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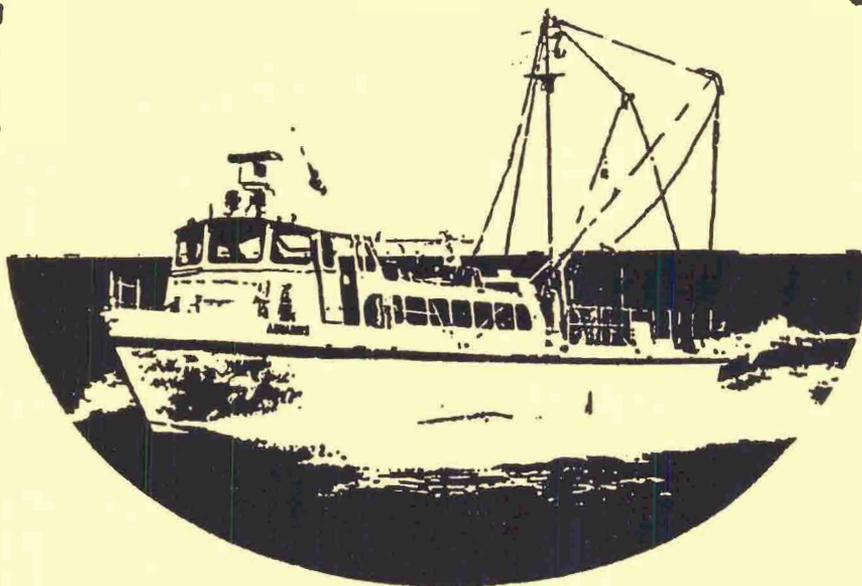
**UNIVERSITY of MARYLAND SYSTEM**

**USA**

# **Chesapeake Bay**

## **Water Quality Monitoring Program**

**ECOSYSTEMS PROCESSES  
COMPONENT  
(EPC)**



**LEVEL ONE DATA REPORT #11**

**Part 1: Interpretive Report**

**A Program Supported by the  
Maryland Department of the Environment  
State of Maryland**

**March 1994**

MARYLAND DEPARTMENT OF THE ENVIRONMENT  
**MARYLAND CHESAPEAKE BAY WATER QUALITY  
MONITORING PROGRAM**

**ECOSYSTEM PROCESSES COMPONENT (EPC)**

**LEVEL ONE REPORT NO. 11**

**INTERPRETIVE REPORT**

(July 1984 - December 1993)

**PREPARED FOR:**

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Baltimore, MD 21224

March, 1994

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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 text describes the temporal and spatial behavior of all the variables measured. The results of an anaerobic metabolism study in Section 7.

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 1993 is submitted in 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, Table A-1, Level 1 No. 7 Interpretive Report Part II: Data Tables (Boynton *et al.*, 1990), 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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##### B-4. CORE PROFILES:

Vertical profiles of percentage H<sub>2</sub>O particulates  
and pore water nutrients at SONE stations  
**FILENAME: CORPRFxx**

Complete data set, 1984 to 1986, is found in Volume I  
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## ABSTRACT

The 1993 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 1993 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 1993 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. This report only includes sediment-water nutrient and oxygen exchanges (SONE) data collected during the nine years of the monitoring program. Data collected during the 1993 monitoring period is evaluated, a discussion of significant ecological trends and interpretation of relationships observed during the monitoring program form the body of the report.

During the winter-spring period of 1993, all four of the major systems monitored, Susquehanna (Maryland mainstem bay), Potomac, Patuxent and Choptank Rivers, experienced both exceptionally high 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 1993 was much larger than previous years. Flows for the remaining portion of the year were average or below average.

Temperature ranged from 12.5 - 28.5 C and salinity conditions ranged between 3.3 - 30 ppt during 1993. 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<sup>-1</sup> at Ragged Point [RGPT] in May, 1993) which is not normally the case and was probably caused by the high river flow of 1993. A synoptic, mainstem bay map of sediment chlorophyll-a concentrations produced using data collected during a cruise in early May, 1993 (following the sinking of the spring algal bloom) indicated intense deposition in the region of the mainstem bay from the mouth of the Patuxent River to the Rappahannock River (Boynton *et al.*, 1993a). This pattern is thought to have shifted more to the south than usual possibly due to the especially strong freshet from the Susquehanna River during April, 1993. Sediment mapping, during and following deposition of the spring bloom, is recommended as a possible future monitoring tool.

During 1993, rates of sediment-water fluxes of oxygen (SOC) in the Patuxent River ranged from near zero to -2.80 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup> while sediment oxygen consumption (SOC) at all other monitoring stations ranged from near zero to -2.0 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>. In part, these low rates were the result of severely depressed oxygen concentrations in bottom waters which

occurred earlier than normal in 1993 and were even depressed in one area not generally exposed to hypoxic conditions (Horn Point [HNPT] in the lower Choptank River).

Ammonium ( $\text{NH}_4^+$ ) fluxes in the Patuxent River were higher (38% 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 1993. 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 nutrient loads. Ammonium ( $\text{NH}_4^+$ ) fluxes were also higher than normal in the lower Potomac River (Ragged Point [RGPT], lower mainstem bay (Point No Point [PNPT]) and in the lower Choptank River (Horn Point [HNPT]). Average or below average mainstem bay (R-64) ammonium ( $\text{NH}_4^+$ ) fluxes possibly resulted from lower than normal deposition in this zone of the bay in 1993 due to the down bay transport indicated above. Fluxes of nitrate plus nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ ) were larger than usual at most stations and with few exceptions (Buena Vista [BUVA] in June, 1993) were directed into sediments in response to high nitrate concentrations in bottom waters.

During 1993, inorganic phosphate (DIP or  $\text{PO}_4$ ) fluxes generally followed the pattern of ammonium ( $\text{NH}_4^+$ ) fluxes with enhancements at most stations. Silicate fluxes ( $\text{Si}(\text{OH})_4$ ) tended to be slightly above average at most stations in the Patuxent River but average or slightly below average at the remaining sites.

Efforts to detect relationships between major EPC Program and other Water Quality Monitoring Program variables (e.g., water column production and algal biomass, sediment-water oxygen and nutrient fluxes and deposition rates) and selected environmental variables were continued using 1993 data. The following patterns were indicated:

- (1) Integrated water column chlorophyll-a mass collected from four different zones of the bay was found to be strongly correlated with nutrient loading rates after these loading rates were scaled for water residence time and mean depth at each site. Data from two other estuarine systems also fit this relationship suggesting that the relationship was robust rather than simply unique to Chesapeake Bay. Additionally, a long-term record of algal biomass, deposition rates and sediment-water fluxes at a site (R-64) in the mainstem Chesapeake were all strongly correlated with indices of nutrient loading rates. These analyses lend additional support to the concept that these water quality variables are responding to changes in nutrient loading rates and that the time scale of this response is on the order of months to years rather than years to decades.
- (2) Summer season (June through August) sediment fluxes were very strongly correlated with winter-spring surficial sediment concentrations of total chlorophyll-a at a series of three stations (Still Pond [SLPD], R-64 and National Science Foundation - Land Margin Ecosystem's station SB) located along the salinity gradient of the mainstem bay. Similar relationships were also found for several other SONE stations. Strong correlations were shown to exist between sediment fluxes and sediment particulate nitrogen (BN) concentrations while sediment fluxes were less strongly correlated with sediment particulate carbon (PC) concentrations and not at all with sediment particulate phosphorus (PP) concentrations.

- (3) Sediment releases of ammonium ( $\text{NH}_4^+$ ) and phosphorus ( $\text{PO}_4$ ) tended to be enhanced in 1993 compared to other years and especially to 1992. These enhancements occurred in a year with higher than normal run off and thus increased diffuse source nutrient loading rates. Deep water dissolved oxygen (DO) concentrations tended to be lower in both spring and summer of 1993 than in previous years at most stations.
- (4) The results from a series of statistical analyses which were performed using the sediment-water nutrient and oxygen exchanges (SONE) flux data base (Boynton *et al.*, 1993b) to examine long term trends, to develop estimates of the levels of detection and to determine the power of the current sampling procedure were reevaluated. The analyses used data for eight stations in three estuaries and the Chesapeake mainstem bay, and 5 flux variables for which data was available for more than three months and more than three years for the period 1985 through 1991. Consistent trends were detected for most flux variables in the Potomac River. These trends were decreasing and were consistent with conditions expected when nutrient loads decrease. Power analysis indicated that small differences (10% of average fluxes) could be detected. These levels of detection will improve as additional years of sampling are added.

## 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.*, 1992a). 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 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, Figure 1-1., 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.

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 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 are to:

- 1) Characterize the present state of the bay (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and oxygen consumption and the rate at which organic and inorganic particulate materials reach deep waters and the sediment surface.
- 2) Determine the long-term trends that develop in sediment-water exchanges and deposition rates 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).

## Dual Nutrient Positive Feedback on Eutrophication

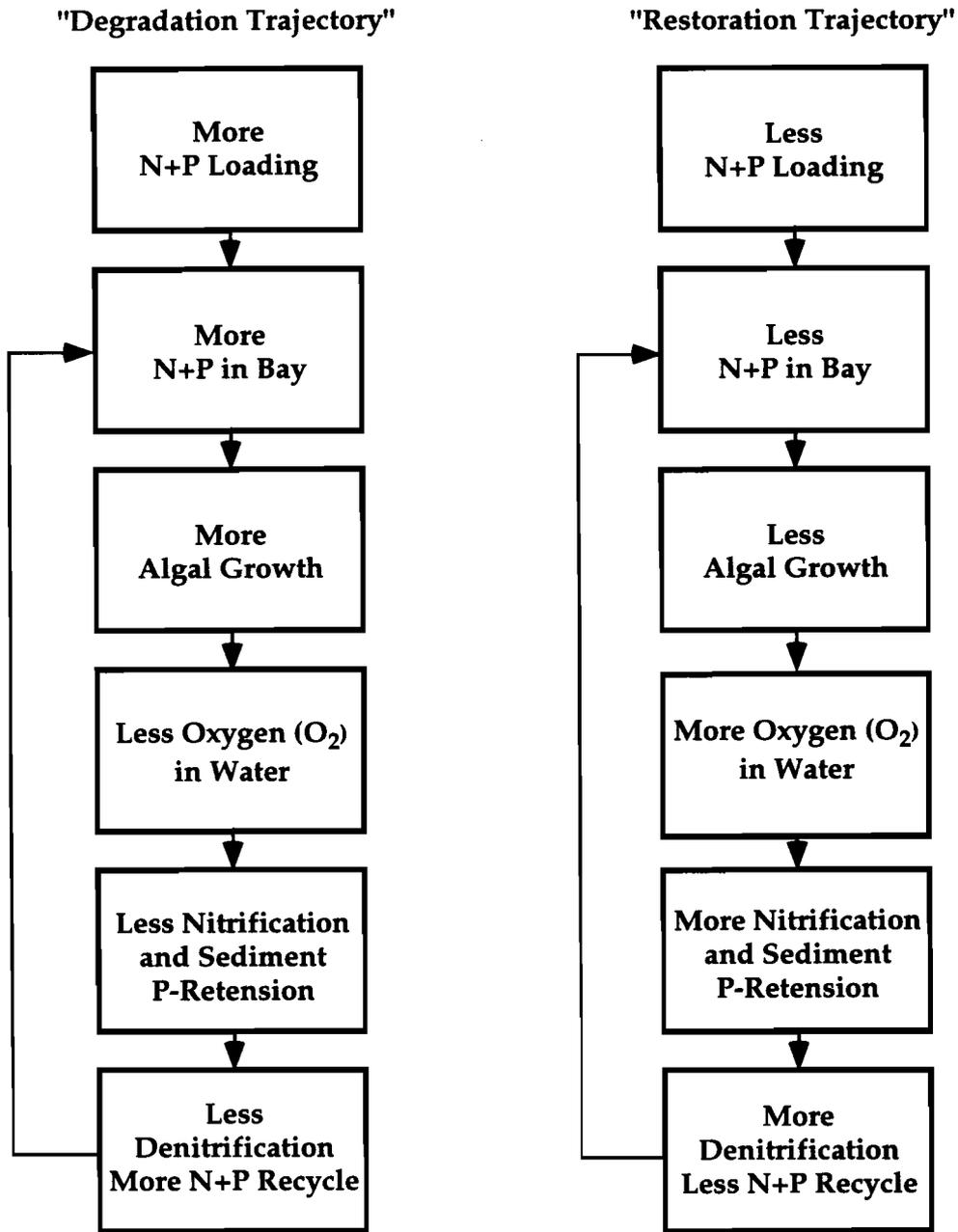


Figure 2-1. Nitrogen (N) and phosphorus (P) loads to the Chesapeake Bay affect coupled sediment nitrification-denitrification and sediment nitrogen and phosphorus cycling. High nitrogen and phosphorus inputs will ultimately result in less nitrogen and phosphorus removal from the benthos, while significant 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.*, 1985a, 1986, 1987, 1988, 1989, 1990, 1991, 1992b, and 1993b). 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.

Ecosystem Processes Component (EPC) program data collected during 1993 are presented in this report and the results of a statistical analysis conducted by Boynton *et al.* (1993b) reevaluated to (1) attempt to explain the magnitude and significance of trends in sediment-water exchanges identified and (2) to relate sediment-water oxygen and nutrient exchanges to nutrient loading rates and *in situ* environmental conditions.

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

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

During 1993, 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 and details 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 1993. 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 1993, 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) portion of this 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 ( $\text{NH}_4^+$ ), phosphate ( $\text{PO}_4^-$ ) and silicate ( $\text{Si}(\text{OH})_4$ ).
- 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 ( $\text{NH}_4^+$ ), phosphate ( $\text{PO}_4^-$ ) and silicate ( $\text{Si}(\text{OH})_4$ ) and occasional nitrate release.

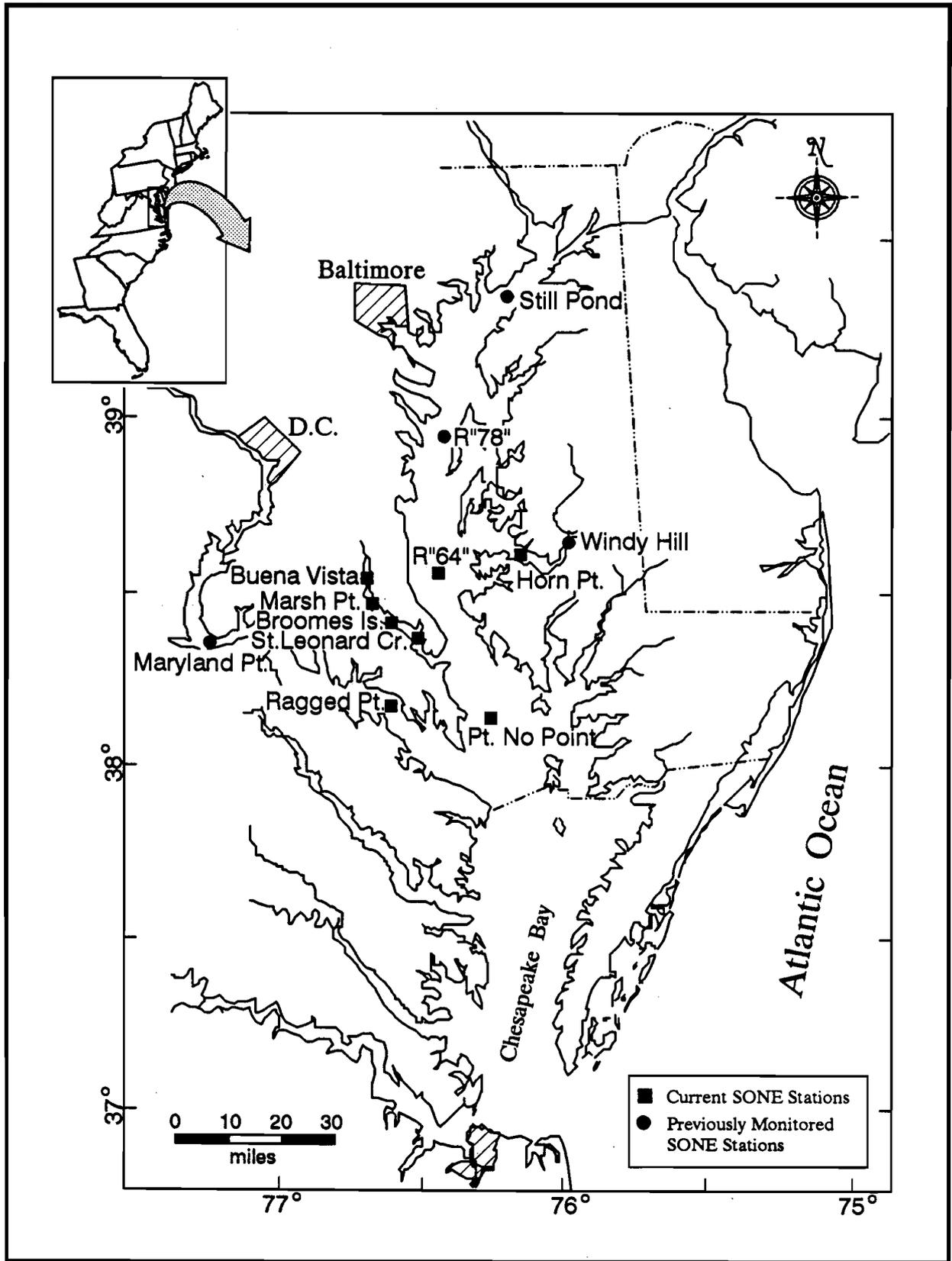


Figure 3-1. Location of Current and Previously sampled Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations in the Maryland Portion of Chesapeake Bay (1984 - 1993).

**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 samples in SONE 1 - 20, August 1984 - June 1989. Numerical Ranking indicates the order in which they appear in the data tables.

B = Stations sampled beginning with SONE 21 and future samples. Numerical ranking indicates the order in which they 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 and 1993 (May, June, July, August, September and October).

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

<b>STATION CODE NAME</b>	<b>LATITUDE DEG MIN</b>	<b>LONGITUDE DEG MIN</b>	<b>STATION DEPTH</b>	<b>MDE STATION</b>	<b>BAY SEGMENT</b>
<b>Patuxent River</b>					
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
<b>Choptank River</b>					
HNPT	38° 37.18'	76° 08.09'	8.2	MET5.2	ET5
<b>Potomac River</b>					
RGPT	38° 09.86'	76° 35.52'	16.5	XBE9541	LE2
<b>Chesapeake Mainstem</b>					
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
<b>Patuxent River</b>	
STLC	7.5 nautical miles upstream of Patuxent River mouth. (R km <sup>1</sup> = 12.1)
BRIS	10 nautical miles upstream of Patuxent River mouth. (R km <sup>1</sup> = 16.1)
MRPT	14.5 nautical miles upstream of Patuxent River mouth. (R km <sup>1</sup> = 23.4)
BUVA	0.75 nautical miles north of Route 231 Bridge at Benedict, MD. (R km <sup>1</sup> = 31.5)
<b>Choptank River</b>	
HNPT	4.0 nautical miles downstream of Route 50 Bridge at Cambridge, MD. (R km <sup>1</sup> = 18.6)
<b>Potomac River</b>	
RGPT	1.5 nautical miles WNW of Bouy 51-B. (R km <sup>1</sup> = 29.8)
<b>Chesapeake Mainstem</b>	
PNPT	3.2 nautical miles east of Point No Point. (R km <sup>1</sup> = 129.0)
R-64	300 yards north east of Channel Buoy R-64.* (R km <sup>1</sup> = 177.4)

**NOTES:**

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

<sup>1</sup> River kilometers (R km) are measured from the mouth of the river or Chesapeake Bay.

**Table 3-2. Station Salinity**

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

**The Salinity Zone layer codes are as follows:**

<b>SALINITY CODE</b>	<b>DESCRIPTION</b>
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 when fluxes are very low due primarily to low temperature. No samples are collected during this period (December - March).

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, 1993, SONE41 through SONE46. A complete listing giving the sampling dates of all SONE cruises (1984 - 1993) 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  $\mu\text{m}$  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 ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), dissolved inorganic phosphorus corrected for salinity (DIP or  $\text{PO}_4^-$ ), silicic acid ( $\text{Si}(\text{OH})_4$ ), particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations and seston content.

Measurements of total dissolved nitrogen (TDN:  $\text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^- + \text{DON}$ ), and total dissolved phosphorus (TDP:  $\text{DIP} + \text{DOP}$ ) 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 (SONE31) 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 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

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

and for the Pooles Island Reconfiguration Assessment (PIRAS) Study

PLIS in Jun, Jul and Aug 1993

GWST in Jun 1993

GTST in Jun and Jul 1993

GW-1 in Aug 1993

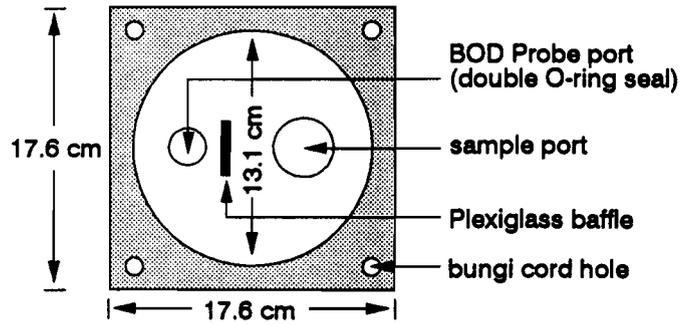
### 3.3.4 Sediment Cores

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 Plexiglass 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.

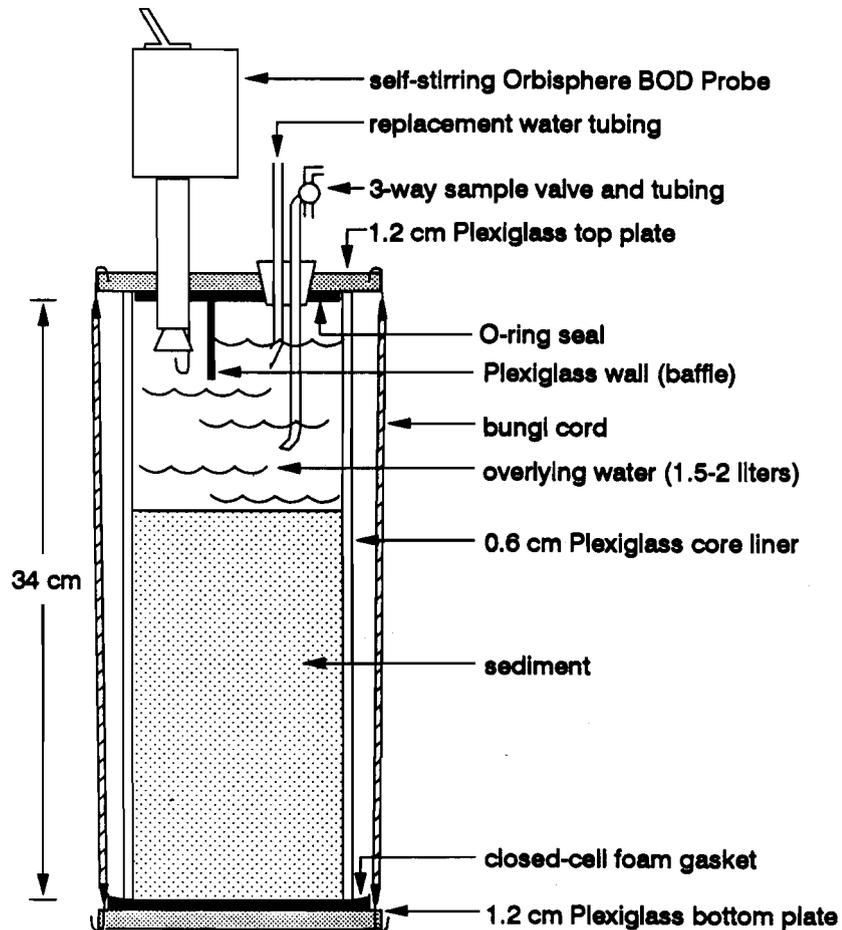
Three intact cores are used to estimate net exchanges of oxygen and dissolved nutrients between sediments and overlying waters (Figure 3-2.). Prior to beginning flux measurements, the overlying water in the core is replaced by fresh bottom water to ensure that water quality conditions in the core closely 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 Plexiglass 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  $PO_4^{3-}$ ) and silicic 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 ( $< 2 \text{ mg l}^{-1}$ ) 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 1992 and 1993, a series of preliminary measurements of sulfate reduction ( $SO_4^{2-}$ ) were made. It appears that this method may be useful for measuring anaerobic metabolism (the majority of which is carried out via sulfate [ $SO_4^{2-}$ ] reduction, the dominant form of anaerobic metabolism in Chesapeake Bay). The method is relatively inexpensive and can be incorporated into the monitoring program with ease. In brief the method involves incubation of intact sediments under anaerobic conditions with sulfate concentration measured during the incubation period using ion chromatography as a detection method. A complete description of the method used is presented in Section 6.3 Methodology for Measurement of Sulfate Reduction Rates. Results from 1993 are presented in chapter 6 Anaerobic Metabolism, Section 6.4 Sulfate estimates at SONE stations during May - October, 1993. If this approach proves successful, a complete description of the method will be inserted into the data dictionary (Boynton and Rohland, 1990).

### Enlarged View of Top Plate



### Cross Section of Incubation Chamber



**Figure 3-2. Schematic Diagram of the Incubation Chamber**

### 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 ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), and dissolved inorganic phosphorus (DIP or  $\text{PO}_4^-$ ) are measured using the automated method of EPA (1979); silicic acid ( $\text{Si}(\text{OH})_4$ ) 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.
- Dissolved nutrients in comparison with 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  $[DIP \text{ or } PO_4^-]$  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.*, 1992b).

Appendix B of this report contains SONE data table listing for variables measured between May and October, 1993, the six months when field measurements were taken. 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 1993 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 be submitted as a data dictionary file to fulfill the requirements of the EPA Chesapeake Bay Liaison Office (EPA/CBLO).

SAS reference files are being compiled for each data set containing detailed station and variable information as well as other pertinent information related to missing data.

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

A statistical study of sediment-water fluxes was completed in 1992 (Boynton *et al.*, 1993b) in consultation with Larry Douglass, Research Statistician at the University of Maryland, College Park. This study examined temporal and spatial trends and determined the statistical power inherent in this study (*i.e.* the estimation of the magnitude of change in flux values needed for statistical significance). The results are summarized in chapter 7, Examination of Sediment-water Fluxes for Long Term Trends and Relationships to Nutrient Loading Rates and Significant Long-term Trends, reevaluated and interpreted in the light of the management phase of the Maryland Chesapeake Bay Water Quality Monitoring Program.

**Table 3-5. Analysis Problem Codes**

<b>ANALYSIS PROBLEM CODE</b>	<b>DESCRIPTION</b>
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 AND NUTRIENT LOADING

### 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 previous reports river flow has been used as an indication of nutrient loading rates. However, management actions designed to reduce nutrient loading rates have been implemented so this relationship is probably changing. In this report direct measurements of nutrient loading rates are used for the period 1985 through 1993 (nitrogen loading rates are estimated for 1993). These loads include fall line loads and any major point source loads below the fall line. Below fall line loads are not included in any of these estimates. Nutrient loads are presented as a series of averages (annual monthly load, December through February average load and October through June average load) as it was found that some variables were responsive to only portions of the total annual load (Boynton *et al.*, 1993b). Finally, loads are presented for the Susquehanna River fall line load (mainstem bay), Potomac, Patuxent and Choptank Rivers. Nutrient loads are presented as total nitrogen (TN) and total phosphorus (TP) and the portion of total nitrogen (TN) and total phosphorus (TP) which is in the dissolved inorganic form (dissolved inorganic nitrogen [DIN] and dissolved inorganic phosphorus [DIP]). All nutrient loading data were obtained from the Maryland Department of the Environment (Summers, *pers. comm.*).

