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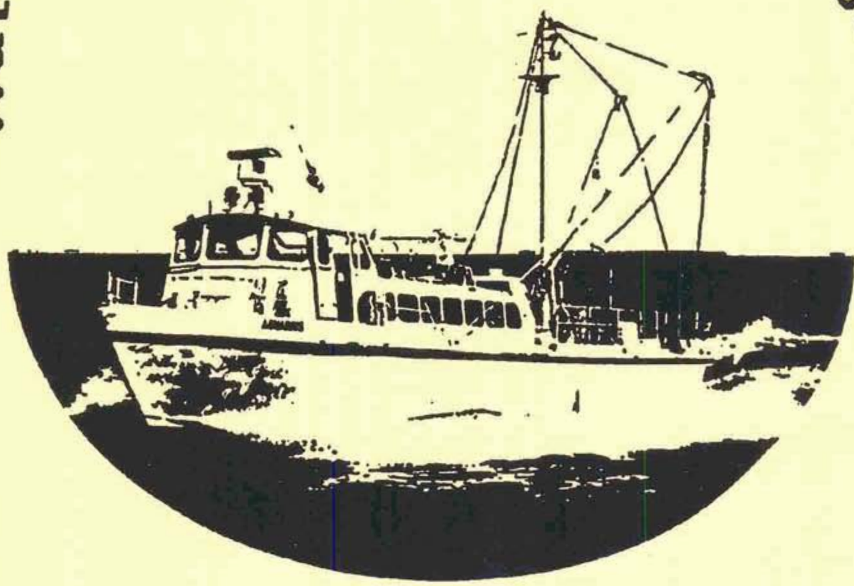
Water Quality Monitoring Program

ECOSYSTEMS PROCESSES COMPONENT (EPC)



LEVEL ONE REPORT #13

Part 1: Interpretive Report

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MARYLAND DEPARTMENT OF THE ENVIRONMENT

MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT NO. 13

INTERPRETIVE REPORT

(July 1984 - December 1995)

PREPARED FOR:

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(January - December 1994)

PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in Contract **GD-001-96-001** between the Maryland Department of Natural Resources (DNR), Resource Assessment Administration, Tidal Water Ecosystem Assessment Division 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 report examines the long term trends and spatial features of sediment-water fluxes.

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 1992 and Volume IV contains VFX data for 1990 through 1992 (Appendix C). The VFX program was terminated on 3rd June, 1992 when the sediment traps were finally retrieved. The VFX data set is now complete. These two volumes were part of Level One, Report No. 9 [UMCEES]CBL Ref. No. 92-042 (Boynton *et al.*, 1992). SONE data for 1992, 1993 and 1994 was submitted with the yearly Interpretive Reports (Boynton *et al.*, 1992, 1993, 1994). Volume V which contains data sheets for the years 1993, 1994 and 1995 is submitted as part of this deliverable. Additionally, the SONE data for 1995 are also submitted as Part II: Data Tables: Appendix B of 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 Chesie are listed in Appendix A: Data Tables, and in the EPC Data Dictionary (Boynton and Rohland, 1990). Entries are arranged alphabetically using the MDE/EPC table names.

A copy of the Ecosystem Processes Component Data Dictionary is available on request from Ms Reneè Karrh (Maryland Department of Natural Resources) 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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ABSTRACT

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 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 five times during 1995 between mid-May and mid-September at two locations in the mainstem bay (measurements were not made at Point No Point [PNPT] after July, 1995), 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 1995 with one major exception. The collection of data to determine the rate of deposition of organic matter to deep waters and sediments at one site (R-64) in the Maryland mainstem bay (referred to as the Vertical Flux [VFX] study of this monitoring program in previous reports) was discontinued after June 3, 1992 due to fiscal constraints of the monitoring program. Data collected during the 1995 monitoring period is evaluated in detail in this report. A discussion of significant ecological trends and interpretation of relationships observed during the eleven years of the sediment-water oxygen and nutrient exchanges (SONE) monitoring program are presented.

During the winter-spring period of 1995, all four of the major systems monitored, Susquehanna (Maryland mainstem bay), Potomac, Patuxent and Choptank Rivers, experienced both freshwater flows and nutrient loads which were associated with the spring freshet from the major rivers entering these systems (Susquehanna, Potomac, Patuxent and Choptank Rivers). In all cases the freshet of 1995 was much smaller than in previous years with the exception of 1992. Flows for the remaining portion of the year closely followed the pattern of previous years and were close to average in magnitude.

Nutrient loading data (monthly fall line load of total nitrogen [TN] and total phosphorus [TP] and both above and below fall line point source loads of total nitrogen [TN] and total phosphorus [TP]) for the Patuxent River were also reviewed for the period 1984 through 1995. Fall line loads of total phosphorus ([TP] which include above fall line point source inputs) have decreased dramatically between 1984 and 1995 (4 - 5 fold); recent loads would be even lower except for very high inputs associated with flood events (*e.g.* May 1989, March 1993 and March 1994). Fall line loads of total nitrogen (TN) have also decreased over this period but not by nearly as great a degree as for total phosphorus (TP). It was evident that the same increased loads were associated with flood events. Both total nitrogen and total phosphorus loads during 1995 were, or were close to, the lowest on record since 1984.

During the monitoring period temperature ranged from 15.2 - 29.0 C and salinity conditions ranged between 10.3 - 24.7 ppt during 1995. Bottom water salinities were lower than usual in spring due to the strong winter-spring freshet and higher than usual during late summer.

At the mainstem bay location (R-64) and at the lower Potomac River location (Ragged Point [RGPT]) there were very low dissolved oxygen (DO) concentrations observed during July, August and September which were not expected to be as severe due to the reduced high river flows of 1995. However, dissolved oxygen conditions at SONE locations in the

Patuxent River were generally good with the exception of one observation at Marsh Point (MRPT) in July 1995. At both the Broomes Island (BRIS) and St. Leonard Creek (STLC) locations summer dissolved oxygen (DO) conditions were considerably improved compared to previous years. Dissolved oxygen concentrations in the Choptank River (Horn Point [HNPT]) are typically high (> 4 mg l^{-1}) during summer. However, in August, 1995 dissolved oxygen concentrations dropped to very low levels. Inspection of salinity measurements indicated that this low dissolved oxygen condition was most probably due to intrusion of deep water from the bay into the Choptank River rather than low dissolved oxygen conditions developing due to local processes. This event, while not usual at this location, provides evidence that these systems are all connected and can influence one another.

Rates of sediment-water fluxes of oxygen (SOC) in the Patuxent River during 1995 ranged from -0.77 g O_2 m^{-2} day^{-1} to -3.24 g O_2 m^{-2} day^{-1} while sediment oxygen consumption (SOC) at all other monitoring stations ranged from near -0.14 g O_2 m^{-2} day^{-1} to -2.90 g O_2 m^{-2} day^{-1}. Low rates during the summer at the mainstem bay and lower Potomac River station were in response to low dissolved oxygen conditions as was the low rate in the Choptank River during August, 1995. Rates of sediment oxygen consumption (SOC) at the two down river stations in the Patuxent River (St Leonard Creek [STLC] and Broomes Island [BRIS]) were possibly a response to improved oxygen conditions in bottom waters during 1995.

Ammonium (NH_4^+) fluxes at the two down river locations (St Leonard Creek [STLC] and Broomes Island [BRIS]) in the Patuxent River were lower than those recorded in earlier years probably in response to the small spring river flow (and associated diffuse source nutrient load) which occurred in 1995. The reduced ammonium fluxes and improved dissolved oxygen (DO) conditions are both positive improvements in sediment quality. Ammonium (NH_4^+) fluxes were also reduced in the lower Potomac River (Ragged Point [RGPT]) and in the lower Choptank River (Horn Point [HNPT]) except in August when low dissolved oxygen conditions were present. With few exceptions, fluxes of nitrate plus nitrite (NO_2^- + NO_3^-) were considerably more positive (*i.e.* directed from sediments to water column) than usual at most stations. Positive nitrate fluxes (or smaller fluxes directed into sediments) is a definite sign of sediment nitrification activity which is a microbial process which converts ammonium to nitrate and requires that oxygen be present. Positive nitrate fluxes are a sign of improved sediment quality. The fact that this occurred during a year of lower than normal nutrient loading rates is another indication that bay sediments are responsive to loading rates.

During 1995, inorganic phosphate (DIP or PO_4^-) fluxes were more reduced than ammonium (NH_4^+) fluxes and this most probably resulted from more oxidized sediment conditions. The reduction in phosphorus fluxes was most noticeable in the Patuxent River where reductions were large (up to a factor of 2). Silicate fluxes ($Si(OH)_4$) tended to be average at most stations during May and June, 1995. Measurements of silicate fluxes ($Si(OH)_4$) were discontinued after June, 1995.

Selected environmental variables (river flow, nutrient loads and bottom water dissolved oxygen concentrations) and key sediment nutrient fluxes (ammonium and phosphate) were examined for selected portions of the monitoring period. Strong relationships of flux to river flow and/or nutrient loads were found and the importance of low dissolved oxygen concentrations on sediment phosphorus and nitrate fluxes further confirmed from both field and laboratory measurements. It appears that considerable improvements in sediment quality can be achieved if dissolved oxygen (DO) concentrations in deep water can be maintained at or above 2 mg l^{-1} and further improvements can be achieved if dissolved oxygen (DO) concentrations remain above 4 mg l^{-1}.

A method for measuring total sediment metabolism which is consistent with the needs of a monitoring program has been implemented. Recently developed and reliable technology is used to detect changes in total inorganic carbon flux (TCO_2 flux) at a reasonable cost. Data based on inorganic carbon (TCO_2) fluxes were compared with sediment oxygen consumption (SOC) rates, and as expected, were found to be appreciably larger. The technique completely avoids the low dissolved oxygen problems associated with sediment oxygen consumption (SOC) rate measurements. Rates of inorganic carbon (TCO_2) appear to be positively correlated with sediment organic matter content and with nutrient loading rates.

A focused review of Sediment Oxygen and Nutrient Exchanges (SONE) data for trends was completed for stations in the Patuxent River. The following trends indicate improving water and sediment quality conditions in response to reduced nutrient loading rates in the Patuxent River system:

- Significant reductions in total nitrogen (TN) and total phosphorus (TP) loading were found.
- Bottom water dissolved water (DO) concentrations have been increasing since 1990.
- Sediment chlorophyll-a mass appears to be declining although trends were not highly significant.
- Sediment oxygen (SOC) fluxes are increasing in response to better dissolved oxygen (DO) conditions in deep waters.
- Ammonium (NH_4^+) and phosphate (PO_4^- or DIP) fluxes are generally decreasing and trends were significant for some months.
- Nitrite plus nitrate fluxes have also responded to improved dissolved oxygen (DO) conditions in deep water.

2. INTRODUCTION

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

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

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

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

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

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

2.3 Objectives of the Water Quality Monitoring Program

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

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

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

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

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

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

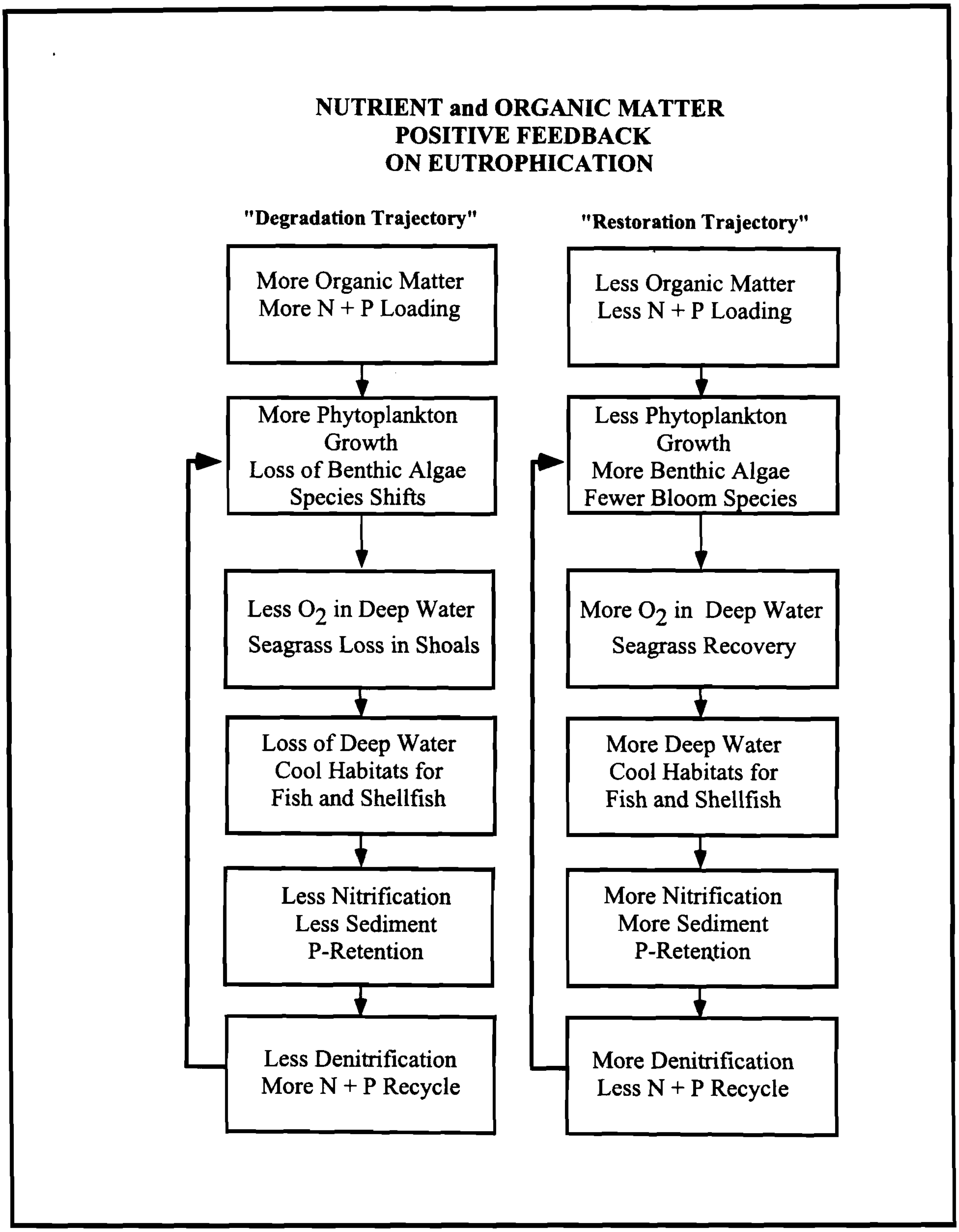

Figure 2-1. Nitrogen (N) and phosphorus (P) loads to the Chesapeake Bay affect coupled sediment nitrification-denitrification and sediment nitrogen and phosphorus cycling. High nitrogen and phosphorus inputs will ultimately result in less nitrogen and phosphorus removal from the benthos, while significant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

The first phase of the study was undertaken over a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation, which were keys in the identification of problem areas. The EPC measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and the sediment surface. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of EPC monitoring have been summarized in a series of interpretive reports (Boynton *et al.*, 1985, 1986, 1987, 1988, 1989, 1990, 1991a, 1992, 1993, 1994 and 1995a). 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.*, 1991a).

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

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

Sediment Oxygen and Nutrient Exchanges (SONE) program data collected during 1995 are presented and interpreted in this report. Sediment-water fluxes are examined for trends and relationships connected with water quality variables measured; laboratory measurements are presented which show relationships of sediment fluxes to water quality conditions; new measurements of dissolved inorganic carbon (TCO_2) flux under both anoxic and oxic conditions are presented representing a new approach to monitoring of sediment metabolism.

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

3.1 Location of Sediment Oxygen and Nutrient Exchanges (SONE) Stations[1]

During 1995, measurements of sediment-water oxygen and nutrient exchanges (SONE) were made five times at eight locations; two stations in the mainstem bay (one station after July) and at least one station in each of three major tributary rivers (Patuxent, Choptank, and Potomac Rivers). These locations shown in Figure 3-1. (specific location details are given in Tables 3-1.1., 3-1.2. and 3-1.3. also EPC Data Dictionary, Boynton and Rohland, 1990; Figure B-6. and Tables B-5.2. and B-5.3.) were selected based on prior knowledge of the general patterns of sediment-water nutrient and oxygen exchanges in Chesapeake Bay.

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

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

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

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

In a few instances (Patuxent River stations and Choptank River 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 1995. 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

[1] 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.

