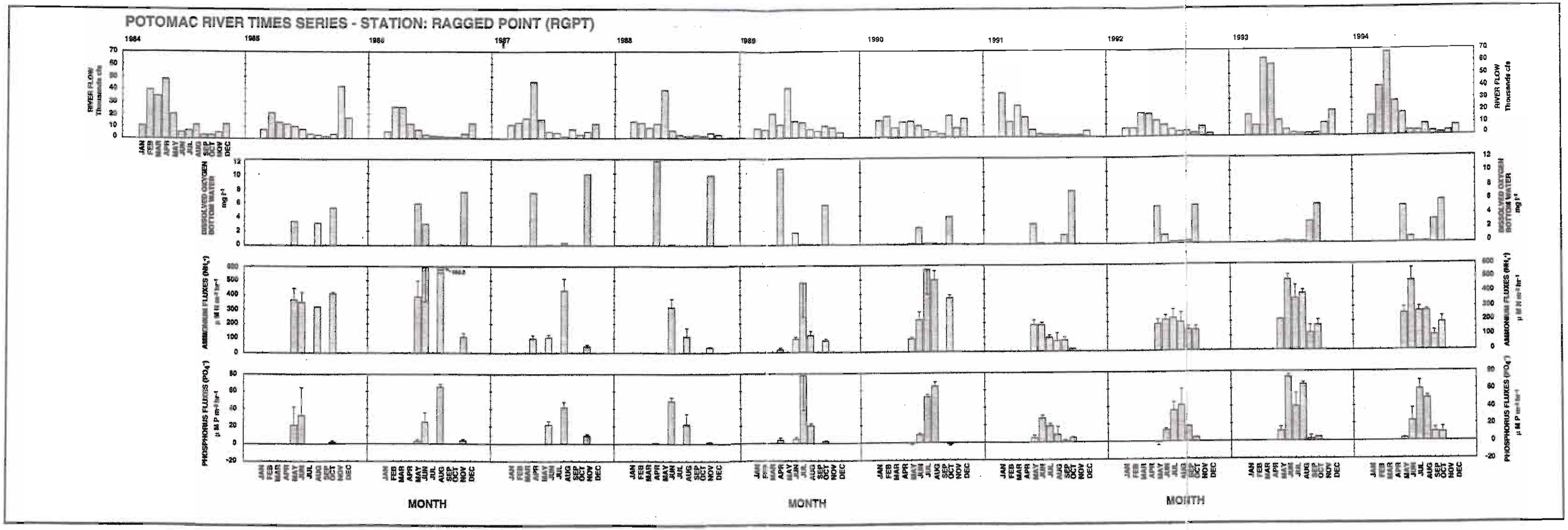

Figure 6-1.4. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Potomac River at SONE station, Ragged Point (RGPT).

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Figure 6-1.5. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Susquehanna River at SONE station, Point No Point (PNPT).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in four months, May, June, August and October from 1985 through 1988, in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus (PO_4^-) monthly mean flux values and standard deviations are calculated using on one set of triplicate flux measurements available for a specific month at each station from 1985 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.

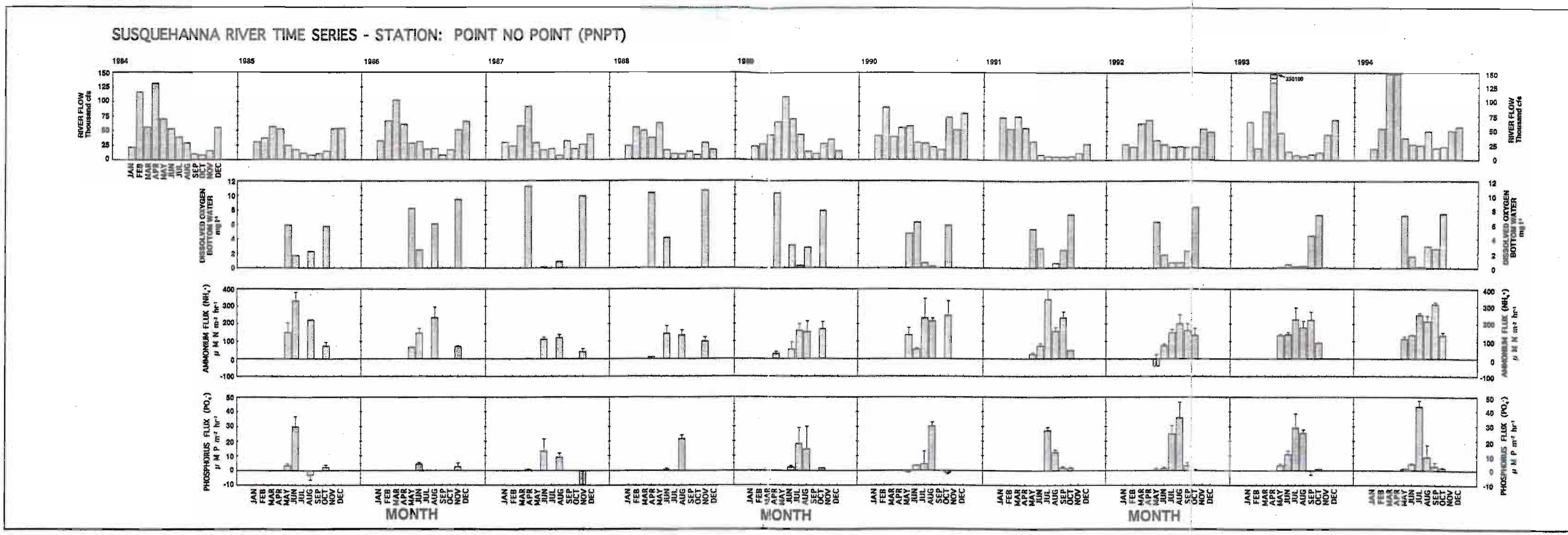

Figure 6-1.5. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Susquehanna River at SONE station, Point No Point (PNPT).

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Figure 6-1.6. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Susquehanna River at SONE station, R-64 (R-64).

- Station location is shown in Figure 3-1.
- River flows are measured at the fall line and represent averages for each month from 1985 - 1994. Data used are provided by US Geological Survey (James *et al.*, 1990; James *pers. comm.*, 1994).
- Dissolved oxygen and flux observations were made with the following frequency; measurements were made in four months, May, June, August and October from 1985 through 1988, in five months in 1989 and 1990 and six months in 1991 through 1994.
- Dissolved oxygen concentration values in bottom waters represent single measurements made at SONE station.
- Ammonium (NH_4^+) and phosphorus (PO_4^-) monthly mean flux values and standard deviations are calculated using on one set of triplicate flux measurements available for a specific month at each station from 1985 through 1994. (September values for all stations only include three years data, 1991 through 1993). Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993b) were excluded in the calculation of average fluxes and standard deviations.
- Negative flux values indicate fluxes from water to sediment.

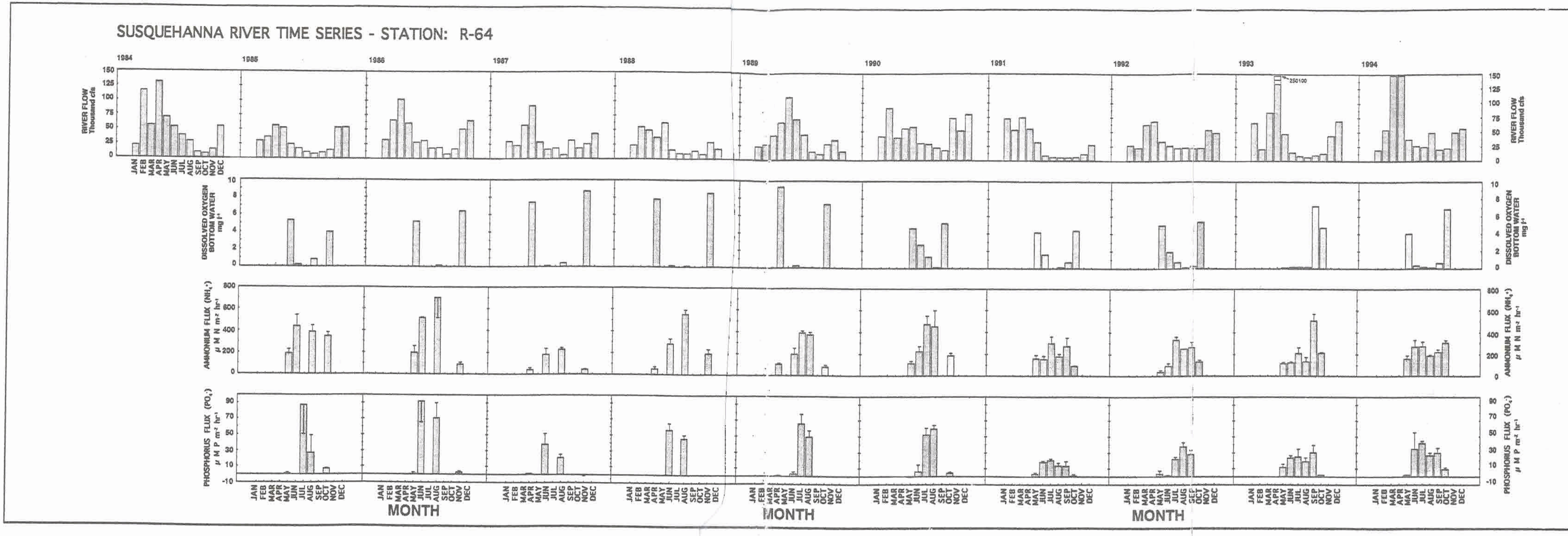


Figure 6-1.6. A time series (bar graphs) of river flow, dissolved oxygen concentrations in bottom waters (water quality) and sediment flux variables, ammonium (NH_4^+) and phosphorus (PO_4^-), measured in the Susquehanna River at SONE station, R-64 (R-64).

especially high flow (*e.g.* 1989, 1993 and 1994) it appears that the spring bloom is transported farther south prior to deposition. In these cases deposition at R-64 is less than expected as is also the case for sediment fluxes. Under the low to moderate flow regimes, sediment fluxes at the more southerly mainstem bay station (Point No Point [PNPT]) are lower than those at the more northerly station (R-64); however, under higher flow regimes (*e.g.* 1993 and 1994) the pattern is reversed. While more complex, these observations indicate that there can be substantial spatial shifts in ecological processes and this argues for adequate spatial coverage in monitoring programs.

A second class of load-flux relationships is particularly apparent for phosphorus fluxes. Assuming that there is an adequate supply of phosphorus coming from overlying waters, phosphorus fluxes appear to be controlled largely by two mechanisms. In the first case, phosphorus fluxes generally follow the annual temperature pattern, when temperature are low (cool) then fluxes are low and fluxes are correspondingly high when temperatures are warmer during summer. This pattern has been observed most clearly at Buena Vista (BUVA) in the upper Patuxent River. The most likely mechanism for these large seasonal fluxes is that the flux is maintained by the burrowing and irrigation activities of the large macrofaunal community at this site. At these types of locations (shallow and non-stratified) hypoxic or anoxic conditions are not known to occur and under these conditions phosphorus fluxes are typically low. However, this site has an ample organic matter supply and hence an ample phosphorus supply. Normally, phosphorus would be sequestered in these sediments resulting in a small flux. The large macrofaunal community circumvents this storage mechanism.

The second mechanism controlling phosphorus fluxes involves oxygen conditions in deep waters proximal to the sediment surface. Typically, much of the phosphorus in estuarine sediments is complexed as oxyhydroxides and is quite insoluble. However, under anoxic conditions phosphorus becomes soluble and can diffuse from sediments to overlying waters. This pattern is particularly evident at several SONE stations. In the lower Choptank River (Horn Point [HNPT, Figure 6-1.3]) in 1985 through 1988 dissolved oxygen conditions in bottom waters were never measured below 4 mg l^{-1} and phosphorus fluxes were uniformly low. However, in August, 1989 bottom water dissolved oxygen concentrations dropped to about 1 mg l^{-1}, probably in response to the large freshet of 1989. Under these low dissolved oxygen conditions sediments responded quickly (same month) with the largest releases of phosphorus on record up to that time. This pattern was repeated again in 1993 when low dissolved oxygen conditions again occurred probably in response to the very large freshet of that year. A pattern of high release of phosphorus from sediments associated with a drop of bottom water dissolved oxygen concentration below about 1.5 mg l^{-1} is repeated throughout the SONE data record(Figures 6.1-1. to 6.1.6.). Once released this phosphorus is again available for phytoplanktonic uptake, algal growth, deposition and decomposition, reinforcing the downward water quality trajectory described earlier in this report (Figure 2-1.). While there are good biological reasons that discourage the maintenance of bottom water dissolved oxygen concentrations at 1.5 mg l^{-1} and indicate that this is too low a goal (*i.e.* too low to support healthy infaunal communities), one benefit of at least achieving this goal would be to drastically reduce the flux of phosphorus from sediments to overlying waters.