### 4.2 Average Annual River Flows

Annual average river flows for the period 1978 through 1993 are shown in Figure 4-1.1. The sixteen year average (1978 - 1993) flows to each system during this period are indicated by horizontal lines on this figure (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993). The sixteen year average in the Susquehanna River (Maryland mainstem bay) was 38,858 cubic feet per second (cfs), in the Potomac River 12,049 cubic feet per second, in the Patuxent River 360 cubic feet per second and in the Choptank River 129 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 sixteen 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 sixteen year average from 1985 through 1988 and above this average in 1989 (except in the Potomac River in 1989). Flows during 1990, 1991 and 1992 were progressively lower than the sixteen year average in all systems except the Susquehanna which was characterized by values above the sixteen year average in 1990 (48,536 cfs) and lower than this average in 1991 (29,750 cfs) and 1992. Flows during 1985 through 1992,

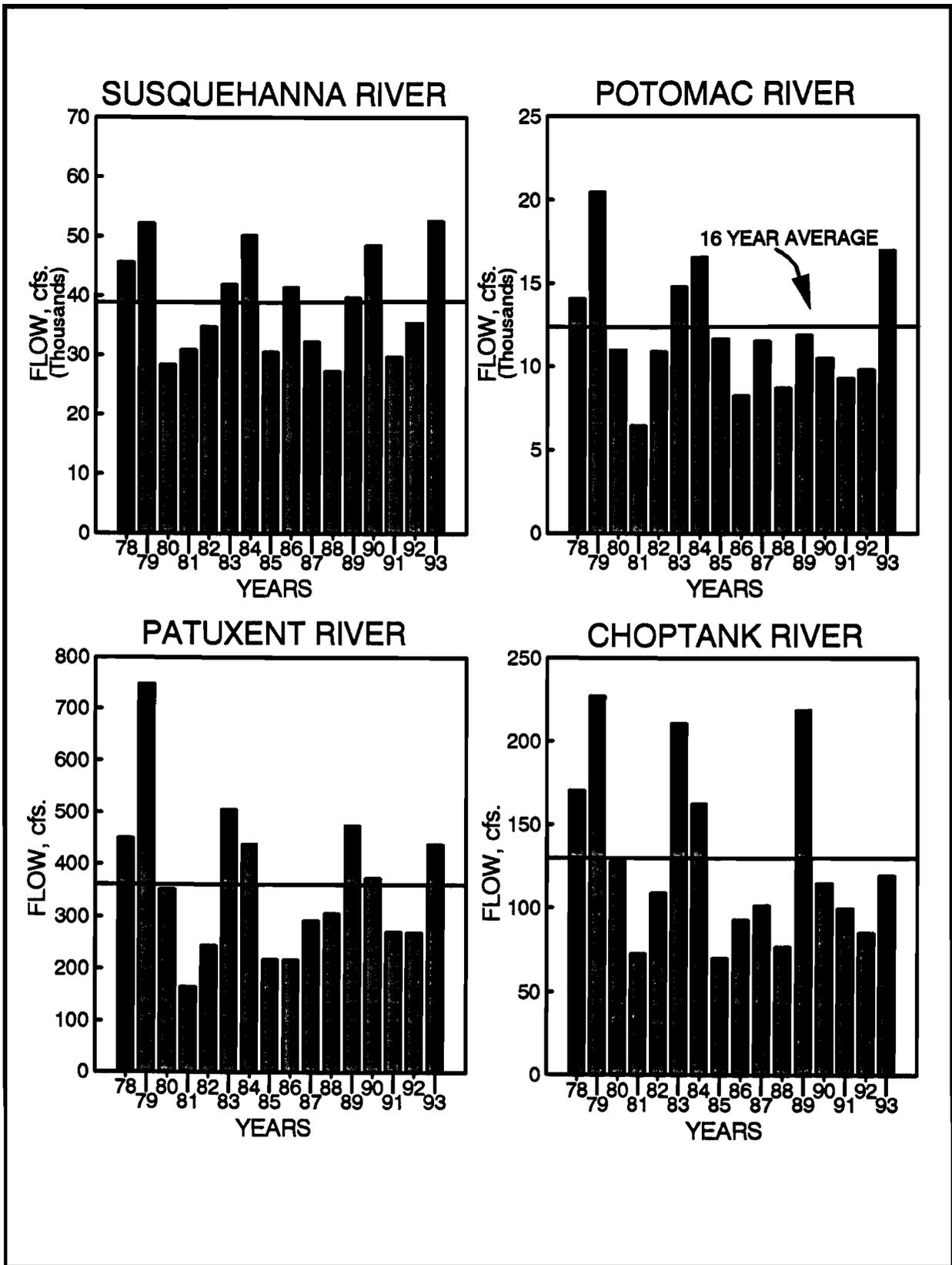


Figure 4-1.1. Bar graphs of average annual river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for the period 1978 through 1993 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993). Flows were measured at Conowingo, MD; Washington, D.C.; Bowie, MD and Greensboro, MD for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

were below the sixteen year average for all years in the Potomac River. In the Susquehanna and Patuxent Rivers flow were below this average with the exception of 1989 and 1990 when flows were above average. Flows in the Choptank River were well below the sixteen year average except in 1989 when flows were above this value. In 1990 flows in the Patuxent and Choptank Rivers were above and below this average respectively while in 1991 and 1992 flows in both of these rivers were again below the sixteen year average.

Flows in three systems were well above average in 1993, in the Susquehanna River 52,505 cfs, Potomac River 16,956 cfs and Patuxent River 438 cfs, and below average in the Choptank River 120 cfs. In general, river flows have either been near the sixteen year average or below this average value during the Ecosystem Processes Component (EPC) monitoring period, 1985 through 1993, with a few exceptions. As a result of this, water column stratification might be expected to be less intense than usual and diffuse nutrient loads to be lower than normal.

### 4.3 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. 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 1993 while the bold dots represent average monthly flows calculated over a longer time period (1978-1993). The data provided by the United States Geological Survey (U.S.G.S.) office are complete for 1993 with the exception of the Patuxent River where data was not available for December 1993. In 1993 flows in all rivers generally followed the sixteen year average with the exception of March and April when large river flows were recorded. In the Susquehanna River 83,200 cfs were recorded in March and 250,100 cfs in April, in the Potomac River 62,740 cfs were recorded in March and 57,850 cfs in April, in the Patuxent River 1,358 cfs were recorded in March and 1,021 cfs in April and in the Choptank River 512 cfs were recorded in March and 312 cfs in April. This was a particularly wet spring as these increased river flows indicate. The flows in December were also larger than average in two of the rivers, in the Susquehanna River 68,800 cfs and in the Potomac River 20,420 cfs were recorded. These data are presented to emphasize the need for careful consideration of temporal relationships between variables such as river flow and ecosystem processes such as 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 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 in governing relationships between nutrient loading rates and sediment-water oxygen and nutrient exchange rates in Chesapeake Bay.

### 4.4 Nutrient Loading Rates

Average nitrogen and phosphorus loading rates from four major rivers (Susquehanna, Potomac, Patuxent and Choptank) have been calculated for the period 1985 through 1993 and are shown as a series of stacked column bar graphs in Figures 4-2.1. - 4-2.3. and 4-3.1. - 4-3.3. Data were obtained from Summers (*pers. comm.*) and Legg (*pers. comm.*) at the Maryland Department of Environment. Nutrient loads for each year are presented as a bar divided into the following nutrient fractions: dissolved inorganic nitrogen (DIN); total nitrogen minus dissolved inorganic nitrogen (equivalent to particulate plus dissolved inorganic nitrogen)(TN-DIN), dissolved inorganic phosphorus (DIP); total phosphorous minus dissolved inorganic phosphorous (equivalent to particulate plus dissolved inorganic

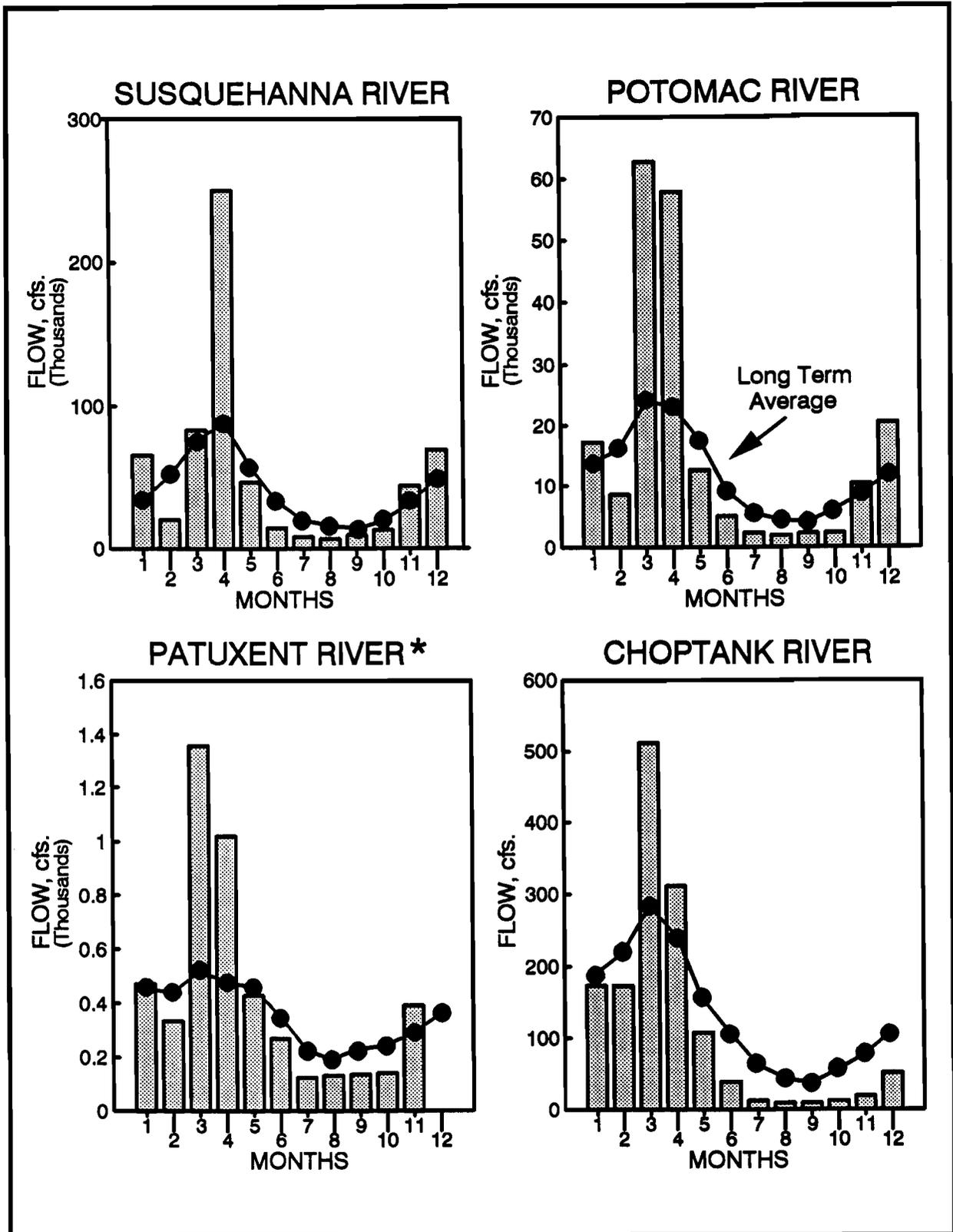


Figure 4-1.2. Bar graphs of average monthly river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for 1993. The bold dots indicate long term average monthly flows calculated for the period 1978 through 1993. Flows were measured at Conowingo, MD; Washington, D.C.; Bowie, MD and Greensboro, MD for the four rivers, respectively.

\* Note data is only available for eleven months in the Patuxent River.

phosphorous)(TP-DIP). These nutrient fractions were used in order to differentiate nutrients which can be directly used by phytoplankton and other autotrophs (dissolved inorganic nitrogen [DIN] and dissolved inorganic phosphorus [DIP]) from those that need to be further oxidized prior to utilization. Additionally, nutrient loads have been separated with reference to source location. Fall line loads include both point and diffuse sources which enter the river above the fall line monitoring station. Point sources in these figures refer to major point sources ( $> 10^6$  gallons day<sup>-1</sup>) entering the river below the fall line in the Patuxent and Potomac Rivers. No below fall line point source data were included in the Susquehanna or Choptank Rivers. Nutrient loads for both sites are under estimated. Diffuse nutrient sources entering these systems below the fall line are not included. Nutrient load data for 1993 are not yet available but estimates of nitrogen loads for 1993 at the fall line were obtained by developing a relationship between load and river flow for the years 1985 through 1992. River flow data are available for 1993 and was used in the estimation of 1993 nitrogen loads. The assumption was made that point source loads below the fall line did not change and was the same in 1993 as it was in 1992, so 1992 data was used as 1993 point source loads. Finally, three different averaging schemes were used to generate annual or seasonal nutrient loads for the years 1985 through 1993 and included: (1) annual average load for the calendar year, (2) annual average load for the water year which begins in October and ends in September and (3) a winter season load which includes the months of December through February. These different averaging schemes were developed because some earlier work has indicated that some processes in the bay respond on these different time scales (Boynton *et al.*, 1993b; Boynton and Kemp, 1993).

Three estimates of nitrogen loads: annual mean nitrogen load, water year mean nitrogen load and winter mean nitrogen load, are shown in Figures 4-2.1, 4-2.2 and 4-2.3 respectively. In all three figures it is clear that dissolved inorganic nitrogen (DIN) dominates the load, suggesting that utilization could potentially be rapid once these nutrients enter the system. There is a factor of two maximum difference in annual loading rates within systems. Interannual differences were much larger in the smaller systems (Patuxent and Choptank Rivers) than in the larger systems (Susquehanna and Potomac Rivers). Interannual patterns of nitrogen loading were also different among systems and this probably plays a strong role in determining water quality trends in these systems. For example, for the period 1985 through 1993 the interannual pattern in the Patuxent and Choptank Rivers was similar with loads generally increasing from 1985 to 1989 and then decreasing loads from 1990 to 1992 and increased loads in 1993. The same pattern was evident in the Susquehanna River but was reduced in amplitude and the 1993 annual loads were not particularly high. Nitrogen loads in the Potomac River decreased only slightly between 1985 and 1992 and increased only slightly in 1993, presumably in response to the strong freshet. In the Patuxent River the influence of management action on point source loads can be seen in the 1992 data and the nitrogen removal at some sewage treatment plants in this system contributed to the record low loads observed in 1992. Winter season (December through February) nitrogen loads (Figure 4-2.3.) exhibit considerably different interannual patterns as might be expected since they are based on only a portion of the year. In the larger systems winter nitrogen loads did not change a great deal in the Patuxent River but varied by over a factor of two in the Choptank River. In both systems, loads were higher in 1986 through 1988 than in later years.

Three estimates of phosphorus loads: annual mean phosphorus load, water year mean phosphorus load and winter mean phosphorus load, are shown in Figures 4-3.1., 4-3.2. and 4-3.3. respectively. In all three figures it is clear that particulate and dissolved organic phosphorous dominate the load suggesting that utilization could potentially be limited once these nutrients enter the system because a large fraction of the load needs to be transformed into dissolved inorganic phosphorus (DIP) before it can be utilized by plants. Thus phosphorus largely enters the system on a non-reactive form in contrast to nitrogen

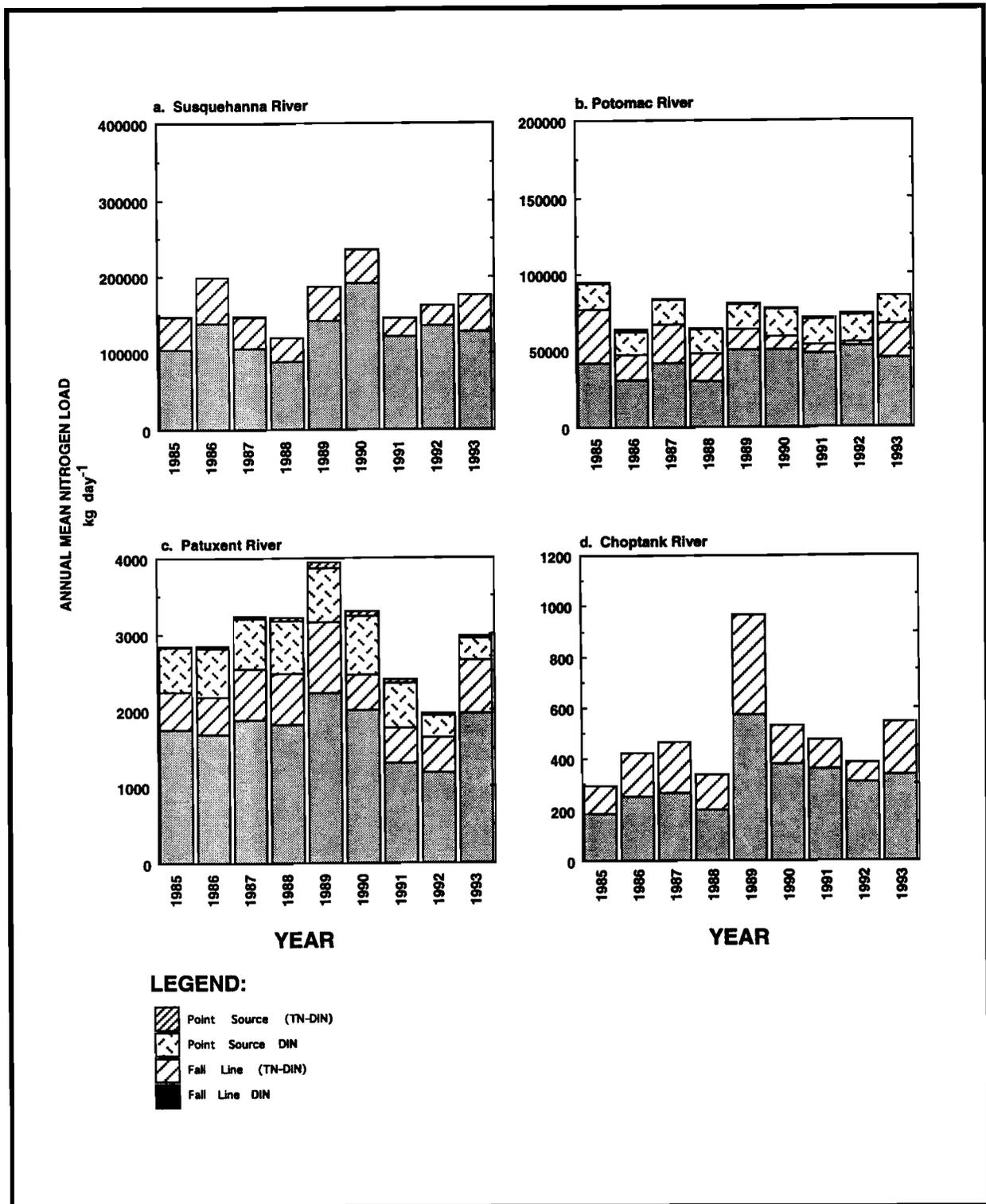
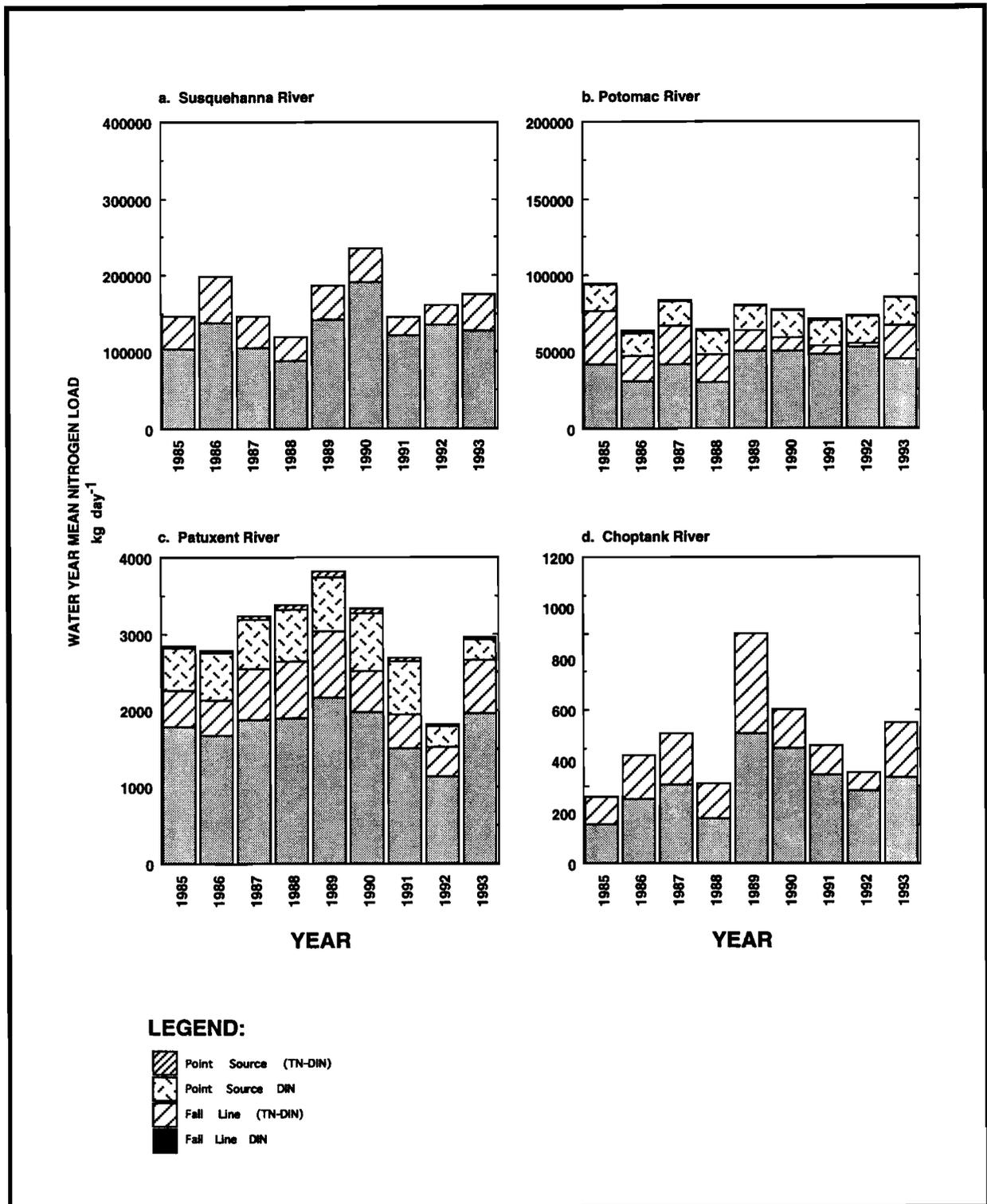


Figure 4-2.1. Stacked column bar graphs showing average nitrogen loads (annual; January through December) from above fall line (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.

Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most of the panels nutrients are represented as dissolved inorganic nitrogen (DIN) and total nitrogen minus dissolved inorganic nitrogen (equivalent to particulate plus dissolved organic nitrogen; TN-DIN).

All four panels have the same units ( $\text{kg day}^{-1}$ ) but the scale of each panel is different.



**Figure 4-2.2. Stacked column bar graphs showing average nitrogen loads (water year; October through September) from above fall line sources (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.**

*Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most of the panels nutrients are represented as dissolved inorganic nitrogen (DIN) and total nitrogen minus dissolved inorganic nitrogen (equivalent to particulate plus dissolved organic nitrogen; TN-DIN).*

*All four panels have the same units (kg day<sup>-1</sup>) but the scale of each panel is different.*

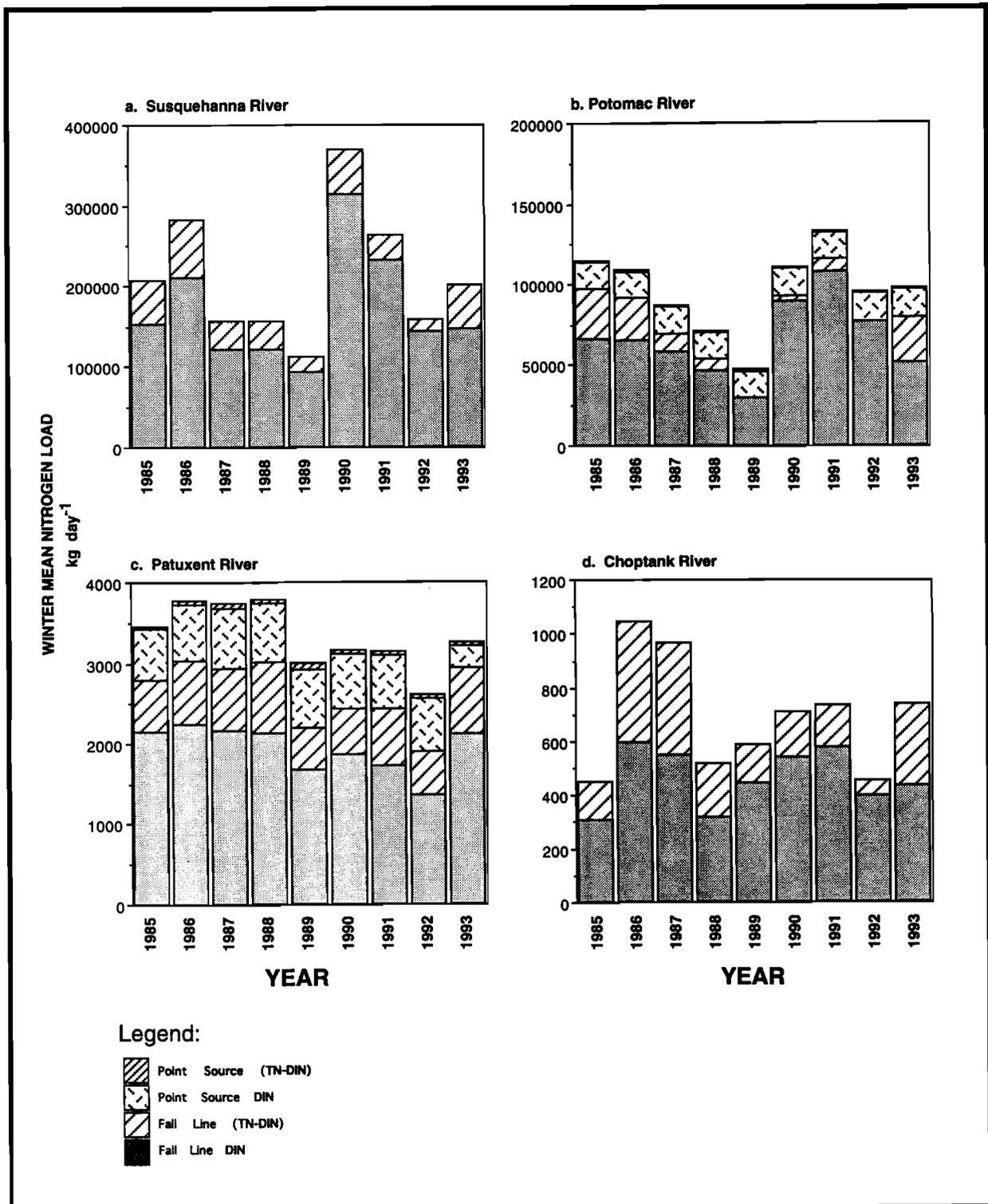


Figure 4-2.3. Stacked column bar graphs showing average nitrogen loads (winter; December through February) from above fall line (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.

Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most of the panels nutrients are represented as dissolved inorganic nitrogen (DIN) and total nitrogen minus dissolved inorganic nitrogen (equivalent to particulate plus dissolved organic nitrogen; TN-DIN).

All four panels have the same units ( $\text{kg day}^{-1}$ ) but the scale of each panel is different.

which enters largely in a reactive form. There is a about a factor of four maximum difference in annual loading rates within systems. Interannual differences were of similar magnitude in the smaller systems (Patuxent and Choptank Rivers) and in the larger systems (Susquehanna and Potomac Rivers). Interannual patterns of phosphorus loading were also different among systems and probably play a strong role in determining water quality trends in these systems. For example, for the period 1985 through 1992 the interannual pattern in the Patuxent and Potomac Rivers was similar with generally decreasing loads. No long term pattern was evident for the Susquehanna River. Loads in the Choptank River exhibited a dramatic peak in 1989 in response to a strong run off event. In the Patuxent River the influence of management action on point source loads is evident in data after 1986 with phosphorus removal at some sewage treatment plants and improved sediment erosion control programs. Winter season (December through February) phosphorus loads (Figure 4-3.3.) exhibit considerably different interannual pattern than expected since they are based on only a portion of the year. In the larger systems, winter phosphorus loads both increased and decreased substantially from 1985 though 1992. In the smaller systems winter phosphorus loads also decreased steadily from 1985 through 1992 but was four times greater in the Patuxent River than in the Choptank River for the same period.