Point [HNPT] and Potomac River: Maryland Point [MDPT] and Ragged Point [RGPT]), 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 1995, 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). The station at Point No Point (PNPT) was not sampled in July, August and September, 1995. Four stations are located in the Patuxent River estuary and one each in the lower mesohaline regions of the Choptank and Potomac Rivers. The salinity characteristics of each station and the four salinity codes are listed in Table 3-2. (also in EPC Data Dictionary, Table B-7.; Boynton and Rohland, 1990).

3.2 Sampling Frequency

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

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

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

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

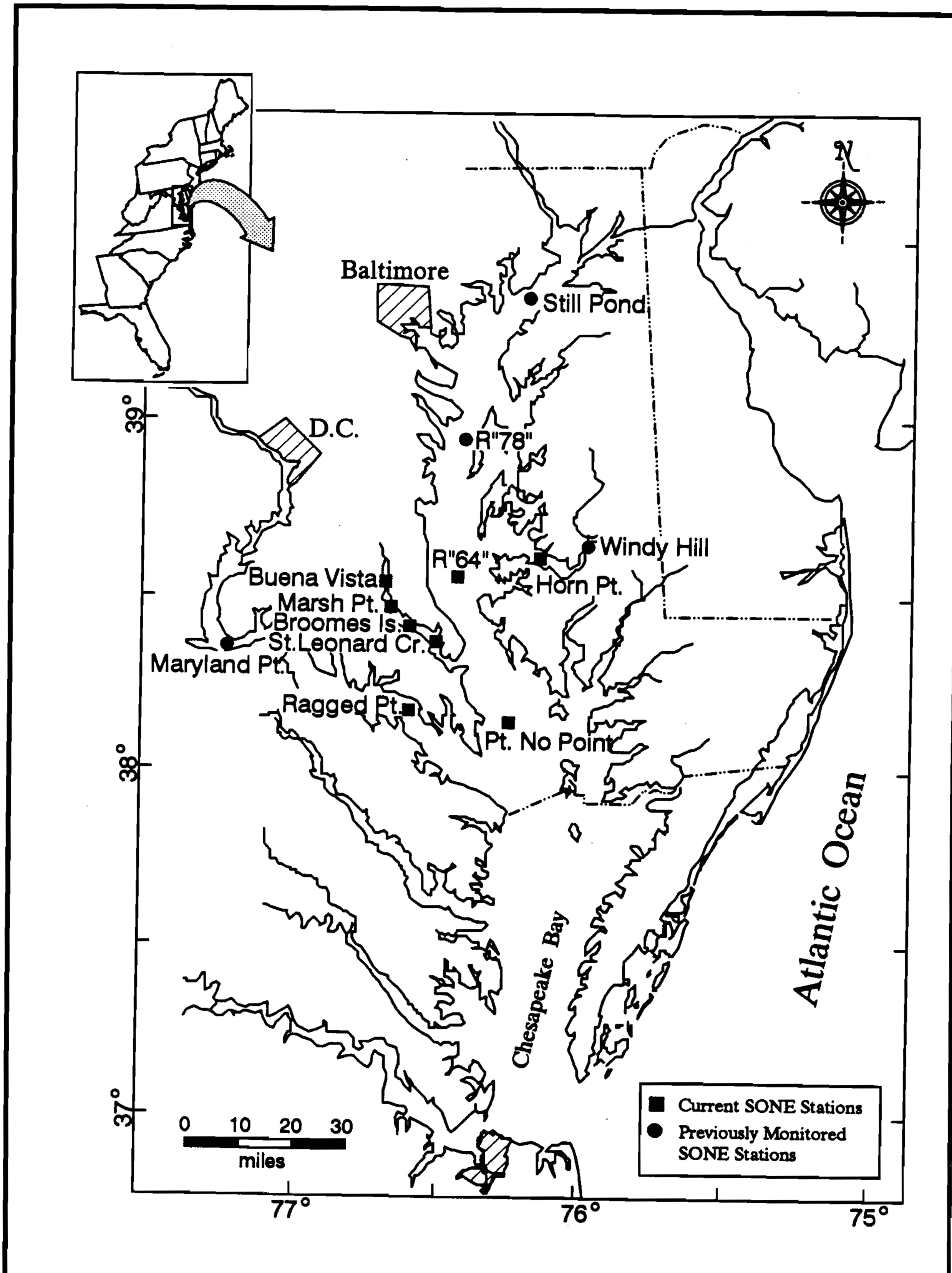

Figure 3-1. Location of Current and Previously sampled Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations in the Maryland portion of Chesapeake Bay (1984 - 1995).

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

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

NOTES:

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

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

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

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

STATION CODE NAME	LATITUDE DEG MIN	LONGITUDE DEG MIN	STATION DEPTH	MDE STATION	BAY SEGMENT
Patuxent River					
STLC	38° 22.88'	76° 30.06'	7.0	XDE2792	LE1
BRIS	38° 23.64'	76° 38.13'	15.0	XDE2792	LE1
MRPT	38° 26.81'	76° 30.06'	5.2	XDE5339	LE1
BUVA	38° 31.12'	76° 39.82'	5.8	XDE9401	RET1
Choptank River					
HNPT	38° 37.18'	76° 08.09'	8.2	MET5.2	ET5
Potomac River					
RGPT	38° 09.86'	76° 35.52'	16.5	XBE9541	LE2
Chesapeake Mainstem					
PNPT	38° 07.99'	76° 15.13'	14.2	MCB5.2	CB5
R-64	38° 33.59'	76° 26.63'	16.8	MCB4.3C	CB4

Table 3-1.3. SONE Station Code and Description

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

NOTES:

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

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

Table 3-2. Station Salinity

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

The Salinity Zone layer codes are as follows:

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

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

Previous studies also indicate that short-term temporal (day-month) variation in these exchanges is small; however, considerable differences in the magnitude and characteristics of fluxes appear among distinctively different estuarine zones (*i.e.*, tidal fresh *vs.* mesohaline regions). In light of these results, the monitoring design adopted for the SONE study involves five monthly measurements made between May and September, 1995 (SONE 53 through SONE 57). A complete listing giving the sampling dates of all SONE cruises (1984 - 1995) 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 (seven stations after July, 1995) SONE stations, 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-bottom[2] (approximately 1/2 meter) water samples are collected using a high volume submersible pump system. Samples are filtered, where appropriate, using 0.7 μm GF/F filter pads, and immediately frozen. Samples are analyzed by Nutrient Analytical Services Laboratory (NASL) for the following dissolved nutrients and particulate materials: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate (NO_2^- + NO_3^-), dissolved inorganic phosphorus corrected for salinity (DIP or PO_4^-), silicious acid ($Si(OH)_4$), particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations and seston content.

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

3.3.3 Sediment Profiles

At each SONE station an intact sediment core is used to measure the redox potential, (Eh, in units of mV) of sediments at 1 cm intervals to about 10 cm. Additionally, surficial sediments are sampled to a depth of 1 cm (2 mm since 9 August 1989) for particulate carbon

[2] Collection of near-surface water samples was discontinued after July, 1991.

Table 3-3. SONE Cruise Identifier

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

NOTES:

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

Table 3-3. SONE Cruise Identifier (Continued)

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

NOTES:

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

Table 3-3. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 53	MAY 1995	18 MAY	21 MAY	Aquarius
SONE 54	JUN 1995*	15 JUN	18 JUN	Aquarius
SONE 55	JUL 1995*	13 JUL	17 JUL	Orion
SONE 56	AUG 1995*	10 AUG	14 AUG	Aquarius
SONE 57	SEP 1995	08 SEP	10 SEP	Aquarius

NOTES:

* Data was also collected for the G-West Hydraulic Monitoring Study at:
PLIS in Jun, Jul and Aug 1995, GW-2 in Jun, Jul and Aug 1995

(PC), particulate nitrogen (PN), particulate phosphorus (PP), and total and active chlorophyll-a concentrations.

3.3.4 Sediment Cores

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

Three intact cores are used to estimate net exchanges of oxygen and dissolved nutrients between sediments and overlying waters (Figure 3-2.). Prior to beginning flux measurements, the overlying water in the core is replaced by fresh bottom water to ensure that water quality conditions in the core closely approximate *in situ* conditions. Gentle circulation of water, with no induction of sediment resuspension, is maintained in the cores during the measurement period via the stirring devices attached to the oxygen (O_2) probes. The cores are placed in a darkened water bath to maintain ambient temperature. Oxygen concentrations are recorded and overlying water samples (35 ml) are extracted from each core every 30 to 60 minutes (depending on the rate of oxygen uptake) over a 2 to 5 hour incubation period. During the incubation period, five overlying water samples are extracted from each core. As a nutrient sample is extracted from a core, an equal amount of ambient bottom water is added. An opaque Plexiglas liner filled with bottom water, incubated and sampled as described above, serves as a blank. Overlying water samples are filtered and immediately frozen for later analysis for ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), dissolved inorganic phosphorous (DIP or PO_4^-), silicious acid ($Si(OH)_4$) (discontinued after July, 1995) concentrations. Oxygen and nutrient fluxes are estimated by calculating the mean rate of change in concentration over the incubation period and converting the volumetric rate to a flux using the volume:area ratio of each core.

It should be noted that at low oxygen concentrations (< 2 mg l^{-1}) sediment oxygen consumption (SOC) rate measurements underestimate actual sediment metabolism because much of the decomposition of organic matter is supported through anaerobic pathways (primarily sulfate reduction). Additionally sediment oxygen consumption (SOC) rates made under low dissolved oxygen (DO) conditions do not capture the eventual oxygen demand that is exerted by the reoxidation of reduced compounds (primarily H_2S) formed during anaerobic periods. Prior to 1989, between five and seven of the sediment oxygen and nutrient exchanges (SONE) stations rarely if ever experienced low bottom water dissolved oxygen (DO) concentrations. Since 1989, SONE stations have been modified and only three of eight stations rarely experience low oxygen concentrations. Hypoxic conditions are common at the remaining stations and influence sediment oxygen consumption (SOC) rates. This represents a methodological limitation which is more serious given the current configuration of stations in the study. A method for measuring total sediment metabolism (dissolved inorganic carbon [TCO_2] flux) has been developed and used in the SONE monitoring program during 1995.

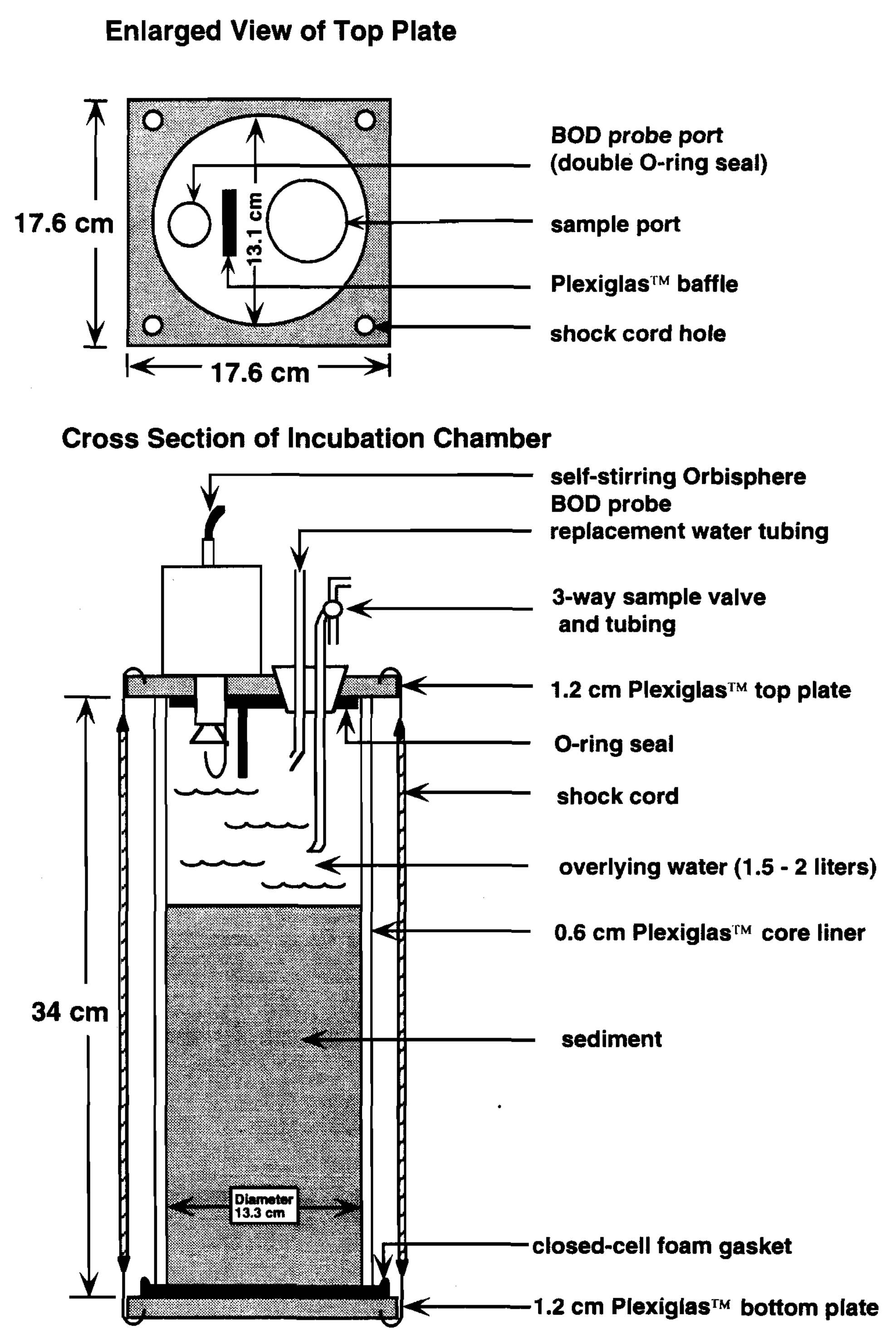

Figure 3-2. Schematic Diagram of the Incubation Chamber

3.3.5. Dissolved Inorganic Carbon (TCO_2) Field and Laboratory Methods

3.3.5.1. Field

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

3.3.5.2. Laboratory

The colorimetric methods of Johnson *et al.* (1987) are used to analyze the water samples for dissolved inorganic carbon (TCO_2).

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

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

3.3.5.3. The Johnson Method

A brief description of the Johnson methodology is as follows: All of the carbon dioxide (CO_2) is released to a free gas, phosphoric acid (10%) is injected into a precise volume of the water sample. The gas is carried in a nitrogen gas stream to a UIC, Inc. colorimeter. The entire system is gas tight.

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

During 1995 the Ecosystem Processes Component (EPC) program measurements of carbon dioxide (CO_2) flux were made at six stations located in a variety of bay habitats. Specifically, measurements were made monthly during May and September, 1995 at a station in the mainstem bay (R-64), three stations in the Patuxent River (St. Leonard Creek [STLC], Broomes Island [BRIS] and Marsh Point [MRPT]) and one station each in the lower Potomac River (Ragged Point [RGPT]) and Choptank River (Horn Point [HNPT]).

3.4. Chemical Analyses

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

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

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

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

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

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

- Quarterly cross calibration exercises with Virginia Institute of Marine Science (VIMS) and Old Dominion University (ODU). The most recent inter-comparison (November 1995) confirmed all parameters routinely analyzed by these laboratories as part of the Chesapeake Bay Monitoring Program. Samples from various salinities and nutrient regimes were analyzed under this exercise.

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

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

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

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

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

3.6. Data Management

Hard copy data table listings of every variable measured during SONE and VFX monitoring programs for August 1984 through December 1991, were submitted in four volumes. Volumes I and II were appended to Level 1, No 7 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 90-062 (Boynton *et al.*, 1990) and Volumes III and IV were appended to Level 1, No 9 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 92-042 (Boynton *et al.*, 1992). Data tables for July through October, 1992 have been added to Volume III for completion. Volume V which comprises hard copy data table listings for 1993, 1994 and 1995 are submitted as part of this report.

Additionally Appendix B (Part II) of this report contains SONE data tables listings of variables measured during 1995. 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.

Dissolved inorganic carbon (TCO_2) values are incorporated in the sediment-water flux data tables (Tables B-6.1. - B-6.5.; SONE 53 through SONE 57), however the initial values are *not* added in the core data file.

3.6.2 Incorporation of Error Codes in Data Tables

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

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

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

3.6.4 Statistical Analysis System (SAS) Files

Lotus files are stripped of headings and converted to ASCII files. The 1994 and 1995 data files, one file for each data set, are to be added to the Statistical Analysis System (SAS) database now resident on the VAX 8650. Additional information regarding the format of the data and details of variable labels, file structure and data and sampling anomalies are to submitted as a data dictionary file to fulfill the requirements of the EPA Chesapeake Bay Liaison Office (EPA/CBLO).