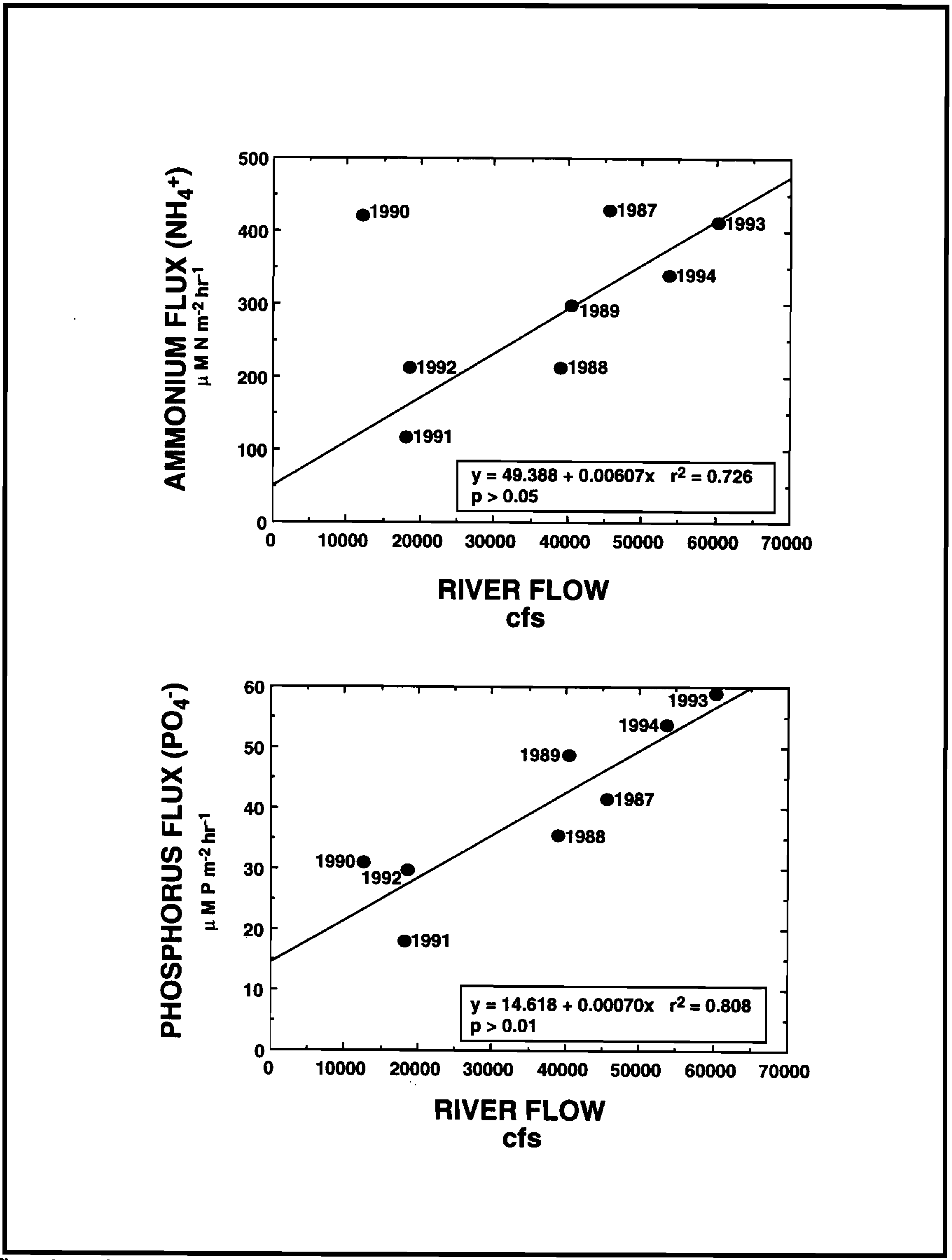
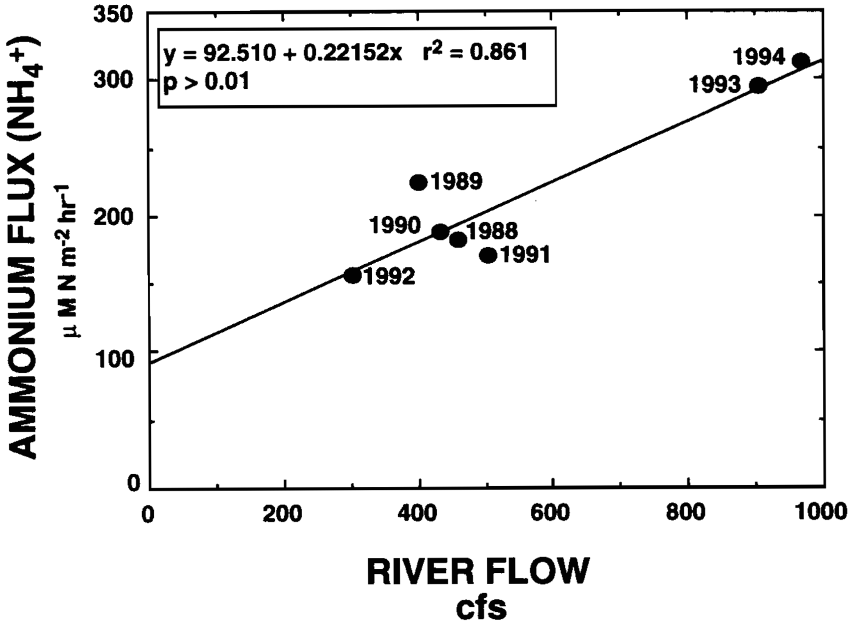


Figure 6-2.1. Scatter plots of average monthly river flow (winter months) versus average summer season ammonium and phosphorus fluxes at a SONE station (Ragged Point [RGPT]) in the lower Potomac River.
Note that the 1990 ammonium flux value was not used in calculating the linear regression model.



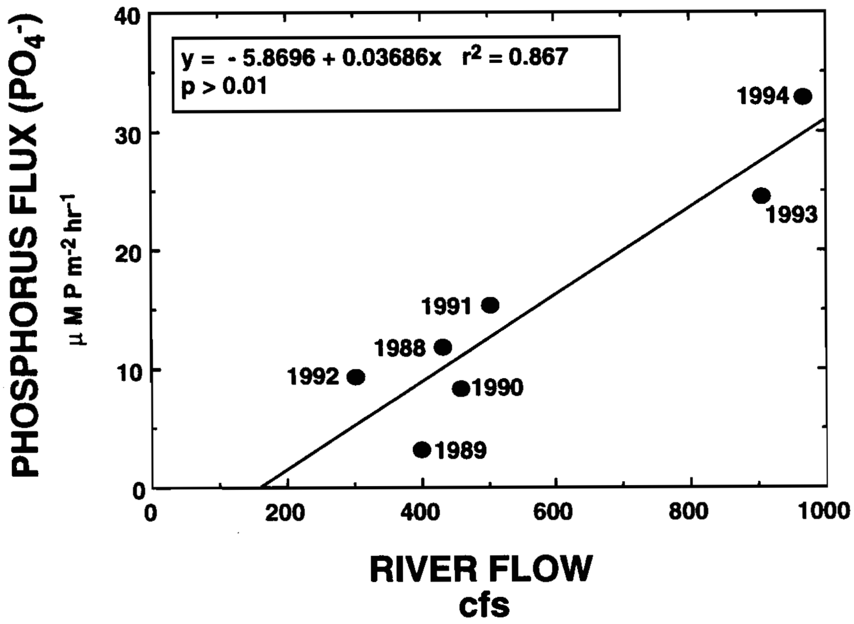


Figure 6-2.2. Scatter plots of average monthly river flow (winter months) versus average summer season ammonium and phosphorus fluxes at a SONE station (St. Leonard Creek [STLC]) in the lower Patuxent River.

An Approach to Extending Spatial Resolution

One issue in all monitoring efforts concerns the spatial resolution of the sampling scheme. In the simplest terms the scheme must be able to differentiate areas according to their status, health or general condition. In the Chesapeake Bay monitoring program there is a substantial gradient in the degree of spatial resolution available from the different components. Water quality monitoring has the greatest spatial coverage with 22 stations in the Maryland portion of the bay and 57 stations in Maryland tributaries. Other components have varying degrees of lesser spatial coverage.

The SONE component of the EPC Program operates with a standard set of 8 stations; two located in the mainstem bay, four stations in the Patuxent River estuary and one each in the lower mesohaline regions of the Choptank and Potomac Rivers. SONE-type data collected at additional stations in other programs provide additional useful information related to spatial coverage: these include the Pooles Island Dredge Disposal Monitoring study which includes several stations in the northern bay; the National Science Foundation (NSF) sponsored Land Margin Ecosystems Program (LMER) with stations in the upper, mid and lower bay; a suite of stations in the Patapsco and Back Rivers as part of the tributaries component of the Chesapeake Bay Monitoring Program and three stations in the upper Potomac as part of a water quality study supported by the Corps of Engineers. With the exception of the monitoring at Pooles Island these are short term studies lasting only a year or two and will not provide long-term data sets. Nevertheless, they certainly are useful in expanding the spatial coverage of SONE measurements.

The relatively limited spatial coverage available for SONE measurements continues to be a problem. In previous interpretive reports (Boynton *et al.*, 1993b, 1994) it has been shown that SONE fluxes are related to nutrient loading rates, are responsive to *in-situ* conditions and have a substantial impact on water quality. However, it has not been possible to make well constrained estimates of flux for full estuarine systems, nor have these types of estimates for depth zones other than those that are monitored been made.

Are there ways to expand this coverage at reasonable costs? If coverage were expanded could important gradients in flux between depth zones and various habitats be observed both in the mainstem bay and in the tributaries? If spatial coverage were sufficient, could annual benthic fluxes be quantitatively mapped? Could these maps be compared with nutrient loads for trends? Could the maps be compared among years for trends in response to climate and management induced changes in loading rates? An approach which involves the development of a SONE mapping system and the use of statistical models which relate easily monitored sediment properties to sediment fluxes is proposed to accomplish these objectives.

Six examples of conceptual SONE flux maps are provided in Figures 6-3.1. - 6-3.6. These maps should be considered preliminary examples of a quantitative display of SONE fluxes. At present these maps are mainly for heuristic purposes. The first example, the map of the Potomac River estuary (Figure 6-3.1.) shows three different depth zones (channel, flank and shoal) and the estuary divided into three different longitudinal sections (tidal fresh, turbidity maximum and mesohaline). These divisions represent a first approximation to the spatial areas among which the magnitude and characteristics of SONE fluxes might vary in important ways. While the EPC Program does not routinely collect data from each of these zones, SONE measurements coupled with those from other programs suggest that fluxes probably vary spatially in the following ways:

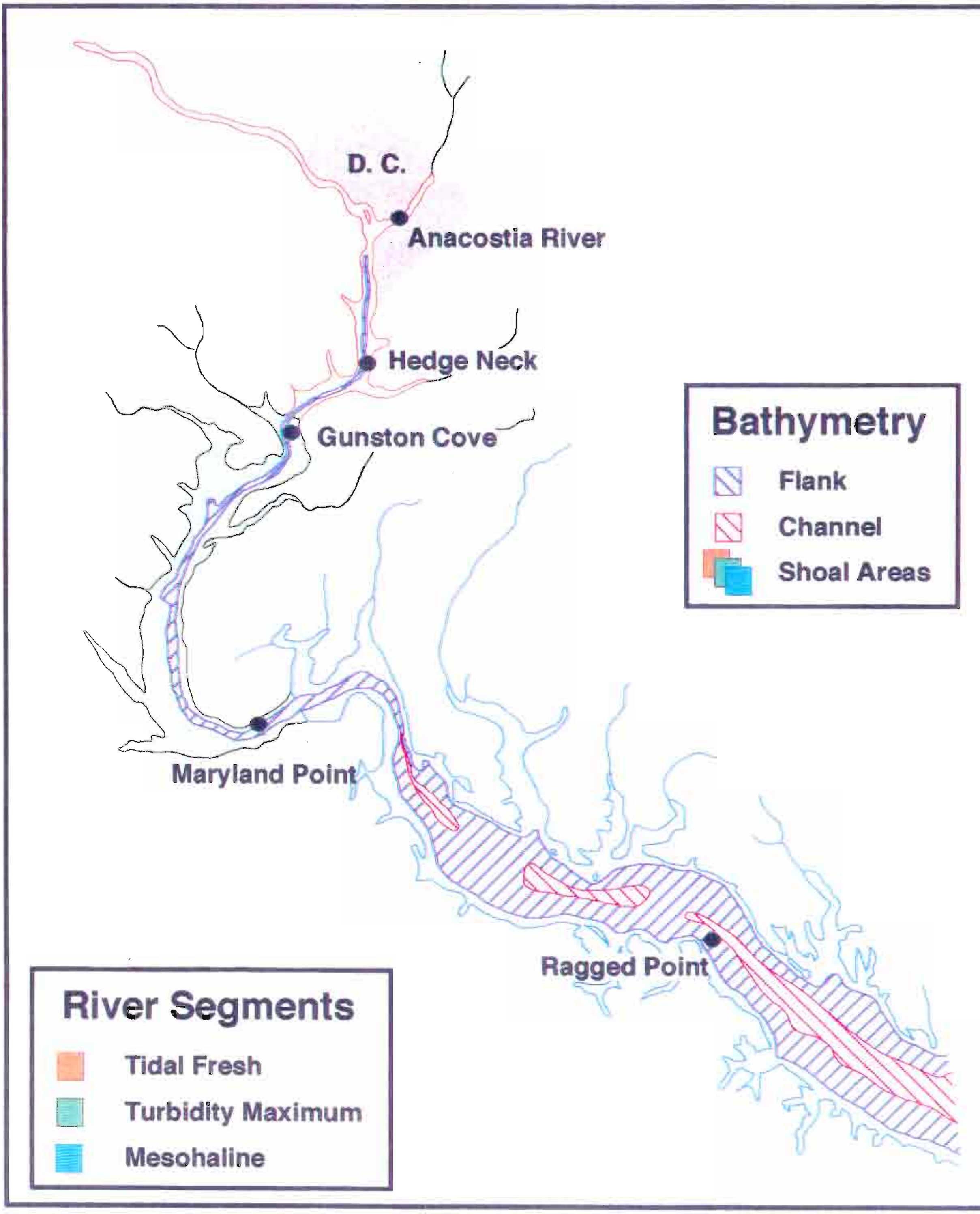


Figure 6-3.1. A color coded map of bathymetry and river segments (estuarine zones) for the Potomac River estuary.
Current and past SONE stations at Ragged Point (RGPT) and Maryland Point (MDPT), respectively, are indicated by bold dots. Stations at Gunston Cove and Hedge Neck were sampled during summer, 1994; several summer measurements were also made in the Anacostia River during 1990.

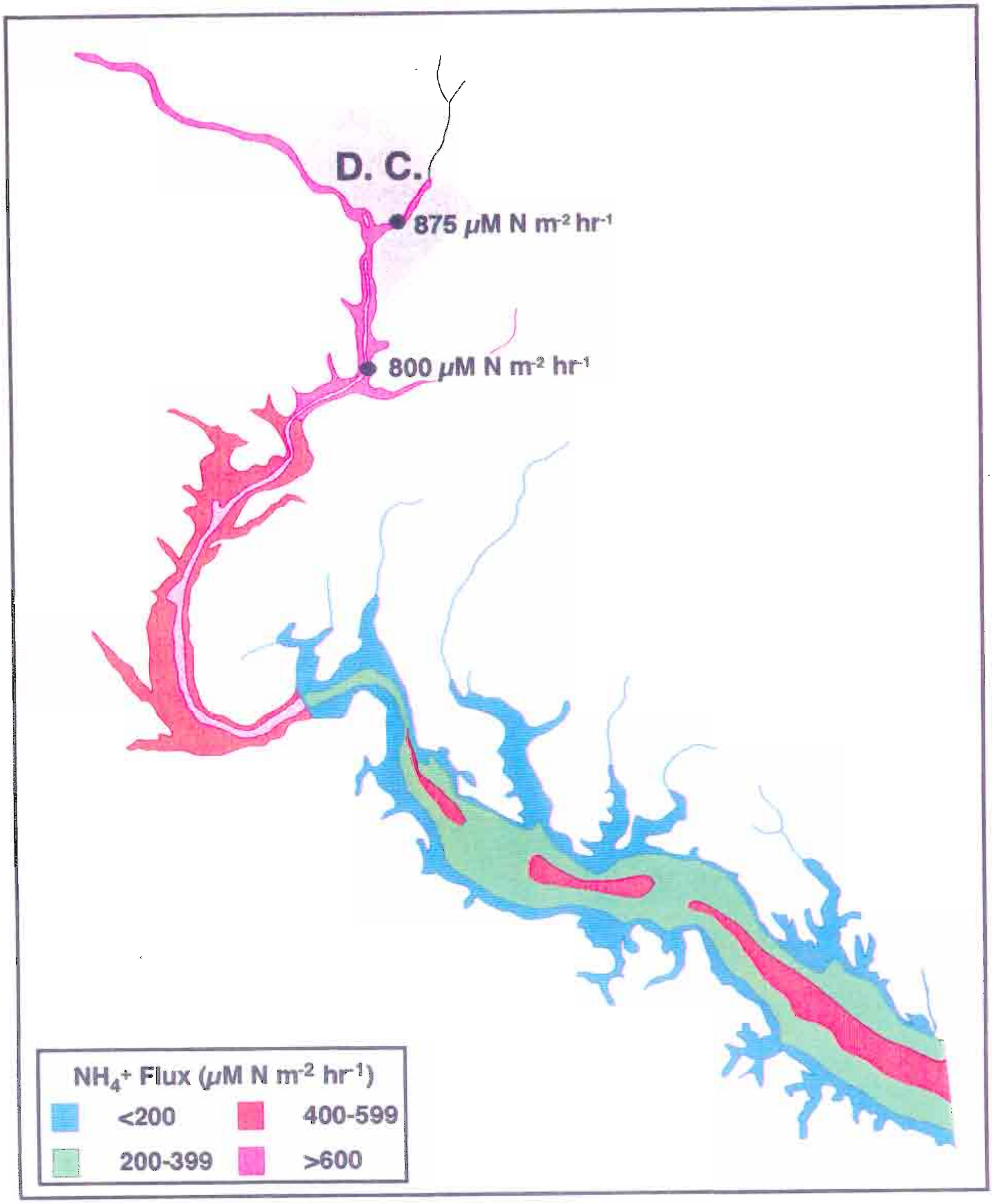


Figure 6-3.2. A color coded map of estimated summer ammonium flux (1985 - 1992) in three zones and three depth habitats of the Potomac River estuary.
Highest measured values are shown in the diagram.

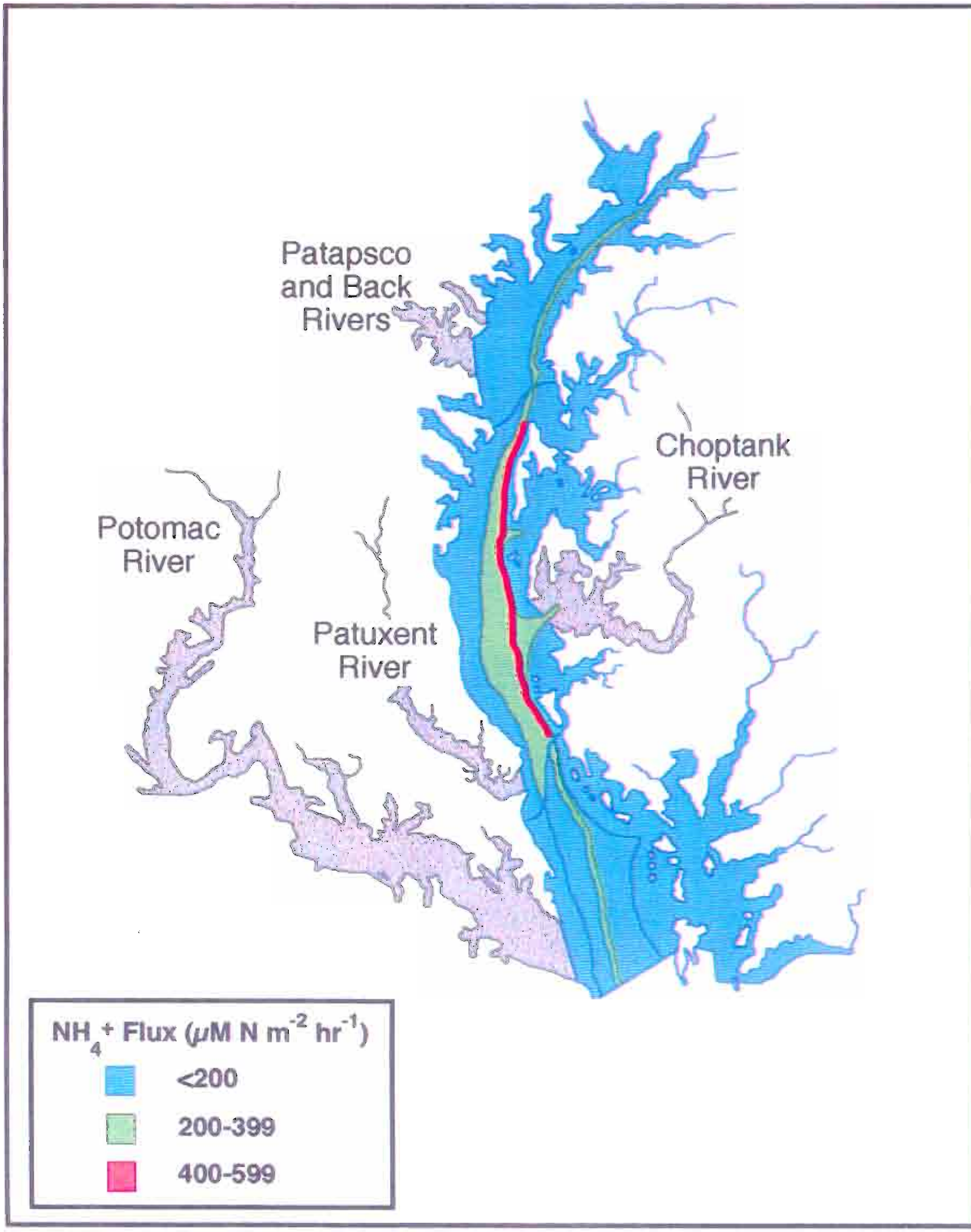


Figure 6-3.3. A color coded map of estimated summer ammonium flux (1985-1992) in three zones and three depth habitats of the Maryland mainstem bay.