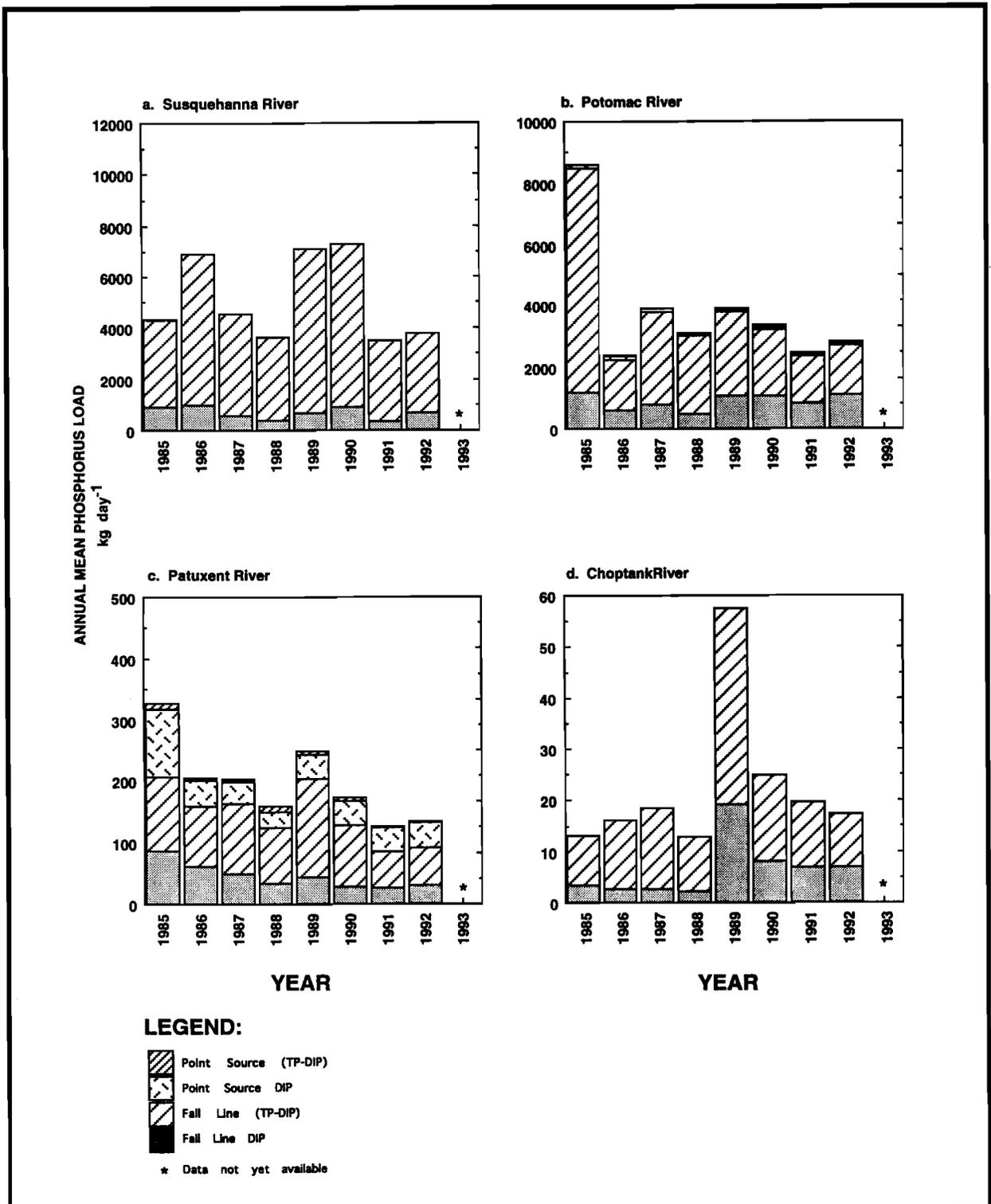


Figure 4-3.1. Stacked column bar graphs showing average phosphorus loads (annual; January through December) from above fall line (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.

Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most panels nutrients are represented as dissolved inorganic phosphorus (DIP) and total phosphorus minus dissolved inorganic phosphorus (equivalent to particulate plus dissolved organic phosphorus; TP-DIP).

All four panels have the same units ( $\text{kg day}^{-1}$ ) but the scale of each panel is different.

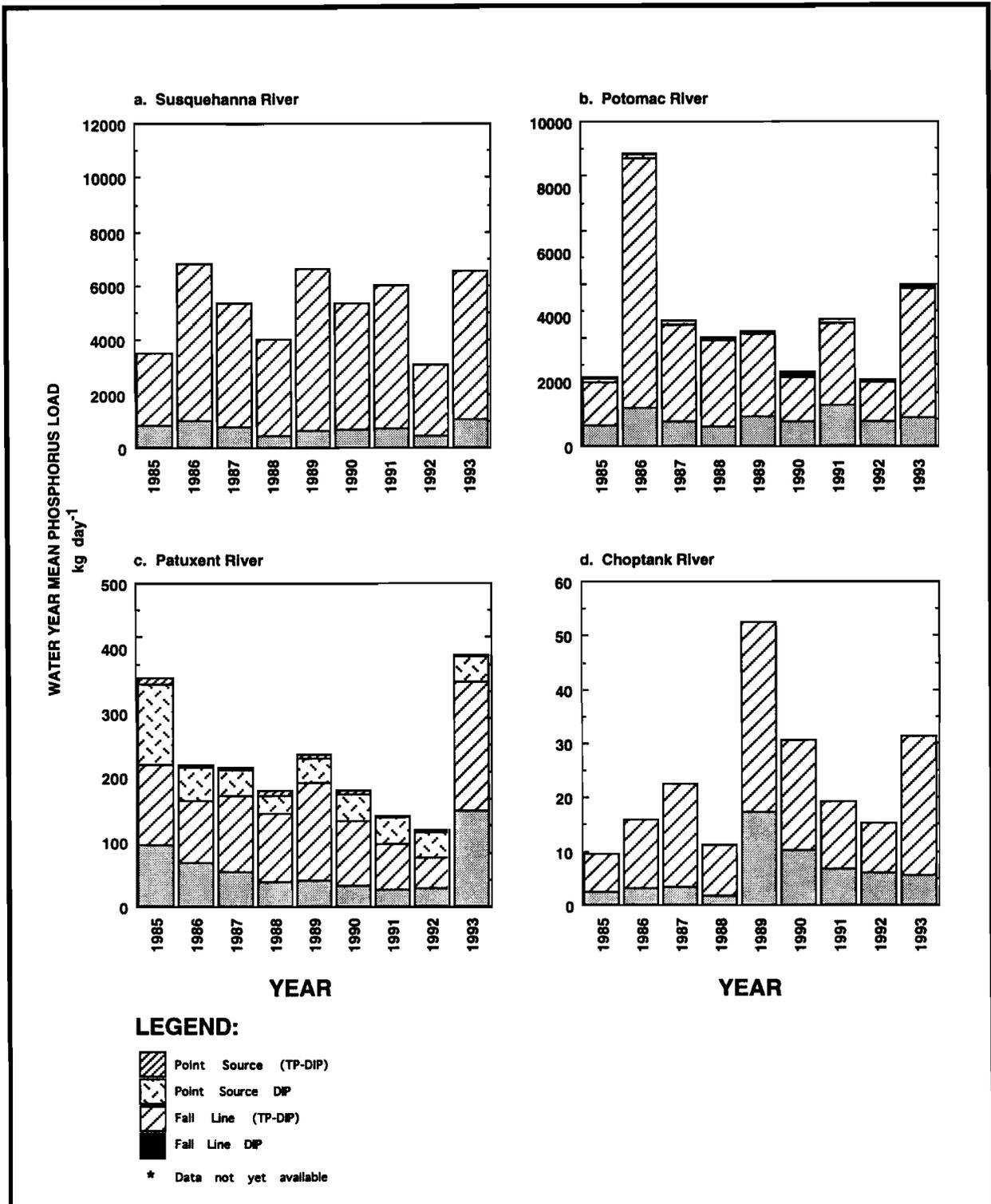


Figure 4-3.2. Stacked column bar graphs showing average phosphorus loads (water year; October through September) from above fall line (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.

Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most panels nutrients are represented as dissolved inorganic phosphorus (DIP) and total phosphorus minus dissolved inorganic phosphorus (equivalent to particulate plus dissolved organic phosphorus; TP-DIP).

All four panels have the same units ( $\text{kg day}^{-1}$ ) but the scale of each panel is different.

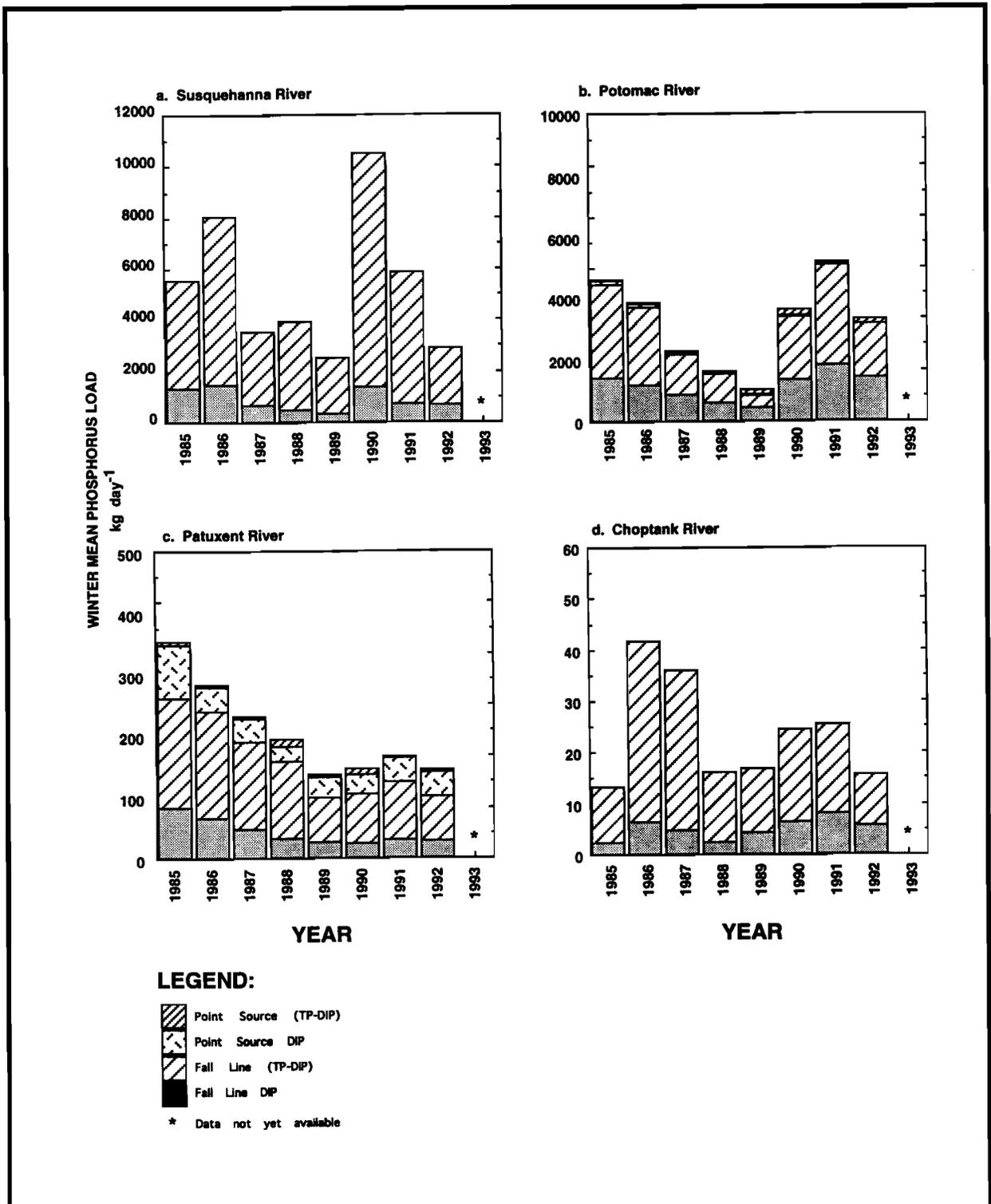


Figure 4-3.3. Stacked column bar graphs showing average phosphorus loads (winter; December through February) from above fall line (diffuse and point source loading) and below fall line point sources for four major tributaries; Susquehanna, Potomac, Patuxent and Choptank Rivers.

Note: Below fall line point sources are not included for the Susquehanna and Choptank Rivers. In most panels nutrients are represented as dissolved inorganic phosphorus (DIP) and total phosphorus minus dissolved inorganic phosphorus (equivalent to particulate plus dissolved organic phosphorus; TP-DIP).

All four panels have the same units ( $\text{kg day}^{-1}$ ) but the scale of each panel is different.

## 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 ( $\text{NH}_4^+$ ), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), phosphate ( $\text{PO}_4^-$ ), and silicate ( $\text{Si}(\text{OH})_4$ ). Data collected over a period of nine calendar years, 1985 through 1993, were used to calculate these averages. Each bar represents the mean flux value for a particular month for 1985 through 1992, an eight year period, 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 1993 (SONE cruises 41 [May 1993] through SONE cruise 46 [October 1993]; 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 1993, ranged from zero (0.01) (Broomes Island [BRIS]) to  $-2.80 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  (Buena Vista [BUVA]) in the Patuxent River, from  $-0.07 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  to  $-1.42 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  in the Choptank River (Horn Point [HNPT]), from zero through  $-0.71 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  in the Potomac River (Ragged Point [RGPT]) and from  $0.06 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  (Point No Point [PNPT]) through  $-1.80 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  (R-64) in the mainstem of the bay (Figure 5-1.1.; Tables B5-41. - B5-46.). 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 values indicate larger rates of SOC.*

The 1993 data closely followed the seasonal pattern, evident in the 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 lower but slightly increased rates in the fall (October). The largest fluxes were recorded in May and June, with a secondary peak recorded in October.

Fluxes at hypoxic stations (where hypoxia is defined as less than  $1.0 \text{ mg l}^{-1}$  dissolved oxygen), St. Leonard Creek (STLC), Buena Vista (BUVA) and Horn Point (HNPT; Figure 5-2.3.)

were depressed in July 1993 as was the case in all previous years with the exception of July 1992 when aerobic sediment metabolism (*i.e.*, sediment oxygen consumption [SOC]) persisted longer than in previous years because of higher dissolved oxygen (DO) concentrations in these waters. In 1992, river flow to the Patuxent estuary was quite low (Figure 4-1.2.) and as a result diffuse source nutrient loads were probably lower than normal. In addition, nitrogen removal was instituted at a major sewage treatment plant (Western Branch; river mile 35 which is upstream of all SONE stations) during fall of 1991.

Spring and fall (July and August) sediment oxygen consumption (SOC) rates at three sediment oxygen and nutrient exchanges (SONE) stations, St. Leonard Creek (STLC), Buena Vista (BUVA) and Horn Point (HNPT), are of sufficient magnitude to constitute a substantial direct dissolved oxygen loss (Kemp and Boynton, 1992). Sediment oxygen consumption (SOC) is not an adequate measure of sediment metabolism during periods of low oxygen conditions which often occur at some SONE stations during summer (*e.g.* August 1993 data at Ragged Point [RGPT]; Figure 5-2.3f.). The sediment oxygen consumption (SOC) rates reported here during periods of low oxygen concentrations grossly underestimate sediment metabolism and eventual oxygen demand exerted by reduced sulphur compounds (Roden, 1990). The results of anaerobic sediment metabolism measurements used as an estimate of total sediment oxygen demand are presented in the following chapter of this report (Chapter 6. Anaerobic Metabolism).

### 5.3 Ammonium (NH<sub>4</sub><sup>+</sup>) Fluxes

Average monthly ammonium (NH<sub>4</sub><sup>+</sup>) fluxes in 1993, ranged from 89.2  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  (St. Leonard Creek [STLC]) to 571.8  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  (Buena Vista [BUVA]) in the Patuxent River, from 68.8  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  to 482.0  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  in the Choptank River (Horn Point [HNPT]), from 150.8  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  to 487.3  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  in the Potomac River (Ragged Point [RGPT]) and from 90.1  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  (Point No Point [PNPT]) through 508.8  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  (R-64) in the mainstem of the bay (Figure 5-1.2.; Tables B5-41. - B5-46.).

At five stations the highest values were recorded in July 1993, at two stations Broomes Island (BRIS) and Ragged Point (RGPT) in June 1993 and at one station R-64 in September 1993. Several interesting spatial patterns were also evident (Figure 5-1.2.). For example, ammonium (NH<sub>4</sub><sup>+</sup>) fluxes tended to increase from the mouth to the turbidity maximum zone of the Patuxent River. This qualitative pattern reflects the expected trend of deposition rates of organic matter to the sediment surface which serves as a substrate supporting ammonium and other fluxes. In fact, deposition rates measured at six sites along the longitudinal axis of the Patuxent River in the late 1970's indicated a deposition maximum in the area of Buena Vista (BUVA) (Boynton *et al.*, 1982b). The values recorded in 1993 generally followed temporal trends exhibited in previous years, but the magnitude of fluxes at sites in the Patuxent, Potomac and Choptank Rivers were exceptionally high in some 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 an large loading event. However, this pattern was not evident at one station (R-64) in the mainstem bay. At this station the magnitude of ammonium (NH<sub>4</sub><sup>+</sup>) fluxes was below mean values for most months of 1993 and fluxes at a station downstream of R-64 (Point No Point [PNPT]) were much higher than normal (Figure 5-2.1b.). In a previous report (Boynton *et al.*, 1993a) it was reported that spring algal bloom deposition to sediments occurred farther downstream than usual. As a result, nutrient fluxes at R-64 were lower than normal and fluxes at Point No Point (PNPT) were higher than normal. The unusual flow pattern of 1993 may not only influence the magnitude

**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 - 1992.
- 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 1992. 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 1992.
- September values for all stations only include two years data, 1991 and 1992.
- The bold solid dots indicate average monthly fluxes recorded in 1993; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.
- \* = Stations occasionally display hypoxic conditions, 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<sup>-1</sup> dissolved oxygen

SEDIMENT OXYGEN CONSUMPTION  
g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>

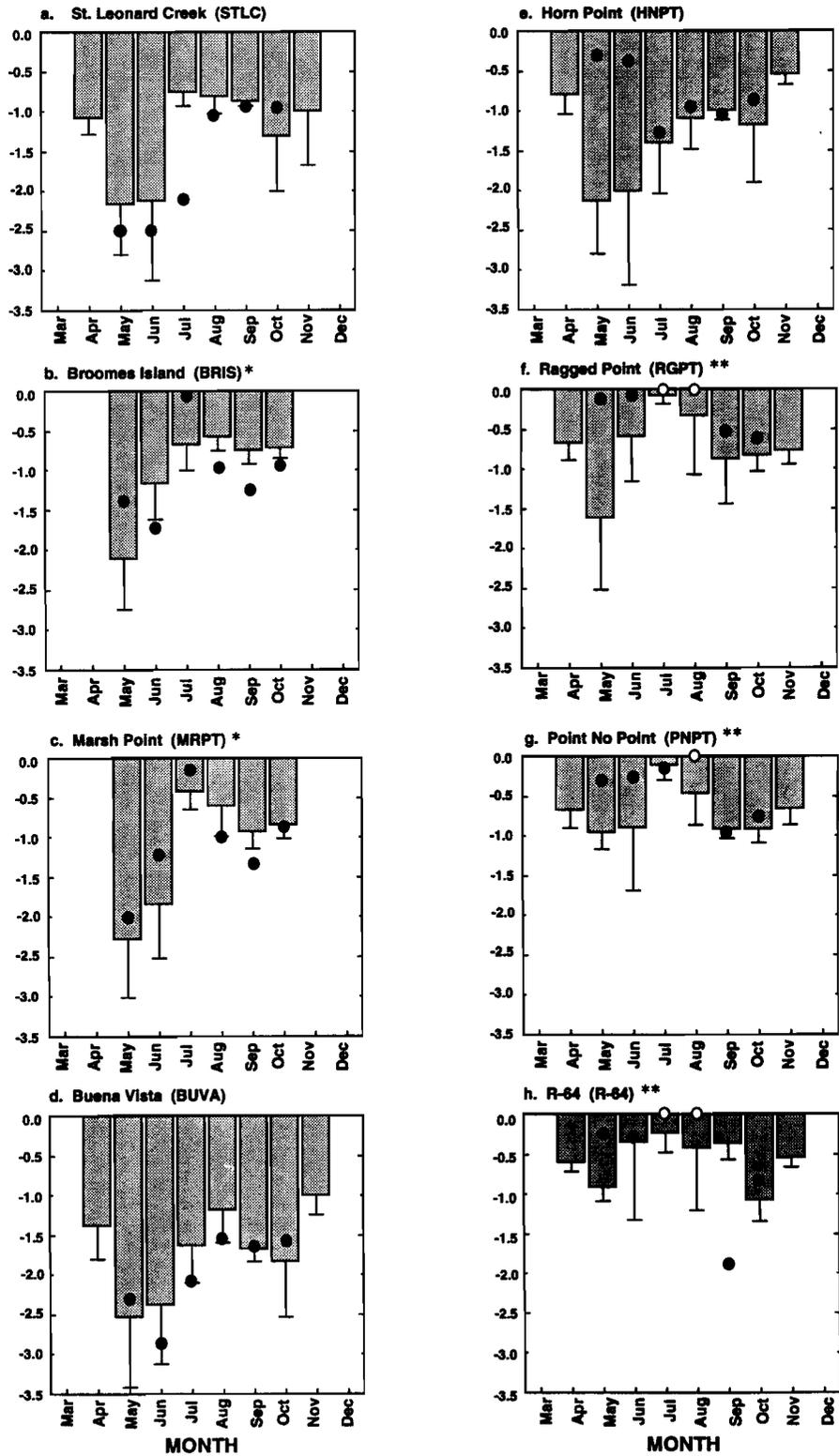


Figure 5-1.1. Mean monthly (April to November) sediment oxygen consumption (SOC) rates at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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**Figure 5-1.2. Mean monthly (April to November) ammonium (NH<sub>4</sub><sup>+</sup>) 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 - 1992.
- 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 1992. 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 1992.
- September values for all stations only include two years data, 1991 and 1992.
- The bold solid dots indicate average monthly fluxes recorded in 1993; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water.

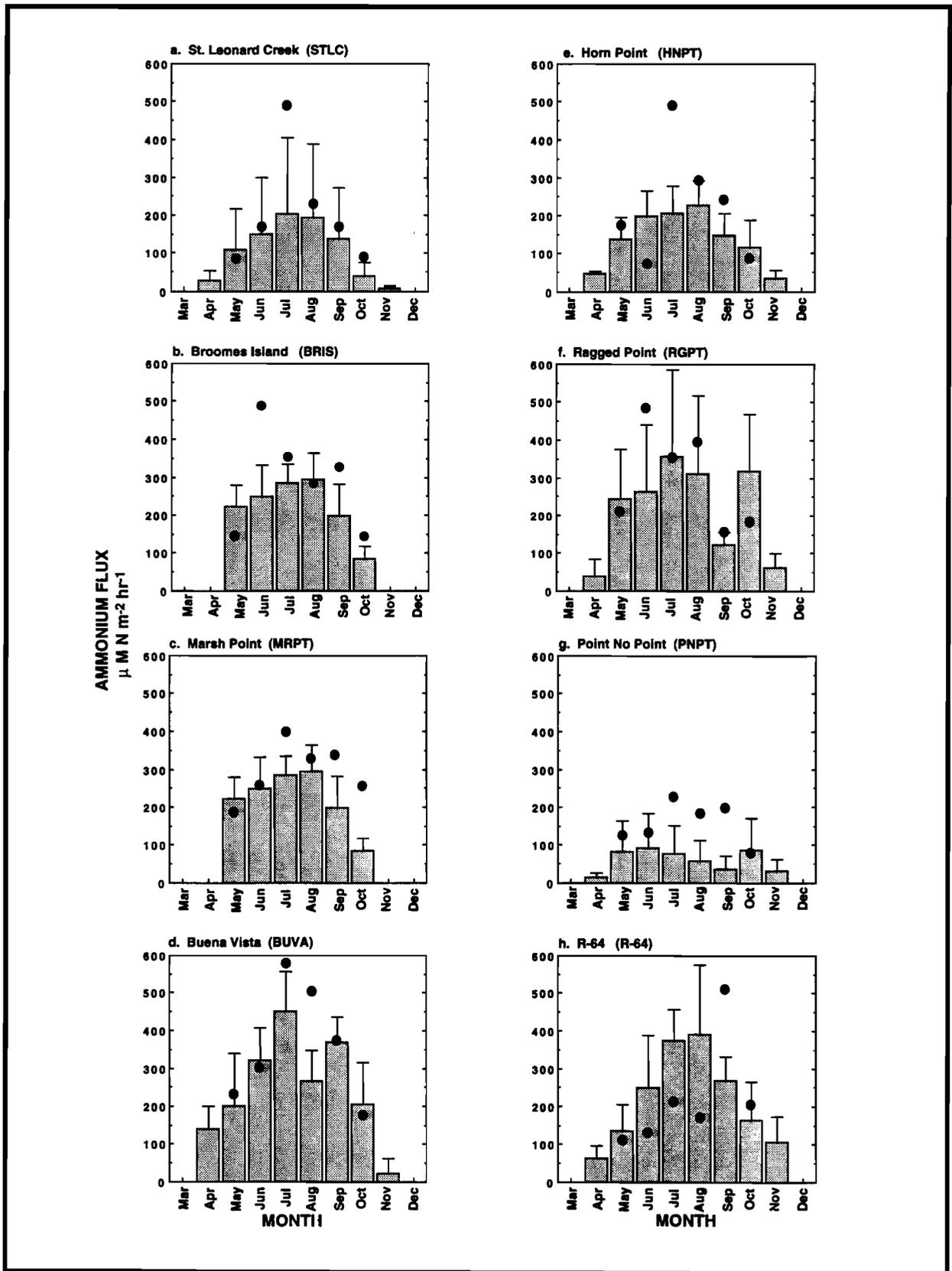


Figure 5-1.2. Mean monthly (April to November) ammonium (NH<sub>4</sub><sup>+</sup>) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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**Figure 5-1.3. Mean monthly (April to November) nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) 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 - 1992.
- 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 1992. 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 1992.
- September values for all stations only include two years data, 1991 and 1992.
- The bold solid dots indicate average monthly fluxes recorded in 1993; 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.

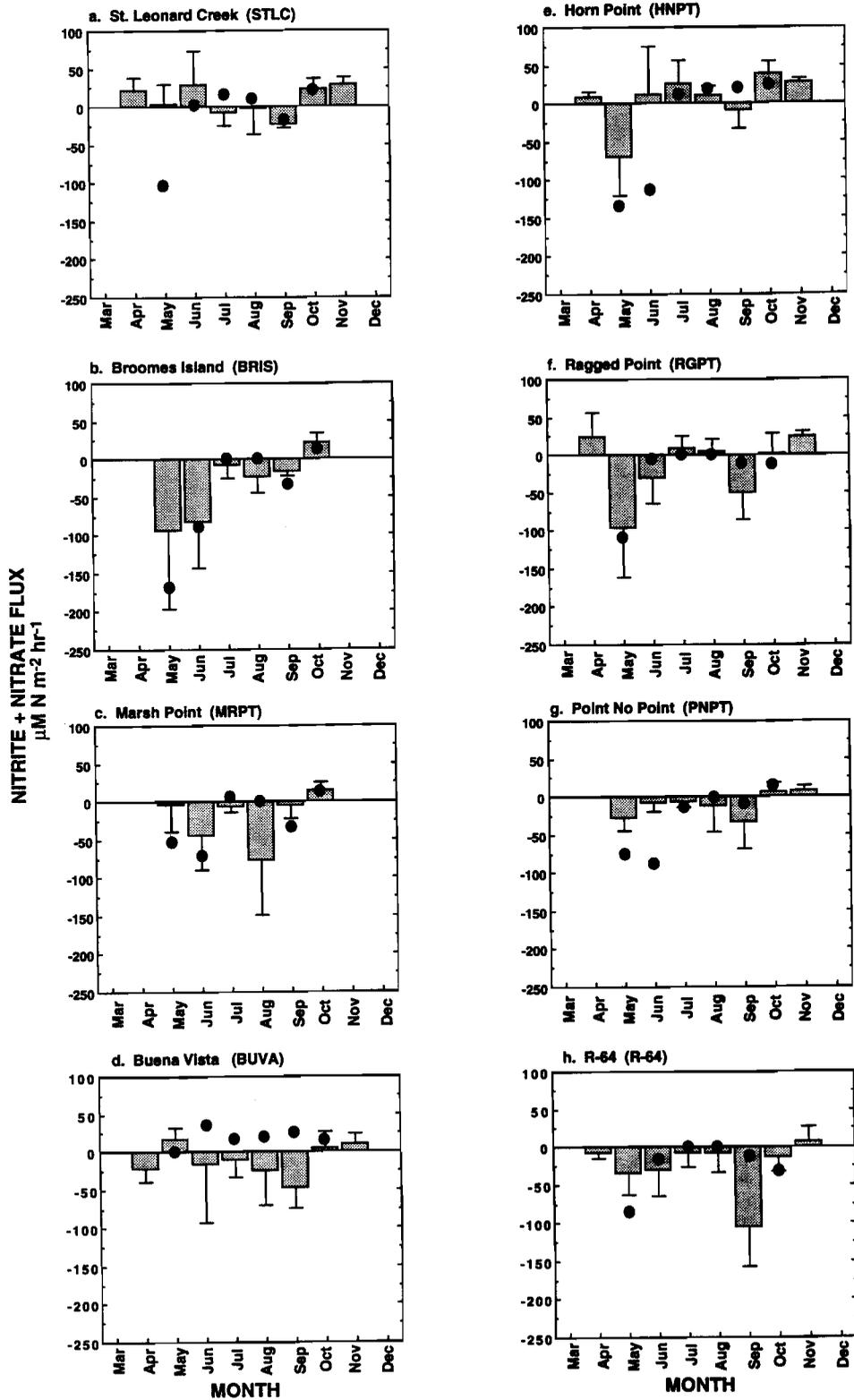


Figure 5-1.3. Mean monthly (April to November) nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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**Figure 5-1.4. Mean monthly (April to November) phosphorus ( $\text{PO}_4^{3-}$  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 - 1992.
- 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 1992. 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 1992.
- September values for all stations only include two years data, 1991 and 1992.
- The bold solid dots indicate average monthly fluxes recorded in 1993; 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.