Two complete sets of SAS data files for 1994 and 1995 are submitted with this report to DNR. SAS reference files for each data set containing detailed station and variable information as well as other pertinent information related to missing data will be submitted to DNR during 1996 to complete the existing Water Quality database.

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

Table 3-4. Analysis Problem Codes

ANALYSIS PROBLEM CODE	DESCRIPTION
A	Laboratory accident
B	Interference
C	Mechanical/materials failure
D	Insufficient sample
N	Sample lost
P	Lost results
R	Sample contaminated
S	Sample container broken during analysis
V	Sample results rejected due to QA/QC criteria
W	Duplicate results for all parameters
X	Sample not preserved properly
AA	Sample thawed when received
BB	Torn filter paper
CC	Pad unfolded in foil pouch
EE	Foil pouch very wet when received from field, therefore poor replication between pads, mean reported.
FF	Poor replication between pads; mean reported
HH	Sample not taken
JJ	Amount filtered not recorded (calculation could not be done)
LL	Mislabeled
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
PP	Assumed sample volume (pouch volume differs from data sheet volume; pouch volume used)
QQ	Although value exceeds a theoretically equivalent or greater value (e.g., PO4F>TDP), the excess is within precision of analytical techniques and therefore not statistically significant
RR	No sample received
SD	All sampling at station discontinued for one or more sampling periods
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 RATES

4.1. Overview

One of the continuing objectives of the Ecosystem Processes Component (EPC) Program is to explore monitoring program data, as well as other data sources, for relationships between nutrient loading (*e.g.*, point, non-point and atmospheric sources) and responses of sediment and deposition processes. Sediment oxygen consumption (SOC) and sediment nutrient exchanges have been shown to have strong influences on water quality conditions (Boynton *et al.*, 1990) and are ultimately regulated by rates of external nutrient supplies. Freshwater input to the bay and tributary rivers is an important external forcing on bay ecology, largely determining salinity patterns, buoyancy and other features. Moreover, both the magnitude and timing of freshwater flow events have been shown to influence bay water quality (Boicourt, 1992). River flow has been shown to be a good first approximation of nutrient loading rates for many areas of Chesapeake Bay and in this report river flow has again been used as an indication of nutrient loading rates. In the case of the Patuxent River estuary, nutrient loading rates (total nitrogen [TN] and total phosphorus [TP]) measured at the fall line and point source loads both above and below the fall line have been assembled and examined for the period 1984 through 1995.

4.2 River Flow Characteristics in 1995

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

4.2.1 Average Annual River Flows

Annual average river flows for the period 1978 through 1995 are shown in Figure 4-1.1. The eighteen year average (1978 - 1995) flow to each system during this period is indicated by horizontal lines on this figure (James *et al.*, 1990; James, *pers. comm.*, 1994, 1995). The eighteen year average in the Susquehanna River was 38,966 cubic feet per second (cfs), in the Potomac River 12,165 cubic feet per second, in the Patuxent River 359 cubic feet per second and in the Choptank River 131 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 eighteen 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 eighteen year average from 1985 through 1988 (except in the Susquehanna River in 1986) and above this average in 1989 (except in the Potomac River). Flows during 1990 were higher than the eighteen year average in the Susquehanna (48,556 cfs) and Patuxent Rivers and lower than this average in the Potomac and Choptank Rivers. In 1991 and 1992 annual average flows were lower than the eighteen year average in all systems. Flows in three rivers were well above average in 1993 (Susquehanna River 52,504 cfs; Potomac River 9,223 cfs and Patuxent River 446 cfs).

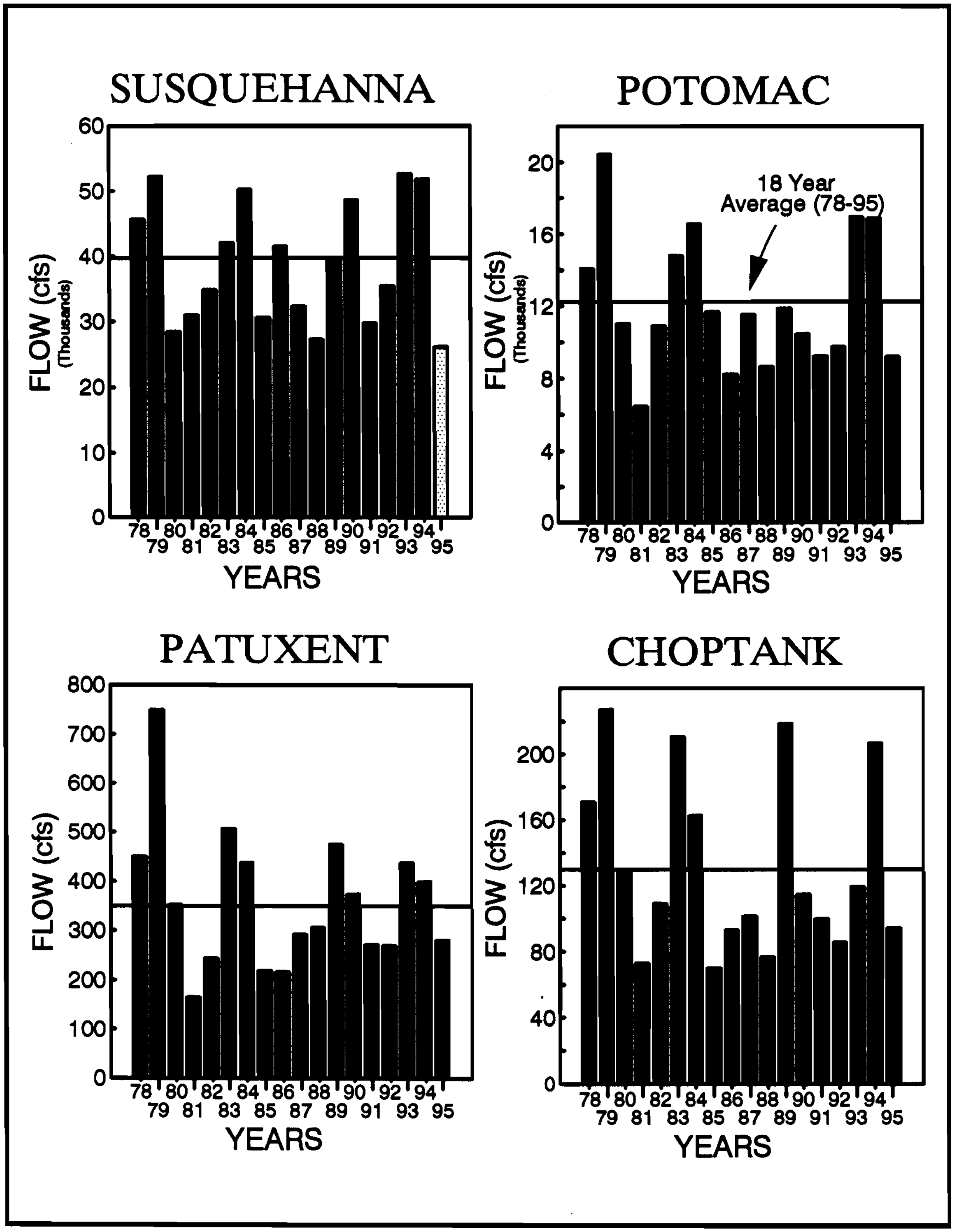

Figure 4-1.1. Bar graphs of average annual river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for the period 1978 through 1995 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers. comm.*, 1994 and 1995). Flows were measured at Conowingo, MD (01578310); Washington, D.C. (01646500); Bowie, MD (01594440) and Greensboro, MD (01491000) for the four systems, respectively.

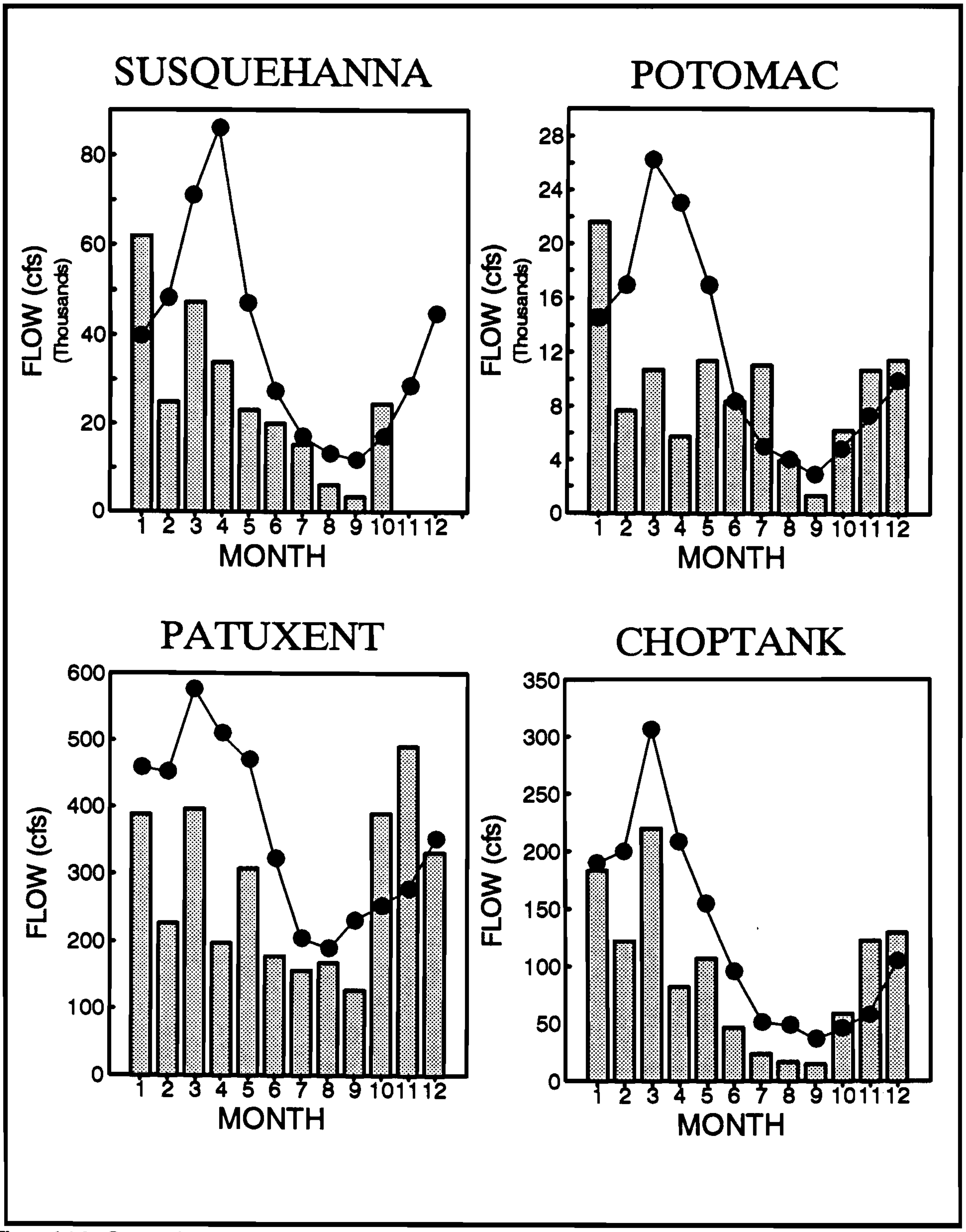

Figure 4-1.2. Bar graphs of average 1995 monthly river flows from the Susquehanna, Potomac, Patuxent and Choptank Rivers. The dot and line plots represent the long-term average flow for the period 1978 through 1995 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers comm.*, 1994 and 1995). Flows were measured at Conowingo, MD (01578310); Washington, D.C. (01646500); Bowie, MD (01594440) and Greensboro, MD (01491000) for the four systems, respectively.

River flows were well above average in 1994 (Susquehannna River 51,744 cfs; Potomac River 16,871 cfs; Patuxent River 399 cfs and Choptank River 207 cfs). River flows have either been near or below the eighteen year average value during the Ecosystem Processes Component monitoring period with a few exceptions (1989, 1993 and 1994). As a result of this, water column stratification might be expected to be less intense than usual and diffuse source nutrient loads to be lower than normal in most years. Data for 1995 indicate that this was a below normal year with regards to freshwater and diffuse source nutrient inputs which were largely associated with the very low flows recorded during the winter-spring period.

4.2.2 Average Monthly River Flows

One of the more obvious characteristics of estuarine systems is the time and space variability associated with many variables as is the case for river flow (and diffuse source nutrient loading). Monthly average river flows for all of the main Maryland tributary rivers are shown as a series of bar graphs (Figure 4-1.2.). In this figure the vertical bars represent average monthly flows for 1995 while the bold dots represent average monthly flows calculated over longer time periods (1978 - 1994). The data provided by the United States Geological Survey (U.S.G.S.) office for 1995 are complete except for the last two months of 1995 for the Susquehanna River.

Peak flows during 1995 were recorded between January and March in the four rivers. The Susquehanna had a flow rate of 62,170 cfs (January), the Potomac 21,260 cfs (January), the Patuxent 398 cfs (March) and the Choptank 221 cfs (March; Figure 4-1.2.). In 1995, late winter-early spring flows from all rivers were substantially reduced compared with the eighteen year average flow. For example, flows during these months from the Susquehanna were more than a factor of two less than the long term average; a similar situation was evident in the Potomac River as well. The low flow conditions generally persisted through the summer in all tributary systems and flows did not increase to more normal rates until October.

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

4.3 Patuxent River Freshwater and Nutrient Loading Rates

The Patuxent River is one of the prime tributaries targeted and undergoing management actions, a special emphasis has been placed on examining river flow, point and fall line nutrient loads over the entire monitoring period. These data are related to the sediment oxygen and nutrient exchanges (SONE) measurements in a subsequent section of this report but are provided here with comment on important patterns. Monthly average river flow (Figure 4-2.1) at the fall line (Bowie, MD) for the period 1984 through 1995 indicates a general repetitive pattern of flow with higher values in winter-spring and lower values in summer-fall. Superimposed on this baseline pattern are important variations. In four years (1984, 1989, 1993 and 1994) winter or spring flows were much enhanced; conversely, during

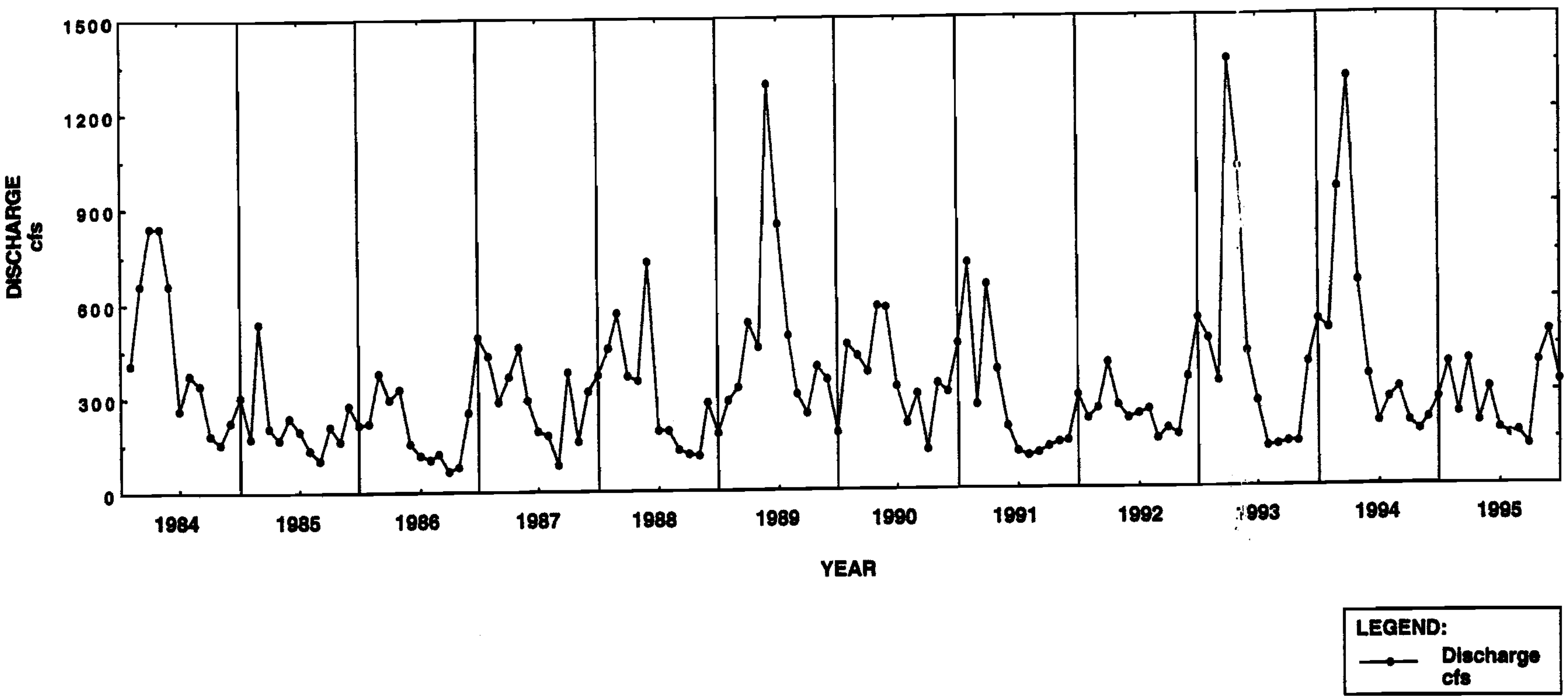

Figure 4-2.1. Monthly average river flow in the Patuxent River, discharge (cfs), measured at Bowie, MD for the period 1984 - 1995.