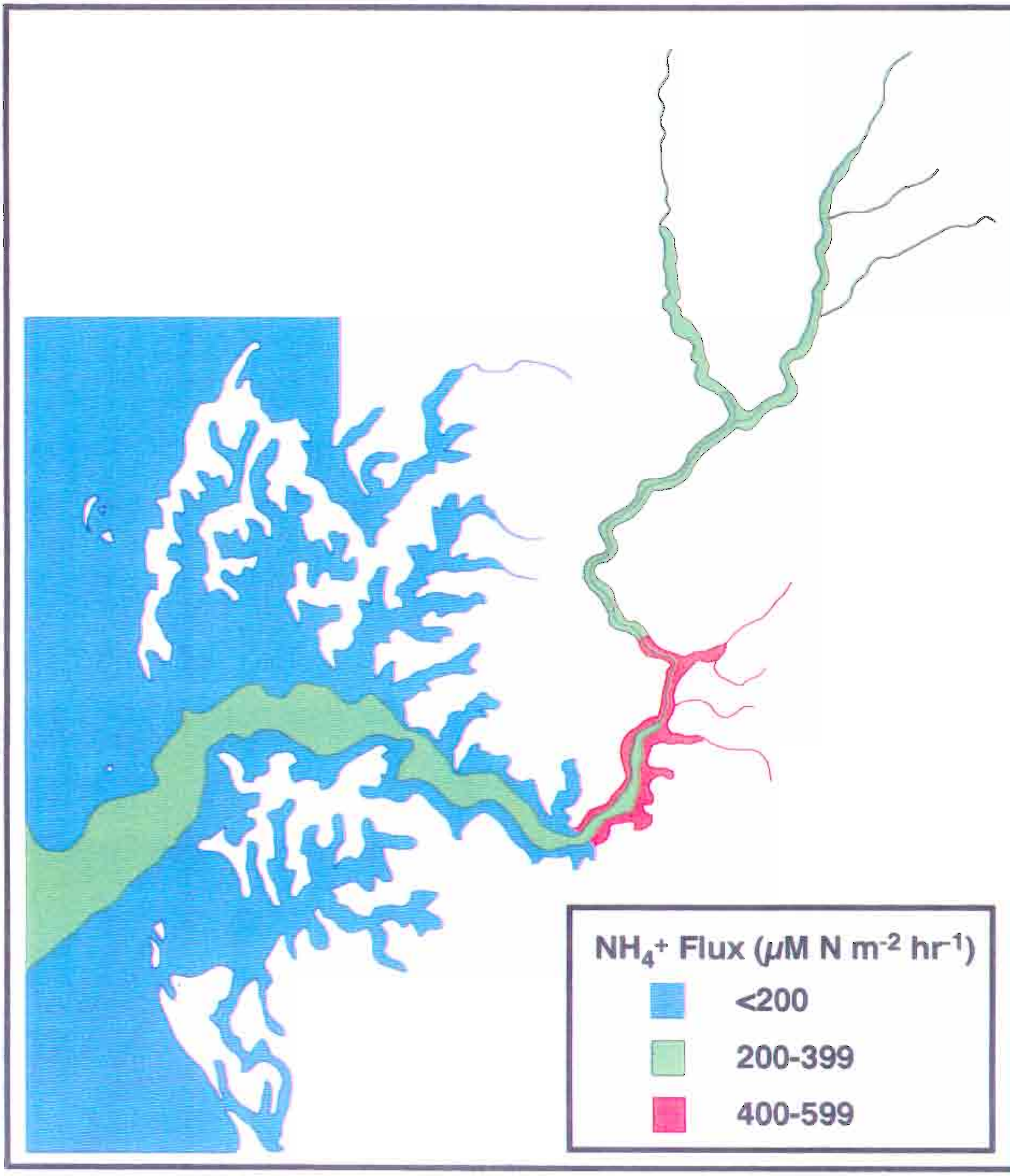


Figure 6-3.4. A color coded map of estimated summer ammonium flux (1985 - 1992) in three zones and three depth habitats of the Choptank River estuary.

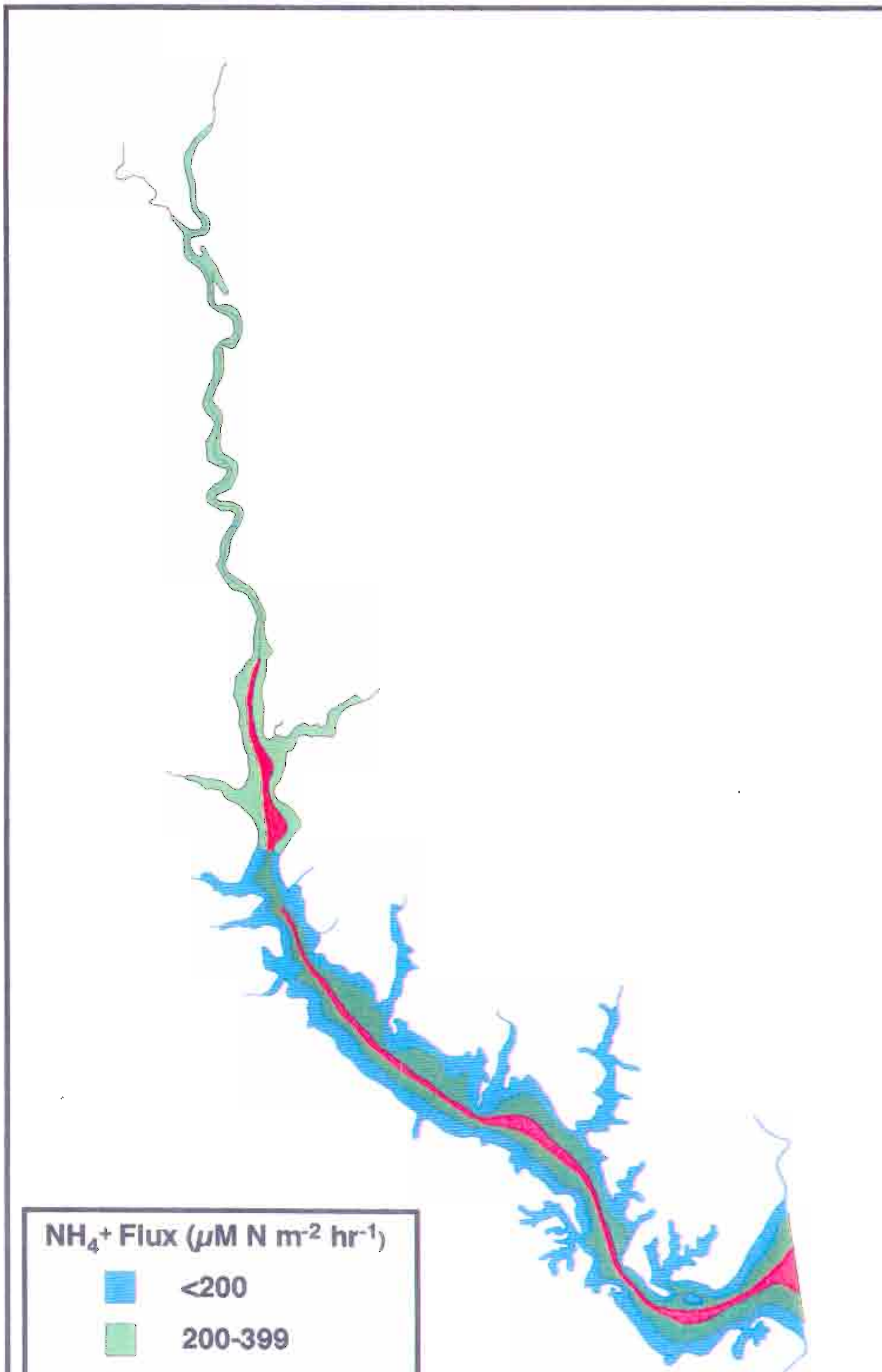


Figure 6-3.5. A color coded map of estimated summer ammonium flux (1979 - 1992) in three zones and three depth habitats of the Patuxent River estuary.

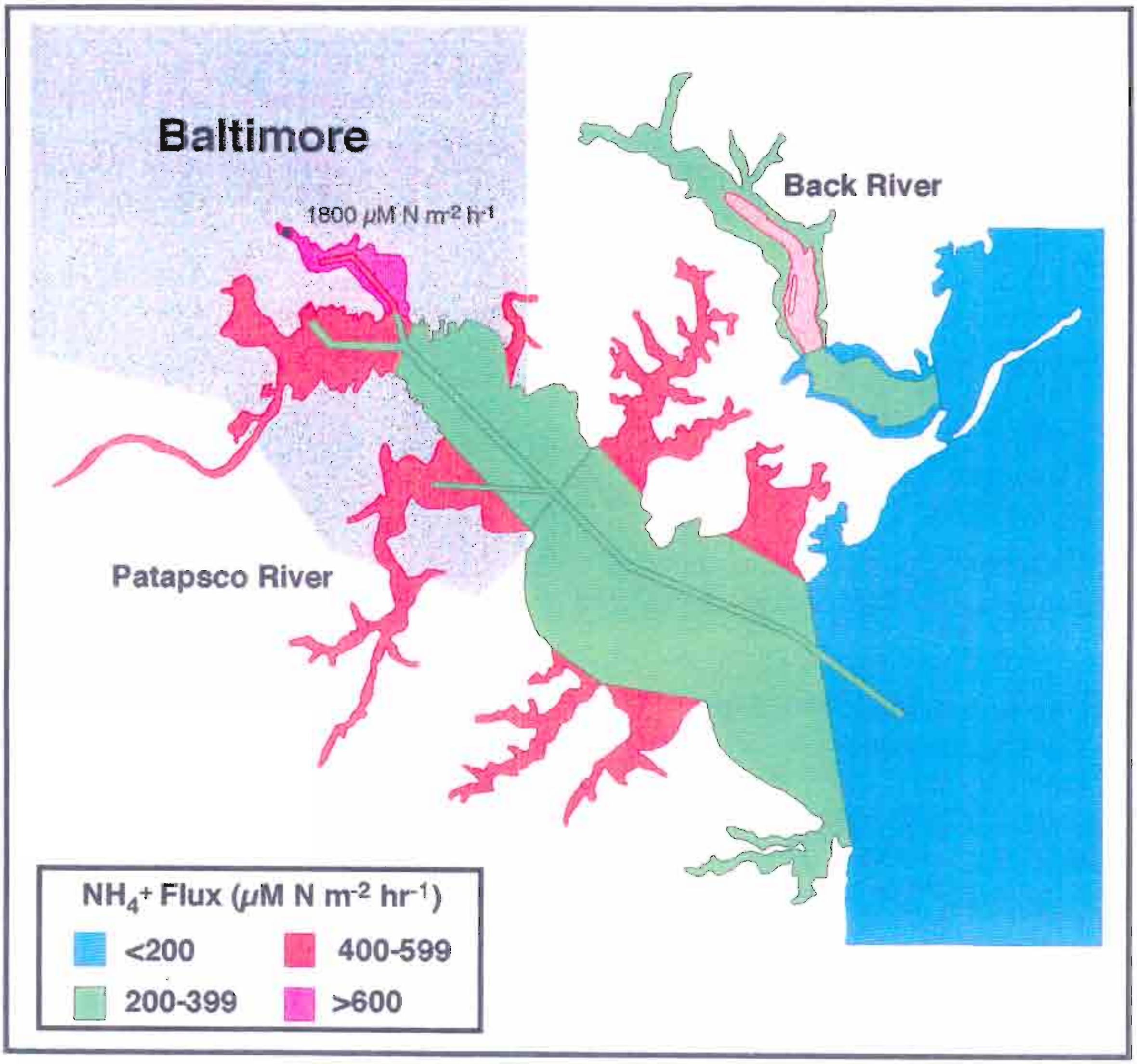


Figure 6-3.6. A color coded map of estimated summer ammonium flux (1994) in three depth zones and three depth habitats of the Patapsco and Back River estuaries.
Highest measured values are shown in the diagram.

(a) fluxes are highest in zones proximal to large sewage and organic matter discharges (*e.g.* upper Potomac River, Anacostia River, Back River and the Inner Harbor region of the Patapsco River),

(b) fluxes are also large in depositional basins (central channels of the mainstem bay and tributary rivers), which receive augmented amounts of particulate materials because of focusing,

(c) fluxes are moderate on the flanks of the bay being fueled by deposition of organic matter from overlying waters,

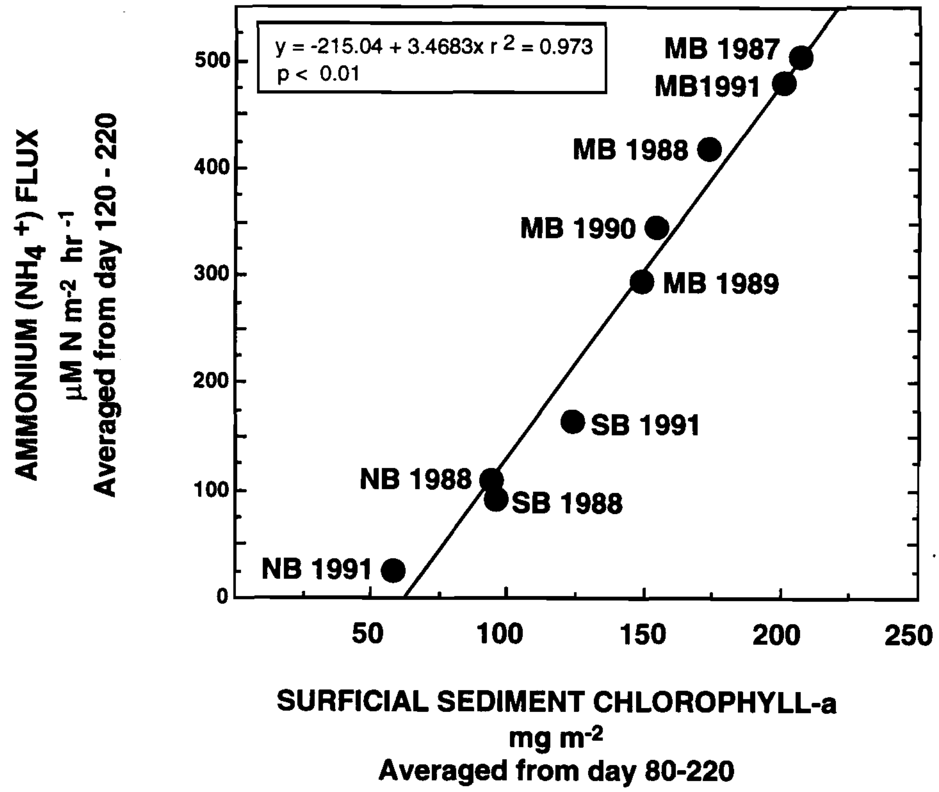
(d) fluxes are low in the shoals because these are not depositional areas and because seagrasses and benthic algae can utilize some of the nutrients which would have been released and

(e) fluxes in the polyhaline portion of the bay are lower than in the mesohaline because organic matter supply rates to sediments are lower in the polyhaline region.