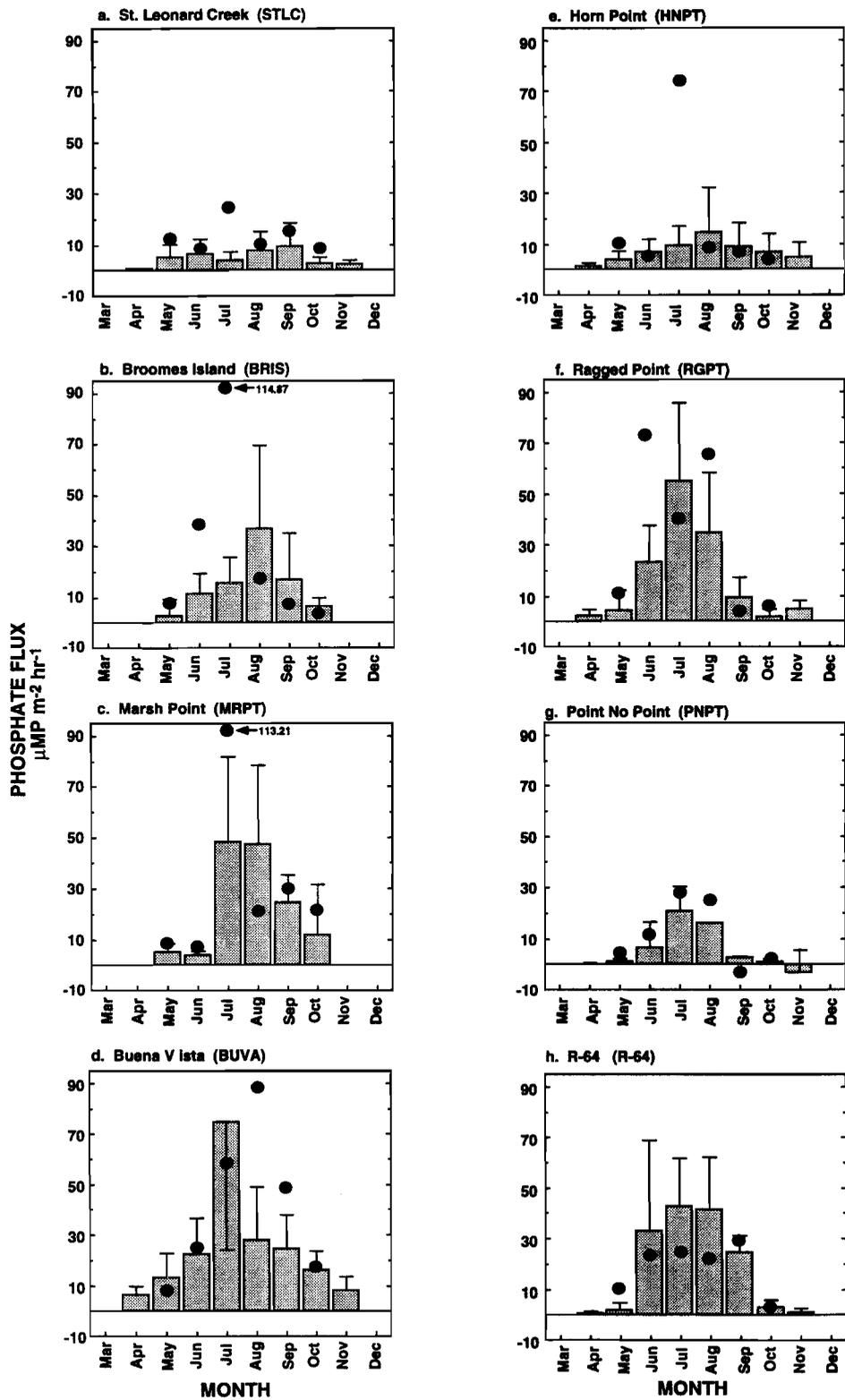


Figure 5-1.4. Mean monthly (April to November) phosphorus ( $\text{PO}_4^{3-}$  or DIP) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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**Figure 5-1.5. Mean monthly (April to November) silicate ( $\text{Si}(\text{OH})_4$ ) 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 - 1992.
- 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 1992. 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 1992.
- September values for all stations only include two years data, 1991 and 1992.
- The bold solid dots indicate average monthly fluxes recorded in 1993; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.

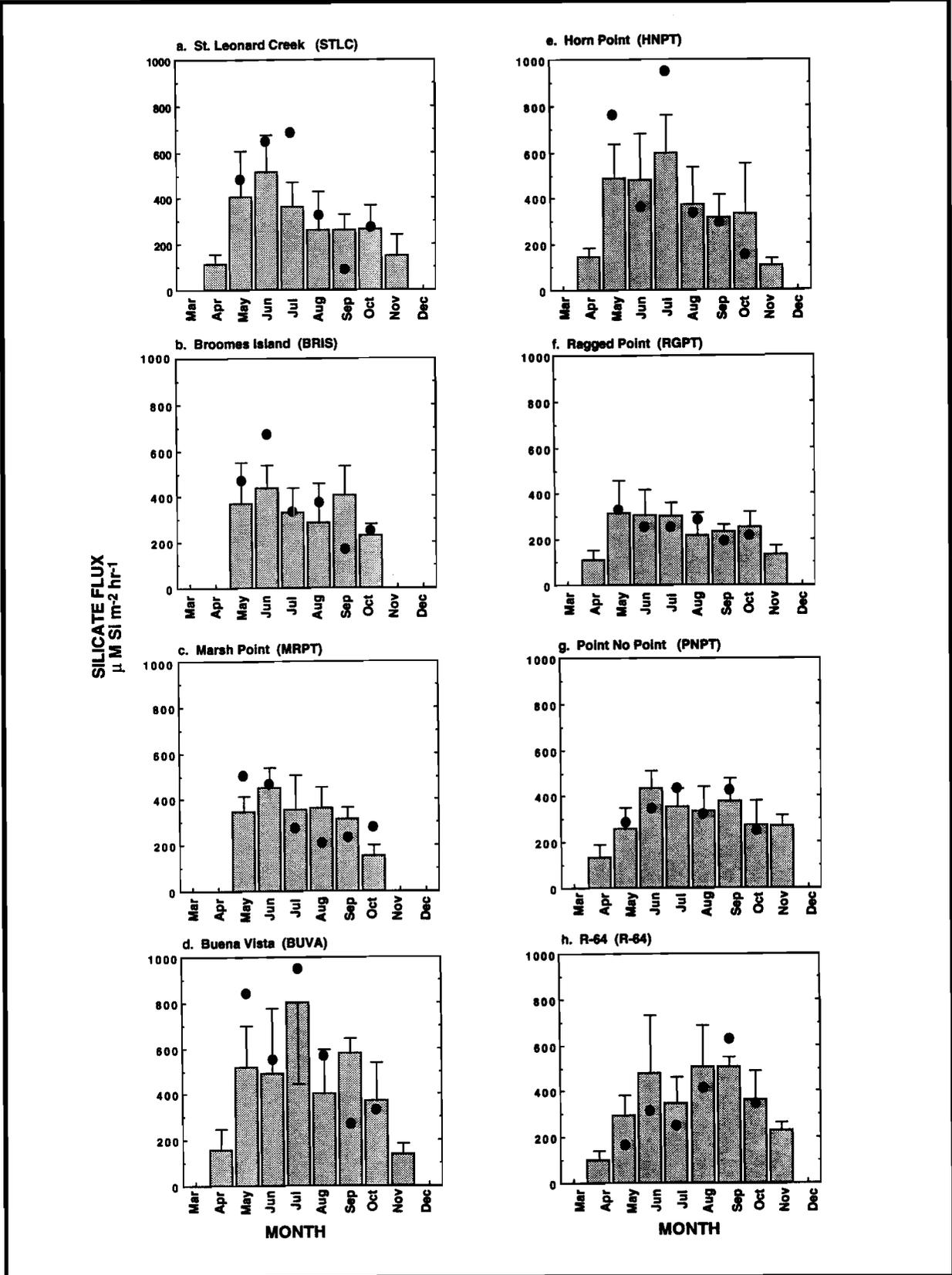


Figure 5-1.5. Mean monthly (April to November) silicate ( $\text{Si(OH)}_4$ ) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

of inputs but also affect the characteristics of sediment processes and the location at which these occur in the bay.

#### 5.4 Nitrite + Nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) Fluxes

Average nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) fluxes for 1993, ranged from zero (Buena Vista [BUVA]) to  $-172.78 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  (Broomes Island [BRIS]) in the Patuxent River, from  $20.03 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  to  $-130.44 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  in the Choptank River (Horn Point [HNPT]), from zero to  $-107.45 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  in the Potomac River (Ragged Point [RGPT]) and from  $9.11 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  (Point No Point [PNPT]) through  $-84.84 \mu\text{MN m}^{-2} \text{ hr}^{-1}$  (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-1.3.; Tables B5-41. - B5-46.). Positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.

In general the range of nitrite plus nitrate fluxes (either into or out of sediments) found at three stations, two in the mainstem bay, Point No Point (PNPT) and R-64, and one in the Patuxent River (Buena Vista [BUVA]) were narrower ranging between 5 and  $-115 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ , while a wider flux range was found at tributary sites, varying between 40 and  $-100 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ .

With a few exceptions (*e.g.*, Broomes Island [BRIS] in May and June, 1991; R-64 in September, 1991), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) fluxes in either direction (into or out of sediments) were small compared to ammonium ( $\text{NH}_4^+$ ) fluxes and even these maximum nitrate fluxes were small compared to maximum ammonium fluxes.

During 1993 the outstanding characteristic of nitrite plus nitrate fluxes ( $\text{NO}_2^- + \text{NO}_3^-$ ) was that the fluxes into sediments were as high or higher than in most previous years with the exception of the site in the upper Patuxent River (Buena Vista [BUVA]) where fluxes were generally small but positive. This is an expected pattern. In years of high river flow nitrate concentrations in overlying waters are typically increased because of enhanced diffuse source run off. With high nitrate concentrations in bottom waters, fluxes of nitrate into sediments are enhanced due to the larger concentration gradient (Table B-2.41.). 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).

At Buena Vista (BUVA) in the upper Patuxent River, nitrite plus nitrate fluxes ( $\text{NO}_2^- + \text{NO}_3^-$ ) were positive departing from previous trends and indicating movement from the sediments into the water. In cases where hypoxic conditions do not occur nitrification of ammonium can occur and at times nitrate plus nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ ) escapes from sediments and is recorded as a flux from sediments to overlying waters. While nitrate plus nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ ) was not released from sediments at all stations (*e.g.* Ragged Point [RGPT]), the Upper Patuxent River (Buena Vista [BUVA]) showed indications of improved water and sediment quality conditions.

#### 5.5 Dissolved Inorganic Phosphorus ( $\text{PO}_4^{3-}$ or DIP) Fluxes

The overwhelming trend, positive values, indicated a net flux of dissolved inorganic phosphorus ( $\text{PO}_4^{3-}$ ) from sediments to the overlying waters. Average monthly dissolved inorganic phosphorus (DIP) fluxes in 1993, ranged from  $6.97 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  (Broomes Island [BRIS]) to  $114.87 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  (Broomes Island [BRIS]) in the Patuxent River, from  $1.75 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  to  $74.21 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  in the Choptank River (Horn Point [HNPT]), from  $2.18 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  to  $72.89 \mu\text{MP m}^{-2} \text{ hr}^{-1}$  in the Potomac River (Ragged Point [RGPT]) and from

-1.61  $\mu\text{MP m}^{-2} \text{hr}^{-1}$  (Point No Point [PNPT]) to 29.42  $\mu\text{MP m}^{-2} \text{hr}^{-1}$  (R-64) in the mainstem of the bay (Figure 5-1.4.; Tables B5-41. - B5-46.). Two large phosphate fluxes were recorded in the Patuxent River, 114.87  $\mu\text{MP m}^{-2} \text{hr}^{-1}$  at Broomes Island (BRIS) and 113.21  $\mu\text{MP m}^{-2} \text{hr}^{-1}$  at Marsh Point (MRPT) 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 ( $\text{PO}_4^{3-}$ ) fluxes were associated with hypoxic or anoxic conditions in overlying waters. It has been suggested that the high dissolved inorganic phosphorus ( $\text{PO}_4^{3-}$ ) 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 1993 generally followed well established temporal trends with some very high fluxes measured during the summer months (June-September). At one station, R-64, there was a marked reduction in the magnitude of dissolved inorganic phosphorus ( $\text{PO}_4^{3-}$ ) fluxes. Fluxes at R-64 during 1993 were only about 40% of the eight year (1985-1992) average. The reduction in phosphorus fluxes at this site (and the enhanced fluxes at the station downstream at Point No Point [PNPT]) are consistent with an earlier observation that the intense Susquehanna River flow during April, 1993 caused development and deposition of the spring bloom to occur farther south in the bay than usual. Lower fluxes of ammonium and phosphorus resulted at R-64 because of lower organic matter deposition rates; higher fluxes occurred at Point No Point (PNPT) because deposition rates were enhanced at this more down bay site. It is possible that even higher fluxes occurred farther down bay (outside of the Maryland Chesapeake Bay Monitoring area) because it appears, based on examination of sediment chlorophyll-a maps, that the focus of the 1993 spring bloom occurred in this area (Boynton *et al.*, 1993a).

## 5.6 Dissolved Silicate ( $\text{Si}(\text{OH})_4$ ) Fluxes

Average monthly silicate fluxes in 1993, ranged from 92  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (St. Leonard Creek [STLC]) to 841  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (Buena Vista [BUVA]) in the Patuxent River, from 179  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  to 780  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  in the Choptank River (Horn Point [HNPT]), from 202  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  to 319  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  in the Potomac River (Ragged Point [RGPT]) and from 188  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (R-64) to 414  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-1.5.; Tables B5-41. - B5-46.).

Silicate fluxes followed the general pattern of previous years although two large values were recorded in July 954  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (Buena Vista [BUVA]) and 886  $\mu\text{M Si m}^{-2} \text{hr}^{-1}$  (Horn Point [HNPT]). In fact, the most striking aspect of these monthly data is the similarity among sites, especially in light of the very different total nitrogen (TN) and total phosphorus (TP) loading rates to which different sites are exposed. In addition, seasonal patterns were not well developed at most stations. For example, while such flux variables as ammonium ( $\text{NH}_4^+$ ) and dissolved inorganic phosphorus ( $\text{PO}_4^-$ ) exhibited higher values during the summer, this was not consistently true for silicate ( $\text{Si}(\text{OH})_4$ ) even though at times values for the months of June or July were slightly higher than in adjacent months, May and August. Consistent with the qualitative relationships between flux and river flow-organic matter deposition, the relatively high silicate ( $\text{Si}(\text{OH})_4$ ) fluxes in the Patuxent and Choptank Rivers were related to the very high flows which occurred during March and April, 1993. Generally lower fluxes were observed at R-64 in the mainstem bay, consistent with the lower deposition rates suspected to have occurred at this station during 1993.

## 5.7 Sediment-water Fluxes and *in situ* Environmental Conditions

### 5.7.1 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. While a number of significant correlations were found between specific sediment-water fluxes (*e.g.*, inorganic dissolved phosphorus [ $\text{PO}_4^-$ ] fluxes) and environmental variables (*e.g.*, bottom water dissolved oxygen levels, or sediment characteristics), the  $r^2$  values were generally low indicating non significant relationships and a lack of predictive power. These earlier evaluations were primarily used to establish which of the suspected relationships or trends were worth continued investigation.

### 5.7.2 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 ( $\text{mg m}^{-2}$ ) and Eh (mV) values (corrected for the hydrogen electrode) in sediments (Figures 5-2.4. and 5-2.5.) averaged over eight years (1985-1992). The data from 1993 are superimposed as bold dots.

#### 5.7.2.1 Temperature

Bottom water temperature conditions during 1993 ranged from 16.0 C (Marsh Point [MRPT]) - 28.1 (Buena Vista [BUVA]) in the Patuxent River, from 16.2 C - 27.7 C in the Choptank River (Horn Point [HNPT]), from 13.4 C - 25.5 C in the Potomac River (Ragged Point [RGPT]) and from 12.5 C (R-64) - 25.8 (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-2.1.; Tables B1-41. - B1-46.). Temperature conditions followed the pattern observed in previous years but were generally slightly lower during spring, probably in response to the larger freshet.

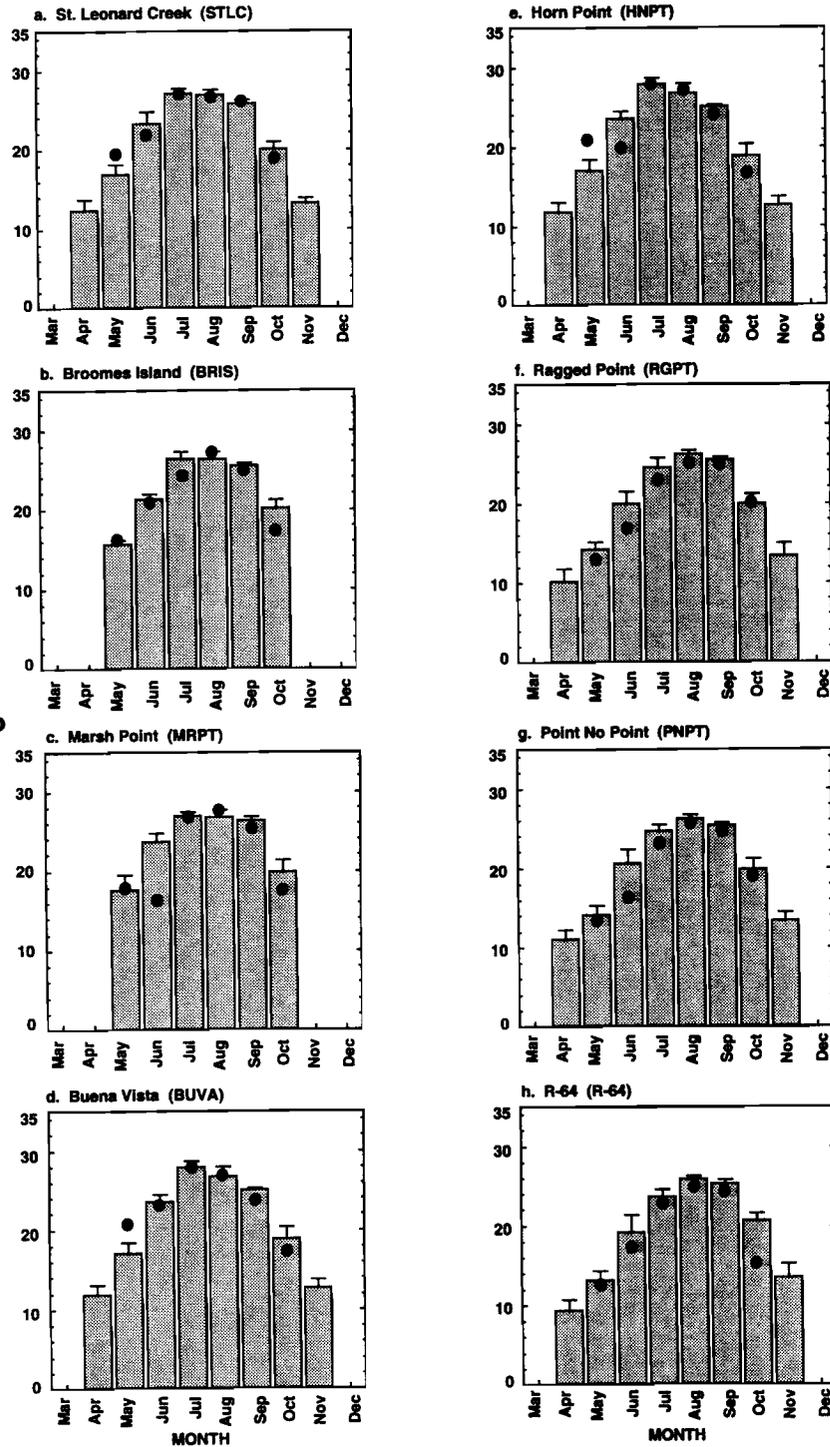
#### 5.7.2.2 Salinity

Bottom water salinity conditions during 1993 ranged from 3.3 ppt (Buena Vista [BUVA]) - 20.3 ppt Broomes Island (BRIS) in the Patuxent River, from 6.4 ppt - 14.0 ppt in the Choptank River (Horn Point [HNPT]), from 11.9 ppt - 24.1 ppt in the Potomac River (Ragged Point [RGPT]) and from 14.4 ppt Point No Point (PNPT) - 29.0 ppt (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-2.2.; Tables B1-41. - B1-46.). The influence of the strong 1993 freshet can be seen as depressed salinity conditions even in the bottom waters of the Patuxent and Choptank Rivers. 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).

#### 5.7.2.3 Dissolved Oxygen

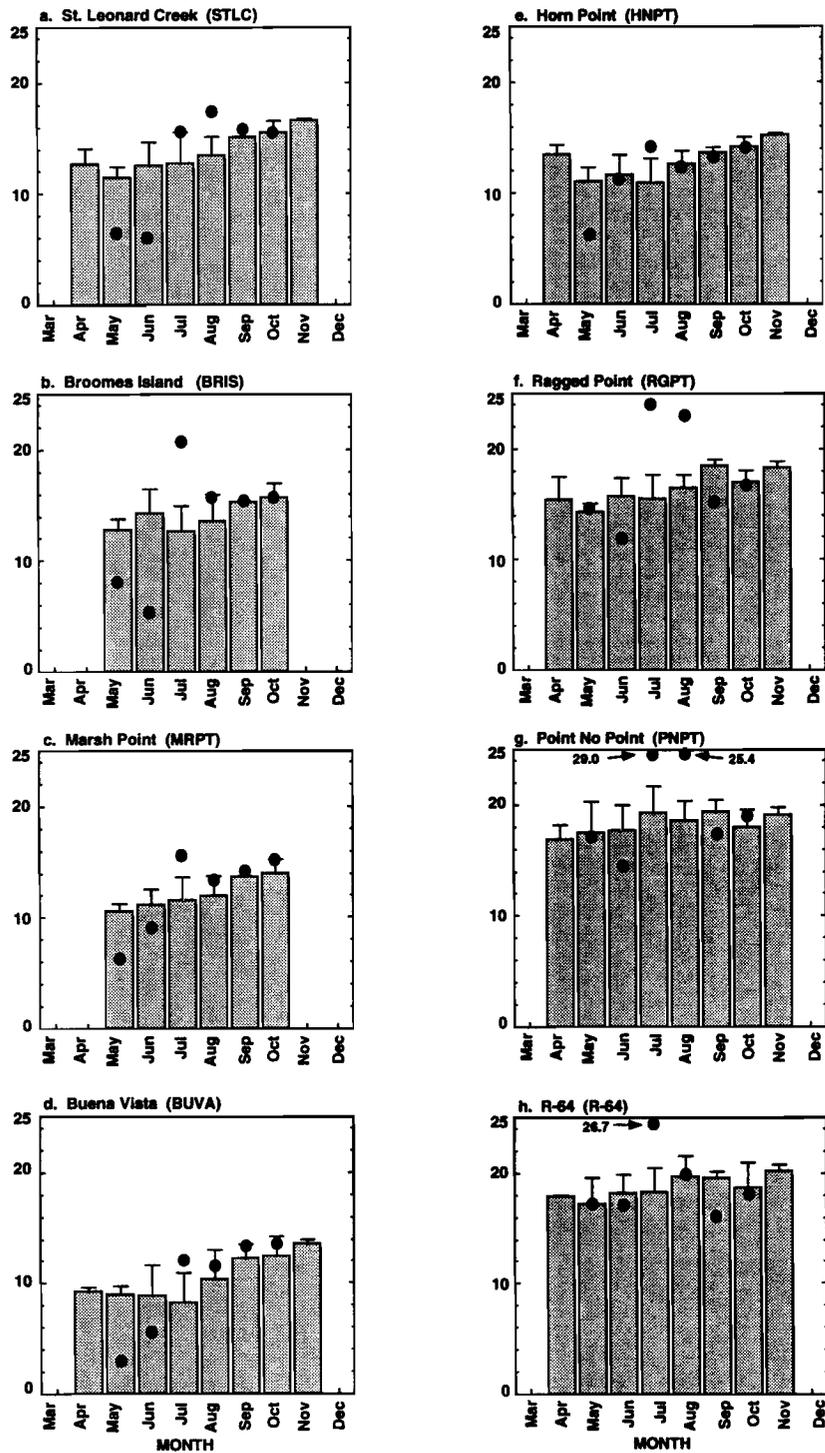
Bottom water dissolved oxygen conditions during 1993 ranged from 0.11  $\text{mg l}^{-1}$  (Broomes Island [BRIS]) - 8.67  $\text{mg l}^{-1}$  (St. Leonard Creek [STLC]) in the Patuxent River, from 0.27  $\text{mg l}^{-1}$  - 10.17  $\text{mg l}^{-1}$  in the Choptank River (Horn Point [HNPT]), from 0.15  $\text{mg l}^{-1}$  - 5.40  $\text{mg l}^{-1}$  in

TEMPERATURE  
C



**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 1992. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1992. The bold dots indicate average monthly values for 1993. Station locations are shown in Figure 3-1.

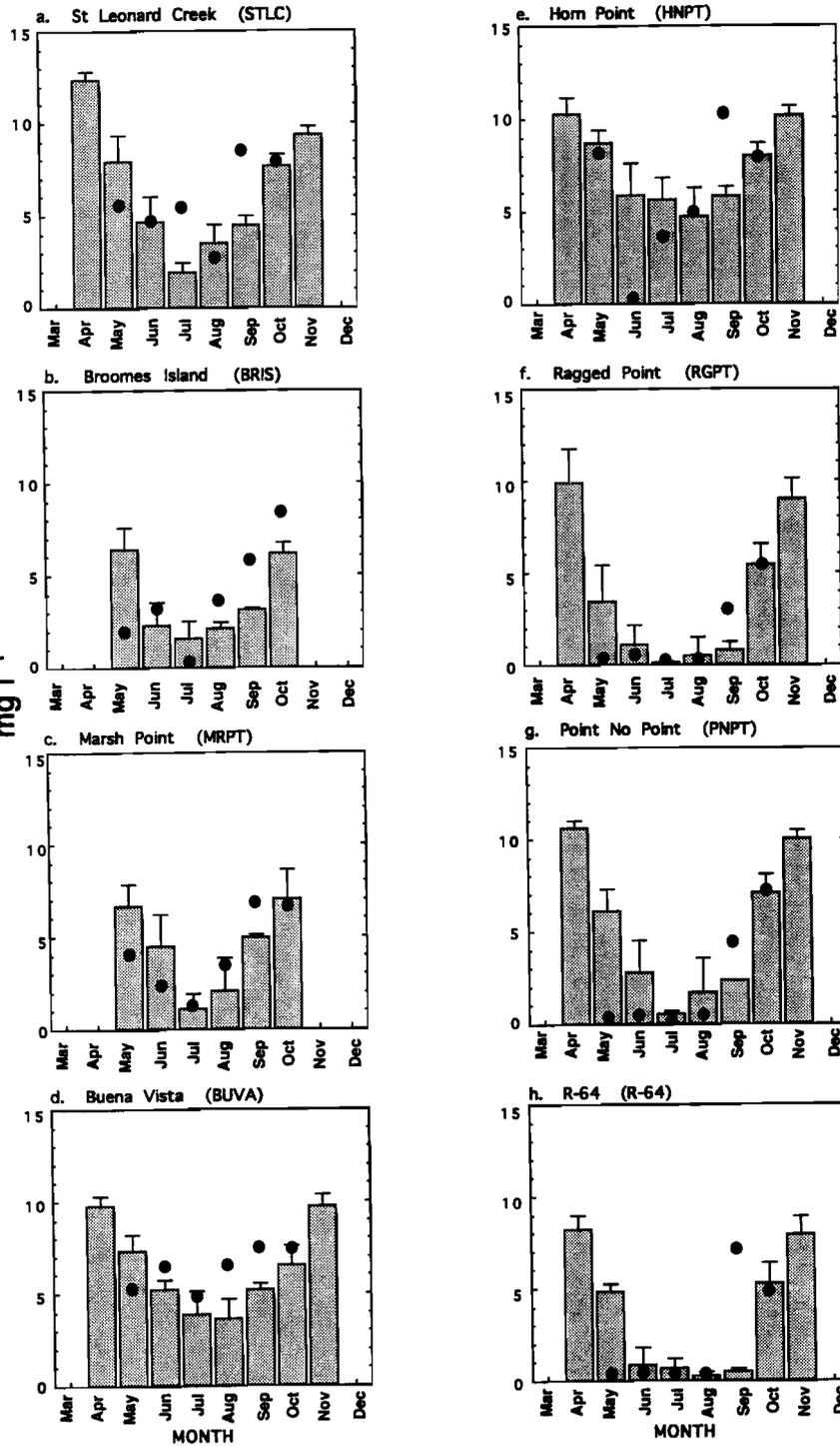
SALINITY ppt



**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 1992. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1992. The bold dots indicate average monthly values for 1993. Station locations are shown in Figure 3-1.

DISSOLVED OXYGEN

mg l<sup>-1</sup>



**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 1992. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1992. The bold dots indicate average monthly values for 1993. Station locations are shown in Figure 3-1.

the Potomac River (Ragged Point [RGPT]) and from 0.10 mg l<sup>-1</sup> (Point No Point [PNPT]) - 7.28 mg l<sup>-1</sup> (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-2.3.; Tables B1-41. - B1-46.).

During 1993 river flows to three portions of the Maryland bay monitored in the Chesapeake Bay Program were higher than the long term sixteen year average (Figure 4-1.1.) while the Choptank River was below this average. 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. Except for stratification 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 1993 dissolved oxygen (DO) concentrations in deep waters were expected to be somewhat depressed. In the Patuxent River (deep stations at Broomes Island [BRIS] and Marsh Point [MRPT]), dissolved oxygen (DO) concentrations were lower than average in 1993 but rebounded to very acceptable levels (~4.0 mg l<sup>-1</sup>) in 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. A similar pattern was evident in the Choptank River (Figure 5-2.3.). At the mainstem bay stations and in the lower Potomac River dissolved oxygen (DO) conditions in bottom waters were very depressed and this occurred earlier than usual, presumably in response to the large freshet. The reasons for the improvement in oxygen conditions in September (Figure 5-2.3.) are not clear.