Data are supplied by personal communication with the United States Geological Survey: James et al., 1990; J. Manning, pers. comm., 1992 and 1993; R. James, pers comm., 1994 and 1995.

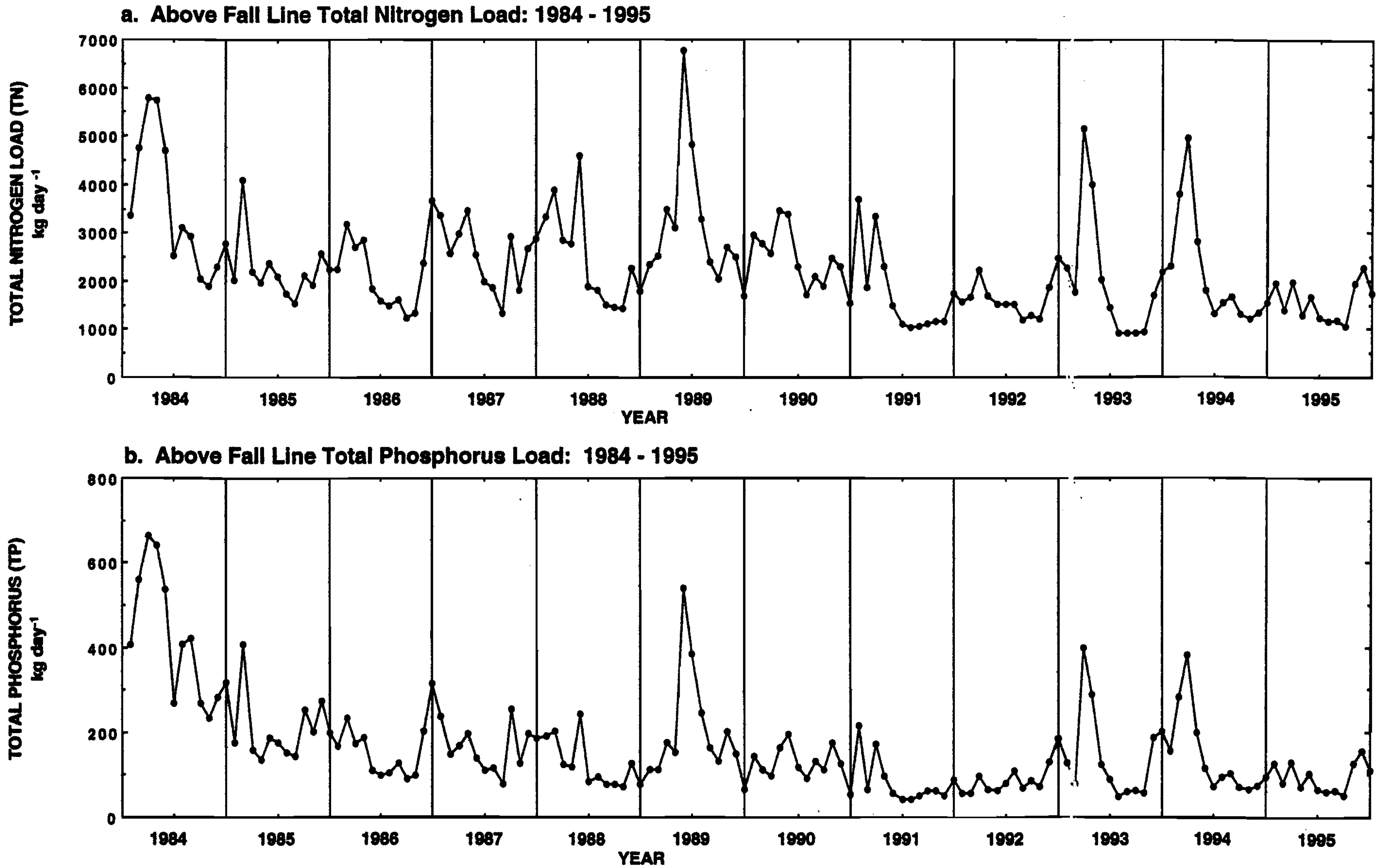

Figure 4-2.2. Monthly average fall line total nitrogen (TN) and total phosphorus (TP) loads for the period 1984 - 1995.
Data are from Wong (Department of Natural Resources (DNR), pers. comm.).

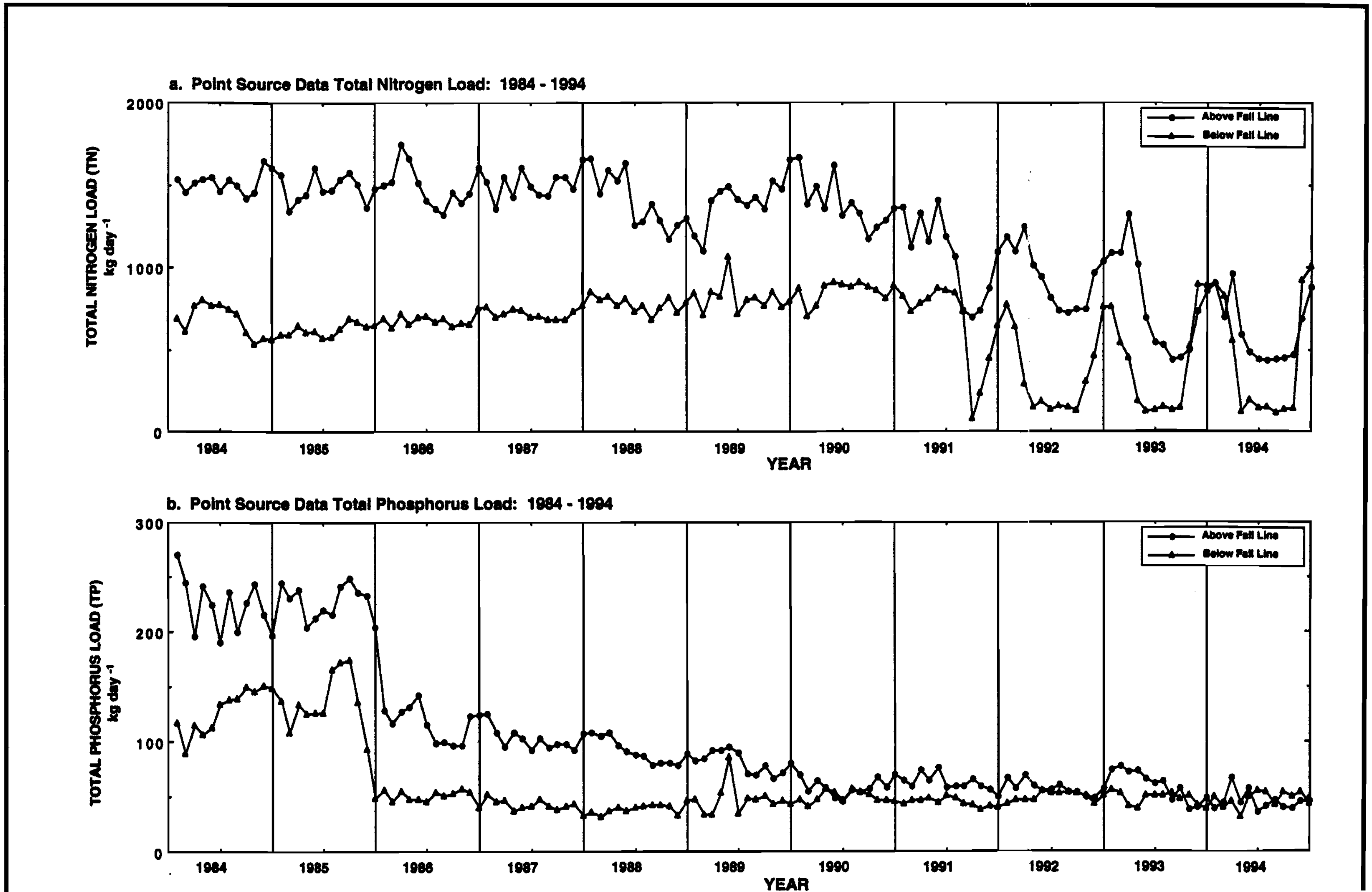

Figure 4-2.3. Monthly average point source total nitrogen (TN) and total phosphorus (TP) loads for the period 1984 - 1995.
Data are from Wong (Department of Natural Resources (DNR), pers. comm).

1985, 1986, 1992 and 1995 flows were particularly low with little indication of a winter-spring freshet. The obvious but important point is that interannual variability in flow is very substantial and will contribute to the difficulty in separating the effects of management actions from local climatic variability. Despite this difficulty, large variations in flow (and the effects of flow on delivery of nutrients, sediments and estuarine stratification) provide an opportunity to compare processes among years and in this way gain some important clues as to how the system will respond to longer term nutrient reductions.

Monthly average total nitrogen (TN) and total phosphorus (TP) loads measured at the fall line (Bowie, MD) for the period 1984 through 1995 are provided in Figure 4-2.2. These data include both point and diffuse sources of total nitrogen (TN) and total phosphorus (TP) from above the fall line. On an interannual basis total nitrogen (TN) loads vary by just over a factor of two. As with freshwater flow there are similar intra-annual patterns with total nitrogen (TN) loads generally being associated with strong freshwater flow events. Additionally, there appears to be a significant decrease in loading rate over the period of record ($r = 0.37$; $p < 0.01$) amounting to about 9 kg $month^{-1}$ or about 100 kg yr^{-1}. The fall line total phosphorus (TP) loads exhibited a sharp decline between 1984 and 1988 (Figure 4-2.2) and then slower declines to the present excepting loading spikes associated with strong freshets in 1989, 1993 and 1994. Loadings of total phosphorus (TP) at the fall line were a factor of four lower in 1995 compared with 1984, a very substantial decline.

Monthly average point source load of total nitrogen (TN) and total phosphorus (TP) from the period 1984 through 1994 are presented in Figure 4-2.3. As expected from the spatial distribution of sewerage treatment plants along the river both total nitrogen (TN) and total phosphorus (TP) loads were greater above than below the fall line; most of the below fall line load is associated with the Western Branch facility. Point sources of total nitrogen (TN) exhibited little seasonal variation between 1984 and 1990. However, starting in 1991 sharp seasonally in load was introduced from plant upgrades to remove nitrogen via biological nitrogen removal which is more effective during warm portions of the year. The distribution of point source loads of total phosphorus (TP) from above and below the fall line were similar to those for total nitrogen (TN). However, sharp load reductions occurred several years earlier (in 1985 and 1986) and did not exhibit the same degree of seasonal variability as observed for total nitrogen (TN). The point source total phosphorus (TP) load reductions were due to sewage plant upgrades and the phosphate detergent ban.

Over the monitoring period (1984 through 1995) combined fall line plus below fall line point source loads have substantially decreased; total nitrogen (TN) loads by a factor of 2.2 (5687 kg day^{-1} in 1984 to 2622 kg day^{-1} in 1995) and total phosphorus (TP) loads by a factor of 4.1 (770 kg day^{-1} in 1984 to 189 kg day^{-1} in 1995).

5. CHARACTERISTICS OF SEDIMENT-WATER OXYGEN AND NUTRIENT EXCHANGES

5.1. Overview

Monthly average sediment-water fluxes are summarized in the form of bar graphs (Figures 5-1.1. through 5-1.5.) for five variables: sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate ($NO_2^- + NO_3^-$), phosphate (PO_4^-), and silicate ($Si(OH)_4$). Data collected over a period of eleven calendar years, 1985 through 1995, were used in the preparation of these graphics. Each bar represents the arithmetic mean flux value for a particular month calculated using individual flux values for the ten calendar year period 1985 through 1995, while the error bar indicates the population standard deviation from this mean. Outlier values identified in statistical testing of SONE data (Boynton *et al.*, 1993) 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 1995 (SONE 53 [May 1995] through SONE 57 [October 1995]; 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]). It is important to note that no measurements were made at Point No Point (PNPT) in July, August and September, 1995 and silicate measurements were discontinued at all stations during July, August and September, 1995.

5.2 Sediment Oxygen Consumption (SOC)

Mean monthly sediment oxygen consumption (SOC) for 1995, ranged from -0.77 g O_2 m^{-2} day^{-1} in July, 1995 at Marsh Point (MRPT) to -3.24 g O_2 m^{-2} day^{-1} in May, 1995 at St Leonard Creek (STLC) in the Patuxent River, from -0.29 g O_2 m^{-2} day^{-1} in August to -2.90 g O_2 m^{-2} day^{-1} in May in the Choptank River (Horn Point [HNPT]), from -0.14 g O_2 m^{-2} day^{-1} in July, 1995 through -0.81 g O_2 m^{-2} day^{-1} in May, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem of the bay mean monthly sediment oxygen consumption (SOC) values at Point No Point (PNPT) ranged from -0.85 g O_2 m^{-2} day^{-1} in June to -0.86 g O_2 m^{-2} day^{-1} and from -0.21 g O_2 m^{-2} day^{-1} in July, 1995 to -1.28 g O_2 m^{-2} day^{-1} at R-64 (Figure 5-1.1.; Tables B6-47. - B6-52.). Values were generally larger in magnitude in the Patuxent and Choptank Rivers than at other sites. *Note that: larger negative sediment oxygen consumption (SOC) flux indicate larger rates of oxygen loss to sediments.*

At most stations the 1995 showed markedly increased rates of sediment oxygen consumption (SOC) early in the sampling period (May, June and July), depressed values in the summer (August) with only a slight increase in rates at the beginning of September. The largest fluxes were recorded in May and June as is typical; however, as no samples were taken in October it is not clear if the secondary peak recorded in previous years occurred. However, spring rates of SOC were considerably enhanced at all stations in the Patuxent River and at Horn Point (HNPT) in the Choptank River. Bottom water dissolved oxygen levels remained high at these sites during 1995 and were probably responsible for the enhanced rates. In general sediment oxygen consumption (SOC) tends to be higher in low flow years when bottom water dissolved oxygen concentrations remain higher.

Fluxes at hypoxic stations (where hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters) were depressed in July but not as markedly in August, 1995 as was the case in all previous years with the exception of July 1992 when aerobic sediment metabolism persisted longer than in previous years because of higher dissolved oxygen (DO) concentrations in these bottom waters. In both 1991 and 1992, river flow to all sites was quite low (Figure 4-1.2.) and as a result diffuse source nutrient loads were probably lower than normal as was organic matter enrichment of bottom waters and sediments. It is important to note a strong deviation from SOC patterns in the lower Choptank River during August, 1995 (Figure 5-5.1). Sediment oxygen consumption (SOC) rates were at record low levels at this time. It appears that water characterized by low dissolved oxygen content had advected into the Choptank River from the mainstem bay; high salinity deep water at this station clearly indicates a mainstem bay influence. Low dissolved oxygen conditions presumably limited SOC rates at this time. This sort of event is evidence of the connections that exist between tributaries and the mainstem bay. In this case, a site that normally has reasonably good water quality conditions during summer experienced a period of poor water quality not because of local processes but because of an influence from the mainstem bay which experiences chronic water quality problems during summer periods.

5.3 Ammonium (NH_4^+) Fluxes

Average monthly ammonium (NH_4^+) fluxes in 19954, ranged from 0 (zero) μMN m^{-2} hr^{-1} in June, 1995 at St. Leonard Creek (STLC) to 496.6 μMN m^{-2} hr^{-1} in July, 1995 at Buena Vista (BUVA) in the Patuxent River, from 56.5 μMN m^{-2} hr^{-1} in June, 1995 to 206.9 μMN m^{-2} hr^{-1} in May, 1995 in the Choptank River (Horn Point [HNPT]), from 113.2 μMN m^{-2} hr^{-1} in May, 1995 to 278.3 μMN m^{-2} hr^{-1} in July, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem of the bay at Point No Point (PNPT) average monthly ammonium (NH_4^+) fluxes ranged from 47.1 μMN m^{-2} hr^{-1} in May, 1995 to 104.1 μMN m^{-2} hr^{-1} in June, 1995 and at R-64 from 107.5 μMN m^{-2} hr^{-1} in May, 1995 to 386.4 μMN m^{-2} hr^{-1} in September, 1995 (Figure 5-1.2.; Tables B6-47. - B6-52.).