In Figures 6-3.2. - 6-3.6. ammonium fluxes are mapped according to the expected magnitude of the flux and are useful at this point mainly as examples of the approach. For example, in the Potomac River measurements were available from the Anacostia River and four other sites, all of which were located in the flank depth zones. In developing the ammonium flux map measured ammonium fluxes from these sites were color coded according to magnitude. Shoal areas were assumed to have lower fluxes and deep channels higher fluxes. Each of the maps from other regions of the bay were coded in a similar fashion (*i.e.* available flank measurements were used to set a baseline; shoal and channel fluxes were set lower and higher, respectively). Even in this qualitative form the maps provide a spatial picture showing where fluxes would be expected to be highest and which of these systems might be most susceptible to changes in sediment processes.

Two steps need to be taken to operationalize this approach and make it a useful addition to the monitoring program. First, a GIS (Geographic Information System) map of the bay would need to be prepared which would serve both as a mapping/display tool but even more importantly as a mechanism for calculating flux totals over various zones of the bay and for calculating (and displaying) interannual differences in flux totals. In addition, the GIS would hold data concerned with the sediment properties which would be used as flux predictors (see section 6.3) and as a tool for interpolating fluxes to all zones of the bay and tributary rivers. This task is tedious but can be readily accomplished with available hardware and software.

The second step is more difficult. Specifically, this step involves relating some easily measured feature of estuarine water quality/sediment quality to sediment nutrient fluxes. Numerous regression analyses (Boynton *et al.*, 1994) have been conducted and from these it has been concluded that measurement of total chlorophyll-a in surficial sediments (0.3 - 1.0 cm depth) is the best predictor available of ammonium, phosphate and silicate fluxes. In addition, dissolved oxygen concentration in deep waters and surficial sediment Eh are also helpful when predicting nitrate and phosphorus fluxes. Examples of relationships between sediment chlorophyll-a and ammonium and phosphate flux are given in Figures 6-4.1. and 6-4.2. and additional examples can be found in Cowan and Boynton (1995) and Boynton *et al.* (1994). The basic concept thus involves converting readily measured sediment properties into quantitative flux estimates.



LEGEND:

NB **Northern Bay**
Station: Still Pond (SLPD)

MB **Central Bay**
Station: Adjacent to R-64

SB **Southern Bay**
Station: Ajdjacent to York Spit,VA

Figure 6-4.1. Scatter plot of surficial sediment total chlorophyll-a mass versus ammonium (NH_4^+) at three locations along the longitudinal axis of Chesapeake Bay.
Surficial sediment chlorophyll-a data at each station were averaged between day 80-220 for each year of measurement. Sediment nutrient fluxes measured at each station were averaged between days 120-220 for each year of measurement. Station designations and locations are as follows: NB = North Bay (located at the earlier SONE site at Still Pond [SLPD]; MB = Mid Bay (located at SONE station R-64); SB = South Bay (located adjacent to York Spit near the mouth of the York River, VA).

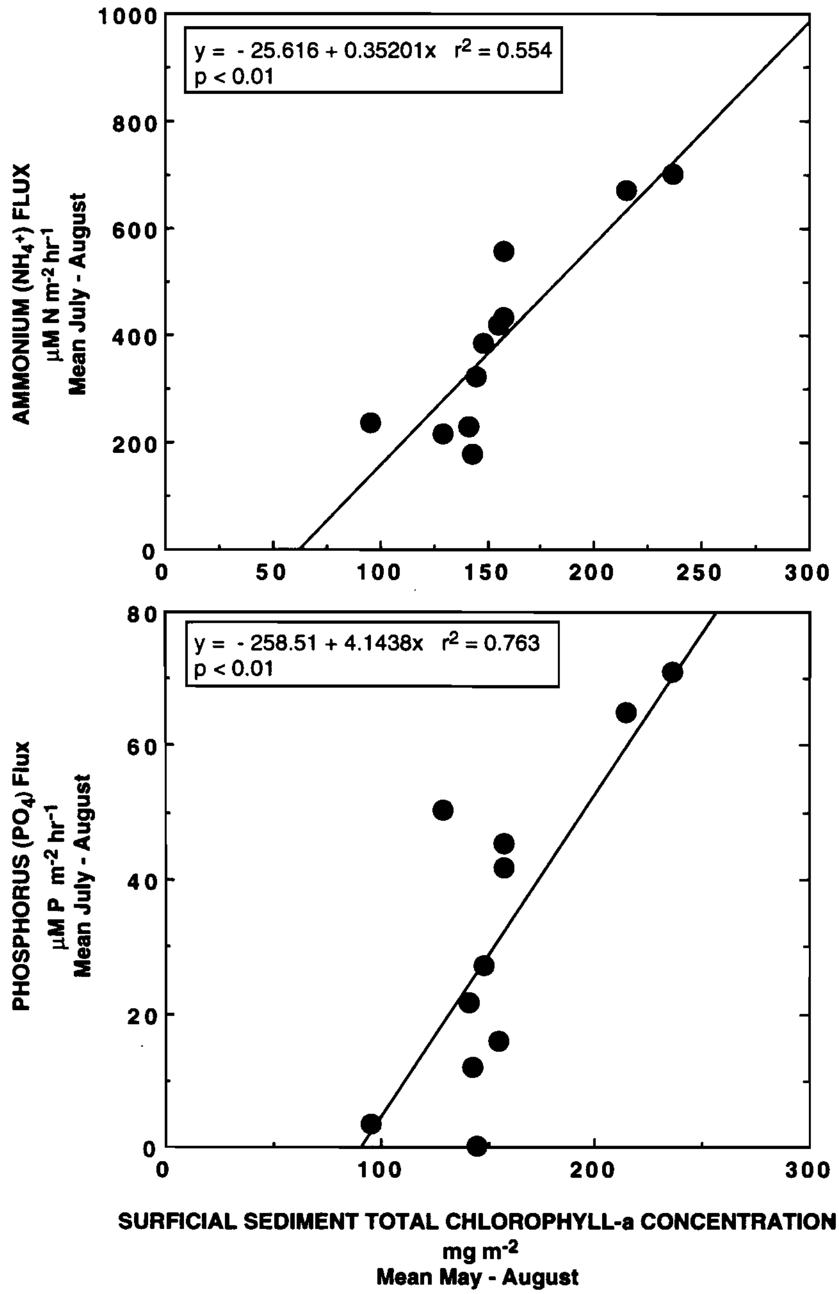


Figure 6-4.2. Graphs depicting the relationship between surficial total chlorophyll-a, ammonium (NH_4^+) flux and phosphorus (PO_4^-) flux at three SONE stations, Buena Vista (BUVA), R-64 and Ragged Point (RGPT) for May through August data from 1985 to 1988.

Several distinct steps are necessary in order to make this suggested procedure operational. First, sediment chlorophyll-a, Eh and bottom water dissolved oxygen maps need to be produced using spatial and temporal scales appropriate to the above objectives. The regression analyses referred to above indicate that early spring (March) through early summer (July) chlorophyll-a levels in surficial sediments are by far the most important predictors of flux. Thus, several maps should be made using data collected between early spring and early summer. The desired spatial resolution would require sampling in three estuarine zones and at three depth habitats within each zone. The chlorophyll-a maps of the mainstem Chesapeake Bay presented in Boynton *et al.* (1994) were based on about 60 samples. It is anticipated that an estuary such as the Patuxent River could be mapped (for chlorophyll-a, Eh and bottom water dissolved oxygen) in one day and would result in some 40 samples, a number adequate to cover estuarine zones and depth habitats (with replication within zones and depths to assess small-scale variability [meters to sub-kilometers]). The final step would be to verify the fluxes predicted from map distributions with direct flux measurements (as currently done in the SONE Program) in areas predicted as having low, medium and high fluxes. It is suggested that a pilot effort be initiated in the Patuxent River estuary in late spring 1995 with assessment of the concept and technique completed in late fall 1995.

6.3 Water Quality Impacts of Sediment-Water Fluxes

The main focus of the Ecosystem Processes Component (EPC) study has been monitoring sediment-water nutrient and oxygen exchanges. Particular attention has been focused on understanding relationships of these fluxes to nutrient loading and other environmental variables. Mass balance calculations (Boynton *et al.*, 1994) clearly indicate the importance of sediments in determining water quality conditions in the bay and hence it is of particular interest to understand factors controlling these fluxes and the likely responses of these processes to reduced nutrient loading rates. In this section, computations are presented which start with nutrient inputs from terrestrial and atmospheric sources. Nutrients derived from sediment-water fluxes are ultimately driven by these inputs then tracked through phytoplanktonic uptake and eventually to decomposition and oxygen consumption in bottom waters. The purpose of the calculations is to estimate the impact of benthic nitrogen releases on dissolved oxygen conditions in deep waters.

The results of these measurements and calculations are summarized in Figure 6-5. Nutrient loading rates used (as total nitrogen from point, non-point and direct atmospheric deposition to estuarine surface waters) for Baltimore Harbor were estimated by Stammerjohn *et al.* (1991) and other nutrient loading rates represent total nitrogen loads averaged for the years 1985 and 1986 (Summers, 1989). Clearly, there is a very considerable range in loads and, as has been observed in this and other components of the Monitoring Program, a considerable range in water quality and biological responses (Figure 6-5.a.). Fluxes of ammonium from these sites have been measured for 5 - 10 years except for the station in Baltimore Harbor which was first monitored during summer, 1994. Again, there is a distinct proportionality between loading rates and sediment ammonium fluxes. The utility of making measurements at sites with different loading rates is clearly evident in this example. The ammonium fluxes at R-64 and mid-Patuxent River SONE stations are large and moderate, respectively while fluxes observed during summer in the Inner Harbor region of the Patapsco are truly huge, reflecting the heavy concentration of organic matter in those sediments (Figure 6-5.b.).

The final two panels in Figure 6-5. represent calculations aimed at estimating the water quality impact of nutrient loads and sediment-water nutrient fluxes (Figure 6-5.c. and 6-5.d.). In Figure 6-5.c. algal production is calculated based on the amount of nitrogen that is