#### **5.7.2.4 Total Chlorophyll-a**

Surficial sediment total chlorophyll-a mass during 1993 ranged from 31.3 mg m<sup>-2</sup> (St. Leonard Creek [STLC]) - 79.2 mg m<sup>-2</sup> (Broomes Island [BRIS]) in the Patuxent River, from 33.7 mg m<sup>-2</sup> - 65.6 mg m<sup>-2</sup> in the Choptank River (Horn Point [HNPT]), from 44.4 mg m<sup>-2</sup> - 102.5 mg m<sup>-2</sup> in the Potomac River (Ragged Point [RGPT]) and from 38.0 mg m<sup>-2</sup> (R-64) - 147.1 mg m<sup>-2</sup> (R-64) in the mainstem of the bay (Figure 5-2.4.; Tables B3-41. - B3-46.). In general, sediment chlorophyll-a levels were similar to or somewhat lower than values recorded in previous years (Figure 5-2.4.). It maybe that chlorophyll-a values were not collected early enough to "capture" the effects of the spring bloom.

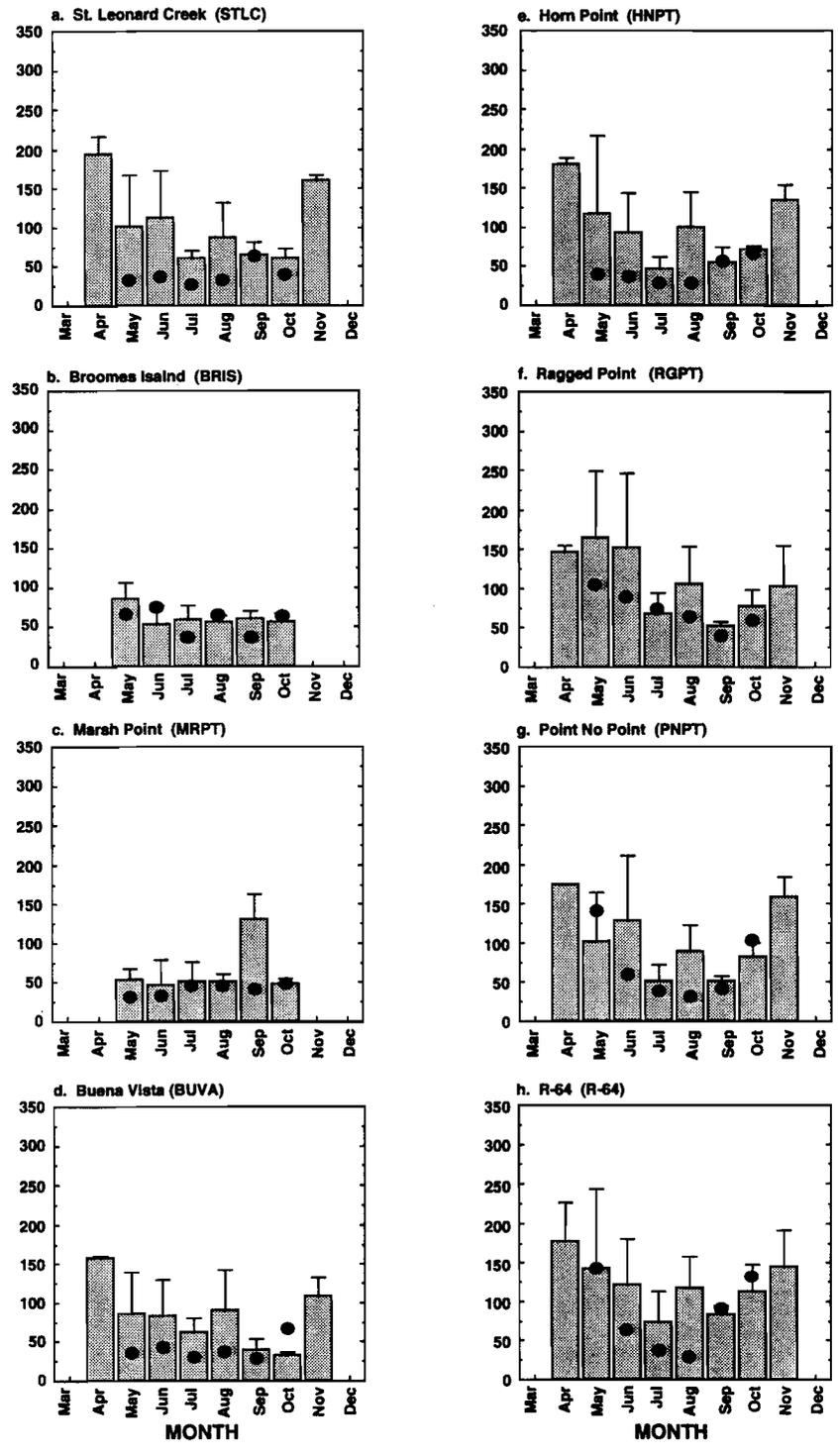
#### **5.7.2.5 Sediment Eh**

Sediment Eh values measured at the sediment-water interface at all sediment oxygen and nutrient exchanges (SONE) stations are shown as a series of bar graphs in Figure 5-2.5. The 1993 values ranged from 172 mV (Marsh Point [MRPT]) - 371 mV (Buena Vista [BUVA]) in the Patuxent River, from 298 mV - 340 mV in the Choptank River (Horn Point [HNPT]), from 1 mV - 329 mV in the Potomac River (Ragged Point [RGPT]) and from -53 mV (Point No Point [PNPT]) - 341 mV (Point No Point [PNPT]) in the mainstem of the bay (Figure 5-2.5.; Tables B3-41. - B3-46.).

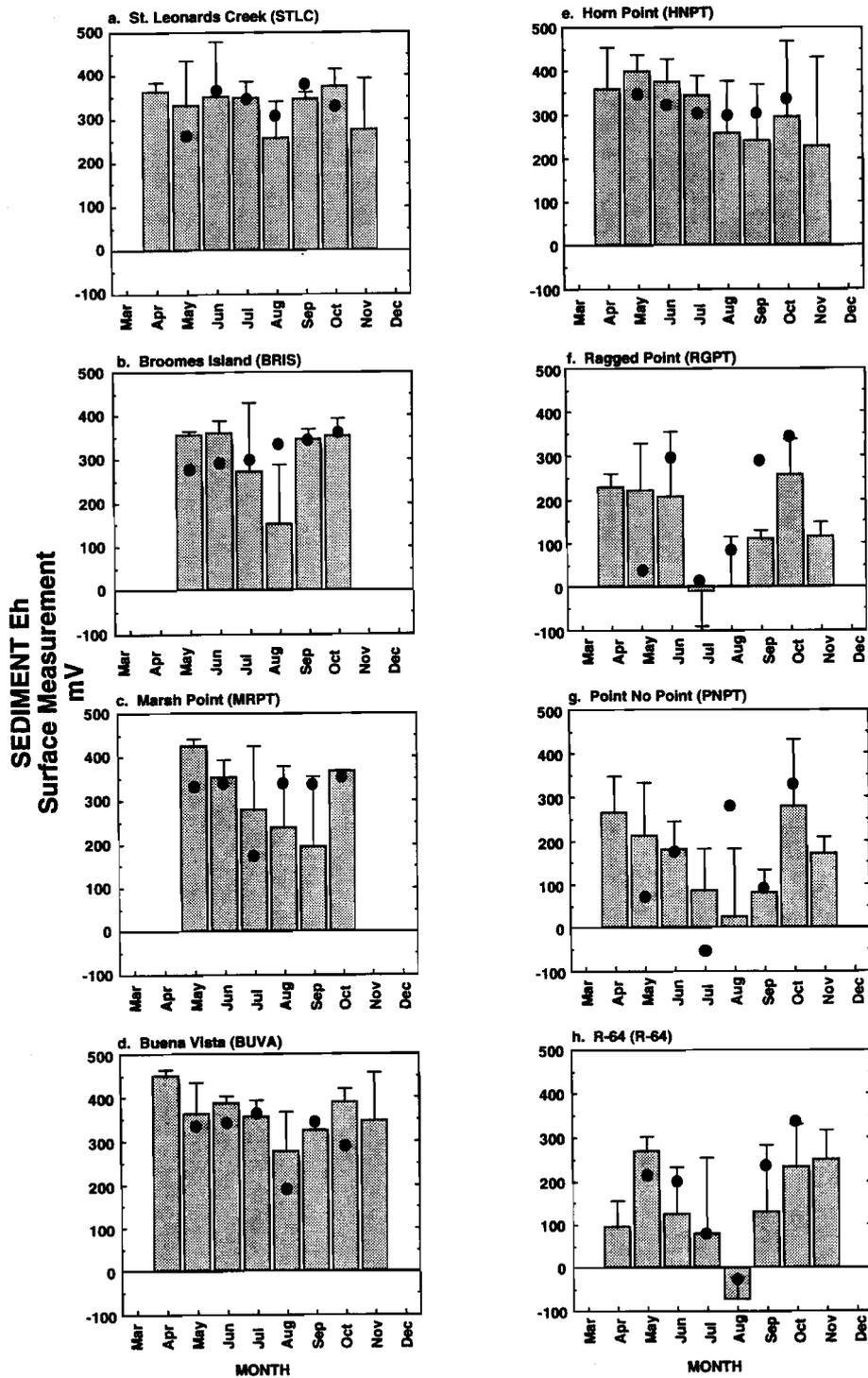
There is considerable scatter among 1993 values, but there are instances in which Eh was more positive (or less negative) in 1993 than the long term eight year (1985-1992) average.

In the Patuxent River values were elevated (or less negative) at most stations during July and August. Likewise, Eh values in the mainstem (R-64 and Point No Point [PNPT]) were elevated during spring and early summer and again in fall. 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. Under these conditions, nitrification (probably coupled to denitrification in deeper anaerobic sediments) and sequestering of phosphorus in insoluble phases are probably active and responsible for the reduced fluxes of ammonium ( $\text{NH}_4^+$ ) and dissolved inorganic phosphorus ( $\text{PO}_4^-$ ) seen at many sediment oxygen and nutrient exchanges (SONE) sites during 1993.

SEDIMENT TOTAL CHLOROPHYLL-a  
mg m<sup>-2</sup>



**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 1992. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1992. The bold dots indicate average monthly values for 1993. 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 1991. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1991. The bold dots indicate average monthly values for 1993. Station locations are shown in Figure 3-1.**

## 6. ANAEROBIC METABOLISM

### 6.1 Introduction

During the last several years a method for measuring anaerobic metabolism has been developed which was compatible with the Ecosystem Processes Component (EPC) monitoring program. Recent measurements indicate that anaerobic metabolism is an important and often a dominating process in sediments of the bay (Roden *et al.*, 1994; Marvin, *pers. comm.*) and therefore needs to be measured. The importance of anaerobic processes is obvious in those zones of the bay that become seasonally hypoxic or anoxic but it is now clear that anaerobic sediment metabolism is also important in areas of the bay where bottom waters remain oxygenated (Roden *et al.*, 1994; Kemp and Boynton, 1992). In order to make such measurements in the context of a monitoring program the methodology needs to be reasonably inexpensive, readily and rapidly conducted under field conditions. Several approaches to the measurement of anaerobic metabolism exist and have been widely used (Section 6.2). These tend to be either too expensive, too time consuming or both for use in the monitoring context. The methodology adapted here focuses on sulfate reduction, the dominant form of anaerobic metabolism in Chesapeake Bay. The specific approach is based on the time dependent disappearance of sulfate from pore waters of intact sediment cores incubated under anoxic conditions at ambient temperature for the period of one month.

This section of the report contains:

- (1) a review of anaerobic metabolism in aquatic systems in order to summarize the anaerobic metabolism process in sediments which has not been discussed at any length in previous interpretive reports
- (2) a description of the methodology used to estimate sulfate reduction and
- (3) the presentation and analysis of sulfate reduction data collected at eight sediment-water nutrient and oxygen exchanges (SONE) stations during 1993.

### 6.2 Anaerobic Metabolism Review

Diagenic processes have, in the last decade, been reasonably well documented in a number of estuaries throughout the world (Fenchel and Blackburn, 1979; Skyring, 1987). It has been shown that estuarine sediments play a quantitatively important role in nutrient recycling and storage within an estuary (Boynton *et al.*, 1994) and thus have a significant affect on water quality. With this in mind, the quantification of sediment respiration has been incorporated into the sampling regime of the Ecosystem Processes Component (EPC) Water Quality monitoring program (Boynton *et al.*, 1993b). Parameters such as sediment oxygen consumption (SOC) and sediment-water nutrient exchange are typically measured either *in situ* using benthic chambers or domes or via intact sediment cores which are incubated on shipboard or in the laboratory. In both approaches the change in oxygen or nutrient concentration is measured as a function of time. The fluxes can be calculated from the slope of the rate of change curve. In the case of oxygen fluxes this methodology provides a reasonable estimate of aerobic respiration but provides little insight into anaerobic processes which, according to recent investigations, may account for over 50% of the

catabolism of deposited organic matter. As a result of this potential underestimation of sediment metabolism, it was decided to attempt to monitor sediment anaerobic metabolism at eight sediment-water nutrient and oxygen exchanges (SONE) stations via measurement of sulfate ( $\text{SO}_4$ ) reduction.

### 6.2.1 Benthic Microbial Metabolic Pathways with particular reference to sulfate reduction

The composition of particulate organic matter (POM) which fuels benthic metabolic processes varies temporally and spatially within each system. In Chesapeake bay, deposited particulate organic matter (POM) during the spring primarily comprises intact diatom cells due to blooms caused by the excessive nutrient input contained in the spring run-off. During the summer, elevated zooplankton grazing causes a shift in the deposited particulate organic matter (POM) to zooplankton fecal pellets and then finally a return to intact diatom cells with the advent of the fall blooms. Decreases in temperature and sunlight and the frequent turnover of the water column during the winter negatively affect primary productivity and therefore particulate organic matter (POM) deposition to the sediment is lessened. In the vicinity of the mouth of the Susquehanna River, terrestrial debris may make up a larger portion of the deposited particulate organic matter (POM). Once this (POM) reaches the sediment surface, it is decomposed via the metabolic activities of benthic microbes and metazoans which then excrete inorganic nutrients (Kemp and Boynton, 1992). These nutrients are then cycled back into the water column where they are consumed by phytoplankton. This cycle of production, deposition, decomposition, nutrient release to the water column and continued algal production is referred to as *benthic pelagic coupling* and is a very important process in estuarine ecosystems.

The various pathways responsible for the metabolism of deposited organic material may fall into one of two categories; processes which occur under aerobic conditions or those which occur under anaerobic conditions. Aerobic benthic metabolism is governed by both macrofauna (various benthic invertebrates) and microbes (protozoa, bacteria and fungi) while anaerobic benthic metabolism is almost exclusively bacterial. Although most organisms are either exclusively aerobic or exclusively anaerobic, there are some species which can exist, at least temporarily, as facultative aerobes or facultative anaerobes. For instance, some species of sulfate reducing bacteria are capable of aerobic metabolism (Canfield and Des Marais, 1991) while some metazoans are facultatively anaerobic (Fenchel and Riedl, 1970).

Metabolism refers to the process via which an organism releases the energy stored in its "food" and transfers this energy to adenosine triphosphate (ATP) which in turn supplies energy for all the life processes of the organism. During metabolism, the "food" or organic matter is oxidized. As with any oxidation reaction, the compound being oxidized must give up electrons which are then "donated" to another compound that, by accepting these electrons, becomes reduced. The compound being oxidized is called the reducing agent or electron donor and the compound being reduced is the oxidizing agent or electron acceptor. It is the electron acceptor, or "terminal" electron acceptor as it is referred to in a metabolic context, which distinguishes aerobic metabolism from anaerobic metabolism.

The terminal electron acceptor in aerobic metabolism is oxygen ( $\text{O}_2$ ). Through the oxidation-reduction process, oxygen ( $\text{O}_2$ ) is reduced to carbon dioxide ( $\text{CO}_2$ ) and water. An important consequence of aerobic metabolism in aquatic systems is the potential depletion of oxygen from the surrounding water. During the summer this depletion, coupled to a stratified water column, can lead to hypoxia or anoxia in bottom waters (Kemp and Boynton, 1992; Boicourt, 1992) and a switch to anaerobic metabolism.

In anaerobic environments metabolic processes are more complicated as anaerobic metabolism can proceed along two very different pathways. The first pathway is anaerobic respiration which uses a different electron acceptor than does aerobic respiration ( $O_2$ ). Examples of these electron acceptors include sulfate ( $SO_4$ ), nitrate ( $NO_3$ ), and carbon dioxide ( $CO_2$ ; Singleton, 1993). The second anaerobic metabolic pathway is fermentation. Fermentation is fundamentally different than other forms of metabolism in that it is not considered to be a respiratory process because it has no separate electron donors and electron acceptors. The electrons generated in the oxidation of the substrate are used to reduce a compound generated from that oxidation. The electron donor and acceptor have the same origin. Only organic compounds are involved in fermentation unlike the respiratory processes which consumes inorganic compounds such as oxygen ( $O_2$ ), sulfate ( $SO_4$ ), or nitrate ( $NO_3$ ; Singleton, 1993). Some end products of fermentation are acetate, propionate, carbon dioxide ( $CO_2$ ) and alcohols (Valiela, 1984). These end products are very important because they are subsequently metabolized by other anaerobic microbes, most importantly in this case, the sulfate reducers.

Anaerobic respiration within estuarine sediments proceeds via one of three major processes: nitrogenous oxide reduction, sulfate reduction, or methanogenesis (methane production; Day *et al.*, 1989). Nitrogenous oxide reducing microbial species require nitrite ( $NO_2^-$ ) or nitrate ( $NO_3^-$ ) as their terminal electron acceptor. Moving down through the sediments, there is a respiratory process gradient caused by the hierarchical depletion of available electron acceptors. The gradient,  $O_2 > NO_3 > SO_4 > CO_2$ , is based upon the decreasing energy yield provided by each successive electron acceptor (Day *et al.*, 1989). After sulfate ( $SO_4$ ) is depleted, which may occur a few centimeters to several meters below the sediment surface, the terminal oxidative process is methanogenesis (Jorgensen and Revsbech, 1989). Sulfate ( $SO_4$ ) is the third most prevalent ion in sea water after chloride and sodium and is the most abundant ion which is biologically active (Day *et al.*, 1989). The ready availability of sulfate ( $SO_4$ ) makes sulfate reduction an important metabolic process in estuarine environments. Reduction inhibition via sulfate depletion does not occur under normal salinity conditions. For example, if the oxygen concentration in the bottom waters and surficial sediments of the estuary is 0.2 mmol of  $O_2$  per liter ( $6.5 \text{ mg l}^{-1}$ ), this amount of oxygen is sufficient to oxidize 0.2 mmol of organic carbon. However, in 15 ppt estuarine water, sulfate is present in concentrations of  $\sim 12.1$  mmol which has the capacity to oxidize 24.2 mmol of organic carbon (Jorgensen, 1982), over 100 times more than that of oxygen (Crill and Martens, 1987).

### **6.2.2 Description of sulfate reducing organisms and their physiology**

Some of the requirements for growth of sulfate reducing bacteria include an anoxic environment, an inorganic electron acceptor ( $SO_4$ ), a carbon source-electron donor, a source of nutrients (nitrogen [N], phosphorus [P] and iron [Fe]), and a surrounding medium with low oxidation-reduction potential (Eh; Gibson, 1990). With few exceptions, sulfate reduction is an exclusively anaerobic process. It is believed that oxygen ( $O_2$ ) deactivates several of the enzymes involved in and necessary for the sulfate reduction process (Canfield and Des Marais, 1991).

Once thought to be a very taxonomically and metabolically restricted group, the sulfate reducers now comprise at least 14 genera capable of metabolizing a variety of different substrata (Singleton, 1993). They are, however, incapable of breaking down starch, glycogen, proteins or lipids and dependent on the fermenters to do this (Hansen, 1988). Of primary importance in the marine environment is the fermentation end product, acetate. In one study, acetate was shown to support 90% of the sulfate reduction (Mackin and Swider,

1989). The methanogens also use acetate as an electron source but are outcompeted by the sulfate reducers which have a higher affinity for acetate (Capone and Kiene, 1988). Shaw *et al.* (1984) determined that over 95% of the acetate oxidized in a study in Skan Bay, Alaska was accomplished via sulfate reduction.

The sulfate reduction process carried out by sulfate reducing bacteria refers to dissimilatory sulfate reduction as opposed to assimilatory reduction. Dissimilatory sulfate reduction is a bioenergetic process while assimilatory reduction involves the reduction and incorporation of sulfate into the biological compounds which make up the organism in question. The generalized reaction of assimilatory sulfate reduction is (Singleton, 1993):



The electron donor is represented by  $\text{AH}_2$  and of the three end products, hydrogen sulfide ( $\text{HS}^-$ ) is perhaps the most important. One of the more familiar characteristics of sulfide is its "rotten egg" odor. This "odiferous physiology" (Singleton, 1993) of the sulfate reducers has some important consequences within the benthic environment. Sulfide is not only toxic to a variety of organisms but it is also a strong reducing agent and as such can inhibit the growth of aerobic organisms (Gibson, 1990). Sulfide produced within the sediment may be precipitated with iron ( $\text{Fe}^{+3}$ ) to form pyrite (Day *et al.*, 1989). Most of the sulfide remains in solution, however, and diffuses to the aerobic-anaerobic boundary where it is reoxidized to sulfate. Ninety percent (90%) of the sulfide produced by the sediments in Limfjorden was reoxidized to sulfate (Jorgensen, 1977a). The oxidation of sulfide to sulfate may be responsible for a significant portion of oxygen consumption attributed to sediments. Jorgensen (1982) determined that the ratio of oxygen consumed to sulfate reduced by the sediments averaged 4:1 in Danish fjords and seas. One mole of sulfate ( $\text{SO}_4$ ) can oxidize as much carbon as two moles of oxygen ( $\text{O}_2$ ) producing a ratio of 2:1. Since almost all of the sulfide produced from sulfate reduction is reoxidized to sulfate, 50% of the oxygen consumed is used in the reoxidation of sulfide at these Danish sites. The ratio of organic carbon oxidized aerobically to that oxidized via sulfate reduction is then 1:1. Roden (1990) found that the amount of oxygen necessary to reoxidize the amount of sulfide released to anoxic bottom waters by the sediment of a mesohaline station in Chesapeake bay was equal to or greater than what was supplied by estimated eddy-diffusive reaeration. This would indicate that bottom water anoxia was maintained through sulfur cycling alone.

It is important to realize that, even though sulfate reduction is an anaerobic process, it occurs in systems that may appear to be aerobic because of moderate to high oxygen concentrations in bottom waters. In fact the penetration depth of oxygen into the sediments is small, millimeters to centimeters, in most sediments. According to Berner (1985), over 90% of medium to fine grained sediments are anoxic below the top few centimeters. In a study of fourteen sediment stations, Jorgensen and Revsbech (1989) found that the oxic zone only penetrated to a depth of 1.3 - 5.6 mm. The boundary between the aerobic and anaerobic layers is the area where the oxidation-reduction potential (Eh) of the sediment is 0 mV. The depth of this boundary will vary with the season (Jorgensen, 1977a). Jorgensen (1977a) found this boundary to be as deep as 3 centimeters in the winter and as shallow as a few millimeters during the summer in Limfjorden, Denmark due to increased oxygen consumption and production of reducing compounds by benthic organisms during the summer. It is also possible for sulfate reduction to occur in completely oxic environments in reduced microniches (Jorgensen, 1977b). These microniches are in the form of fecal pellets 50 to 200  $\mu\text{m}$  in diameter.

The depth and intensity within sediments where sulfate reduction can occur is dependent on several factors. Sulfate will penetrate deeper into the sediments with increased salinity due

to the higher concentration of sulfate in more saline water (Jorgensen and Sorensen, 1985). This will increase the potential for sulfate reduction to occur at depth. It has also been shown that there is a direct correlation between the rate of sulfate reduction and the rate of sedimentation (Berner, 1978; Jorgensen, 1989). In high sedimentation areas, the rate of organic matter deposition may be too fast for aerobic metabolic processes to keep up, therefore a large amount of freshly deposited material is buried that can then be decomposed through sulfate reduction (Roden, 1990; Jorgensen, 1989). Due to the ready supply of metabolizable organic material in highly depositional areas ( $> 1 \text{ cm yr}^{-1}$ ), most of the sulfate reduction occurs in a sharp peak of activity just below the aerobic-anaerobic boundary within the sediments while those areas experiencing low deposition will exhibit a broad peak that can extend several meters into the sediment (Westrich and Berner, 1988; Jorgensen, Bang and Blackburn, 1990). Deep mixing of the sediment in high deposition areas can cause a broadening of the zone of elevated sulfate reduction due to the importation of fresh organic matter deeper into the sediment (Jorgensen, Bang and Blackburn, 1990). If deposition occurs at a rate which is high enough such that the aerobic decomposers deplete bottom water oxygen, a significant portion of the sulfate reduction activity may take place within the anoxic water overlying the sediments (Indrebo *et al.*, 1979). The relationship between deposition and sulfate reduction is dependent on the depth of the system. With increasing depth, more of the sedimenting organic matter is degraded in the water column before reaching the bottom (Capone and Kiene, 1988).

Sulfate reducing bacteria have a  $Q_{10}$  of about 3.4 across the natural temperature range (Jorgensen, 1977b). In their study of sulfate reduction in salt marsh sediments, Nedwell and Abrams (1979) found that temperature was more important in controlling rates than the electron donor-acceptor concentration. Westrich and Berner (1988) found temperature to be more important in sediments with low rates of sulfate reduction. Their findings indicated that the reactivity of the deposited organic matter was the most important factor and since the sulfate reducers are dependent upon the fermenters for a metabolizable supply of "food", it is the rate of fermentation which is the ultimate controlling factor of sulfate reduction.

At concentrations  $< 3 \text{ mM SO}_4$ , sulfate reduction within the sediments starts to become limited by the sulfate supply (Boudreau and Westrich, 1984). When sulfate reduction becomes limited due to a lack of an electron acceptor, then a different anaerobic metabolic process which is not likewise inhibited will become the dominant form of anaerobic metabolism. This switching of dominant metabolic pathway is seen in estuaries due to the characteristic salinity gradient which influences the availability of terminal electron acceptors. In fresh waters, decreasing sulfate concentrations start to limit particulate organic matter (POM) oxidation through sulfate reduction. In Norsminde Fjord, Jorgensen and Sorensen (1985) found that there was a change in the relative importance of sulfate and nitrate reduction (denitrification, nitrate reduction, and sulfate reduction were measured) at stations located at the estuary mouth versus the headwaters of the estuary. At the estuary mouth, sulfate was more abundant and therefore sulfate reduction was the dominant anaerobic process while in the fresher river outflow, sulfate was scarce and nitrate more prevalent causing a shift to nitrate reduction.

Eh data for the eight SONE stations indicates that R-64, Ragged Point (RGPT) and Point No Point (PNPT) have the greatest potential for high sulfate reduction rates due to relatively shallow oxygen penetration into the sediments, particularly in the summer. With the anoxic zone relatively close to the surface, the potential for sulfide diffusion to the overlying waters and subsequent sulfur cycling induced anoxia is increased. A highly depositional station such as R-64, where the ready availability of catabolizable substrate is high during spring and early summer leading to rapid depletion of  $\text{O}_2$  in the overlying waters, would be very likely to be a system where the dominant form of benthic metabolism

was sulfate reduction. None of the eight stations exhibit salinity levels low enough (< 4 ppt) during any of the months studied presently (May through October) or historically (April through November) to indicate that sulfate concentration might be limiting to sulfate reduction.

### **6.2.3 Methods used in the determination of sulfate reduction**

Quantification of the rate at which sulfate is reduced within the sediments of several different ecosystems throughout the world has been undertaken using a variety of methods (Table 6-1.). These include mathematical modeling, direct chemical and radiometric measurements and indirect measurements (Skyring, 1987). Mathematical modeling requires diffusion coefficients.

Sulfate concentrations at various depths and sedimentation rates for the given system are incorporated into equations which compute sulfate reduction rate. Rates determined by this method may not be accurate in sediments that are bioturbated or mixed (Skyring, 1987). Direct chemical methods involve the measurement of increasing or decreasing sulfate concentration within sealed containers of sediment. These increases or decreases can then be used to determine the rate of sulfate reduction. Sulfate reduction can be determined radiometrically using radiolabeled sulfate ( $^{35}\text{S}$ ) and subsequently measuring the amount of radiolabeled sulfide present in the pore water of the inoculated sediment after incubation. Since sulfide is an end product of the sulfate reduction the accumulation of radioactive sulfide over time indicates the rate at which sulfate is reduced. Ammonia ( $\text{NH}_4^+$ ) is always an end product of anoxic metabolism (Skyring, 1987), so ammonia buildup within anoxic sediments can be used to provide an indirect measurement of sulfate reduction.