The values recorded in 1995 generally followed temporal trends exhibited in previous years. However, the magnitude of fluxes was below the mean values recorded in previous years; fluxes were particularly low in the lower Choptank River (Horn Point [HNPT]) in June 1995 and in May and June, 1995 at the two down river stations in the Patuxent River (St. Leonard Creek [STLC] and Broomes Island [BRIS]). In general the magnitude of ammonium (NH_4^+) fluxes was below mean values for most months of 1995 at Ragged Point (RGPT) while in the mainstem bay fluxes at R-64 were higher than normal for all months sampled except August, 1995 (Figure 5-2.1.b.). Depressed ammonium fluxes (NH_4^+) are expected during years of lower than normal nutrient loading and better than normal oxygen conditions in deep waters. Both of these conditions were evident in the lower Patuxent and Choptank Rivers during 1995.

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

- Monthly means and standard deviations were calculated using flux data for a specific month at each station from 1985 - 1994.
- 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 1995. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993) 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 1994.
- September values for all stations only include five years data, 1991 through 1995.
- The bold solid dots indicate average monthly fluxes recorded in 1995; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.
- * = Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT).
  ** = Very hypoxic stations are Ragged Point (RGPT), Point No Point (PNPT) and R-64.

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

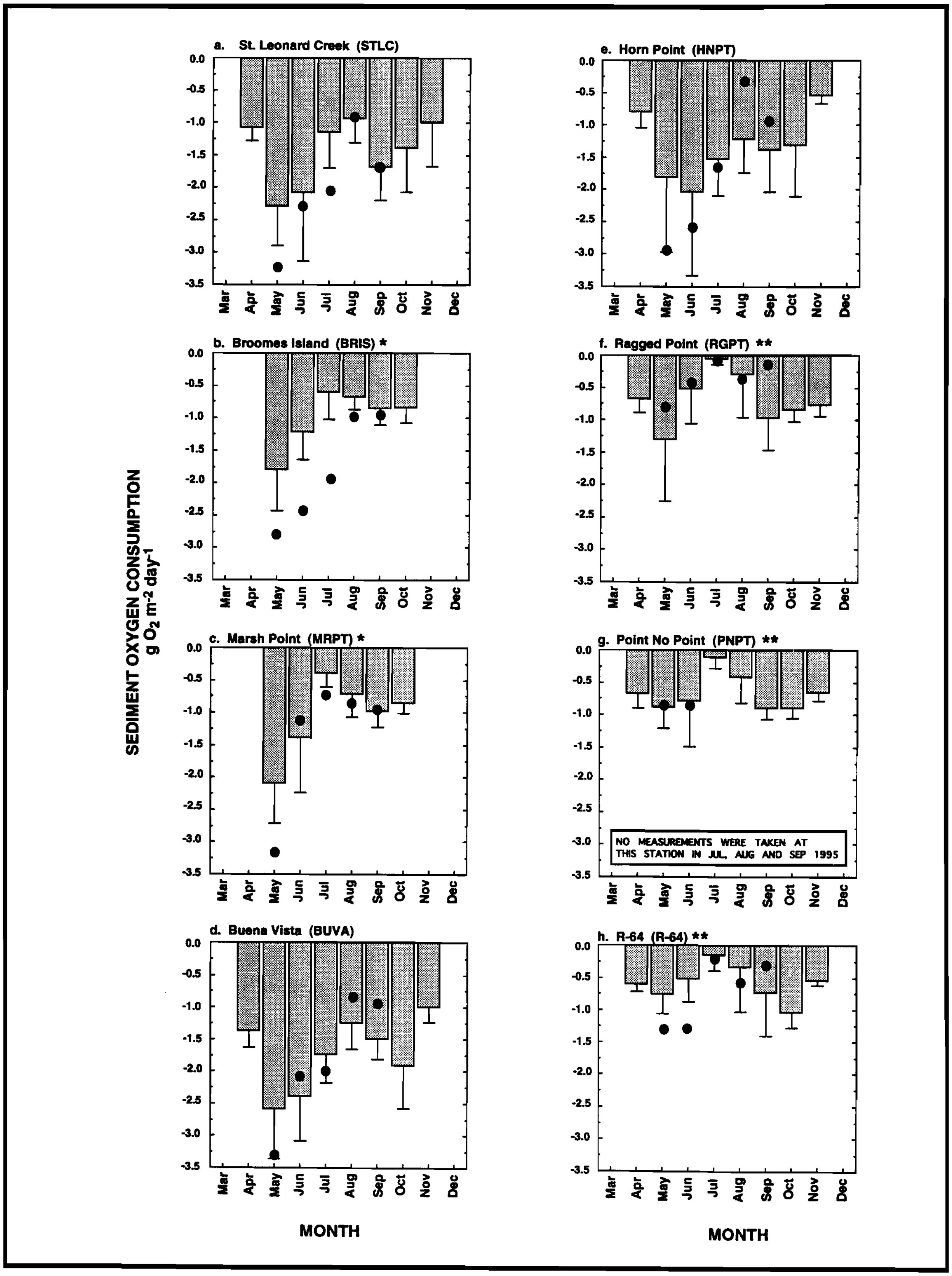

Figure 5-1.1. Mean monthly (April to November) sediment oxygen consumption (SOC) rates at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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

- Monthly means and standard deviations were calculated using data available for a specific month at each station from 1985 - 1994.
- 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 1995. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993) 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 1994.
- September values for all stations only include five years data, 1991 through 1995.
- The bold solid dots indicate average monthly fluxes recorded in 1995; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water.

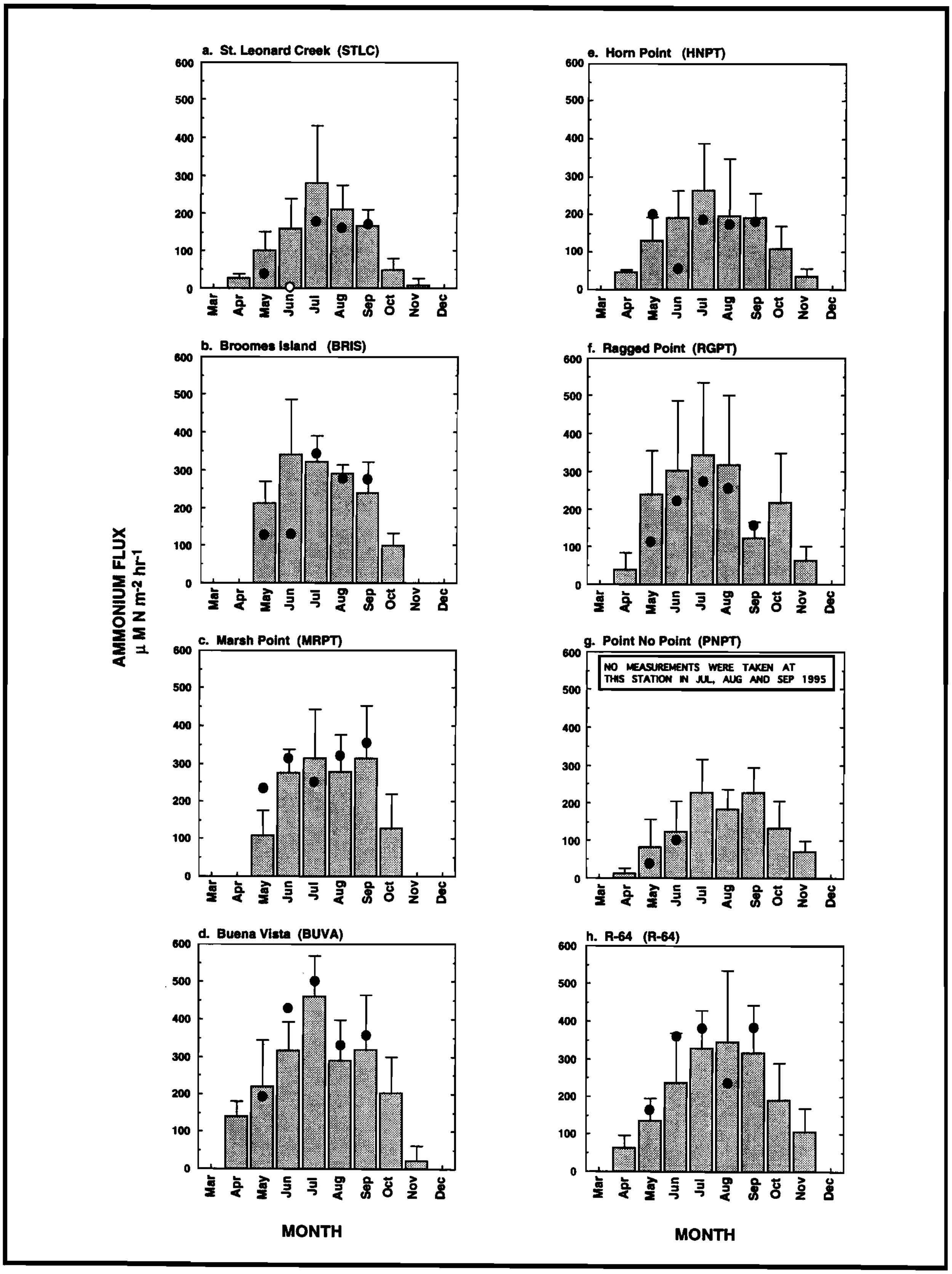

Figure 5-1.2. Mean monthly (April to November) ammonium (NH_4^+) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1994.
- 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 1995. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993) 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 1994.
- September values for all stations only include five years data, 1991 through 1995.
- The bold solid dots indicate average monthly fluxes recorded in 1995; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.

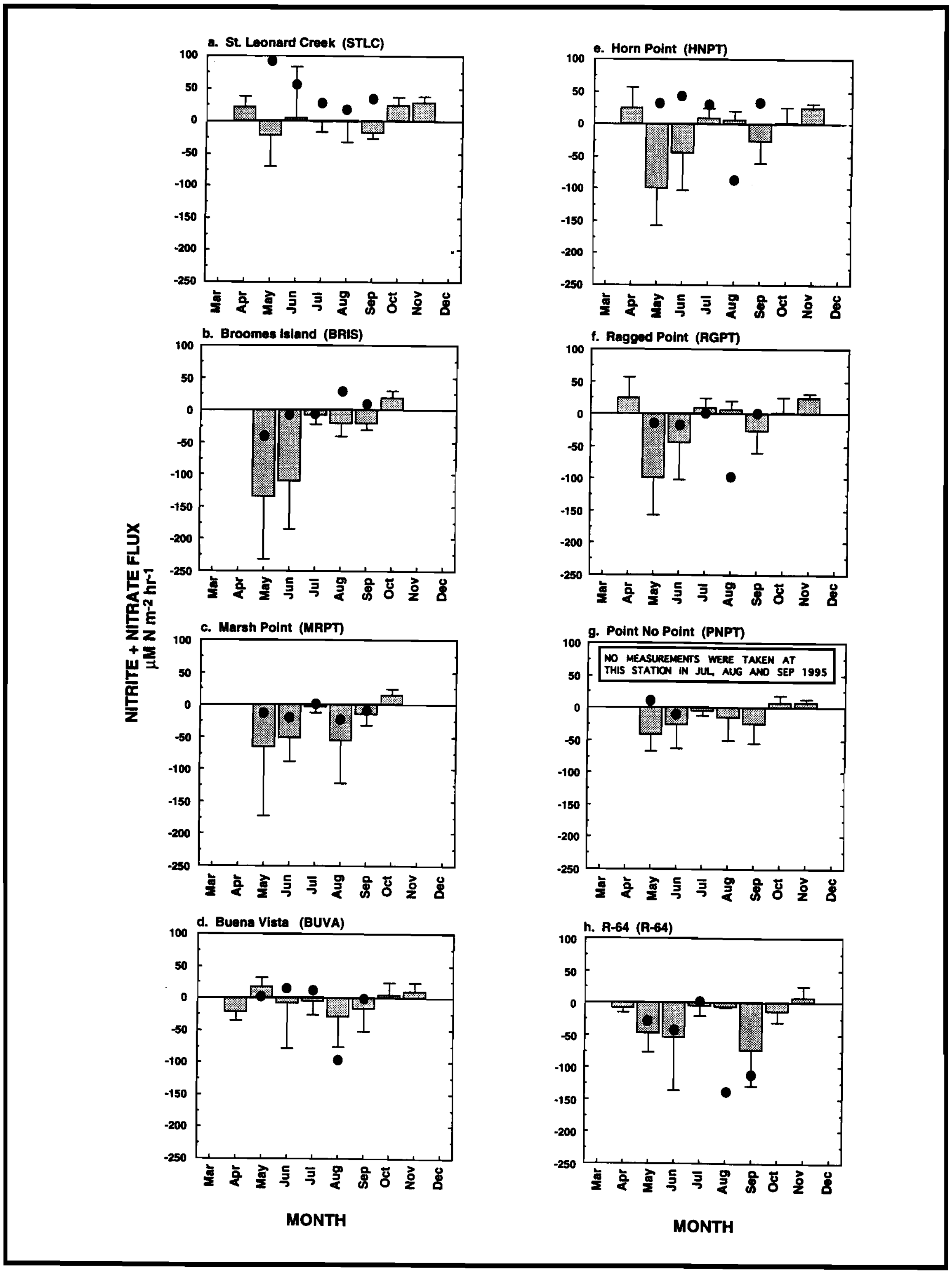

Figure 5-1.3. Mean monthly (April to November) nitrite plus nitrate (NO_2^- + NO_3^-) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1994.
- 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 1995. Outlier values identified during the statistical testing of SONE data (Boynton *et al.*, 1993) 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 1994.
- September values for all stations only include three years data, 1991 through 1995.
- The bold solid dots indicate average monthly fluxes recorded in 1995; bold open circles indicate average flux for that month was 0.0 (zero).
- Positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.

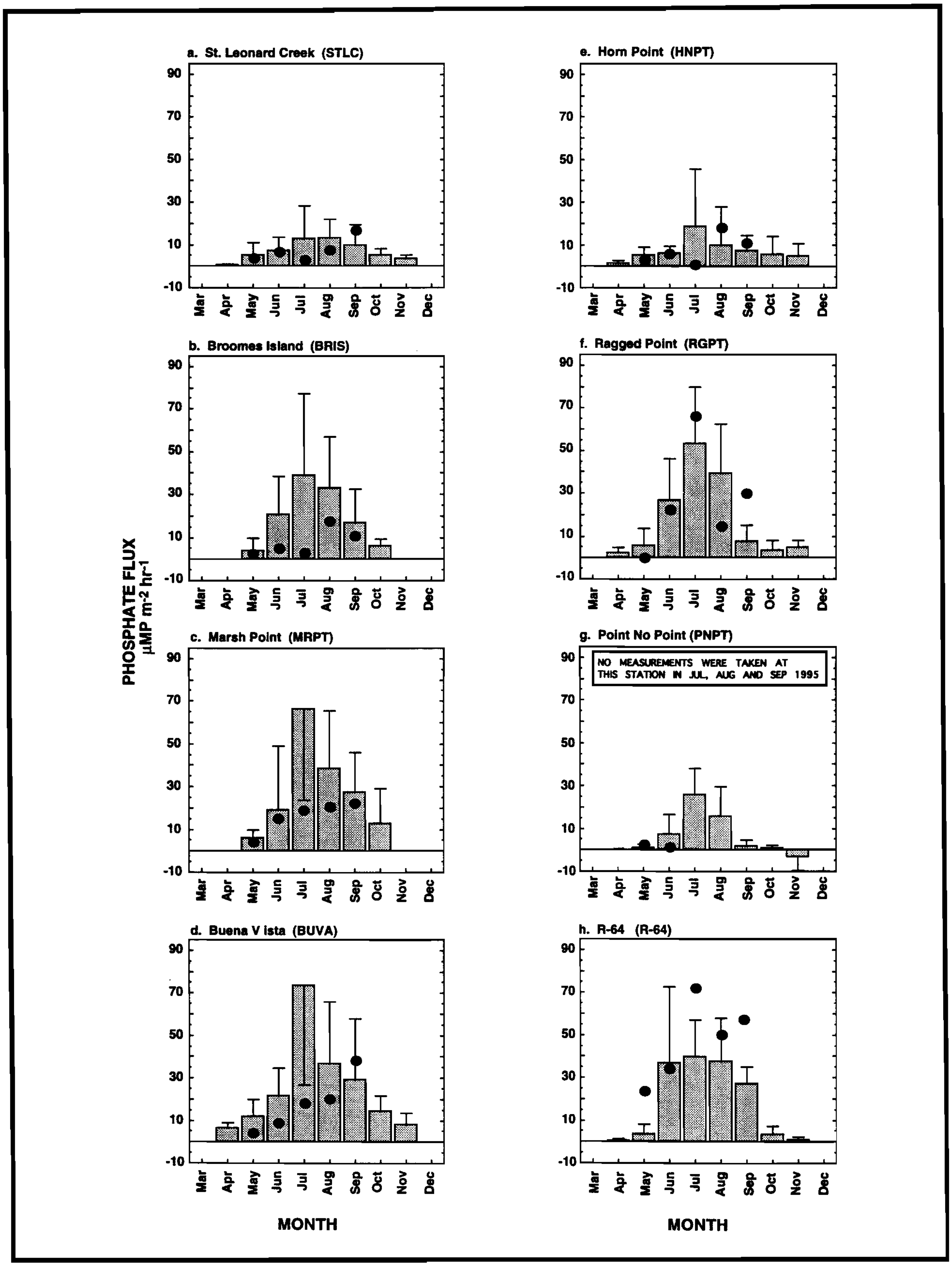

Figure 5-1.4. Mean monthly (April to November) phosphorus (PO_4^- or DIP) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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

- Monthly means and standard deviations were calculated using flux data available for a specific month at each station from 1985 - 1994.
- 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 1995. 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 1994.
- September values for all stations only include three years data, 1991 through 1995.
- The bold solid dots indicate average monthly fluxes recorded in 1995; bold open circles indicate average flux for that month was 0.0 (zero).
- Negative values indicate fluxes from water to sediment.