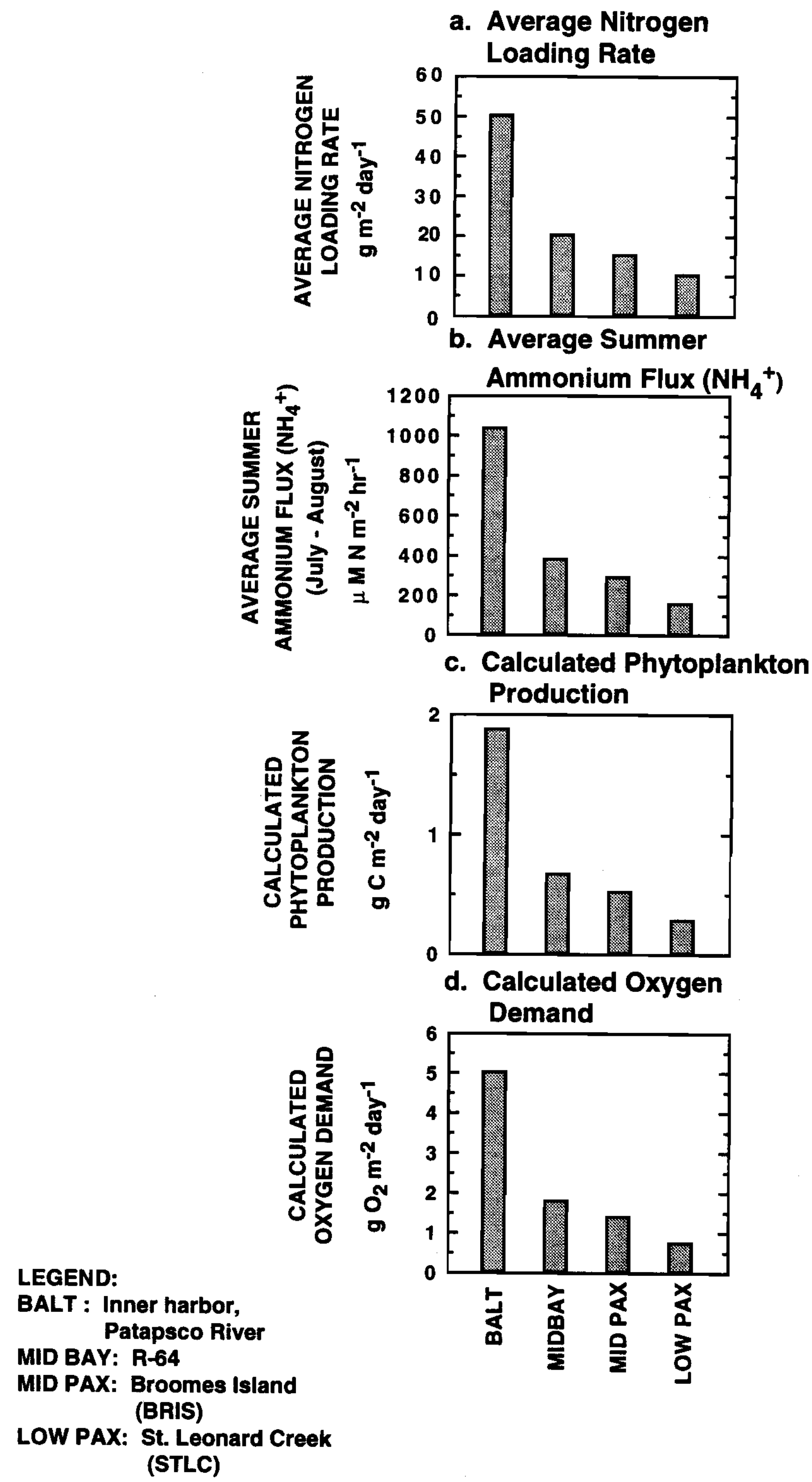


Figure 6-5. A summary of measurements and calculations relating nitrogen loading rates, sediment ammonium (NH_4^+) fluxes, calculated phytoplankton production and calculated oxygen consumption rates. Data are from a selection of Chesapeake Bay locations spanning a large gradient in nutrient loading rates. Details of the calculations are given in the test.

released from sediments. The calculation assumes that for every nitrogen atom available, 6.25 atoms of carbon are photosynthetically produced. Again, rates are very high in Baltimore harbor, moderate in the mid-bay (R-64) and mid-Patuxent (Broomes Island [BRIS]) and relatively small in the lower Patuxent. Nevertheless, at all sites sediment nutrient releases are capable of supporting readily measured amounts of primary production. Finally, the amount of organic matter produced by phytoplankton was oxidized to inorganic end products (*e.g.* CO_2 and inorganic nutrients) and the amount of oxygen needed for this oxidation calculated (Fig 6-5.d.). Oxygen consumption rates ranged from 0.75 to 5.00 g O_2 m^{-2} day^{-1} in this selection of systems. These rates of respiration can be considered to range from modest to very high as would be their impact on water column water quality conditions. For example, the water column at the Inner Harbor station is about 7 meters with about half of it below the pycnocline. If this deep water were saturated with oxygen, it would hold about 25 g O_2 m^{-2} during summer temperature and salinity conditions. If sediment oxygen consumption were the only oxygen demand (assuming water column respiration to be zero) the oxygen in the water column would be depleted in only five days. If water column respiration were included, oxygen depletion time would be even faster. Unfortunately, water column respiration data for this and most other SONE sites are not available. At the rest of the stations shown in Figure 6-5. the impact of fluxes on dissolved oxygen conditions is less than at the highly enriched Inner Harbor site but still large, especially at the mid-Patuxent River station where the water column beneath the pycnocline is relatively short and thus has a limited oxygen storage capacity. Overall, nutrient input reductions would be expected to be mirrored by sediment nutrient release reductions and then reductions in oxygen consumption rates, similar to the pattern of events shown in Figure 2-1 of this report.

7. NEW APPROACHES FOR ECOSYSTEM MONITORING

7.1 Monitoring Sediment Metabolism Under Anoxic and Oxic Conditions: TCO_2 Flux Approach

One of the goals of the Ecosystem Processes Component of the Chesapeake Bay Monitoring Program is to assess temporal and spatial variabilities in the fate of organic matter reaching estuarine sediments. In the conceptual model shown in Figure 2-1. nutrient enrichment leads to larger algal stocks and deposition of organic matter to sediments. This, in turn, leads to higher rates of sediment metabolism, nutrient releases and low dissolved oxygen conditions.

Since the beginning of the monitoring program sediment oxygen consumption (SOC) measurements have been used as the prime tool for estimating sediment metabolism as well as a tool for directly assessing the impact of sediments on water column oxygen conditions. In previous reports (Boynton *et al.*, 1993b, 1994) the limitations of this approach (SOC) for estimating the fate of organic matter were discussed and some alternate techniques suggested. In brief, the sediment oxygen consumption (SOC) technique is a good method for estimating oxygen uptake by sediments. However, the technique fails when oxygen concentrations are low (< 2 mg l^{-1}) because sediment oxygen consumption (SOC) rates become proportional to oxygen concentrations and the technique provides no information concerning metabolism when anoxic conditions are present. The sediment oxygen consumption (SOC) technique is still an important tool but falls short of providing all of the information needed to assess total sediment metabolism.

With this problem clearly identified, the Ecosystem Processes Component (EPC) Program initiated a series of trial measurements of sulfate reduction rates in order to obtain estimates of anaerobic sediment metabolism which could be used in conjunction with sediment oxygen consumption (SOC) rates to provide estimates of total sediment metabolism. The technique and early results have been reported in detail in Boynton *et al.* (1994) and additional measurements taken during 1994 are provided in this report. While this approach appears reasonable, the technique is incredibly labor intensive, requiring extensive handling on the research vessel, month-long incubations of sediment cores under temperature controlled laboratory conditions and tedious analytical analyses.

Until recently this approach was the only way to obtain reasonable measurements of total sediment metabolism. However, new analytical technology has now made it possible to routinely measure total CO_2 concentrations with great precision. The importance of this rests on the fact that CO_2 is the end product of both aerobic and anaerobic respiration (Boynton *et al.*, 1994). Prior to the development of this analytical technology it was not possible to confidently measure relatively small changes in CO_2 concentration in seawater against the huge background concentrations which are present.

7.1.1. TCO_2 Field and Laboratory Methods

7.1.1.1. Field

Water samples are slowly transferred from a syringe to a small BOD bottle and are then quickly injected with mercuric chloride ($HgCl_2$) to stop metabolism. Note that $HgCl_2$ works in both oxic and anoxic conditions. Glass stoppers are dropped into place, the bottles are shaken and then stored in a dark humid environment.

7.1.1.2. Laboratory

The coulormetric methods of Johnson *et al.* (1987) are used to analyze the water samples for total CO_2.

$$TCO_2 = CO_2(aq) + H_2CO_3 + HCO_3^- + CO_3^{-2}$$

Ninety nine percent of CO_2 in marine systems is in the form of HCO_3^-. A calcium carbonate correction is calculated separately.

7.1.1.3. The Johnson Method

In brief the Johnson methodology is as follows:

All of the CO_2 is released to a free gas, phosphoric acid (10%) is injected into a precise volume of the water sample. The gas is carried in a nitrogen gas stream to a UIC, Inc. coulometer. The entire system is gas tight.

The CO_2 gas reacts with the UIC solution to form a weak acid lowering the pH which causes the solution to change color. This change in light transmission is detected by a photometer. The coulometer generates OH^- ions (by hydrolysis) to back-titrate the weak acid. Titration is complete when the photometer detects initial conditions. The electrical current used to generate OH^- can be accurately, precisely and easily measured. The precision of this technique is 0.1%. In the Chesapeake Bay, with a TCO_2 background averaging 2000 μM, a 5 μM change can be detected. During the four hour period that flux measurements were taken changes of TCO_2 of between 20 and 50 μM were detected.

During 1994 the Ecosystem Processes Component (EPC) program was able to make CO_2 flux measurements at ten stations located in a variety of bay habitats. Specifically, measurements were made in June, July and November, 1994 at 6 sites in the very enriched Patapsco and Back Rivers (Table 7-1.a., Figure 7-1.3.). Measurements were also made through the SONE sampling period at SONE station R-64 in the mainstem bay (Table 7-1.b., Figure 7-1.1.) and at three sites in the upper Potomac River in May, July, August and October, 1994 (Table 7-1.c., Figure 7-1.2.). Note that in Tables 7-1.a. through 7-1.c., simultaneous measurements of sediment oxygen consumption (SOC in molar units) are provided for direct comparison.

These data indicate several points relevant to the Ecosystem Processe Component (ECP) program. First, rates are higher, at times much higher, in those areas proximal to nutrient and organic matter sources. For example, rates in the Inner Harbor(INHB) area of the Patapsco River averaged 11.5 mM m^{-2} hr^{-1} during summer of 1994 (equivalent to about 3.3 g C m^{-2} day^{-1}). Lower rates were observed in the outer portions of the harbor, as expected. Similarly, rates in the upper Potomac River (Hedge Neck [HGNK] and Gunston Cove [GNCV]) were higher than those farther downstream (Maryland Point [MDPT]) and these were generally higher than those measured in the Maryland mainstem bay at R-64 (Table 7-1.b.). It appears that CO_2 fluxes respond well to gradients of enrichment, as expected and as required of a monitoring tool.

Second, it appears that CO_2 fluxes provide reasonable estimates of sediment metabolism, even under anoxic conditions when sediment oxygen consumption (SOC) fluxes do not occur. At R-64 in the Maryland mainstem bay sediment oxygen consumption (SOC) fluxes were at or near zero in July and August, 1994 while CO_2 fluxes indicate moderate metabolic

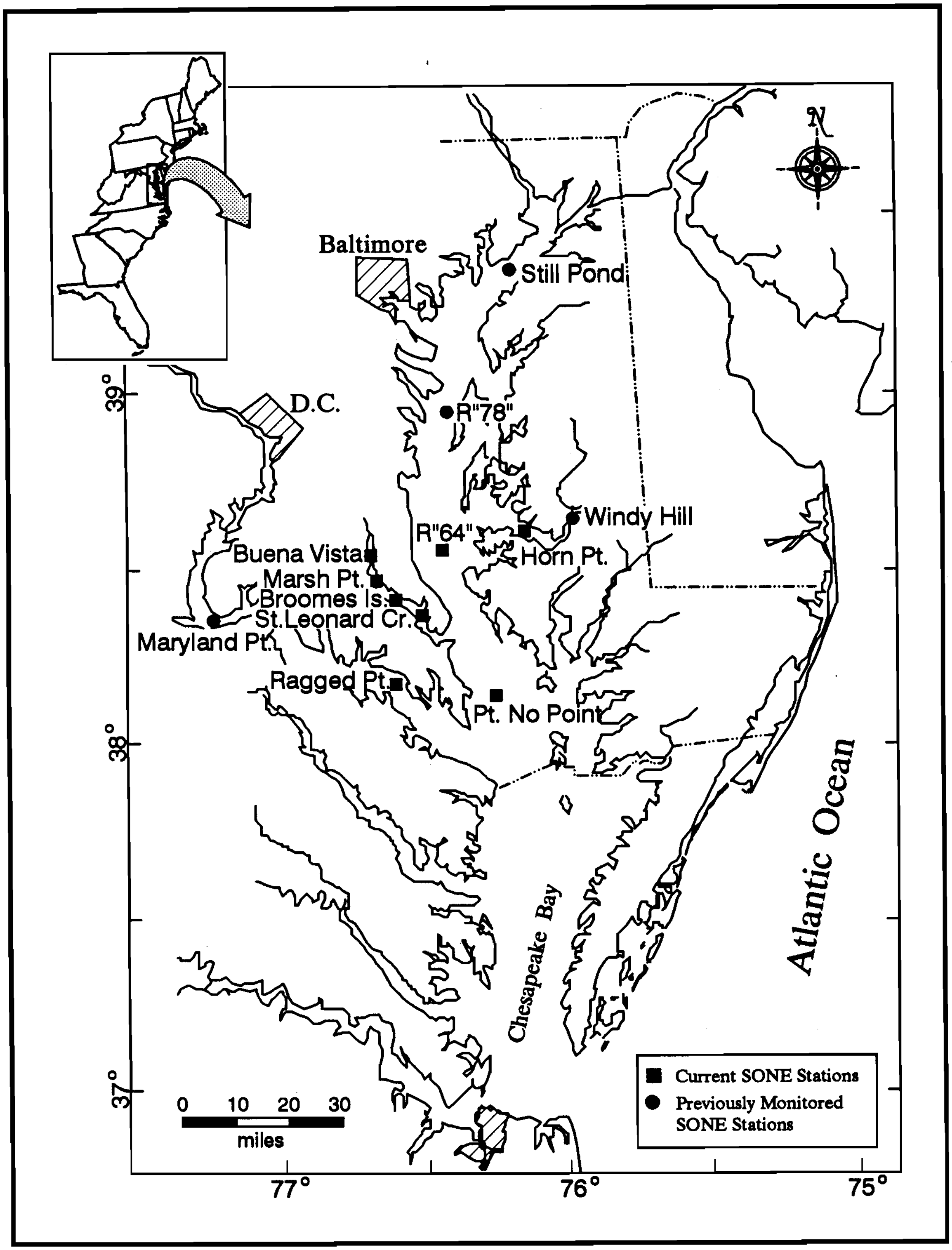


Figure 7-1.1. Location of Current and Previously sampled Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations in the Maryland portion of Chesapeake Bay (1984 - 1994).
Sediment oxygen consumption (SOC) and Total Carbon Dioxide (TCO_2) fluxes were measured at R-64 in 1994.