## **6.3 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 of one month.

### **6.3.1 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

**Table 6-1. Sulfate reduction rates and system characteristics of a variety of systems throughout the world. Rates are integrated over the sediment depth indicated (Adapted from Skyring, 1987).**

Place	Ecosystem	Sediment Type	Water Depth m	Sediment Depth cm	Season Temp (°C)	Sulfate Reduction Rate Calculated mmol m <sup>-2</sup> day <sup>-1</sup>	Reference
<b>Estuaries, Shallow Seas and Continental Shelf</b>							
Colne Point, UK	Tidal Creek	mud	tidal	0-20	annual	45	Senior et al. (1982).
Limfjorden, Denmark	Restricted Fjord		4 - 12	0-10	summer	15	Jorgensen (1977a).
					winter	2.5	
					annual	7	
			10	0-14	5 - 25	20	Blackburn (1979).
					spring-winter		
Kysing Fjord, Denmark	Restricted Fjord	sand/silt	0.5	0-15	summer	18	Troelsen and Jorgensen (1979).
					winter	4	
	Restricted Fjord	sand/silt	0.5	0-15	summer	15	Sorensen et al. (1979).
					winter	5.8	
Randers Fjord, Denmark	Open Fjord		0.5	0-15	summer	7.8	Sorensen et al. (1979).
					winter	1.9	
Long Island Sound, USA	Estuarine mud	organic mud	0-2			0-1.4	Goldhaber et al. (1977).
			0-8			5.4	
			11 - 14			9	
			10-80			2.7	
		clay/silt	0-10	22	8 - 10	Aller and Yingst (1980). Bordreau and Westrich (1984).	
		organic mud	5-100	room (20-25?)	22-48		
		organic mud					
		3-4%	0-12	22	75	Berner and Westrich (1985).	
		1.5-2.5%	0-9	23	17		
		1-1.4%	0-12	22	17		
		1.3-2.0	0-30	21	42		
Great Bay Estuary, USA	Estuarine mud	clay/silt	shallow	0-6	winter	1.5	Hines et al. (1982).
					summer	15	
	Bioturbated Non-bioturbated	clay/silt	0.5	0-12	annual	16	Hines and Jones (1985).
					summer	4	
Bioturbated Non-bioturbated				0-6	42		
				0-6	10		
Branford Bay, USA.	Estuarine mud	mud		surface	32	28	Nakai and Jensen (1964).
Cape Lookout Bight, USA.	Zostera, Haladule, Spartina debris	organic mud	tidal	0-35	summer	62-106	Crill and Martens (1983).
				0-3	26	24-41	
					winter		
					11		

**Table 6-1. Sulfate reduction rates and system characteristics of a variety of systems throughout the world. Rates are integrated over the sediment depth indicated (Adapted from Skyring, 1987)(Continued).**

Place	Ecosystem	Sediment Type	Water Depth m	Sediment Depth cm	Season Temp (°C)	Sulfate Reduction Rate Calculated mmol m <sup>-2</sup> day <sup>-1</sup>	Reference
<b>Estuaries, Shallow Seas and Continental Shelf</b>							
Kattegat Skagerrak	Shallow Seas		0-2 2 - 20	0-15 0-15		14-50 4 - 20	Jorgensen (1982).
Azov Sea, USSR.	Shallow Sea	organic		0-2	sum to fall	14.5	Tolokonnikova (1977).
San Fransisco Bay, USA	Enclosed Shallow Sea	mud	tidal	0-40	21-23	92	Oremland and Silverland (1979).
Pacific Ocean, Mastalan	Continental Shelf	silt	140	15-30		0.11	Ivanov et al. (1980).
Atlantic Ocean	Continental Shelf		158	0-5		0.05	Battersby and Brown (1982).
Gulf of Oman	Continental Slope		520	0-200		0.56	Ivanov et al. (1980).
Gulf of California, USA	Continental Shelf			35-40		0.02	
Chesapeake Bay, USA	Estuarine Mud						
	Oligohaline	organic mud	8	0-20	5 - 30	1 - 10	Marvin (Pers. Comm.)
	Mesohaline	silt	15	0-20	5 - 30	5-70	
	Polyhaline	sandy clay	10	0-20	5 - 30	5-40	
<b>Coastal Basins, Enclosed Seas and Deep Fjords</b>							
Saanich Inlet, Canada	Deep Fjord	organic mud	225	0-25	10	6 - 9	Devol et al. (1984).
Danish Fjords	Fjord		20-200	0-15		0.2-7	Jorgensen (1982).
By Fjord, Sweden	Coastal Basin	dredge spoils	48	1 - 10	1 - 6	3	Dryssen and Hallberg (1979).
Scottish Fjords:							
Loch Linnhe	Restricted marine fjords		48	0-5		0.005	Battersby and Brown (1982).
Loch Creran			13	0-5		0.2	
Loch Eil	Polluted		18	0-5		0.5	
			30	0-5		0.75	
			49	0-5		7.5	
Ellis Fjord, Antarctica	Fjord	mud	50	surface 0-5		0.04	Franzmann et al. (1985).
Black Sea	Shelf	carbonate silt	180	0-6	9	2.3-3.6	Sorokin (1962;1983).
	Slope		1600-1700	0-6		1.4-1.9	
	Bathypagic Slope		2000	0-6		.4-.7	
	Halistatic Centers		2000	0-6		.001-.003	
Baltic Sea	Enclosed Sea	organic	10	0-20	winter 6 Apr-Dec 10 - 16	14  11	Bagander (1977;1980)
				surface		5.3	Volikov and Rozanov (1983).

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.

### 6.3.2 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.

### 6.3.3 Sulfate Analysis

Sulfate (SO<sub>4</sub>) 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 from May through August, 1993 were obtained using standards of 0.0, 0.25, 1.0, 5.0, and 15.0 ppm for the standard curve, while data from September and October, 1993 were obtained using standards of 0.0, 0.5, 5.0, 10.0, and 20.0 ppm for the standard curve. Standards were run after every ten samples throughout the analysis.

### 6.3.4 Porosity Analysis

Porosity is the percent of pore water in 1 cubic centimeter (cm<sup>3</sup>) 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 (2.5g cm<sup>-3</sup>).

### 6.3.5 Flux Calculations

Depletion rate of sulfate (SO<sub>4</sub>) was estimated from sulfate (SO<sub>4</sub>) concentrations in the pore water of the minicores using the following equation:

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

where F = sulfate flux (mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>),  
d[SO<sub>4</sub>]/dt = rate of change of sulfate concentrations over time (mg l<sup>-1</sup> day<sup>-1</sup>),

V = sediment volume (l),  
P = porosity, and  
K = conversion constant (to convert volumetric rate to areal flux).

Sediment volume of each minicore was 0.0507 liters and each minicore had a surface area of 5.07 cm<sup>2</sup>.

#### 6.4 Sulfate Reduction estimates at SONE Stations during May-October, 1993

Estimates of sulfate reduction rates (Figure 6-1.) were completed at eight sediment oxygen and nutrient exchanges (SONE) stations during regularly scheduled SONE cruises for the first time during 1993, May through October. At all eight stations highest rates were observed either during July or August, 1993 and at most stations rates were lower in the spring and fall. In general, fall rates were lower than spring rates. Sulfate reduction rates ranged from 4 to 24 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> during 1993 at stations in the Patuxent River. During the period May through October average sulfate reduction rates were 12.8 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at St. Leonard Creek [STLC], 15.9 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at Broomes Island [BRIS], 16.5 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at Marsh Point [MRPT] and 9.9 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> 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 ranged between 4 and 36 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>. 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, 1993 was almost identical (16.0 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>) to Patuxent River rates at Broomes Island (BRIS) and Marsh Point (MRPT). At the lower Potomac River site (Ragged Point [RGPT]) sulfate reduction rates were very high ranging from 6 to 36 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> and averaging 22.7 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> for May through October, 1994. The lowest sulfate reduction rates were observed at the two stations in the mainstem bay, 8.7 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at Point No Point (PNPT) and 10.2 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at R-64.

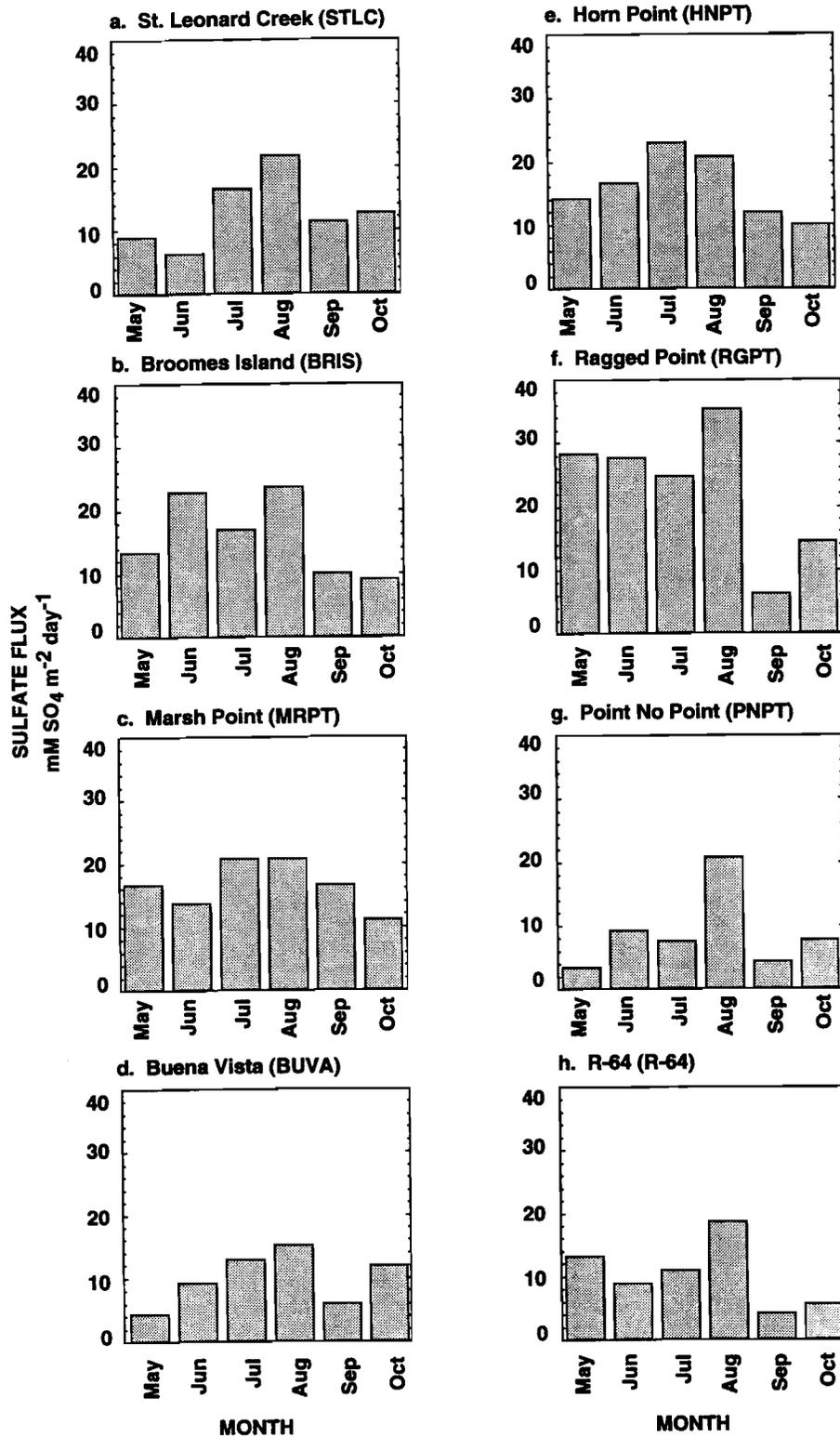


Figure 6-1. Average (mean of triplicate minicores) sulfate reduction rates at eight SONE stations for the months of May through October, 1993.

## 6.5 Factors regulating Sulfate Reduction at SONE stations

There was a factor of 2.5 between the lowest and highest average sulfate reduction rates measured at eight SONE stations during 1993. Sulfate reduction rates were lowest at Point No Point (PNPT) and highest at Ragged Point (RGPT). 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. It is of considerable interest to find out if these rates are proportional to nutrient loading rates or other water quality parameters. Since data have only been collected for one year this is difficult to determine. At this point an examination of sulfate reduction rates at stations which receive different nutrient loading rates can be used to determine if any qualitative relationships between nutrient enrichment and anaerobic metabolism are evident.

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 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 1993. In general, areal nutrient loading rates to the Potomac River are higher than at other SONE stations as are chlorophyll-a concentrations and other sediment-water exchanges. It follows that 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 the two mainstem bay stations, Point No Point (PNPT) and R-64, 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. At these two stations sulfate reduction rates were relatively low during the entire sampling period, May through October, 1993 (Figure 6-1.). 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.) 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. 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.

## 6.6 Comparison of Ecosystem Processes Component Sulfate Reduction Data with other available estimates

It is of particular interest to compare the first annual sulfate reduction measurements with measurements from other coastal and aquatic systems as well as other measurements previously made in Chesapeake Bay using different methods (Table 6-1.). In general, the minicore measurements of sulfate reduction were similar to those reported from other productive coastal systems. For example, rates in Long Island Sound ranged from less than 1 to 75 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> with most measurements in the range of 5 to 20 mM SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup>. Rates were higher in areas such as Cape Lookout Bight where organic matter deposition rates are unusually high ( 3-4 g C m<sup>-2</sup> day<sup>-1</sup>). Rates measured in the sediment-water nutrient exchanges (SONE) program were higher than most made in deeper and colder systems. Previous measurements of sulfate reduction available for Chesapeake Bay are similar to or slightly larger than those measured using minicores during 1993. The similarity of rates measured using radiolabeled sulfur (see examples in Table 6-1. and in Roden *et al.*, 1994) with those measured using the simplified minicore incubation technique suggests that this technique captured the essence of this anaerobic process.

## 6.7 Comparison of Sediment Oxygen Consumption and Sulfate Reduction Rates

The major motivation for developing an anaerobic metabolism methodology is to obtain a reliable measurement of both the processing of carbon and the consumption of oxygen by sediments. This is important because sediments act as a major source of nutrients during warm periods of the year as well as a sink for oxygen. Both of these processes have serious impacts on water quality and the habitat. The magnitude of both processes is proportional to organic matter loading rates to sediments and in turn to nutrient loading rates from the land and atmosphere. As management programs are implemented, nutrient inputs decrease, the production of organic matter decreases, deposition of organic matter to sediments also decreases as does sediment consumption of carbon and oxygen and the release of dissolved nutrients. In the earlier stages of the Ecosystem Processes Component (EPC) monitoring program, sediment oxygen consumption (SOC) rates were used as a measure of sediment oxygen and carbon consumption rates. However, as diagenic processes in sediments have become better understood, it has become clear that while sediment oxygen consumption (SOC) is a useful measurement of sediment oxygen and carbon consumption rates in sediments that are not exposed to low oxygen conditions (< 1 mg l<sup>-1</sup>), it is not useful in assessing sediment oxygen demand or estimating organic matter decomposition rates when such conditions exist. Under these conditions oxygen demand is grossly underestimated and measurements are not possible under anoxic conditions. For these reasons the measurement of anaerobic metabolism has become important. Fortunately, measurements of sulfate reduction can be converted to oxygen equivalents (*i.e.* the amount of oxygen required to reoxidize the sulfur which was reduced) using stoichiometric relationships (1 mol reduced sulphur (S) requires 2 mol oxygen (O<sub>2</sub>) for reoxidation) and thus can be combined with sediment oxygen consumption (SOC) measurements to provide a much improved estimate of total oxygen demand by estuarine sediments. Average seasonal (May through October) estimates of sulfate reduction ranged from 8 to 22 mmol SO<sub>4</sub> m<sup>-2</sup> day<sup>-1</sup> at SONE stations during 1993. Conversion of these rates to oxygen equivalents yields values of 0.5 to 1.4 g O<sub>2</sub> m<sup>-2</sup> day<sup>-1</sup>. Oxygen equivalent rates of this magnitude represent from 50 to almost 100% of observed sediment oxygen consumption (SOC) measurements. Continued measurements of both sediment oxygen consumption (SOC) and sulfate reduction (SO<sub>4</sub>) will finally provide a reasonable estimate of sediment metabolism under both oxic and anoxic conditions.

## 7. EXAMINATION OF SEDIMENT-WATER FLUXES FOR LONG TERM TRENDS AND RELATIONSHIPS TO NUTRIENT LOADING RATES

### 7.1 Introduction

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 nine complete years of monitoring data have been accumulated. A new component was added to the Ecosystem Processes Component (EPC) Program in 1993 which was designed to examine the sediment flux data base in order to determine (1) long-term trends in sediment-water nutrient and oxygen exchanges and (2) relationships of important water quality variables to nutrient loading rates.

First, statistical analyses were conducted to examine the sediment oxygen and nutrient exchanges (SONE) sediment-water flux data for temporal trends in sediment-water fluxes which have occurred over seven years, 1985 through 1991. Five different SONE flux variables, sediment oxygen consumption (SOC), ammonium ( $\text{NH}_4^+$ ), nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ), dissolved inorganic phosphorus ( $\text{PO}_4^-$ ) and silicate ( $\text{Si}(\text{OH})_4$ ) fluxes were each regressed by year for each of eight SONE stations and the resulting regression coefficients (slopes) were analyzed using analysis of variance to test for temporal and spatial trends. Additionally, power analysis was used to determine the sensitivity of flux measurements (*i.e.*, smallest change that could be detected) within the limits of the present program design. The details of this analysis were reported in Boynton *et al.* (1993b). Findings together with additional comments relevant to achieving the goals of the monitoring program are summarized below.

Second, a conceptual model of the eutrophication process has been under development during the last several years which has employed regression analysis to explore sediment oxygen and nutrient exchanges (SONE) and other monitoring program data sets for relationships and related responses to nutrient loading rates. As an example of this type of activity significant relationships between nutrient loading rates and variables such as nutrient stocks in the water column and sediments (Boynton *et al.*, 1994), algal production and biomass (Boynton and Kemp, 1993) and others have been found. At this stage of the monitoring program it can be argued that the latter activity (statistical relationships to nutrient loading rates versus trend analysis) is the more achievable and important. The main reason for this is that interannual variability in nutrient loading rates to major (but not all) areas of the bay is influenced by seasonal and annual climatic regimes (*i.e.* wet versus dry seasons and years) rather than by management actions designed and implemented to limit nutrient inputs to the bay since the program was initiated. There are of course some exceptions to this such as the phosphorus loading pattern in the Patuxent River (Fig. 4-1.1c.). The importance of climate simply indicates the dominance of diffuse nutrient sources in many portions of the bay system (Boynton *et al.*, 1994). As a result of this, nutrient loading rates in most of these systems have not generally declined over the last nine years (in most cases) but rather have exhibited a variable pattern with both high and low loading years being observed. There is no question that without management actions loading rates would be higher than recorded but the degree to which loads have been reduced is not large enough, in most cases, to overwhelm the year-to-year differences related to climate via

diffuse source loading. As a result of this, long-term ( 8-9 years) trends are expected to be difficult to detect for any variable whose behavior is closely coupled to nutrient loading rates on shorter time scales (seasonal to annual) except in those cases where nutrient loading rates have been linear (steadily increasing or decreasing) over the period of record ( 9 years). Such situations are the exception rather than the rule. As a result of this, increasing or decreasing trends are difficult to observe in many cases but will become more apparent as the bay clean-up programs become implemented and the length of the monitoring data base increases. However, because of the substantial interannual differences in nutrient loading rates it is possible to explore data for quantitative relationships to loads and from these relationships anticipate changes in these variables as loads are reduced.

## 7.2 Statistical Analyses for Long-Term Trends

The basic approach employed in examining sediment oxygen and nutrient exchanges (SONE) sediment-water flux data for long-term trends involved regressing flux variables (e.g. ammonium  $[\text{NH}_4^+]$  flux) collected during a certain month at a particular SONE station by the year in which the data were collected. The slopes of these regressions (after being weighted or adjusted to compensate for individual data points which greatly influenced the slope) were analyzed using analysis of variance (ANOVA). Since the estimates from the regressions were computed using varying numbers of observations (555 - 598), the ANOVA was weighted for the number of observations used to compute the rate of change in units of flux year<sup>-1</sup>. The ANOVA model included the sources of variation for river (4; Susquehanna, Potomac, Patuxent and Potomac), station or stations within river (8; regularly sampled SONE stations), month (7; April through November, omitting September data) and the river by month interaction. In addition to the four ANOVA hypotheses, pair wise contrasts (t test using the MSE) were used to test for differences between rivers, stations with rivers (Patuxent [PTX] and Susquehanna [SUS] Rivers only) and between rivers within month (or between months within river). The change in flux per year was also tested to determine if it was significantly different from zero overall or for any level of aggregation of river, station and month (t test using MSE). The details and an explanation of the statistical method used are given in Boynton *et al.* (1993b).

A summary of results from the analysis of variance is presented in Table 7-1. The table contains the mean square values for change in flux year<sup>-1</sup> with significance indicated for the sources of variation. This table summarizes the least square means for the months April through November (with the exception of September) for each of the rivers and for each SONE flux variable except silicate for which no significant trends were found. The last column on the right contains the least mean square values for rivers summed over all months. This value represents the average change in flux within a river averaged for all months (April through November with the exception of September). The values have letters indicating the significant differences among the mean values.

There were no significant trends for sediment oxygen consumption (SOC) for any specific month in the Potomac and Susquehanna (Maryland Mainstem Bay) Rivers. In the Choptank River there was a definite sign of increasing sediment oxygen consumption (SOC) during June and a smaller decrease during July. The only other trend was a decrease in sediment oxygen consumption (SOC) in the Patuxent River during November. While few statistically significant trends were found, those that were identified are of ecological importance *i.e.* a change of this magnitude would impact dissolved oxygen (DO) conditions (Kemp and Boynton, 1992). When data for all months were analyzed, the annual sediment oxygen consumption (SOC) trends for the Patuxent and Choptank Rivers were not different from one another. However, the Potomac River showed a significant increasing trend in sediment oxygen consumption (SOC) on an annual basis. Sediment oxygen consumption

**Table 7-1. Table of Least Square Means by River for Change in Flux/Year for five SONE variables.**

NOTE: Units are different for sediment oxygen consumption than for nutrient fluxes. (Adapted from Boynton *et al.*, 1993b)

RIVER	-----LEAST SQUARE MEANS (mass m <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> )-----							
	i. Sediment Oxygen Consumption (g O <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> yr <sup>-1</sup> )							
	April	May	June	July	August	October	November	River <sup>1</sup>
CHOP	0.226	-0.100	0.373**	-0.301 <sup>+</sup>	0.025	-0.039	-0.015	0.024 <sup>ab</sup>
POT	0.091	0.210	0.182	0.063	0.161	0.013	0.102	0.117 <sup>*a</sup>
PTX	0.180	-0.112	0.009	-0.124	-0.052	-0.039	-0.412**	-0.079 <sup>b</sup>
SUS	0.056	0.018	0.074	0.089	0.134	0.066	0.093	0.076 <sup>a</sup>
ii. Ammonium (μMN m <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> )								
	April	May	June	July	August	October	November	River <sup>1</sup>
CHOP	-3	7	-23	54	7	-29	1	2 <sup>a</sup>
POT	-40	-37	-44	-177***	-70*	-29	-35	-62*** <sup>b</sup>
PTX	-15	29	8	38 <sup>+</sup>	25	-1	12	14 <sup>a</sup>
SUS	21	-10	-36 <sup>+</sup>	22	-19	-14	34	-0 <sup>a</sup>
iii. Nitrite + Nitrate (μMN m <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> )								
	April	May	June	July	August	October	November	River <sup>1</sup>
CHOP	5.5	-14.0	-28.8***	6.4	-3.2	-0.7	-3.6	-4.5 <sup>a</sup>
POT	-34.1**	-5.9	0.0	1.2	3.5	-2.0	-6.9	-6.9 <sup>a</sup>
PTX	-16.8*	-1.4	-17.3*	14.3	-25.2***	4.1	-5.0	-6.7 <sup>*a</sup>
SUS	0.2	2.6	-3.5	2.4	-7.4	0.5	-6.8	-1.7 <sup>a</sup>
iv. Dissolved Inorganic Phosphorus (μMP m <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> )								
	April	May	June	July	August	October	November	River <sup>1</sup>
CHOP	-0.8	-0.6	0.2	-8.9	0.8	-4.1	-0.7	-2.0 <sup>a</sup>
POT	1.1	-2.1	-2.5	-25.7**	0.9	0.1	-1.2	-4.2 <sup>a</sup>
PTX	-2.1	-0.3	-2.4	1.6	6.4 <sup>+</sup>	-0.4	2.7	-1.6 <sup>a</sup>
SUS	-0.2	0.4	-10.7*	-5.4	2.1	-0.5	2.7	-1.6 <sup>a</sup>

+ p = 0.10 |  
 \* p = 0.05 | Test of no significant change  
 \*\* p = 0.01 | in flux across years  
 \*\*\* p = 0.001 |  
 abc Any means with an identical letter are not significantly different from each other at the 10% level  
 1 t-tests were used to detect differences among rivers across all months.

(SOC) trends for the Patuxent and Choptank Rivers were not significantly different from zero and this was probably due to improving bottom water dissolved oxygen (DO) levels at this station.

Two ecologically significant trends were evident for ammonium ( $\text{NH}_4^+$ ) in the Potomac River. A highly significant ( $p = 0.001$ ) decreasing trend in ammonium was detected during July and a less significant ( $p = 0.05$ ) decrease during August. The Potomac River showed a significant decreasing trend ( $p = 0.001$ ) for ammonium ( $\text{NH}_4^+$ ) on an annual basis and this trend was significantly different from the other three rivers. The trend towards lower ammonium ( $\text{NH}_4^+$ ) fluxes in the Potomac River is consistent with the finding that sediment oxygen consumption (SOC) rates were increasing. The most plausible explanation for this is that annual nutrient loading rates to the Potomac River were reasonably constant during 1985 through 1991 or decreased only slightly. In this case, algal biomass accumulation would be expected to be constant or somewhat reduced because of nutrient limitation, and this would lead to reduced deposition of organic matter to sediments. Reduced organic matter supply rates to sediments would result in relieving intense oxygen demand in deep waters and sediments leaving an oxygen residual in these waters. With some oxygen in deep waters ( $>1\text{-}2 \text{ mg l}^{-1}$ ) sediment oxygen consumption (SOC) rates would tend to increase. The reduction in ammonium ( $\text{NH}_4^+$ ) fluxes probably resulted from both a reduction in organic matter deposition rates to sediments (limiting the amount of nitrogen potentially available for recycling) and the enhancement of sediment nitrification of ammonium ( $\text{NH}_4^+$ ), much of the resulting nitrate being denitrified and lost to the atmosphere as a biologically inert gas. Reduced  $\text{NH}_4^+$  fluxes from sediments during warm periods of the year would lead to lower algal biomass levels during these same seasons. In turn lower algal biomass levels would lead to improved water quality via reduced oxygen demand.

No significant trends for nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) were detected in the Susquehanna River (Maryland Mainstem Bay). Two highly significant ( $p = 0.001$ ) trends were found, one in the Choptank River during June and the other in the Patuxent River during August. Three less significant trends were also detected; two for the month of April in the Potomac ( $p = 0.01$ ) and Patuxent ( $p = 0.05$ ) Rivers, and the other for the month of June in the Patuxent River ( $p = 0.05$ ). The Patuxent River showed a decreasing trend ( $p = 0.05$ ) for nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) on an annual basis, and was different than the other three rivers. The ecological significance of the long-term trends found for this flux is that all trends were towards increased nitrite plus nitrate *uptake* by sediments (increased negative values). This in turn suggests that there is generally more of this compound in deep waters, particularly in the Patuxent River, over the period of record because sediment uptake of nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) is proportional to concentrations in overlying waters. This pattern is generally consistent with annual nutrient loading rates to the Patuxent River for the period 1985 through 1990. Loads were lower in 1991. This form of nitrogen comes primarily from diffuse sources and as sources are controlled the concentrations in bottom waters can be expected to decrease as will fluxes from water to sediments. So a different pattern may emerge for nitrite plus nitrate ( $\text{NO}_2^- + \text{NO}_3^-$ ) fluxes as diffuse source nutrient controls are implemented. More importantly, as loading rates from land decrease so too should algal biomass and organic matter deposition rates to sediments. Excessive organic matter in deep waters and sediments depletes oxygen concentrations and this inhibits sediment nitrification, a bacterial process which transforms ammonium to nitrate. The nitrate produced in this process is largely denitrified (Jenkins and Kemp, 1984) but some nitrate generally escapes from sediments to overlying waters. The magnitude of this flux is small enough to be of little concern as a source of nutrients which could substantially enhance algal production but it is a signal that a self-cleansing process is operative in estuarine sediments. Significant long-term trends which indicate nitrate fluxes from sediment to water could be viewed as a strong sign of improving

sediment quality conditions. In fact, in years of particularly low nutrient loading rates, e.g. 1992, positive nitrate fluxes have been observed (Boynton *et al.*, 1993b).