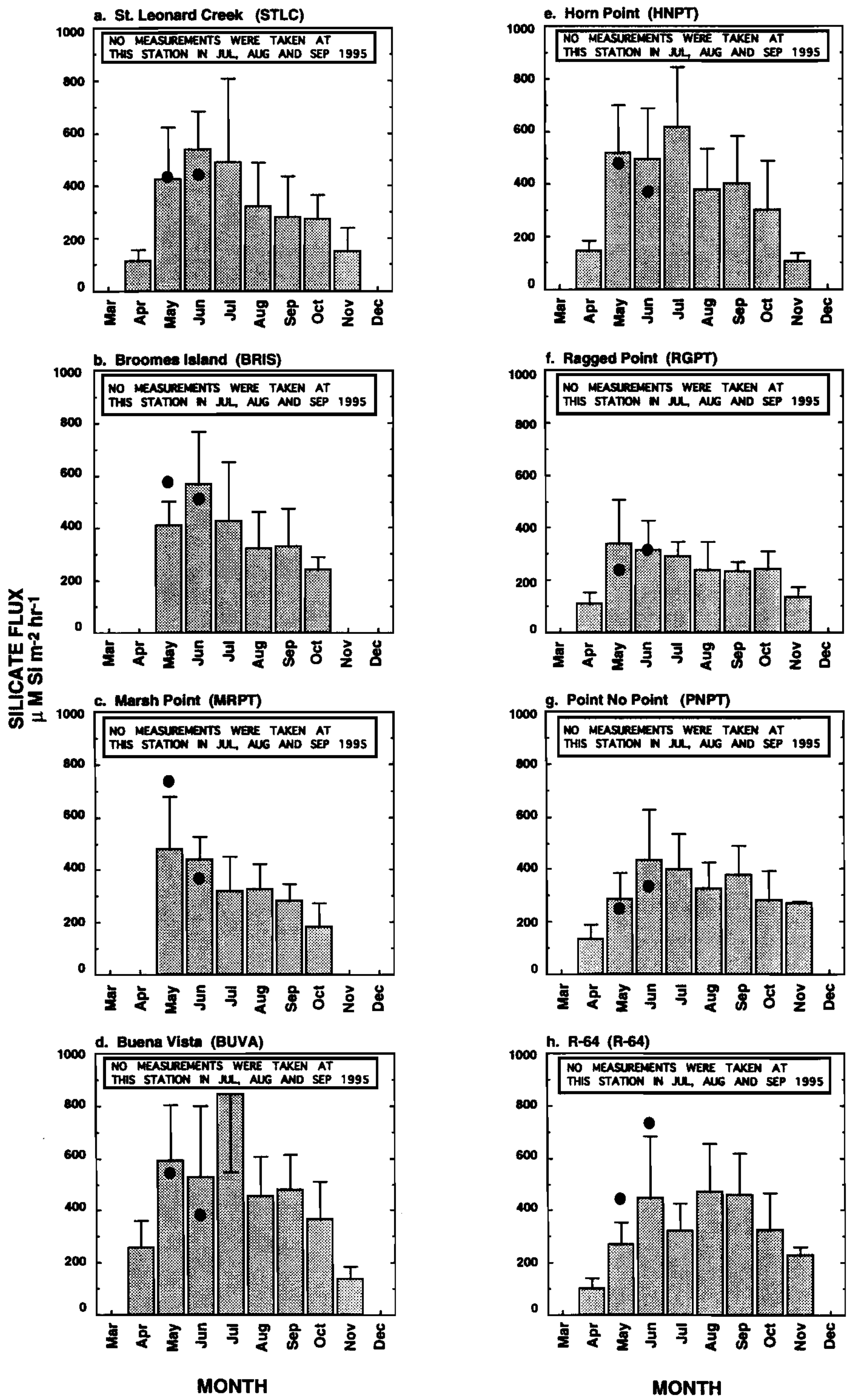

Figure 5-1.5. Mean monthly (April to November) silicate ($Si(OH)_4$) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay.

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

Average nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes for 1995, ranged from -97.72 μMN m^{-2} hr^{-1} in August at Buena Vista (BUVA) to 91.12 μMN m^{-2} hr^{-1} in May, 1995 at St. Leonard Creek (STLC) in the Patuxent River, from -87.76 μMN m^{-2} hr^{-1} in August, 1995 to 43.22 μMN m^{-2} hr^{-1} in June, 1995 in the Choptank River (Horn Point [HNPT]), from -97.90 μMN m^{-2} hr^{-1} in August, 1995 to 0 (zero) μMN m^{-2} hr^{-1} in July, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, average nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes at Point No Point (PNPT) ranged from -14.88 μMN m^{-2} hr^{-1} in July, 1995 (R-64) to 8.91 μMN m^{-2} hr^{-1} in May, 1995 and at R-64 from -145 μMN m^{-2} hr^{-1} in August, 1995 to 0 (zero) μMN m^{-2} hr^{-1} in July, 1995 (Figure 5-1.3.; Tables B6-47. - B6-52.). *Note that positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.*

In general nitrate flux do not constitute a large fraction of the nitrogen exchange between sediments and bottom waters. On occasion, large fluxes from water to sediments do occur. These are almost always associated with high levels of nitrate in the water column and it is probable that this nitrate nitrogen is subsequently denitrified (converted to N_2) after diffusing into surface sediments. However, even small nitrate fluxes from sediments to overlying waters provide a useful indication of sediment constitutions. Specifically, production and release of nitrate from sediments is a strong indication that sediment nitrification is occurring. This process requires at least low levels of dissolved oxygen and is hence an indication that surface sediments have been in contact with oxygenated waters. During 1995, stations in the Patuxent River (with the exception of one measurement) exhibited relatively high rates of sediment nitrate release or much lower rates of nitrogen uptake. In fact, at the St. Leonard Creek (STLC) station sediments released nitrate through the entire monitoring period, a pattern never before observed. A similar pattern was observed in the lower Potomac River (Ragged Point [RGPT]) and lower Choptank River (Horn Point [HNPT]) stations except during August, 1995 when dissolved oxygen conditions were poor. These are the types of nitrate fluxes to be expected under reduced nutrient load conditions (as was the case in 1995) both because these conditions favor improved dissolved oxygen conditions in deep waters and sediments and lower conditions of nitrate in overlying waters. Fluxes of nitrate from sediments to waters appear to serve quite well as an indicator of improved sediment quality.

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

Average monthly dissolved inorganic phosphorus (DIP) fluxes in 1995 ranged from 1.89 μMP m^{-2} hr^{-1} in July, 1995 at Broomes Island (BRIS) to 20.93 μMP m^{-2} hr^{-1} in September, 1995 at Marsh Point (MRPT) in the Patuxent River, from 0 (zero) μMP m^{-2} hr^{-1} in July, 1995 to 18.634 μMP m^{-2} hr^{-1} in August, 1995 in the Choptank River (Horn Point [HNPT]), from -0.24 μMP m^{-2} hr^{-1} in May, 1995 to 65.93 μMP m^{-2} hr^{-1} in July, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, Average monthly dissolved inorganic phosphorus (DIP) fluxes ranged from 0.90 μMP m^{-2} hr^{-1} in May, 1995 to 1.32 in June, 1995 at Point No Point (PNPT) and at R-64 from 26.29 μMP m^{-2} hr^{-1} in May, 1995 to 73.23 μMP m^{-2} hr^{-1} in July, 1995 (Figure 5-1.4.; Tables B6-47. - B6-52.).

Dissolved inorganic phosphorus (PO_4^-) fluxes in 1995 were the most outstanding feature of the SONE program, especially in the Patuxent River. We would predict low phosphorus fluxes during a low flow year because of both low loading rates and more oxidized sediments conditions which tend to reduce phosphorus release from sediments. However, during 1995 fluxes at Patuxent River stations were reduced beyond expectation. Rates at Broomes Island (BRIS) were half those of the long term mean and fluxes were almost as reduced at other stations. Except for the low dissolved oxygen period in the Choptank River during August, 1995 phosphorus fluxes there were also reduced relative to the long term mean. It may be premature to conclude that reduced phosphorus inputs from point and diffuse sources is the cause of the pattern observed in the Patuxent River but the pattern observed during 1995 is what we would expect. Alternatively, the low release rates may have resulted because bottom waters were reasonably well oxidized during 1995 and these conditions reduced phosphorus fluxes. However, the fluxes observed during 1995 were lower than those observed during other low flow years.

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

Average monthly silicate fluxes were only measured in May and June, 1995. Average monthly flux values ranged from 376 μM Si m^{-2} hr^{-1} in June, 1995 at Marsh Point (MRPT) to 733 μM Si m^{-2} hr^{-1} in May, 1995 at Marsh Point (MRPT) in the Patuxent River, from 362 μM Si m^{-2} hr^{-1} in June, 1995 to 495 μM Si m^{-2} hr^{-1} in May, 1995 in the Choptank River (Horn Point [HNPT]), from 250 μM Si m^{-2} hr^{-1} in May, 1995 to 316 μM Si m^{-2} hr^{-1} in June, 1995 in the Potomac River (Ragged Point [RGPT]) and from 264 μM Si m^{-2} hr^{-1} in May, 1995 to 328 μM Si m^{-2} hr^{-1} in June, 1995 in the mainstem bay at Point No Point (PNPT) and from 434 μM Si m^{-2} hr^{-1} in May, 1995 to 715 μM Si m^{-2} hr^{-1} in June, 1995 at R-64 (Figure 5-1.5.; Tables B6-47. - B6-52.).

Silicate fluxes in May and June, 1995 generally followed temporal trends exhibited in previous years. The 1995 data collected in May and June were similar to the long term average at most stations.

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 and in more recent reports a series of regression analyses were presented (Boynton *et al.*, 1994). To date a number of significant correlations have been found between specific sediment-water fluxes (*e.g.*, inorganic dissolved phosphorus [PO_4^-] fluxes) and environmental variables (*e.g.*, bottom water dissolved oxygen levels, or sediment characteristics). The predictive power of these relationships (r^2 values) has increased over the years as more observations have been added and as more has been learned about the mechanistic relationship between sediment fluxes and environmental conditions.

5.7.2 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 (mg m^{-2}) and Eh (mV) values (corrected to the hydrogen electrode) in sediments (Figures 5-2.4. and 5-2.5.) averaged over ten years (1985 - 1994; 5 years, 1990 - 1994, for sediment chlorophyll-a and sediment particulate nutrients). The data from 1995 are superimposed as bold dots.

5.7.2.1 Temperature

Bottom water temperature conditions in the Patuxent River during 1995 ranged from 17.9 C at Broomes Island (BRIS) in May, 1995 to 29.0 at Buena Vista BUVA) in July and August, 1995. In the Choptank River bottom water temperatures at Horn Point (HNPT) ranged from 18.6 C in May, 1995 to 27.2 C in July, 1995. In the Potomac River bottom water temperatures at Ragged Point (RGPT) ranged from 16.4 C in May, 1995 to 27.6 C in August, 1995. In the mainstem of the bay bottom water temperature conditions ranged from 15.8 C in May, 1995 to 21.3 C in June, 1995 at Point No Point (PNPT) and at R-64 from 15.2 C to 26.5 C in August, 1995 (Figure 5-2.1.; Tables B1-47. - B1-52.).

Temperature conditions followed the pattern observed in previous years but were slightly higher at most SONE stations.

5.7.2.2 Salinity

Bottom water salinity conditions during 1995 ranged from 10.3 ppt in May, 1995 at Buena Vista (BUVA) to 16.7 ppt in September, 1995 at Broomes Island (BRIS) in the Patuxent River, from 12.7 ppt in May, 1995 to 17.1 ppt in August, 1995 at Horn Point [HNPT] in the Choptank River, from 14.4 ppt in May, 1995 to 19.8 ppt in September, 1995 at Ragged Point (RGPT) in the Potomac River. In the mainstem bay salinity ranged from 19.1 ppt in June, 1995 to 20.8 ppt in May, 1995 at Point No Point (PNPT) and from 19.1 ppt in May, 1995 to 24.7 ppt in August, 1995 at R-64 (Figure 5-2.2.; Tables B1-47. - B1-52.).

The influence of the low flow year experienced in 1995 was reflected in salinity conditions which are slightly higher than normal. The one particularly large event recorded in August, 1995 in the lower Choptank River (Horn Point[HNPT]) indicates the intrusion of saltier bay water into the tributary. This is further born out by the correspondingly low value for bottom water dissolved oxygen for the same station in August, 1995. While such intrusions are seldom observed in SONE monitoring (because of the timing of the sampling, monthly sampling frequency) they may be more common and could be well documented using high frequency measurements (hourly) at selected locations. As indicated earlier in this report (Sections 5-4 and 5-5) rapid changes in dissolved oxygen conditions can have dramatic effects on sediment-water nutrient processes.

5.7.2.3 Dissolved Oxygen

Bottom water dissolved oxygen conditions during 1995 ranged from 0.94 mg l^{-1} in July, 1995 at Marsh Point (MRPT) to 8.53 mg l^{-1} in May, 1995 at St. Leonard Creek (STLC) in the Patuxent River, from 0.71 mg l^{-1} in June, 1995 to 9.64 mg l^{-1} in May, 1995 at Horn Point(HNPT) in the Choptank River, from 0.19 mg l^{-1} in September, 1995 to 7.68 mg l^{-1} in May, 1995 at Ragged Point (RGPT) in the Potomac River. In the mainstem bay, bottom water dissolved oxygen conditions ranged from 5.60 mg l^{-1} in September, 1995 to 7.99 mg l^{-1} in May, 1995 at Point No Point (PNPT) and at R-64 from 0.05 mg l^{-1} in September, 1995 to 7.26 mg l^{-1} in May, 1995 (Figure 5-2.3.; Tables B1-47. - B1-52.).