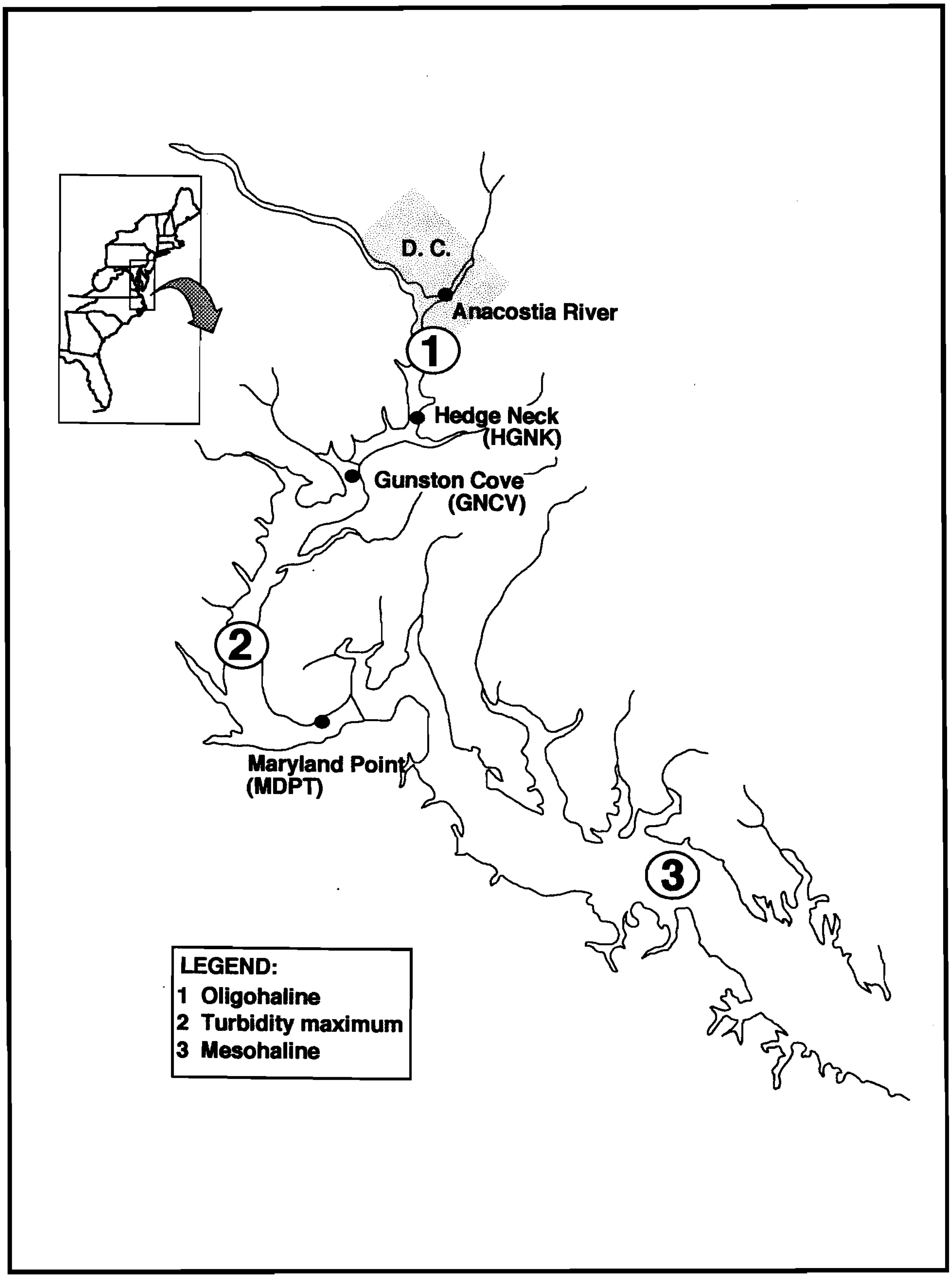


Figure 7-1.2. Location of three stations in the Potomac River at which sediment oxygen consumption (SOC) and Total Carbon Dioxide (TCO_2) fluxes were measured in 1994.

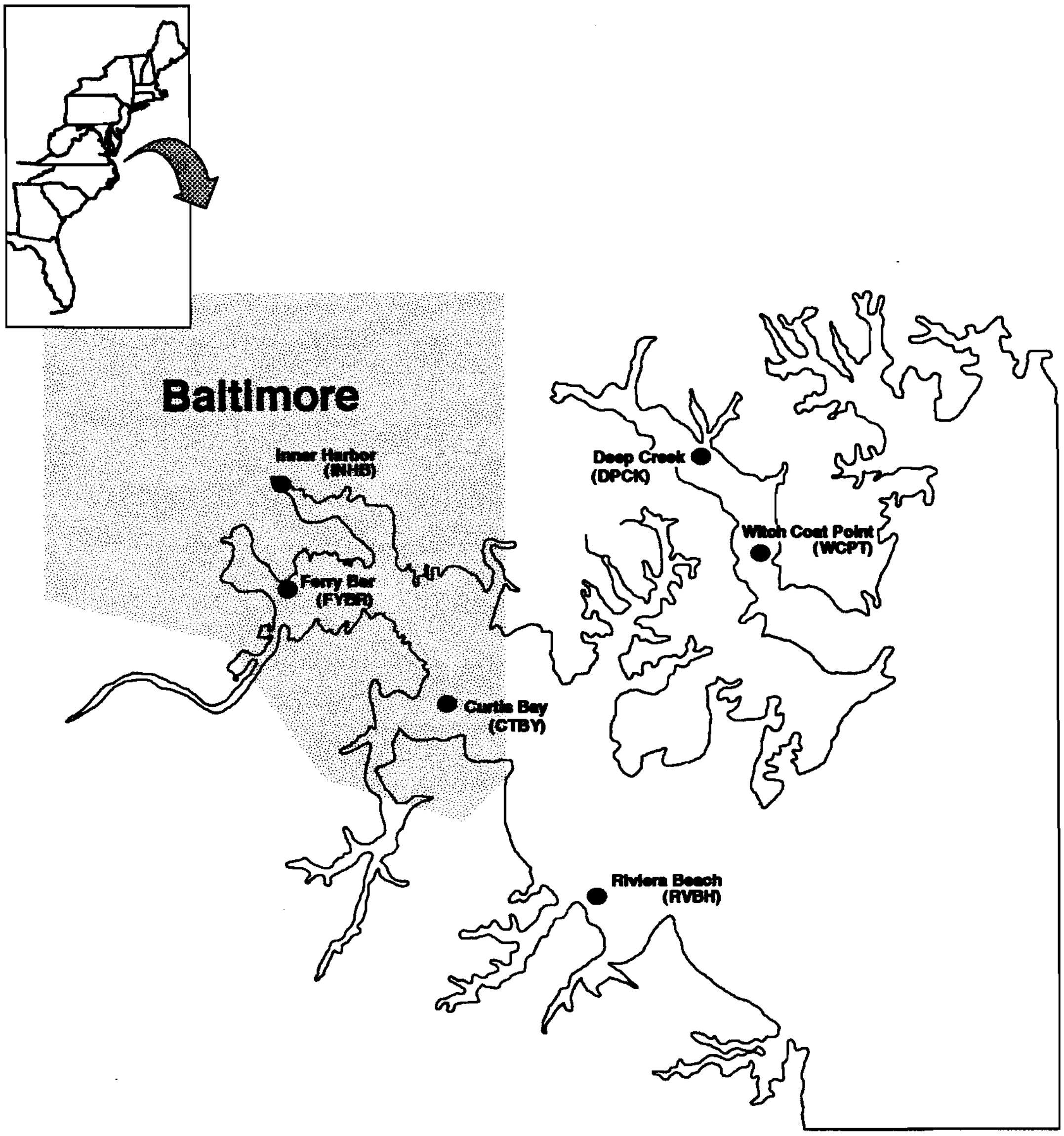


Figure 7-1.3. Location of four stations in the Patapsco River and two stations in the Back River at which sediment oxygen consumption (SOC) and Total Carbon Dioxide (TCO_2) fluxes were measured in 1994.

STATION		JUNE	STD	JULY	STD	NOVEMBER	STD
a. Measurements in the Patapsco and Back Rivers (1994); Figure 7-1.3.							
Patapsco River Inner Harbor (INHB)	SOC	1.24	-0.21	0.49	-0.47	0.99	-0.20
	TCO_2	13.81	2.58	9.22	3.95	5.64	0.56
	O_2/CO_2	**0.09**		**0.05**		**0.18**	
Patapsco River Ferry Bar (FYBR)	SOC	1.42	-0.32	1.45	-0.38	0.87	-0.09
	TCO_2	7.79	0.40	8.58	0.00	1.72	0.00
	O_2/CO_2	**0.18**		**0.17**		**0.51**	
Patapsco River Curtis Bay (CTBY)	SOC	4.06	-0.22	0.98	-0.14	0.92	-0.04
	TCO_2	8.38	0.10	2.06	0.71	2.64	1.88
	O_2/CO_2	**0.48**		**0.47**		**0.35**	
Patapsco River Riviera Beach (RVBH)	SOC	3.80	-0.12	2.51	-0.10	2.64	-0.32
	TCO_2	9.55	0.77	3.47	0.50	1.76	0.38
	O_2/CO_2	**0.40**		**0.73**		**1.50**	
Back River Deep Creek (DPCK)	SOC	2.28	-0.26	1.55	-0.09	1.46	-0.09
	TCO_2	7.93	0.83	3.82	0.49	3.20	0.59
	O_2/CO_2	**0.29**		**0.41**		**0.46**	
Back River Witch Coat Point (WCPT)	SOC	3.28	-0.46	1.65	-0.08	1.07	-0.06
	TCO_2	6.02	1.63	4.90	1.25	1.76	0.15
	O_2/CO_2	**0.54**		**0.34**		**0.61**	

Table 7-1. A summary of sediment oxygen consumption (SOC) and Total Carbon Dioxide (TCO_2) fluxes based on measurements made during 1994 at:
a. the Patapsco and Back Rivers
b. the Potomac River
c. the Mid bay (station R-64)
Units of SOC and TCO_2 fluxes are mM O_2 m^{-2} hr^{-1} and mM CO_2 m^{-2} hr^{-1}.
NOTE: Values not calculated are noted as NC

STATION		MAY	STD	JULY	STD	AUGUST	STD	OCTOBER	STD
a. Measurements in the Potomac River (1994); Figure 7-1.2									
Potomac River Hedge Neck (HGNK)	SOC	3.13	-0.29	1.93	-0.15	2.81	-0.33	2.01	-0.21
	TCO_2	9.62	0.98	2.36	0.36	5.32	0.51	1.45	0.40
	O_2/CO_2	**0.32**		**0.82**		**0.53**		**1.39**	
Potomac River Gunston Cove (GNCV)	SOC	3.03	-0.22	3.13	-0.04	3.98	-1.03	2.05	-0.21
	TCO_2	6.02	2.22	5.47	0.17	7.66	2.80	4.77	1.12
	O_2/CO_2	**0.50**		**0.57**		**0.52**		**0.43**	
Potomac River Maryland Point (MDPT)	SOC	2.93	-0.43	3.38	-0.62	2.15	-0.71	0.02	-0.13
	TCO_2	1.40	0.30	2.78	0.71	2.69	1.39	2.14	2.75
	O_2/CO_2	**2.09**		**1.21**		**0.80**		**0.01**	

	MAY	STD	JUNE	STD	JULY	STD	AUG	STD	SEPT	STD	OCT	STD
c. Mainstem bay - Station R-64; Figure 7-1.1.												
SOC	0.94	-0.04	0.38	NC	0.03	-0.17	0.00	-0.01	0.51	NC	1.72	-0.30
TCO_2	1.74	0.34	NC	NC	1.95	0.56	1.73	0.15	NC	NC	3.66	0.56
O_2/CO_2	**0.54**				**0.01**		**0.00**				**0.47**	

Table 7-1.(Continued) A summary of sediment oxygen consumption (SOC) and Total Carbon Dioxide (TCO_2) fluxes based on measurements made during 1994 at:

a. the Patapsco and Back Rivers

b. the Potomac River

c. the Mid bay (station R-64)

Units of SOC and TCO_2 fluxes are mM O_2 m^{-2} hr^{-1} and mM CO_2 m^{-2} hr^{-1}.