Two significant decreasing trends of ecological importance were indicated for dissolved inorganic phosphorus ( $\text{PO}_4^-$ ), one in the Potomac River ( $p = 0.01$ ) for the month of July and one in the Susquehanna River (Maryland Mainstem Bay;  $p = 0.05$ ) for the month of June. No difference was found between rivers for dissolved inorganic phosphorus ( $\text{PO}_4^-$ ) when data for all months is used. Again, the large decrease in phosphate flux observed in the Potomac River is consistent with lower nutrient loading rates and more oxygenated bottom waters. When bottom waters are more oxygenated phosphate fluxes tend to be reduced because much of the phosphate is bound up with particulate iron oxyhydroxides and as such are not available for diffusion across the sediment-water interface. Additionally, while annual trends of dissolved inorganic phosphorus ( $\text{PO}_4^-$ ) fluxes were not significant, all indicated decreasing fluxes over the period of record (1985 - 1991) and this is also consistent with generally reduced phosphorus loading rates to many portions of the bay.

Relatively few significant trends were detected in the Ecosystem Processes Component (EPC) Program sediment-water flux data although those that were detected were consistent with the conceptual models of eutrophication developed. It might be more accurate to conclude that there were not many trends in these data that emerged based on a *linear model* (i.e., either increasing or decreasing trends that could be best fitted with a straight line) and that "trends" may typically be non-linear.

An example of a typical "non-linear" trend in sediment nutrient fluxes with time is provided in Figure 7-1. Fluxes exhibited a large interannual range (e.g. 1986 versus 1991) and from 1988 - 1992 exhibited a generally decreasing pattern (Figure 7-1.a.). However, a simple pattern of either increasing or decreasing fluxes was not evident when the full data record is considered. These data (average summer flux) can also be plotted as a function of river flow (a good loading rate; Figure 7-1.b.) and when this is done sediment fluxes reflect the pattern of nutrient loading to the bay indicating the linkage between nutrient loading and sediment responses. When nutrient load reductions are large enough to dominate the natural variations due to inter-annual climatic changes, temporal trends in sediment-water fluxes will become more evident in linear trend analyses. The important things to remember are that sediment-water fluxes are responsive to nutrient loading rates, sediments respond quickly to load changes and that reductions in nutrient loads will lead to better sediment quality conditions.

Alternatively, it could be argued that trends were imbedded in the sediment-water nutrient flux data set but that the variability associated with the data was sufficiently large so that the trends could not be detected. In other words, the level of detection was not sufficiently sensitive to detect these trends. At this point it seems far more likely that the lack of temporal trend was related to the former as opposed to the latter explanations given above. Detection levels were shown to be well below those considered to be of ecological significance (Boynton *et al.*, 1993b). In earlier reports (Boynton *et al.*, 1990) it was shown that there were substantial inter-annual differences in the magnitude of specific fluxes at various stations. However, these inter-annual differences generally did not proceed in either an increasing or decreasing pattern. Rather, it appeared that fluxes were related to the magnitude of nutrient loading rates which at most sites has not simply increased or decreased during the monitoring period, except in the Potomac River where a general (although not completely consistent) declining loading rate was evident. Additionally, very strong statistical and experimental relationships have been observed between the magnitude of sediment-water fluxes and the amount of labile organic matter on the sediment surface resulting from the deposition of the spring bloom. Spring bloom deposition, in turn, has been related to nutrient loading rates. Thus, it appears that the natural inter-annual

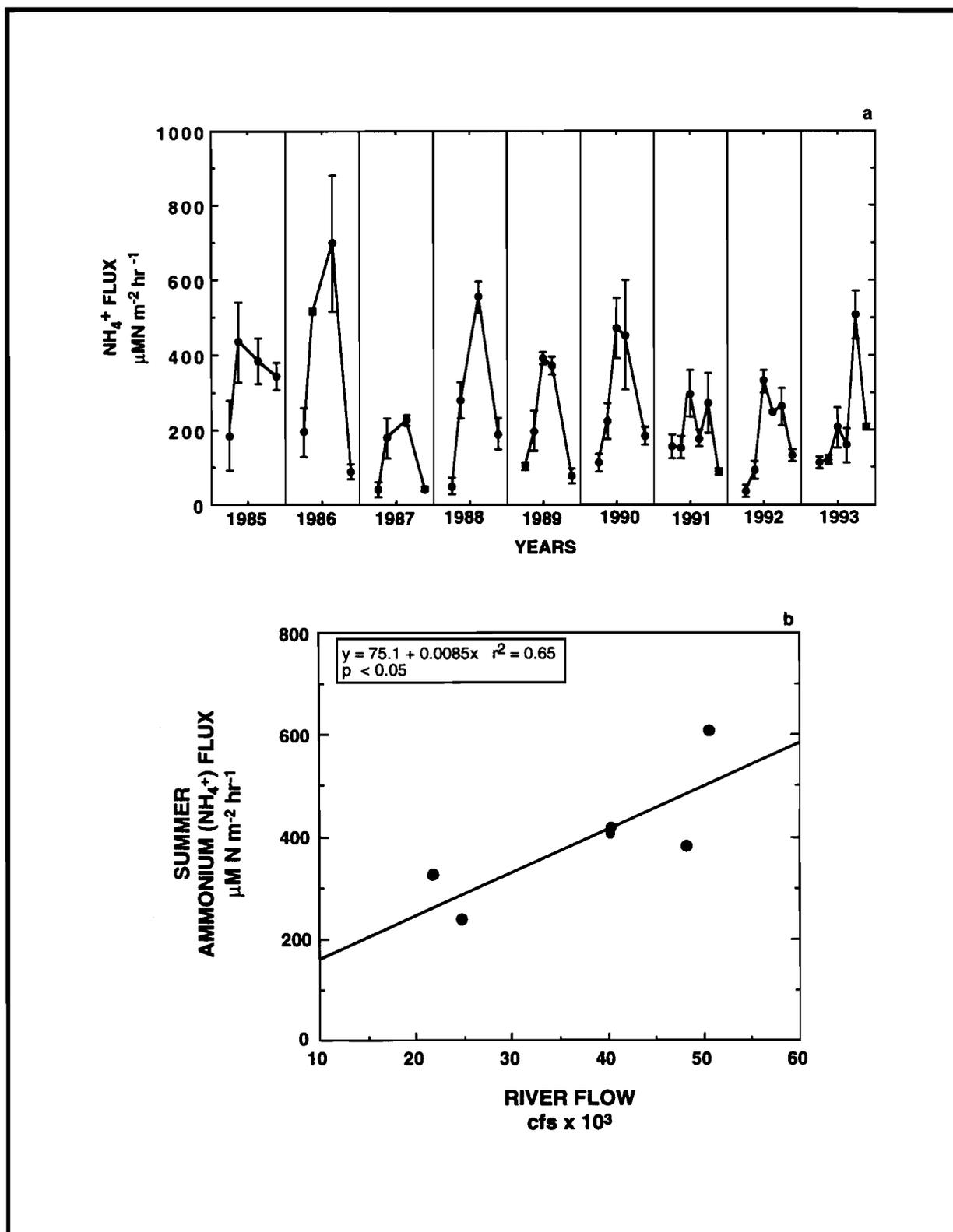


Figure 7-1. a. A time series of sediment ammonium (NH<sub>4</sub><sup>+</sup>) fluxes (mean and standard deviation of triplicate measurements) collected monthly for May through October periods for 1985 - 1993.

b. A scatter plot of summer ammonium (NH<sub>4</sub><sup>+</sup>) flux versus river flow.

Data were collected in the mesohaline region of Chesapeake Bay (R-64).

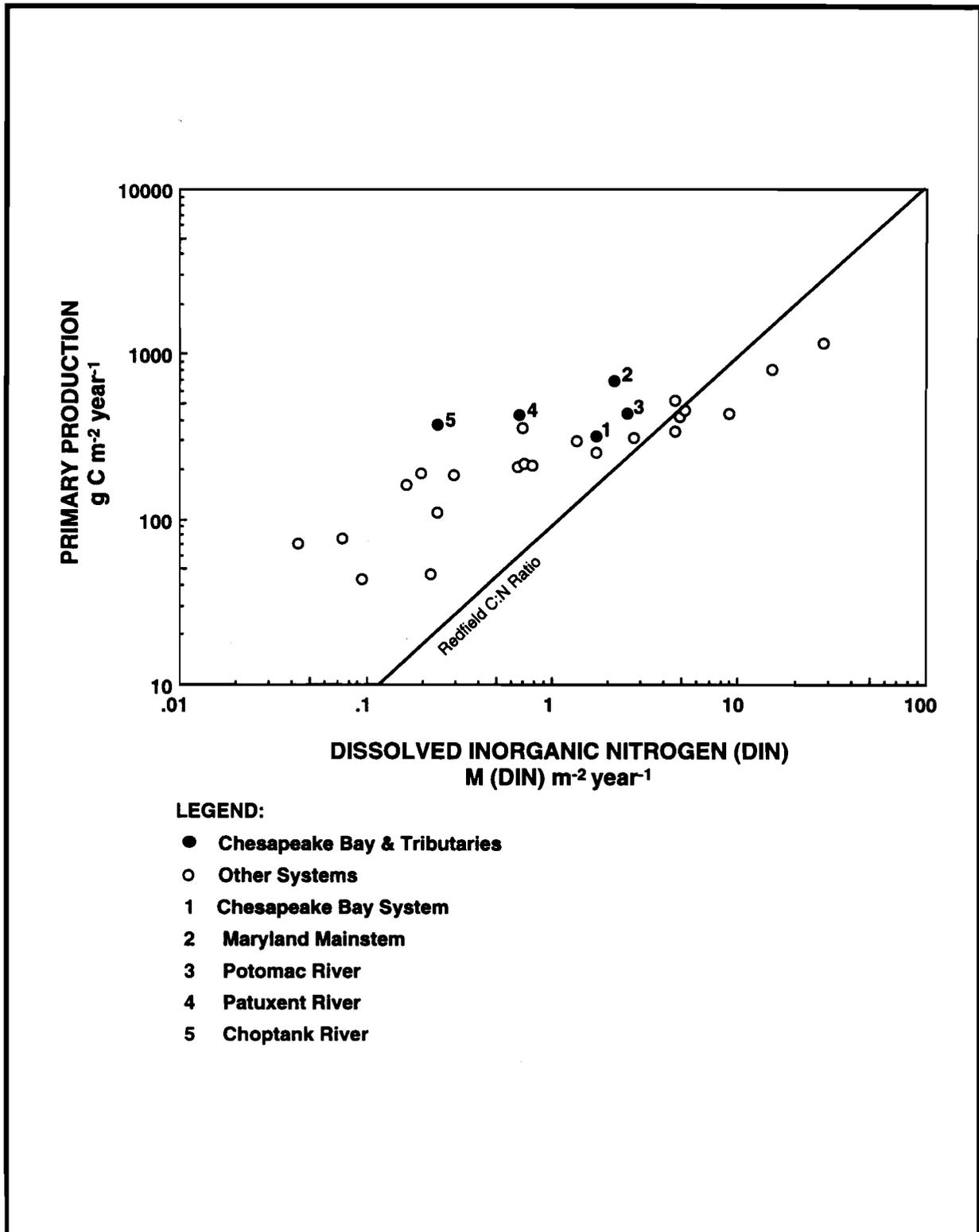


Figure 7-2. Primary production by phytoplankton (<sup>14</sup>C uptake) as a function of the annual input of dissolved inorganic nitrogen per unit area of a wide range of marine ecosystems.

The line represents a Redfield carbon to nitrogen molar ratio of 6.625 and gives a rough indication of how much carbon could be fixed at a given rate of nitrogen input without any recycling of nitrogen. (Adapted from Nixon, 1988)

variability in nutrient loading rates (due to wet and dry years) is providing a larger signal than the nutrient reductions achieved by the management program to date in most cases.

When nutrient load reductions are large enough to dominate the natural variations due to inter-annual climate changes temporal trends in sediment-water fluxes should become evident. In fact a few are evident already. The station in the lower Potomac River (Ragged Point [RGPT]) exhibited significant increases in sediment oxygen consumption (SOC) rates and significant decreases in ammonia ( $\text{NH}_4^+$ ), phosphorus ( $\text{PO}_4^-$ ) and nitrate plus nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ ) fluxes. These changes in flux are consistent with predictions associated with generally lower nutrient conditions which has been the case in the Potomac River. It is important to note that in all the other river systems there has been at least one cycle in high-low nutrient loading during the monitoring period, except in the Potomac River where loads have generally been decreasing during the last several years. As the relationships between nutrient loading rates and ecosystem responses such as sediment-water exchanges become clearer it may be possible to account for inter-annual variations in flux attributable to natural as opposed to anthropogenic causes. This in turn would further improve the ability to detect trends in these data sets.

### 7.3 Detection Limits

In the preceding section it was suggested that the lack of trend detection was possibly due to the inherent variability in sediment-water flux measurements. Power analysis was used to explore this possibility and the detailed results reported in Boynton *et al.* (1993b). It was found that differences in fluxes which can be detected with the present sampling scheme are quite small and in all cases are also small in terms of general ecological impact.

Limits of detection for the changes in flux rates provided in Table 7-2. are all small relative to the average fluxes observed at sediment oxygen and nutrient exchanges (SONE) stations and are very small relative to average fluxes observed during summer periods when fluxes are typically highest (Figures 5-1.1. - 5-1.5.). Sediment oxygen consumption (SOC) fluxes at sediment oxygen and nutrient (SONE) stations range between 0.5 and 2.5  $\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  during spring and early summer. An annual change of about 0.08  $\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1}$  represents an ability to detect a change of between 3 and 16 percent per year. Similar results emerge for other fluxes as well, suggesting that the current sampling regime is adequate. Another way to evaluate the effectiveness of sampling is to compare the level of change in flux which can be detected with some change in another environmental variable of management interest. In this case ammonium ( $\text{NH}_4^+$ ) fluxes provide a good example. During summer periods it appears that nitrogen limits primary production in the mesohaline regions of the bay (Gustafson *et al.*, 1994). During this period of the year sediments are an important source of nitrogen (as well as silicate [ $\text{Si}(\text{OH})_4$ ] and dissolved inorganic phosphorus [ $\text{PO}_4^-$ ]) which supports primary production rates. Summer sediment release rates of ammonium ( $\text{NH}_4^+$ ) are in the range of 250-300  $\mu\text{MN m}^{-2} \text{ hr}^{-1}$  which is an amount capable of supporting primary production rates of about 0.6  $\text{g C m}^{-2} \text{ day}^{-1}$ . Total production rates are about 1-2  $\text{g C m}^{-2} \text{ day}^{-1}$  so it is clear that sediment nutrient supplies are important. It appears that an ammonium ( $\text{NH}_4^+$ ) flux changes of about 24  $\mu\text{MN m}^{-2} \text{ hr}^{-1} \text{ yr}^{-1}$  can be detected. This level of detection is equivalent to an 8% change in primary production rate which is a very small change. Similar results are obtained when other nutrient fluxes are considered in this same context. It would seem that the level of detection, which will continue to improve gradually over the next few years, is adequate for the variables measured in the sediment oxygen and nutrient exchanges (SONE) portion of the Ecosystem Processes Component (EPC) Program.

**Table 7-2. A summary of the detection limits ( $p < 0.95$ ) of changes in sediment-water fluxes estimated from the power analyses. (Adapted from Boynton *et al.*, 1993b)**

Years indicated the year up to which flux data are included (*i.e.*, 1991 included flux data from 1985 through 1991). Later years (*i.e.*, 1992 through 2000) are projections of results based on the inclusion of additional years of data having the same characteristics as the data set collected between 1985 and 1991. Units for data in the table are  $\mu\text{M m}^{-2} \text{ hr}^{-1} \text{ yr}^{-1}$  except for sediment oxygen consumption (SOC) where the units are  $\text{g O}_2 \text{ m}^{-2} \text{ day}^{-1} \text{ yr}^{-1}$ .

FLUX VARIABLE	YEAR				
	1991	1992	1994	1996	2000
Sediment Oxygen Consumption (SOC)	0.08	0.08	0.08	0.07	0.06
Ammonium ( $\text{NH}_4^+$ )	23.8	20.5	17.0	16.0	14.9
Nitrate + Nitrite ( $\text{NO}_2^- + \text{NO}_3^-$ )	6.0	5.5	4.8	4.0	3.5
Dissolved Inorganic Phosphate (DIP)	5.1	4.6	4.0	3.5	2.8
Silicate ( $\text{Si}(\text{OH})_4$ )	40.0	36.3	30.0	27.5	22.5

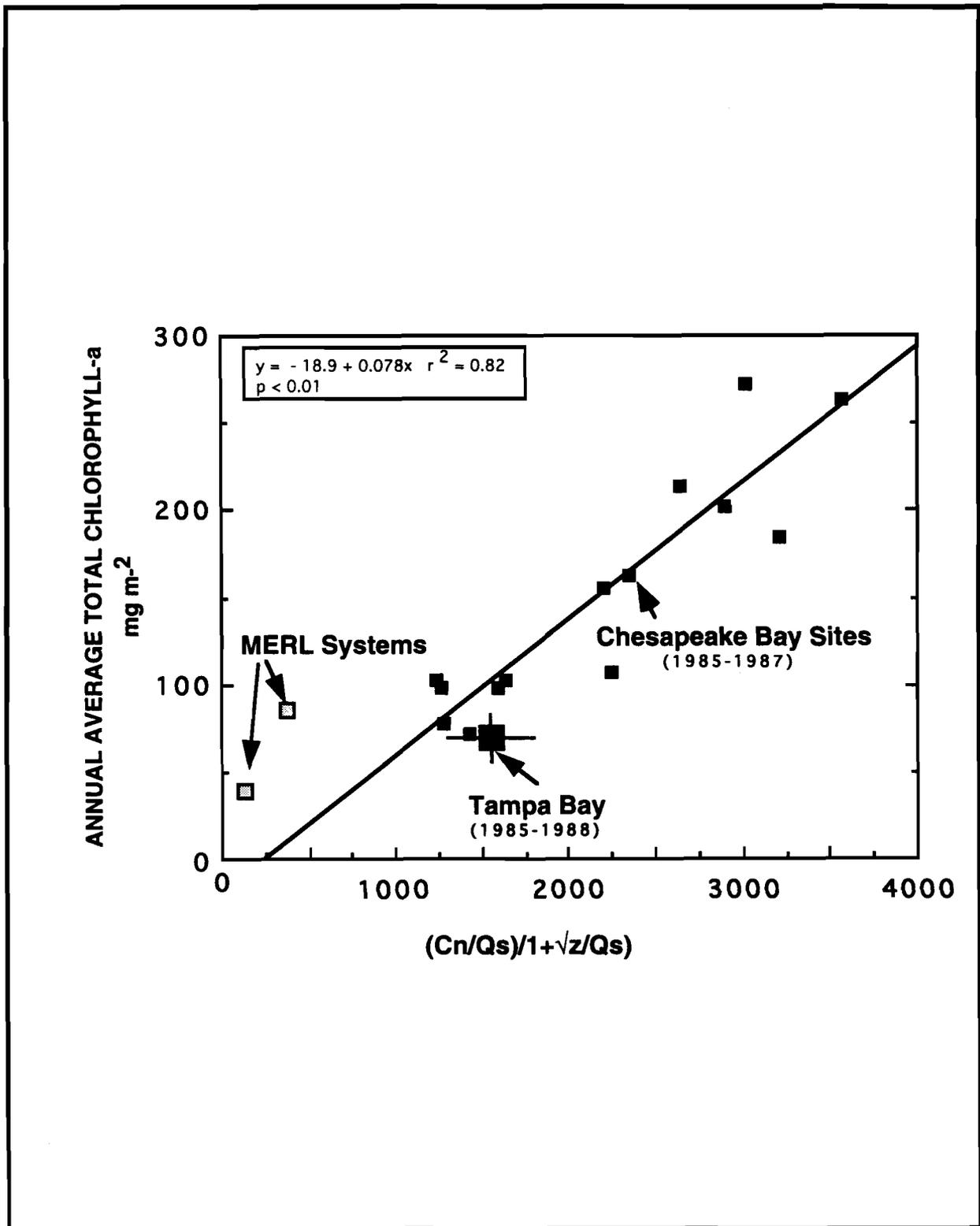
## 7.4 Relationships of Selected Variables to Nutrient Loading Rates

One of the fundamental assumptions underlying the Chesapeake Bay nutrient reduction strategy is that nutrients (nitrogen and phosphorus) are indeed regulating some of the principal water quality characteristics as well as other ecosystem features of the bay system and that these features will respond to changes in nutrient loading rates. The purpose of this section is to provide results of ongoing analyses designed to explore Chesapeake Bay data sets (as well as other data sets) for relationships to nutrient loading rates; in effect to show that the nutrient loading-water quality coupling is sound and to glean some insights as to the nature of the relationship for selected variables.

### 7.4.1 Comparative Analyses of Production and Algal Biomass

In the last few years much has been written in the literature which clearly indicates that nutrient loading rates are a very strong determinate of algal production rates in a variety of systems, including Chesapeake Bay. One of the earliest such efforts was reported by Boynton *et al.* (1982a) but perhaps the most comprehensive description of this relationship is that of Nixon (1988) where he assembled annual production data from some 22 sites and plotted these against annual dissolved inorganic nitrogen (DIN) loading rates (Fig 7-2). Additional estimates of algal production from several areas of Chesapeake Bay have been added to this figure. Nixon (1988) has also indicated the amount of algal production that could be supported if "new nutrients" added to the system were the only nutrients available to support production; in effect the production rate if no nutrient cycling occurred. Several interesting features are evident in this data compilation. First, there is a very definite statistical relationship indicated between dissolved inorganic nitrogen (DIN) loading rate and algal production based on data from a wide variety of coastal systems. Second, the plot indicates that production rates are much higher than expected based solely on loading rate with no recycling; nutrient recycling plays a particularly important role in systems with relatively low nutrient loading rates. Finally, production rates from several Chesapeake Bay sites are particularly high indicating the importance of both the retentive physics of the bay (Boicourt, 1992) and very efficient recycling both in sediments and waters of the bay (Kemp and Boynton, 1992). Thus, a global sampling of coastal sites indicates a tight coupling between nutrient loading and algal production; Chesapeake Bay sites are consistent with these data.

It has previously been observed that algal production rates are less sensitive to nutrient loading rates than is the accumulation of algal biomass (Malone *et al.*, 1994). In addition, algal biomass represents the organic material still available for decomposition after the respiratory costs of production have been met. Thus, algal biomass may be a more relevant variable to be considered than production in cases where oxygen water quality is of concern as it is in the bay. In the mid-1970s limnologists recognized this and developed a series of very useful statistical models relating nutrient loading rates and algal biomass for a large sampling of lakes (*e.g.* Vollenweider, 1976) and ultimately used these relationship to estimate the degree to which nutrient loading rates would need to be decreased to move a particular lake from one trophic state to another. We have initiated efforts to produce a similar type of relationship for estuarine systems and an example of the types of results we have obtained to date is shown in Figure 7-3. We initially attempted a direct duplication of the Vollenweider (1976) model using average annual surface water chlorophyll-a as the dependent variable and annual average phosphorus loading rate (adjusted for the freshwater fill time and mean depth of the receiving water body) as the independent variable. This selection of variables did not produce significant statistical relationships. We then reasoned that because algal blooms often develop in deep waters, particularly in spring in the bay, that integrated water column chlorophyll-a would be a better estimate of algal



**Figure 7-3. A scatter plot of scaled nitrogen loading rate versus annual average total chlorophyll-a concentration.** Nitrogen loading has been scaled according to water residence time and average depth. Details are given in Vollenweider (1976). Chesapeake Bay sites include the Maryland mainstem, Patapsco, Potomac, Patuxent and Choptank Rivers (Sellner, pers. comm.). Data from MERL (University of Rhode Island Marine Experimental Research Laboratory) are from Nixon et al. (1986); Tampa Bay data are from Johnson (pers. comm.)

biomass accumulation. We also used nitrogen as the nutrient of interest and results improved to the degree shown in Figure 7-3. We have also obtained sufficient data to add results of the MERL eutrophication experiment (Nixon, 1986) and portions of Tampa Bay (Johnson, *pers. comm.*). The results of this analysis supports the concept that estuarine systems respond in an understandable fashion to nutrient loading rates. Further, there is some indication that different systems respond in a similar fashion when loading rates are scaled for local conditions of depth and flushing rates. This sort of analysis should be expanded to include other systems because it provides an opportunity to explore the robustness of this relationship and ultimately increases confidence in the conceptual model upon which it is based. Additionally, the scaling of the nutrient load should more thoroughly consider the more complex factors regulating water residence time in tidal estuaries.

#### **7.4.2 Analyses of Mainstem Chesapeake Bay Data**

One of the typical criticisms of comparative work such as that presented in the preceding paragraphs is that interpretable signals emerge in part because there is such an extreme range in the end members of the data set. The conceptual model upon which such analyses are based must still be correct but the utility of the relationships is limited because the overall range is orders of magnitude but questions concerning a particular system are often confined to less than one order of magnitude. We have explored this potential problem with comparative analyses by focusing on one well studied site in mainstem Chesapeake Bay (station R-64) and asked if some of the same sorts of relationships emerge when the range in both independent and dependent variables is much smaller. Results of one set of analyses are shown in Figure 7-3. in which river flow from the Susquehanna River (a good correlate of nutrient loading rate) was regressed against a series of important water quality variables (algal biomass, spring algal deposition rates and summer ammonium flux from sediments). Conceptually, the three dependent variables can also be thought of as linked in a cause-effect chain whereby nutrients generate algal biomass which deposits to sediments and provides organic substrate for decomposition processes which have ammonium ( $\text{NH}_4^+$ ) as an end product. In all cases there was a strong relationship between loading rate and response indicating that even within a limited range of forcing interpretable signals emerge. In the spring deposition analysis (Figure 7-3.b.) data from 1991 fall far from expected. Work by Smith (*pers. comm.*) suggests that this deviation was largely caused by displacement of the spring bloom farther down bay than usual in response to persistently high river flow during the winter period. Such findings remind us that at least a portion of the variability we are attempting to resolve at one point in the bay is the result of similar processes occurring in different locations in different years in response to changes in external forcing. Sampling at many bay sites continues to be important as this example indicates. It is important to note that there were large responses in the dependent variables (a factor of 2 to 3) suggesting that these variables can be expected to change in response to reduced nutrient loading rates in more than trivial ways. Finally, in all cases nutrient loading rates were for the water year immediately preceding (and overlapping) with the year in which measurements of dependent variables were made indicating that responses to changing nutrient loading rates at least for these variables is rapid (months to year) rather than slow (years to decades). Similar rapid responses of these variables have been observed in mesocosm studies as well (Nixon, 1988; Jasinski *pers. comm.*).

#### **7.4.3 Analyses of Sediment-Water Flux Data**

The main focus of the Ecosystem Processes Component (EPC) study has been monitoring sediment-water nutrient and oxygen exchanges and because of this 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.

Seasonal variation in the magnitude of sediment-water nutrient and oxygen fluxes is modified by such factors as temperature, benthic infaunal activity, and nitrification-denitrification rates, but is ultimately controlled by the magnitude of labile organic matter deposition to the sediment surface (Kelly and Nixon, 1984; Jensen *et al.*, 1990). It is also thought that differences in the amount and quality of labile organic deposition between sites determines the spatial variability observed in fluxes. The differences in rates of organic matter deposition that determine spatial and seasonal variability in any one year also determine the inter-annual variability in the magnitude of sediment nutrient and oxygen (SONE) fluxes. The spring bloom event generally supplies the largest amount of organic material to the sediment surface during any one year (Boynton *et al.*, 1990). The bloom occurs when temperatures are low and water column microbial activity and zooplankton populations are reduced, so relatively little phytoplanktonic material is recycled within the water column. In addition, the spring bloom population is largely composed of diatoms that sink quickly once dead, while summer blooms are largely composed of dinoflagellates that sink slowly and so have a greater chance of being consumed in the water column before reaching the sediments (Smith, 1992). Finally, the summer pycnocline may be strong enough to prevent sinking of lighter particulates to deep waters and sediments.