During 1995 river flows to three portions of the Maryland bay monitored in the Chesapeake Bay Program were lower than the long term eighteen year average (Figure 4-1.1.). The conceptual model used to guide the Ecosystem Processes Component (EPC) Program indicates that nutrient loading (associated with river flow) stimulates phytoplankton production which leads to deposition of organic matter to deep waters and sediments. As this material decomposes, oxygen is consumed and nutrients are released from sediments,

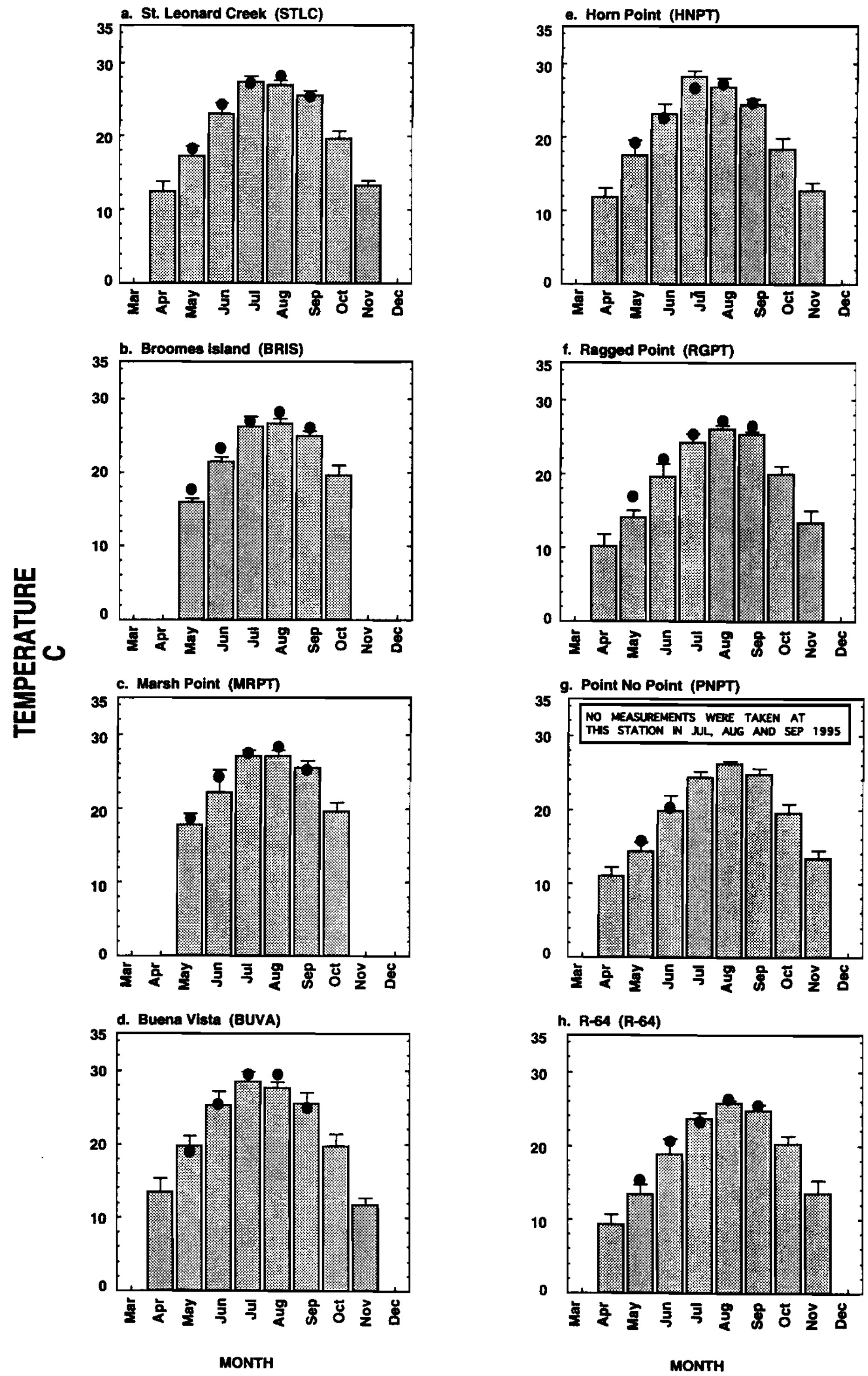

Figure 5-2.1 Monthly (April to November) bottom water temperature measurements at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1995. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

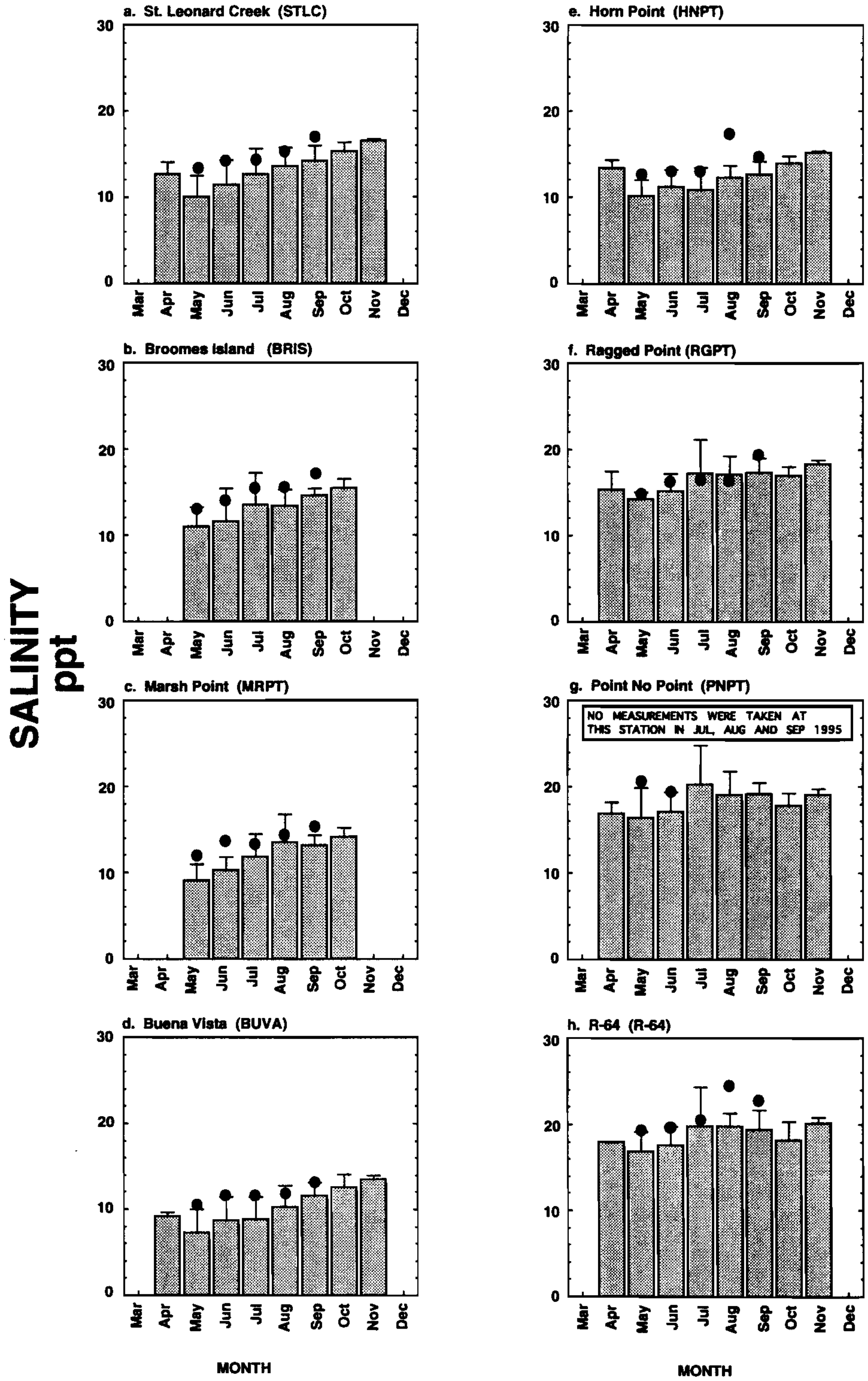

Figure 5-2.2 Monthly (April to November) bottom water salinity at eight SONE stations located in the Maryland portion of Chesapeake Bay.

Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1995. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

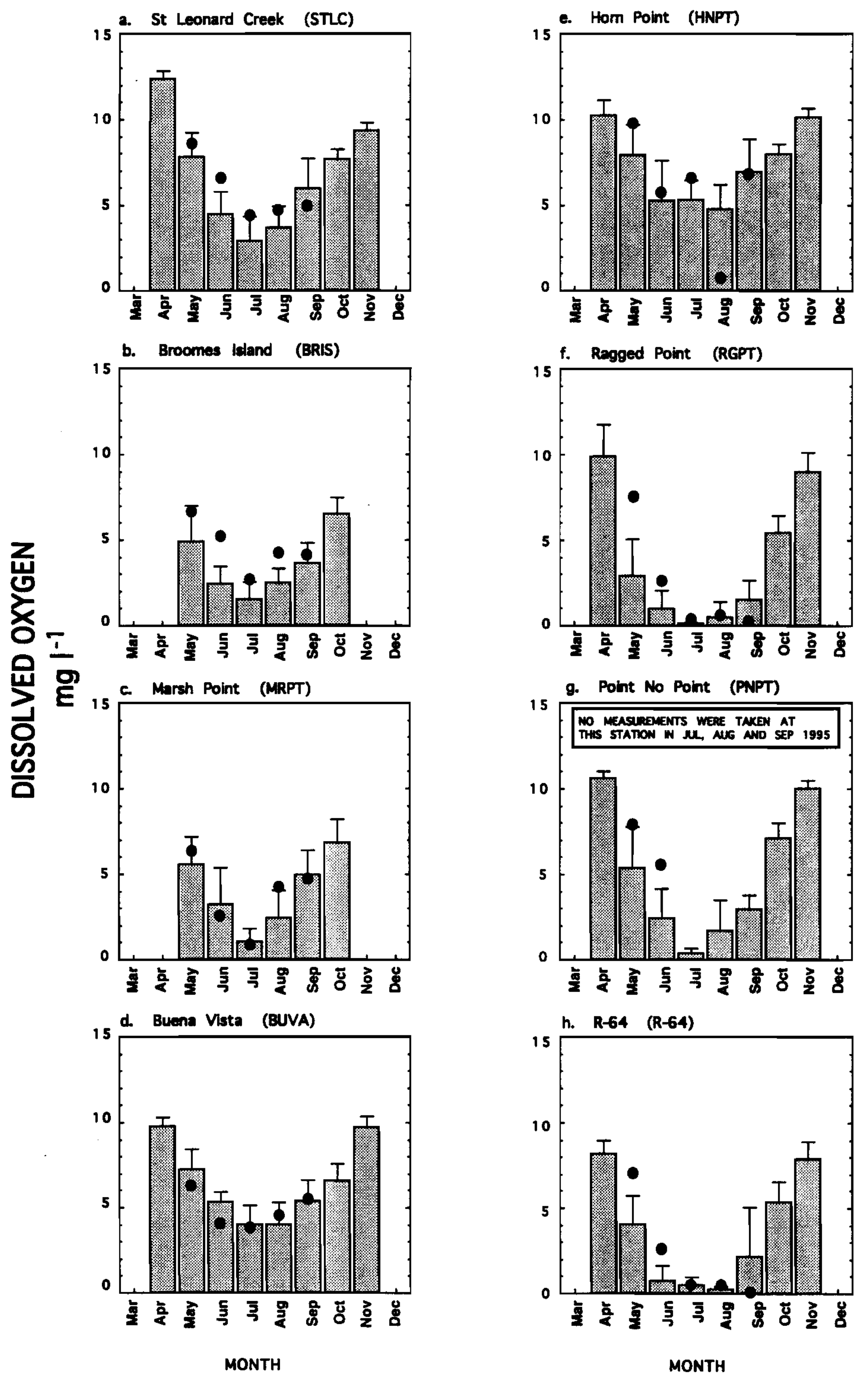

Figure 5-2.3 Monthly (April to November) bottom water dissolved oxygen (DO) concentrations at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1995. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

stimulating further phytoplanktonic production of organic matter and continued low dissolved oxygen conditions. In addition high river flows increased the degree of stratification resulting in lower aeration rates of bottom water. These events are ultimately tied to nutrient loading rates and hence reduction in loading rates is of key importance in improving water and sediment quality conditions.

This scenario is the basis for testing the hypothesis that during 1995 dissolved oxygen (DO) concentrations in deep waters were expected to be above average. In the Patuxent River dissolved oxygen (DO) concentrations were higher than average or close to average in 1995. Oxygen concentrations at St. Leonard Creek (STLC) were well above average for four months (May through August) and even more importantly dissolved oxygen concentrations at Broomes Island (BRIS), which is a deeper station more frequently exhibiting hypoxic conditions, dissolved oxygen conditions were improved throughout the summer period. Even at the station at Marsh Point (MRPT), which is more proximal; to nutrient sources, oxygen conditions were reasonable for all months with the exception of July. At the mainstem bay stations and in the lower Potomac River dissolved oxygen (DO) conditions in bottom waters were markedly above normal through June but eventually reached very low levels from July through September, indicating that sufficient organic matter was available, even under low flow conditions, to exhaust oxygen supplies. The exceptionally low dissolved condition in the lower Choptank River (Horn Point [HNPT]) is correlated with a high salinity value measured in the same month at the same station, and represents a single event where saltier water (presumably with low dissolved oxygen content) from the bay intruded into the tributary.

5.7.2.4 Total Chlorophyll-a

Surficial sediment total chlorophyll-a mass during 1995 ranged from 18.0 mg m^{-2} in August, 1995 at Buena Vista (BUVA) to 40.3 mg m^{-2} in September, 1995 at St. Leonard Creek (STLC) in the Patuxent River, from 16.9 mg m^{-2} in July, 1995 to 30.1 mg m^{-2} in September, 1995 in the Choptank River (Horn Point [HNPT]), from 26.7 mg m^{-2} in September, 1995 to 38.4 mg m^{-2} in May, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, surficial sediment total chlorophyll-a mass ranged from 24.3 mg m^{-2} in June, 1995 to 54.6 mg m^{-2} mg m^{-2} in May, 1995 and at R-64 from 29.1 mg m^{-2} in June, 1995 to 44.5 mg m^{-2} in July, 1995 (Figure 5-2.4.; Tables B3-47. - B3-52.).

The main characteristics of sediment chlorophyll-a mass is that almost all the values measured were well below long term averages at all eight stations. This is consistent with the conceptual model wherein low nutrient loads associated with a low flow year do not encourage the creation of a large spring bloom so that less organic material (*e.g.* phytoplanktonic debris) is deposited at the sediment surface where it is available for summer period decomposition.

5.7.2.5 Sediment Eh

Sediment Eh (corrected to the hydrogen electrode) values measured at the sediment-water interface (sediment depth = 0 cm) at all sediment oxygen and nutrient exchanges (SONE) stations are shown as a series of bar graphs in Figure 5-2.5. The 1995 values ranged from 106 mV in August, 1995 at Marsh Point (MRPT) to 410 mV in May, 1995 at St. Leonard Creek (STLC) in the Patuxent River, from 203 mV in August, 1995 to 353 mV in September, 1995 in the Choptank River (Horn Point [HNPT]), from 44 mV in August, 1995 to 322 mV in June, 1995 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, sediment Eh values ranged from 170 mV in May, 1995 to 320 mV in June, 1995 at Point

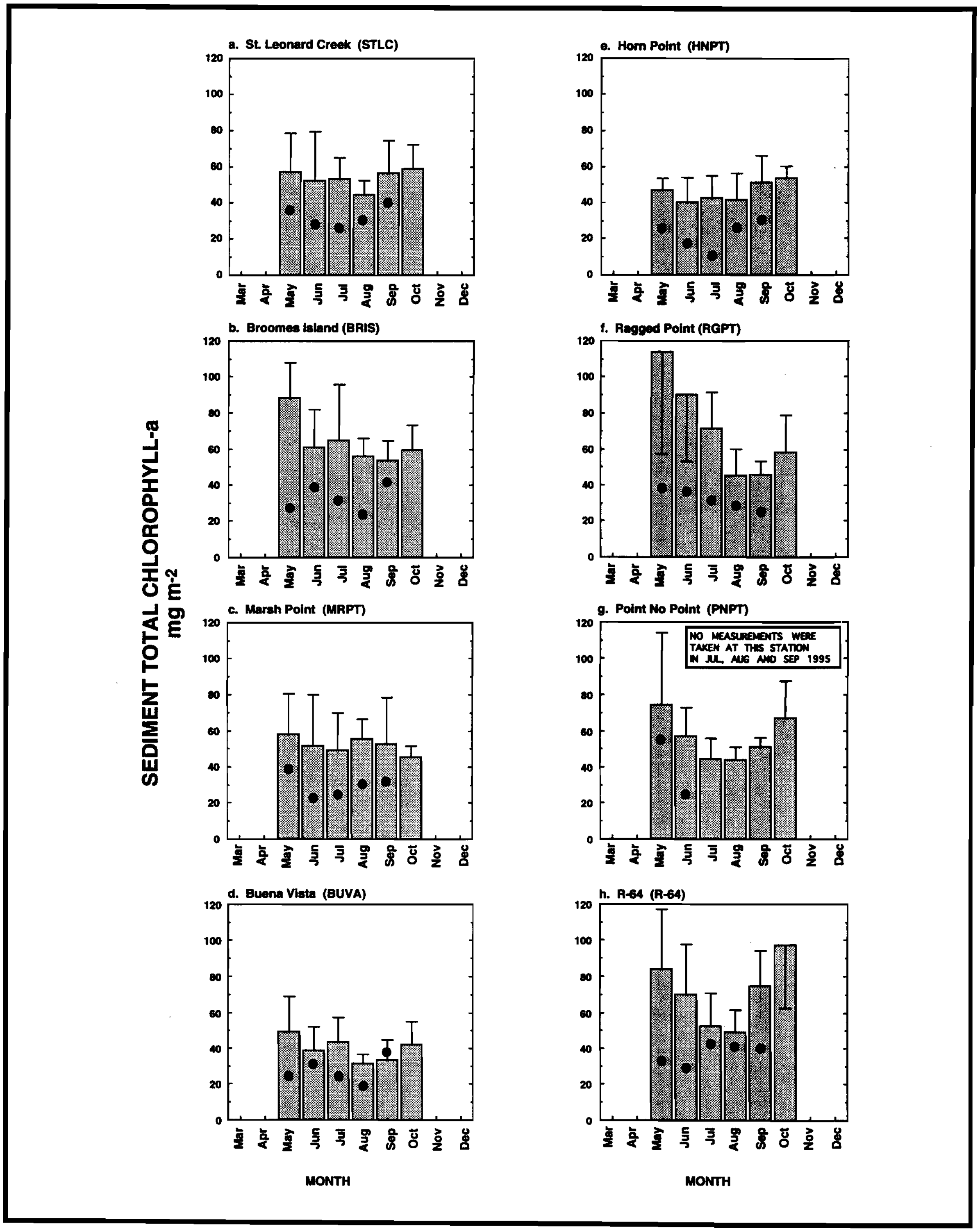

Figure 5-2.4 Monthly (April to November) sediment total chlorophyll-a concentrations at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1995. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