NOTE: Values not calculated are noted as NC rates at these times amounting to about 0.6 to 1.0 g C m^{-2} day^{-1}. These rates are in the range estimated from budget calculations (Kemp and Boynton, 1992).

Finally, on all but a few occasions (3 out of 33) measurements of CO_2 flux were larger than sediment oxygen consumption (SOC) fluxes. This indicates that sediment oxygen consumption (SOC) fluxes underestimate sediment metabolism, often by a large margin (*see* O_2/CO_2 flux ratios in Tables 7-1.a., 7-1.b. and 7-1.c.). The reason CO_2 flux would be larger than sediment oxygen consumption (SOC) flux is that the latter measures aerobic respiration plus the re-oxidation of reduced compounds (mainly inorganic sulfur [S] compounds). Fluxes of CO_2 measure aerobic as well as anaerobic metabolism, CO_2 being the end product of both types of reactions. In determining the fate of organic matter it is imperative to have a reliable estimate of total metabolism. For monitoring purposes is equally necessary to have good estimates of total metabolism to gauge the effects of nutrient reductions which in turn will lead to decreases in sediment metabolic rates. It is recommended that CO_2 fluxes be added to the Ecosystem Processes Component (EPC) Program monitoring agenda as soon as possible.

7.2 Open Water Metabolism Measurements as a Monitoring Tool: An Example from the Patuxent River Estuary

One of the central concepts in estuarine ecology concerns the relationship between nutrient supply rate and phytoplanktonic responses. Nixon *et al.* (1986) has referred to this as the agricultural paradigm wherein addition of fertilizer to agricultural crops leads to a larger yield. In a similar, but certainly less tested fashion nutrient additions to estuarine waters result in modest increases in cell growth rates (D'Elia *et al.*, 1986) but large increases in standing stocks of planktonic algae (Boynton *et al.*, 1982a; Nixon *et al.*, 1986). It is this algal response to "fertilization" which is one of the root causes of estuarine eutrophication. In recognition of this, the monitoring program routinely measures nutrient inputs to the system and phytoplanktonic responses in terms of speciation, production and standing crop. The Ecosystem Processes Component (EPC) Program and others have shown that there are strong relationships between loading rate and algal responses (Boynton *et al.*, 1994; Hagy *pers. comm.*).

While the use of methods such as C-14 primary production and fluorescence-based algal stock estimates for monitoring purposes is certainly justified, they are best used to obtain measures of algal performance at a variety of locations; that is as tools to obtain spatial estimates of rates and stocks. These, indeed most, approaches do not lend themselves to problems involving monitoring of temporal variability at fine scales (*i.e.* days to weeks) simply due to the costs associated with such measurements.

However, there are some methods that are relatively inexpensive and can address fine-scale temporal, as well as longer-scale (*i.e.* months to years) variability of processes of interest when monitoring estuarine system performance. One of these techniques was developed by Odum and Hoskins (1958) and involves estimating both community production and community respiration from changes in dissolved oxygen concentrations over diel periods. In its simplest form, production is estimated from the rate of change of dissolved oxygen during daylight hours. Any increase in dissolved oxygen concentration can be attributed to net photosynthesis of primary producers. In a similar fashion, decreases in dissolved oxygen concentrations during hours of darkness can be attributed to respiration of both primary producers and the full assemblage of heterotrophs. In both cases it is assumed that measurements are being made within the same general water mass over the 24 hour period; in effect, net advective additions or deletions of dissolved oxygen are assumed to be small as would be the case within a generally homogeneous water mass. In very heterogeneous

systems the utility of the system is compromised because of this. Finally, both daytime and nighttime rates of change are corrected for oxygen diffusion across the air-water interface leaving an oxygen signal which is an estimate of biological metabolism.
Several years ago the Ecosystem Processes Component (EPC) Program was able to obtain a data record collected from the Benedict Bridge (Md Route 231; center bridge span) which included almost continuous measurements of dissolved oxygen, temperature, salinity and water height for the period 1964 through 1969. During these years Mr. Robert Cory of the U. S. Geological Survey maintained a monitoring station on the bridge (for details of this study refer to Cory [1965]). Measurements of the four variables listed above were recorded continuously on large format strip chart recorders. Cory tended the monitoring station with unusual intensity, frequently and throughly cleaning the sensors and performing calibrations. Except for some periods when equipment failed or freezing conditions prevailed the record is complete. By normal standards this is a most unusual and valuable record but for the Chesapeake Bay Monitoring Program it represents a window on the past from which good deal can be learnt about the performance of the Patuxent River when water quality conditions were better and nutrient loads to the system were lower than in recent decades.

In 1992 using a modern temperature, salinity and dissolved oxygen instrument (Hydrolab Surveyor 4000), borrowed from the U. S. EPA-EMAP program, a contemporary series of measurements was obtained during April through October at the same site used by Cory during the 1960's. It is important to note that while this modern instrument was compact and had internal data storage, the basic sensors were the same as those used by Cory and the same rigorous schedule of cleaning and calibration (clean and calibrate every 3 - 4 days) was followed.

Both the Cory data set and the 1992 data set have been analyzed by Mr. Brendan Sweeney who is a graduate student at the University of Maryland. Mr. Sweeney has completed the production and respiration computations and is now beginning to write a Masters Thesis based on these measurements. Figure 7-2. shows the estimates of production and respiration (weekly averages and standard deviations) from 1964 and 1992. Average rates during 1992 were much larger than in the past. Rates of daytime net community production (Pa*) in 1992 exceeded those in 1964 by a factor of three (300%) while estimates of community night respiration (Rn) in 1992 were greater than those in 1964 by a factor of two (200%). Preliminary analyses by Sweeney (*pers. comm.*) indicate a statistically significant trend towards higher values for both daytime net community production (Pa*) and community night respiration (Rn) between 1964 and 1968 and significant differences between the data collected in the 1960's and 1992. Furthermore, there have been changes in the seasonal pattern of metabolism between the 1960's and 1992. In the 1960's, daytime net community production (Pa*) exhibited very low values during late winter and then increased sharply at the beginning of May (week 17). With one exception this was the highest value of daytime net community production (Pa*) recorded during the year and probably represents enhanced production associated with the spring algal bloom. By 1992 this pattern had been substantially altered; production was already enhanced by May and rates continued to climb through September generally following the temperature cycle. This change in pattern was probably caused by increased nutrient loading rates and the positive feedback effects associated with increased loads (Figure 2-1). Rates of oxygen consumption (Rn) also increased and during 1992 exhibited a longer period of enhanced rates.

Examination of the Cory and 1992 data sets strongly suggests that use of the diel oxygen technique for measuring community production and respiration would be a powerful and cost effective addition to monitoring efforts in the Patuxent River estuary and possibly other sites as well. It appears that the technique is sensitive to temporal changes in these rates which are known to be strongly impacted by nutrient supply rates. Current technology makes continuous measurements convenient to make, at least relative to older approaches.

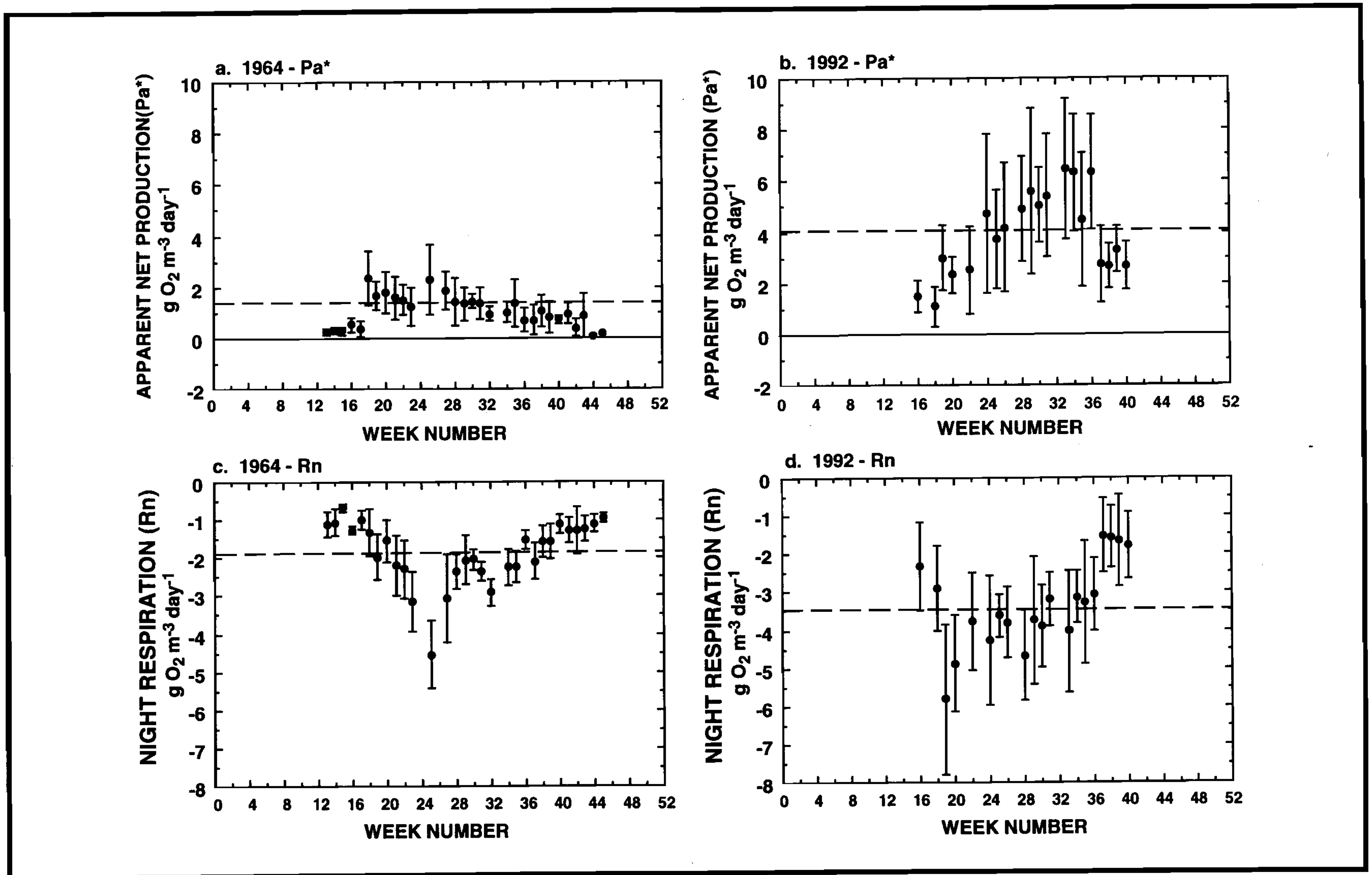


Figure 7-2. A comparison of rates (week averages and standard deviations) of daytime net community primary production (Pa*) and community night respiration (Rn) measured during 1964 and 1992 at the Benedict Bridge (MD Route 231 bridge), Patuxent River. Rates were based on diel measurements of dissolved oxygen and converted to estimates of metabolism using the technique of Odum and Hoskins (1958).
The 1964 data were collected by Cory (pers. comm.) and the 1992 data were collected by Sweeney (pers. comm.).

Finally, the Patuxent River in particular is undergoing intensive management programs aimed at nutrient reduction. It seems prudent to utilize some measurements having fine-scale temporal resolution from which several rate processes which are central to estuarine eutrophication can be inferred and which may also resolve further the issue of time lags related to fall-line nutrient loading and estuarine biological responses. A modern weather station making continuously recording measurements of wind speed, wind direction, precipitation and solar radiation is now available. All these data would be useful for interpretation of the community metabolism data collected.

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