There appears to be an opportunity to investigate inter-annual variation in sediment-water nutrient exchanges by comparing annual nutrient fluxes in different areas of the bay with some index of organic matter supply to sediments. The Ecosystem Processes Component (EPC) Program routinely monitors total chlorophyll-a in surficial sediments during SONE cruises. In addition, another program (the Land Margin Ecosystem Research [LMER] Program funded in Chesapeake Bay by the National Science Foundation [NSF]) also measured sediment chlorophyll-a concentrations and nutrient fluxes at several locations in the bay particularly during the spring bloom period of the year. These data bases have been combined and a search for relationships between organic matter supply and sediment-water nutrient exchanges was initiated. Initially, direct correlation between a specific nutrient flux and sediment chlorophyll-a measurement at a station or group of stations for a season or series of years was completed. While a few significant correlations emerged, most either lacked predictive power or were statistically non-significant. It was thought that labile organic matter produced during the spring might play a major role in supporting sediment-water exchanges during summer. Essentially, a temporal lag between delivery of organic matter to sediments and consumption (and recycling) by sediments was postulated. This lag was induced by temperature effects on respiration. Accordingly, sediment chlorophyll-a data were averaged at each site for which data were available over the spring-early summer period (days 80 - 220). Nutrient fluxes were averaged for each site and year for a shorter period of the year that encompassed the period when large nutrient fluxes occurred (days 120 - 220). Altogether, there were three sites (Still Pond [SLPD], R-64 and National Science Foundation - Land Margin Ecosystem's station SB) and four different years for which adequate data were available. Results of regression analyses where sediment chlorophyll-a mass was used to predict sediment-water nutrient fluxes is shown in Figure 7-4. The key to the success of these analyses was the lag of one month when averaging the chlorophyll-a and flux data. This temporal lag accounts for slower microbial degradation of the deposited spring bloom material in the colder months during and immediately following the spring bloom. These analyses indicate that spring bloom deposition supports nutrient fluxes later in the year. Similar analyses using particulate carbon (PC) or particulate nitrogen (PN) as the independent variables produced similar results although not as statistically significant. Results were not statistically significant using sediment particulate

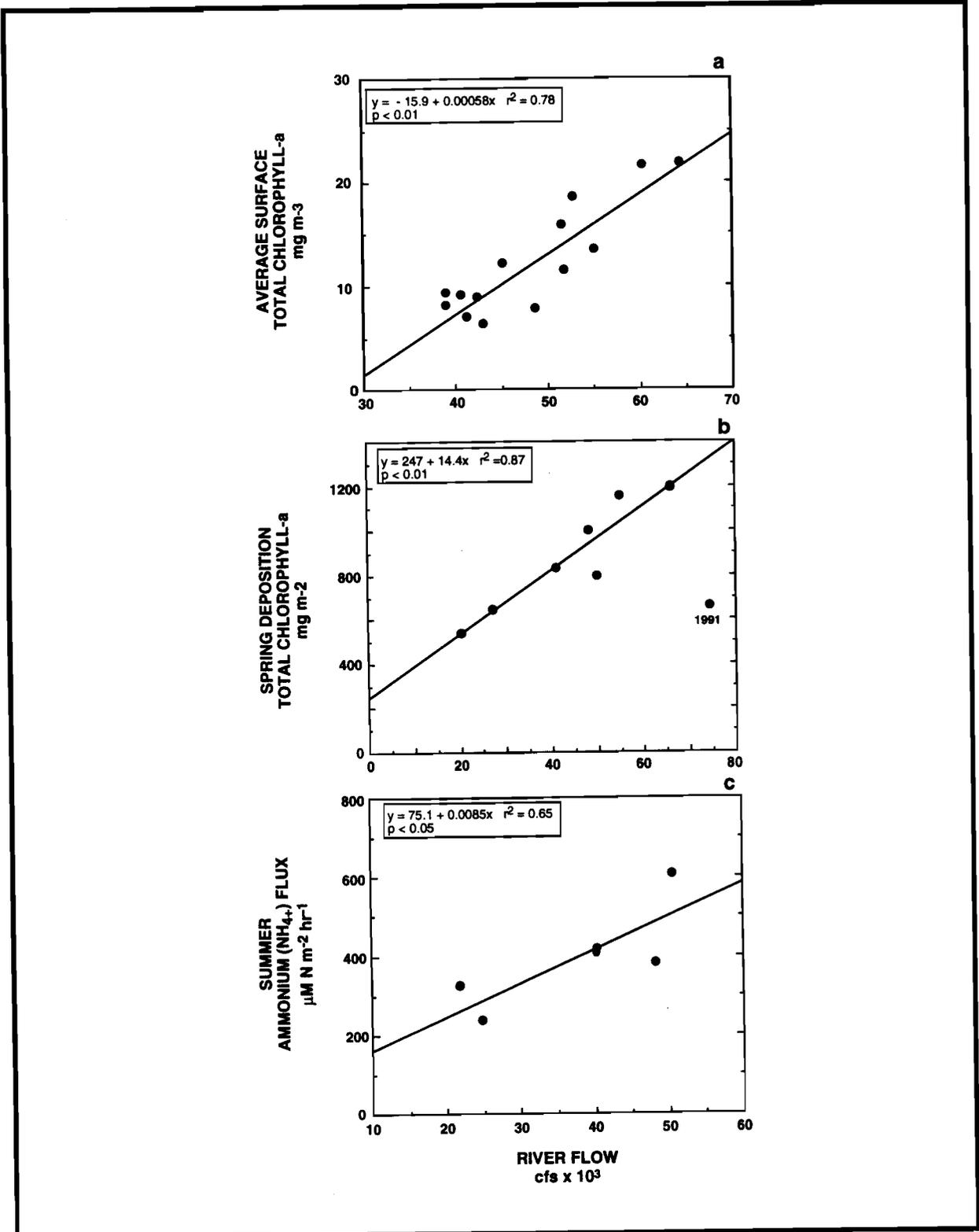
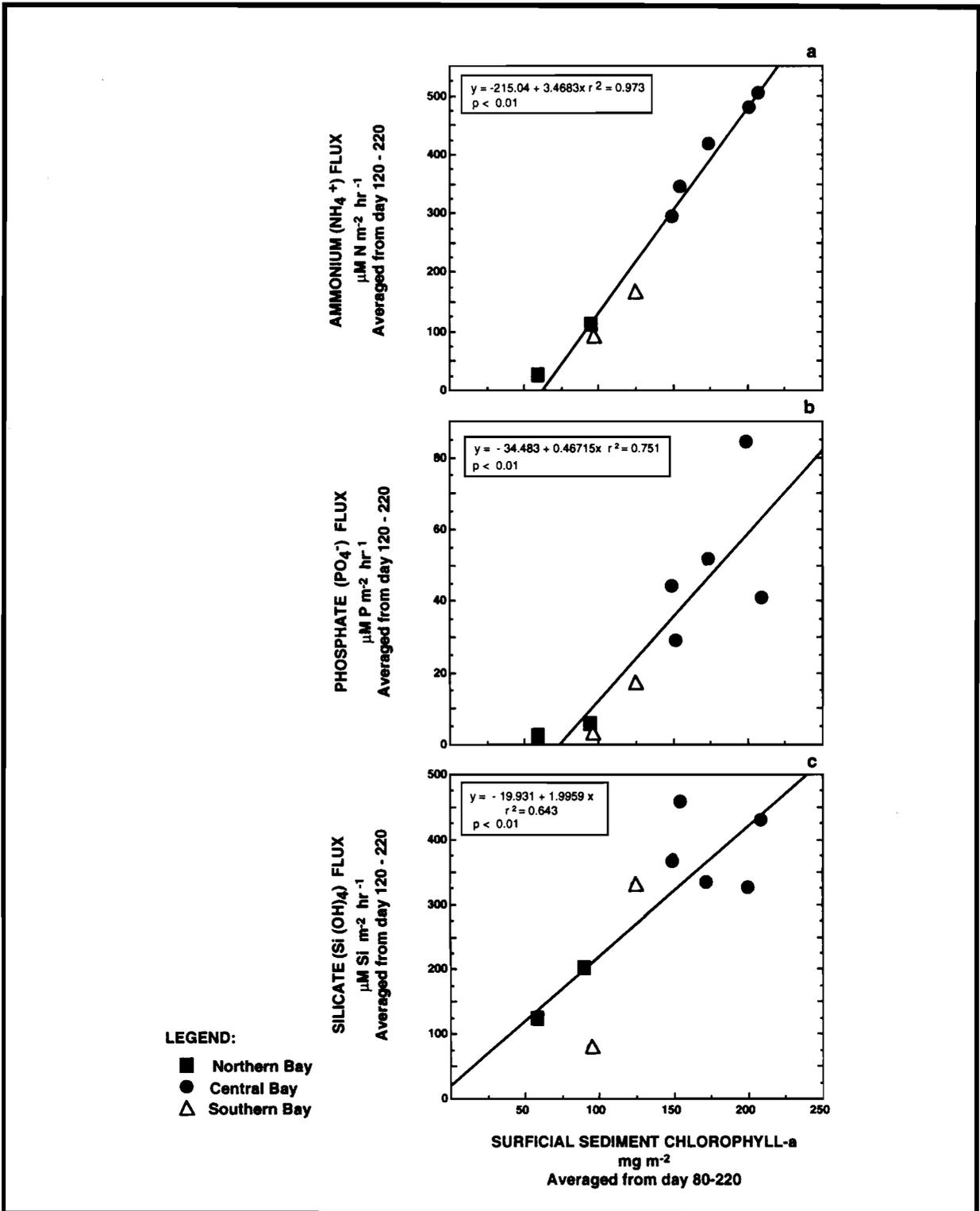


Figure 7-4. Scatter plots indicating statistical relationships between: (a) river flow and algal biomass, (b) river flow and organic matter deposition rates during spring and (c) river flow and nitrogen from sediments during summer. Data were collected from a long-term reference station (R-64) in the mesohaline portion of Chesapeake Bay from 1985 - 1992. River flow has been found to be a good estimation of total nitrogen load in this system. The importance of interannual differences in external forcing is clearly indicated.



**Figure 7-5. Scatter plots of surficial sediment total chlorophyll-a mass versus ammonium (NH<sub>4</sub><sup>+</sup>), dissolved inorganic phosphorus (PO<sub>4</sub><sup>-</sup>) and silicate (Si(OH)<sub>4</sub>) fluxes 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 follow: 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).

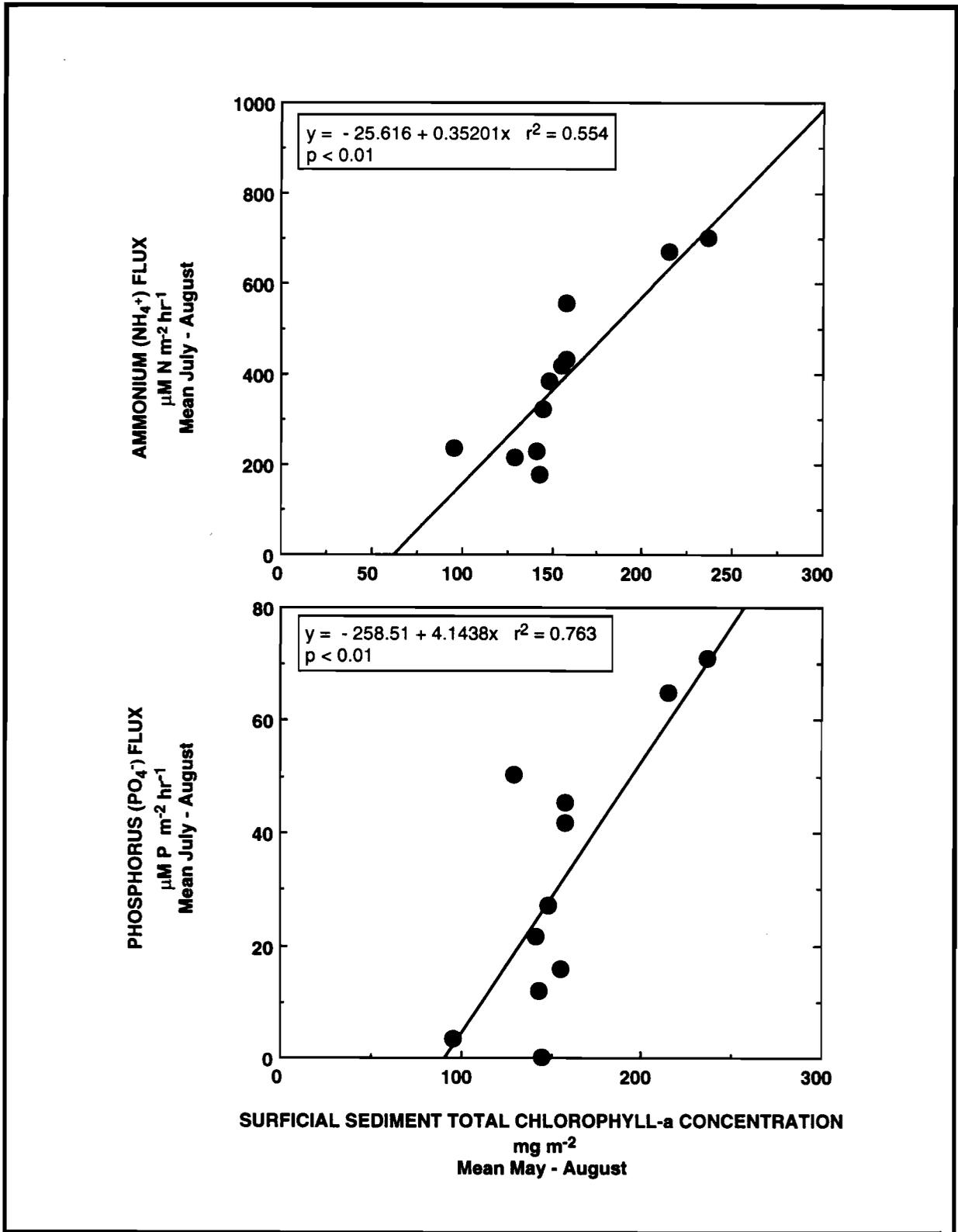


Figure 7-6. Graphs depicting the relationship between surficial sediment total chlorophyll-a, ammonium (NH<sub>4</sub><sup>+</sup>) flux and phosphorus (PO<sub>4</sub><sup>-</sup>) flux at three SONE stations, Buena Vista (BUVA), R-64 and Ragged Point (RGPT) for May through August data from 1985 to 1988.

phosphorus (PP) as the independent variable. These results suggest a strong case for organic matter deposition as the "master" variable regulating sediment-water nutrient exchanges along the mainstem of the bay on an annual basis.

A larger portion of the sediment oxygen and nutrient exchanges (SONE) data base is being examined for relationships between sediment chlorophyll-a and sediment nutrient fluxes. An example of the early results is shown in Figure 7-5. A significant upward slope once again substantiates the important regulating role for labile organic matter. The pattern is stronger for ammonium ( $\text{NH}_4^+$ ) than for phosphate ( $\text{PO}_4^-$ ) and it is probable that redox conditions at the sediment-water interface also influence phosphate fluxes. For example, there is one very low and one very high phosphate ( $\text{PO}_4^-$ ) flux relative to sediment chlorophyll-a indicated in Figure 7-5, and these may have resulted because sediment redox conditions were high and low, respectively, at the time of measurement. These relationships are not as strong as those found for the mainstem bay for several possible reasons. The most important is that sediment chlorophyll-a was measured more often in the early spring (March through June) in the mainstem bay data than is the case in the sediment oxygen and nutrient exchanges (SONE) data base (May through June). It is probable, based on deposition measurements made at SONE station R-64 (Boynton *et al.*, 1992), that intense early spring deposition plays an important role in supporting summer fluxes; in the SONE program sediments are not routinely sampled during this season. Another consideration is that measurements of sediment chlorophyll-a made using the top 1 cm of the sediment column provide a far better estimate of summer flux than do surficial sediment scrapes (top 2-3 mm). Since 1989 surficial sediment scrapes have been the sampling technique employed in sediment oxygen and nutrient exchanges (SONE) program. In May, 1994 we are planning to revert to the earlier method but retaining the scrape methodology as well in the hopes of calibrating one sampling method with the other. These results suggest that the possibility of making routine early spring measurements of sediment chlorophyll-a at all or some sediment oxygen and nutrient exchanges (SONE) stations is worth careful consideration. These data could then be compared to sediment-water nutrient and oxygen fluxes during the warmer periods of the year at SONE stations. If similar relationships emerge, a more quantitative assessment of organic matter loading-sediment nutrient release rates at all SONE stations could be determined. Ultimately, measurements of surficial sediment total chlorophyll-a might be used as a simple and inexpensive monitoring tool which could be used to provide far better *spatial coverage* of sediment processes than is possible with direct measurements of nutrient fluxes.

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## **APPENDIX A**

### **ECOSYSTEM PROCESSES COMPONENT SONE AND VFX PARAMETER LIST**

## INTRODUCTION

Appendix A contains Table A-1 modified from the Ecosystem Processes Component Data Dictionary (Boynton and Rohland, 1990). The data dictionary is an extensive reference document providing a listing and description of all variables used by the Maryland Department of the Environment, Ecosystem Processes Component (MDE/EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program.

Table A-1 lists the variables used in the sediment oxygen and nutrient exchanges (SONE) program. The variables are sorted in alphabetical order using the table name. The table has five columns: table name is followed by the one to eight character CHESSEE variable name, a parameter description, the unit of measure and the unit abbreviation used in the SONE data tables.

**Table A-1. Variable and Parameter List  
Modified from Boynton and Rohland (1990)**

TABLE NAME	CHESSEE VARIABLE NAME	PARAMETER DESCRIPTION	UNIT	UNIT ABBR
AA VIAL NO	SAMPLEID	Basic identification number for water samples.	Number	
BLANK SLOPE DIP	BS_DIP	Time rate of change of phosphorus concentration in a blank chamber.	Micromoles per liter per minute	$\mu\text{M}/(\text{l} \cdot \text{min})$
BLANK SLOPE DO	BS_DO	Time rate of change of dissolved oxygen concentration in a blank chamber.	Milligrams per liter per minute	$\text{mg}/(\text{l} \cdot \text{min})$
BLANK SLOPE H2S	BS_H2S	Time rate of change of hydrogen sulfide concentration in a blank chamber.	Nanomoles per liter per minute	$\text{nM}/(\text{l} \cdot \text{min})$
BLANK SLOPE NH4	BS_NH4	Time rate of change of ammonium concentration in a blank chamber.	Micromoles per liter per minute	$\mu\text{M}/(\text{l} \cdot \text{min})$
BLANK SLOPE NO23	BS_NO23	Time rate of change of nitrite plus nitrate concentration in a blank chamber.	Micromoles per liter per minute	$\mu\text{M}/(\text{l} \cdot \text{min})$
BLANK SLOPE Si(OH)4	BS_DSI	Time rate of change of siliceous acid concentration in a blank chamber.	Micromoles per liter per minute	$\mu\text{M}/(\text{l} \cdot \text{min})$
CHLa ACTIVE	CHL_A	The total chlorophyll-a of a water sample is acidified and measured fluorometrically. Active chlorophyll-a is then determined by subtracting the value obtained following acidification from the total chlorophyll-a value.	Micrograms per liter	$\mu\text{g/l}$
CHLa TOTAL	CHL_T	The total chlorophyll-a concentration of a water sample determined by extraction in 90% acetone and measured fluorometrically. This value includes active chlorophyll-a and some undefined chlorophyll-a degradation products.	Micrograms per liter	$\mu\text{g/l}$
COND	COND	Conductivity of water.	Millimhos per centimeter	$\text{mmho}/\text{cm}$
CORE DEPTH	CORE_Z	Depth either above or beneath (negative values) the sediment water interface at which measurement was taken; a core depth of zero represents the sediment water interface.	Centimeters	$\text{cm}$
CORE H <sub>2</sub> O DEPTH	COREWATZ	Height of water above the sediment surface in a sediment-water flux chamber.	Meters	$\text{m}$
CORE H <sub>2</sub> O VOL	CORE_WAT	Total volume of water overlying sediment in a sediment-water flux chamber.	Milliliters	$\text{ml}$

Table A-1. Variable and Parameter List (Continued)

TABLE NAME	CHESSEE VARIABLE NAME	PARAMETER DESCRIPTION	UNIT	UNIT ABBR
CORE NO	CORE_NO	Chamber replicate identifier.	Alpha or numeric	
CORR DIP	DIP_CORR	Dissolved inorganic phosphorus concentration of a filtered water sample which has been corrected for salinity effects.	Micromolar	$\mu\text{M}$
DATE	DATE	Date of sample collection or measurement, alphanumeric.	Day, Month, Year	DDMMYY
DIP	DIP_MOL	Dissolved inorganic phosphorus concentration of a filtered water sample.	Micromolar	$\mu\text{M}$
DIP FLUX	DIP_FLUX	Net flux of dissolved inorganic phosphorus across sediment water interface.	Micromolar phosphorus per square meter per hour	$\mu\text{MP}/(\text{m}^2 \cdot \text{hr})$
DIP FLUX MEAN	DIP_MFLX	Average of triplicate dissolved inorganic phosphorus flux determinations at a station.	Micromolar phosphorus per square meter per hour	$\mu\text{MP}/(\text{m}^2 \cdot \text{hr})$
DO	DISOXY	Dissolved oxygen concentration.	Milligrams per liter	mg/l
DIP SLOPE	DIP_SLP	Time rate of change of dissolved inorganic phosphorus concentration in overlying waters of a sediment-water flux chamber.	Micromolar phosphorus per liter per minute	$\mu\text{MP}/(\text{l} \cdot \text{min})$
DO FLUX	DO_FLUX	Net flux of dissolved oxygen across sediment-water interface. DO flux is synonymous with sediment oxygen consumption (SOC).	Grams oxygen per square meter per day	$\text{gO}_2/(\text{m}^2 \cdot \text{day})$
DO FLUX MEAN	DO_MFLX	Average of triplicate dissolved oxygen flux determinations at a station.	Grams oxygen per square meter per day	$\text{gO}_2/(\text{m}^2 \cdot \text{day})$
DO SAT	DOSAT	Measured oxygen concentration relative to oxygen saturation concentration at sample temperature and salinity.	Percentage	%
DO SLOPE	DO_SLP	Time rate of change of dissolved oxygen concentration in overlying waters of a sediment-water flux chamber.	Milligrams O <sub>2</sub> per liter per minute	$\text{mg}/(\text{l} \cdot \text{min})$
Eh CORR	EH_CORR	Eh corrected = Eh measured + 244mV. This gives Eh relative to the hydrogen electrode.	Millivolts	mV

Table A-1. Variable and Parameter List (Continued)

TABLE NAME	CHESSEE VARIABLE NAME	PARAMETER DESCRIPTION	UNIT	UNIT ABBR
Eh MEAS	ORP	A measure of the chemical environment (oxidizing or reducing) at a specific depth in the sediment column measured relative to a calomel electrode.	Millivolts	mV
GEAR CODE	GEAR	Sampling Gear Code.	See Boynton and Rohland, 1990	
H2O %	H2O_SED	The percentage (by weight) of water loss by drying for a specified section of the sediment column.	Grams of water per 100 grams of wet sediment	%
H2S	H2S_MOL	Hydrogen sulfide concentration of a filtered water sample.	Micromolar	$\mu M$
H2S FLUX	H2S_FLUX	Net flux of dissolved hydrogen sulfide across sediment water interface.	Micromolar sulfur per square meter per hour	$\mu MS/(m^2 \cdot hr)$
H2S FLUX MEAN	H2S_MFLX	Average of triplicate hydrogen sulfide flux determinations at a station.	Micromolar sulfur per square meter per hour	$\mu MS/(m^2 \cdot hr)$
H2S SLOPE	H2S_SLP	Time rate of change of hydrogen sulfide concentration in overlying waters of a sediment-water flux chamber.	Micromolar sulfur per liter per minute	$\mu MS/(l \cdot min)$
NH4	NH4_MOL	Ammonium concentration of a filtered water sample.	Micromolar	$\mu M$
NH4FLUX	NH4_FLUX	Net flux of dissolved ammonium across sediment water interface.	Micromolar nitrogen per square meter per hour	$\mu MN/(m^2 \cdot hr)$
NH4 FLUX MEAN	NH4MFLX	Average of triplicate ammonium flux determinations at a station	Micromolar nitrogen per square meter per day	$\mu MN/(m^2 \cdot day)$

Table A-1. Variable and Parameter List (Continued)

TABLE NAME	CHESSEE VARIABLE NAME	PARAMETER DESCRIPTION	UNIT	UNIT ABBR
NH4 SLOPE	NH4_SLP	Time rate of change of ammonium concentration in overlying waters of a sediment-water flux chamber.	Micromoles nitrogen per liter per minute	$\mu\text{MN}/(1 \cdot \text{min})$
NO2	NO2_MOL	Nitrite concentration of a filtered water sample.	Micromolar	$\mu\text{M}$
NO2 FLUX	NO2_FLUX	Net flux of dissolved nitrite across sediment water interface.	Micromolar nitrogen per square meter per hour	$\mu\text{MN}/(\text{m}^2 \cdot \text{hr})$
NO2FLUX MEAN	NO2_MFLX	Average of triplicate nitrite flux determinations at a station.	Micromolar nitrogen per square meter per hour	$\mu\text{MN}/(\text{m}^2 \cdot \text{hr})$
NO2SLOPE	NO2_SLP	Time rate of change of nitrite concentration in overlying waters of a sediment-water flux chamber.	Micromolar nitrogen per liter per minute	$\mu\text{MN}/(1 \cdot \text{hr})$
NO2 + NO3	NO23_MOL	Nitrite + nitrate concentration of a filtered water sample.	Micromolar	$\mu\text{M}$
NO2 + NO3 FLUX	NO23FLUX	Net flux of dissolved nitrite + nitrate across sediment water interface.	Micromolar nitrogen per square meter per hour	$\mu\text{MN}/(\text{m}^2 \cdot \text{hr})$
NO2 + NO3 FLUX MEAN	NO23MFLX	Average of triplicate nitrite + nitrate flux determinations at a station.	Micromolar nitrogen per square meter per hour	$\mu\text{MN}/(\text{m}^2 \cdot \text{hr})$
NO2 + NO3 SLOPE	NO23_SLP	Time rate of change of nitrite + nitrate concentration in overlying waters of a sediment-water flux chamber.	Micromolar nitrogen per liter per minute	$\mu\text{MN}/(1 \cdot \text{min})$

Table A-1. Variable and Parameter List (Continued)

TABLE NAME	CHESSEE VARIABLE NAME	PARAMETER DESCRIPTION	UNIT	UNIT ABBR
PC	PC_WAT	Particulate organic carbon concentration of a water sample.	Micrograms per liter	$\mu\text{g/l}$
PN	PN_WAT	Particulate organic nitrogen concentration of a water sample.	Micrograms per liter	$\mu\text{g/l}$
PP	PP_WAT	Particulate phosphorus concentration of a water sample.	Micrograms per liter	$\mu\text{g/l}$
SALIN	SALIN	Salinity of water at sample depth.	Parts per thousand	ppt
SAMPLE DEPTH	SDEPTH	Sample depth from surface of water.	Meters	m
SECCHI DEPTH	SECCHI	Depth from water surface to which Secchi disk can be seen.	Meters	m
SED CHLa ACTIVE	CHLA_SED	The total chlorophyll-a sediment section sample is acidified and measured fluorometrically. Active chlorophyll-a is then determined by subtracting the value obtained following acidification from the total chlorophyll-a value.	Milligrams per square meter	$\text{mg/m}^2$
SED CHLa TOTAL	CHLT_SED	The total chlorophyll-a concentration of a sediment section sample determined by extraction in 90% acetone and measured fluorometrically. This value includes active chlorophyll-a and some undefined chlorophyll-a degradation products.	Milligrams per square meter	$\text{mg/m}^2$
SED PC	PC_SED	Percentage by dry weight of particulate organic carbon for a specified section of the sediment column.	Grams carbon per 100 grams of dry sediment	% (wt)
SED PN	PN_SED	Percentage by dry weight of particulate organic nitrogen for a specified section of the sediment column.	Grams nitrogen per 100 grams of dry sediment	% (wt)
SED PP	PP_SED	Percentage by dry weight of particulate phosphorus for a specified section of the sediment column.	Grams phosphorus per 100 grams of dry sediment	% (wt)

**Table A-1. Variable and Parameter List (Continued)**

<b>TABLE NAME</b>	<b>CHESSEE VARIABLE NAME</b>	<b>PARAMETER DESCRIPTION</b>	<b>UNIT</b>	<b>UNIT ABBR</b>
SESTON	SES_MG	Concentration as dry weight of total particulates in a water sample (seston).	milligrams per liter	mg/l
SILICATE FLUX	DSI_FLUX	Net flux of dissolved silicate across sediment water interface.	Micromolar silicate per square meter per hour	$\mu\text{MSi}/(\text{m}^2 \cdot \text{hr})$
SILICATE FLUX MEAN	DSIMFLUX	Average of triplicate silicate flux determinations at a SONE station.	Micromolar silicate per square meter per hour	$\mu\text{MSi}/(\text{m}^2 \cdot \text{hr})$
SILICATE SLOPE	DSISLOPE	Time rate of change of silicate concentration in overlying waters of a sediment-water flux chamber.	Micromolar silicate per liter per minute	$\mu\text{MSi}/(\text{l} \cdot \text{min})$
Si(OH) <sub>4</sub>	DSI_MOL	Silicious acid concentration of a filtered water sample.	micromolar	$\mu\text{M}$
STATION	STATION	Sampling station identifier.	See Appendix B Table 3-1	
TDN	TDN_MOL	Total dissolved nitrogen concentration of a filtered water sample.	Micromolar nitrogen per liter	$\mu\text{MN}/\text{l}$
TDP	TDP	Total dissolved phosphorus concentration of a filtered water sample.	Micromolar phosphorus per liter	$\mu\text{MP}/\text{l}$
TEMP	WTEMP	Temperature of water at sample depth.	Degrees Centigrade	C
TIME	TIME	Time of day that sample was collected using 24-hour clock.	Hours, minutes in 24-hour time	HHMM
TIME DELTA	TIME_DEL	Time difference between samples.	Minutes	MM

**Table A-1. Variable and Parameter List (Continued)**

<b>TABLE NAME</b>	<b>CHESSEE VARIABLE NAME</b>	<b>PARAMETER DESCRIPTION</b>	<b>UNIT</b>	<b>UNIT ABBR</b>
<b>TIME SUM</b>	<b>TIME_SUM</b>	Summation of the time elapsed from beginning of incubation of a sediment-water flux chamber.	Minutes	MM
<b>TOTAL DEPTH</b>	<b>TDEPTH</b>	Total depth of water column at station.	Meters	m

DATE: 11th April, 1992