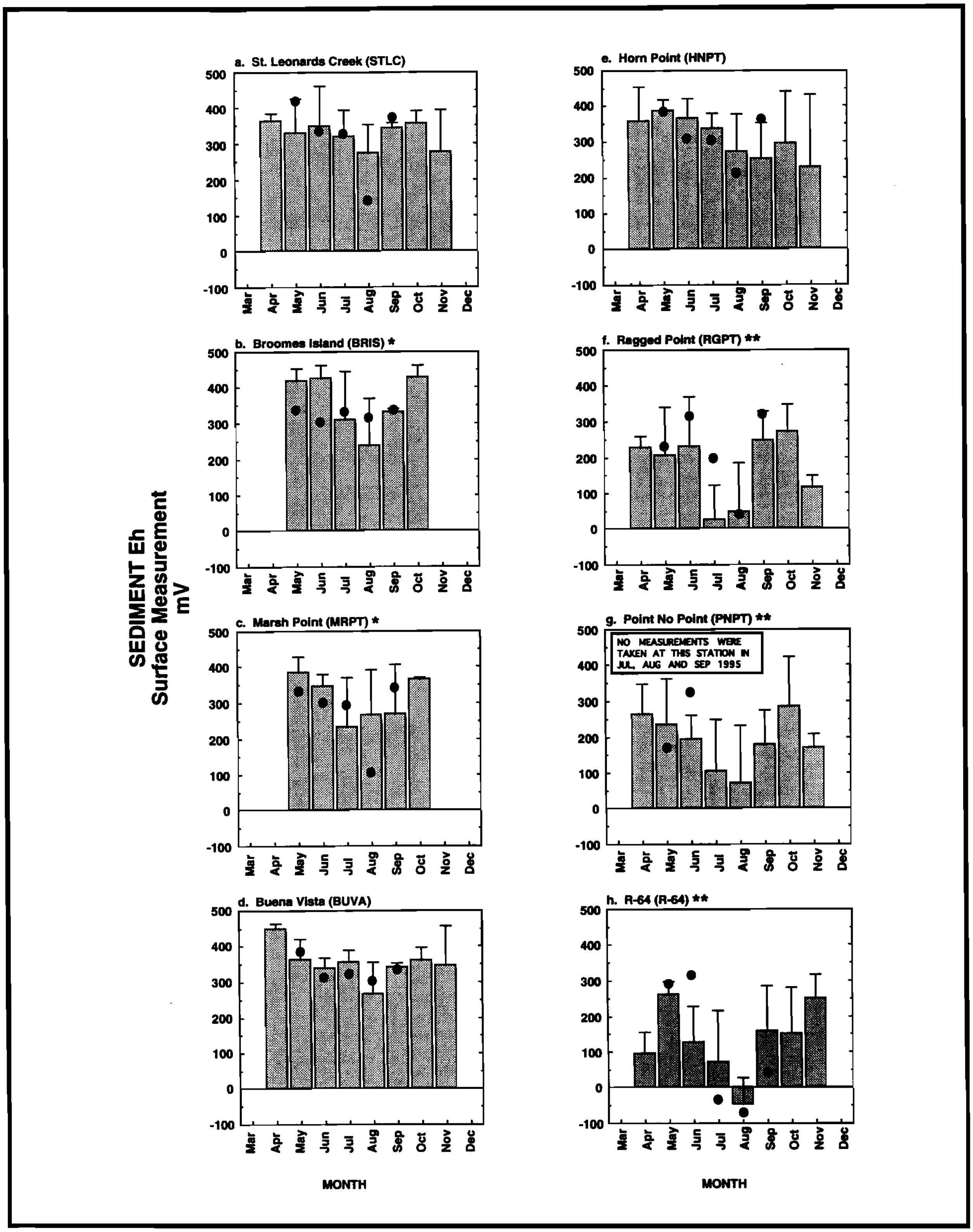

Figure 5-2.5 Monthly (April to November) surficial (sediment-water interface, sediment depth = 0 cm) sediment Eh values (corrected for the hydrogen electrode) at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using all data available for a specific month at each station. In general there was one value available for each month for 1985 through 1995. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1994. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

No Point (PNPT) and from -71 mV in August, 1995 to 310 in June, 1995 at R-64 (Figure 5-2.5.; Tables B3-47. - B3-52.).

The 1995 values were slightly lower than those of previous years although values recorded in June, 1995 at five of the stations were higher than average. In the Patuxent River values followed the temporal trend except for two depressed values in August, 1995 at St. Leonard Creek (STLC) and Marsh Point (MRPT). 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. More positive Eh values are a sign of improving sediment quality.

5.8.2.6 Sediment Characteristics

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

(1) Particulate carbon (PC) ranged from 2.46 percent dry weight in August, 1995 at Buena Vista (BUVA) to 3.77 percent dry weight in June, 19954 at St. Leonard Creek (STLC), from 1.60 percent dry weight in August, 1995 to 1.98 percent dry weight in September, 1995 in the Choptank River (Horn Point, [HNPT]), from 3.32 percent dry weight in August, 1995 to 3.59 percent dry weight in July, 1995 in the Potomac River (Ragged Point [RGPT]) and in the mainstem bay at Point No Point (PNPT) from 3.461 percent dry weight in May, 1995 to 3.73 percent dry weight in June, 1994 and at R-64 from 3.03 percent dry weight in May, 1995 to 3.65 in August, 1995 (Figure 5-2.6.; Tables B3-47. and B3-52.).

(2) Particulate nitrogen (PN) ranged from 0.31 percent dry weight in August, 1995 at Buena Vista (BUVA) to 0.46 percent dry weight at both Marsh Point (MRPT) in May, 1995 and Broomes Island (BRIS) in August, 1995, from 0.22 percent dry weight in August, 1995 to 0.27 percent dry weight in September, 1995 in the Choptank River (Horn Point, [HNPT]), from 0.43 percent dry weight in August, 1995 to 0.49 percent dry weight in July, 1995 in the Potomac River (Ragged Point [RGPT]) and in the mainstem bay at Point No Point (PNPT) from 0.43 percent dry weight in June, 1995 to 0.46 percent dry weight in May, 1995 and at R-64 from 0.40 percent dry weight in May, 1995 to 0.49 percent dry weight in August, 1995 (Figure 5-2.7.; Tables B3-47. and B3-52.).

(3) Particulate phosphorus (PP) ranged from 0.7015 percent dry weight in July, 1995 at St. Leonard Creek (STLC) to 0.17 percent dry weight in June, 1995 at St. Leonard Creek (STLC), from 0.04 percent dry weight in May, July and August, 1995 to 0,05 percent dry weight in June and September, 1995 in the Choptank River (Horn Point, [HNPT]), from 0.06 percent dry weight in August and September, 1995 to 0.09 percent dry weight in June, 1995 in the Potomac River (Ragged Point [RGPT]) and in the mainstem bay at Point No Point (PNPT) from 0.06 percent dry weight in June, 1995 to 0.07 percent dry weight in May, 1995 and at R-64 from 0.06 percent dry weight in July and August 1995 to 0.08 in June, 1995 (Figure 5-2.8.; Tables B3-47. and B3-52.).

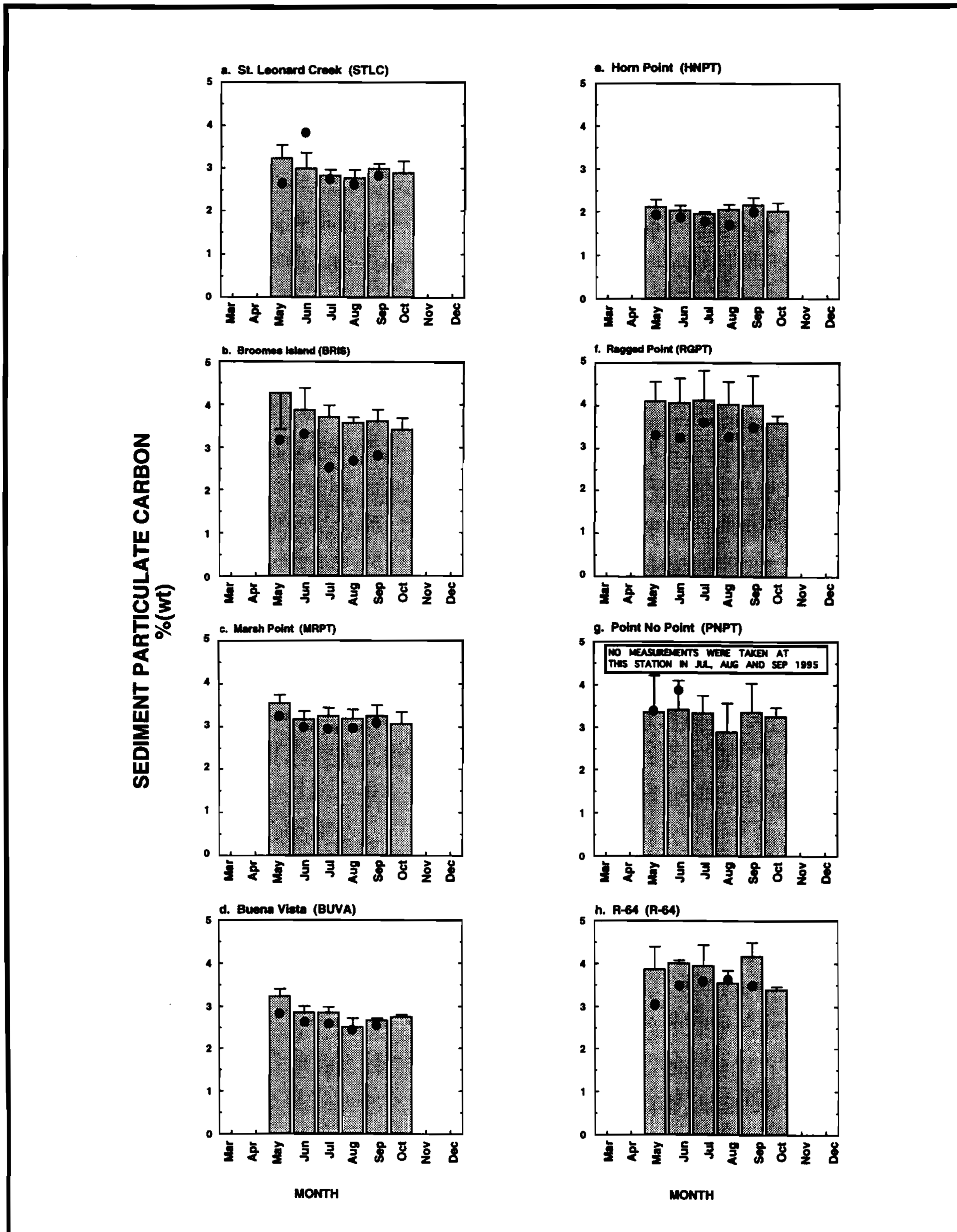

Figure 5-2.6 Mean monthly (April to November) sediment particulate carbon (PC) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1994 for a specific month at each station during which period a standard method was used. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

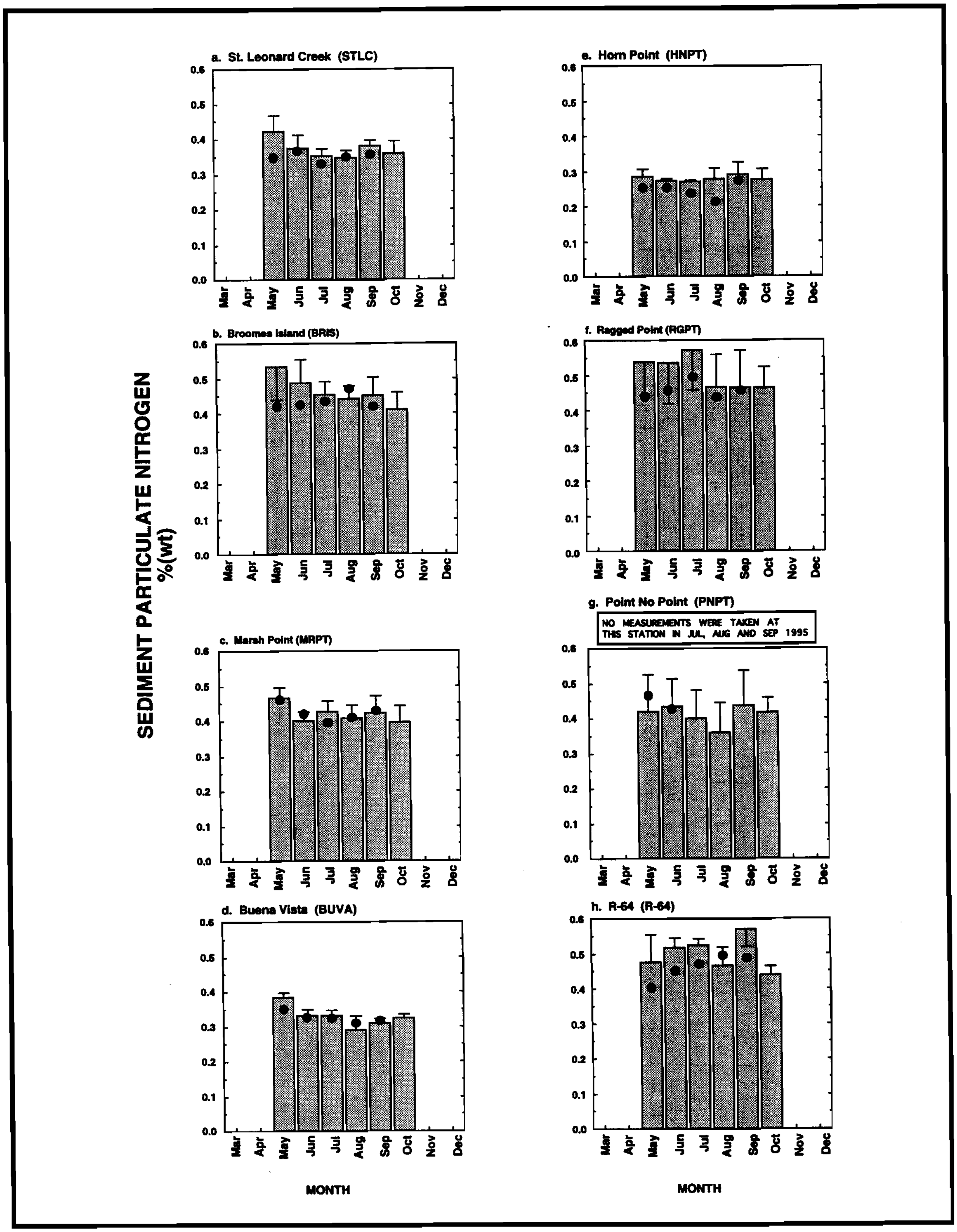

Figure 5-2.7 Mean monthly (April to November) sediment particulate nitrogen (PN) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1994 for a specific month at each station during which period a standard method was used. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

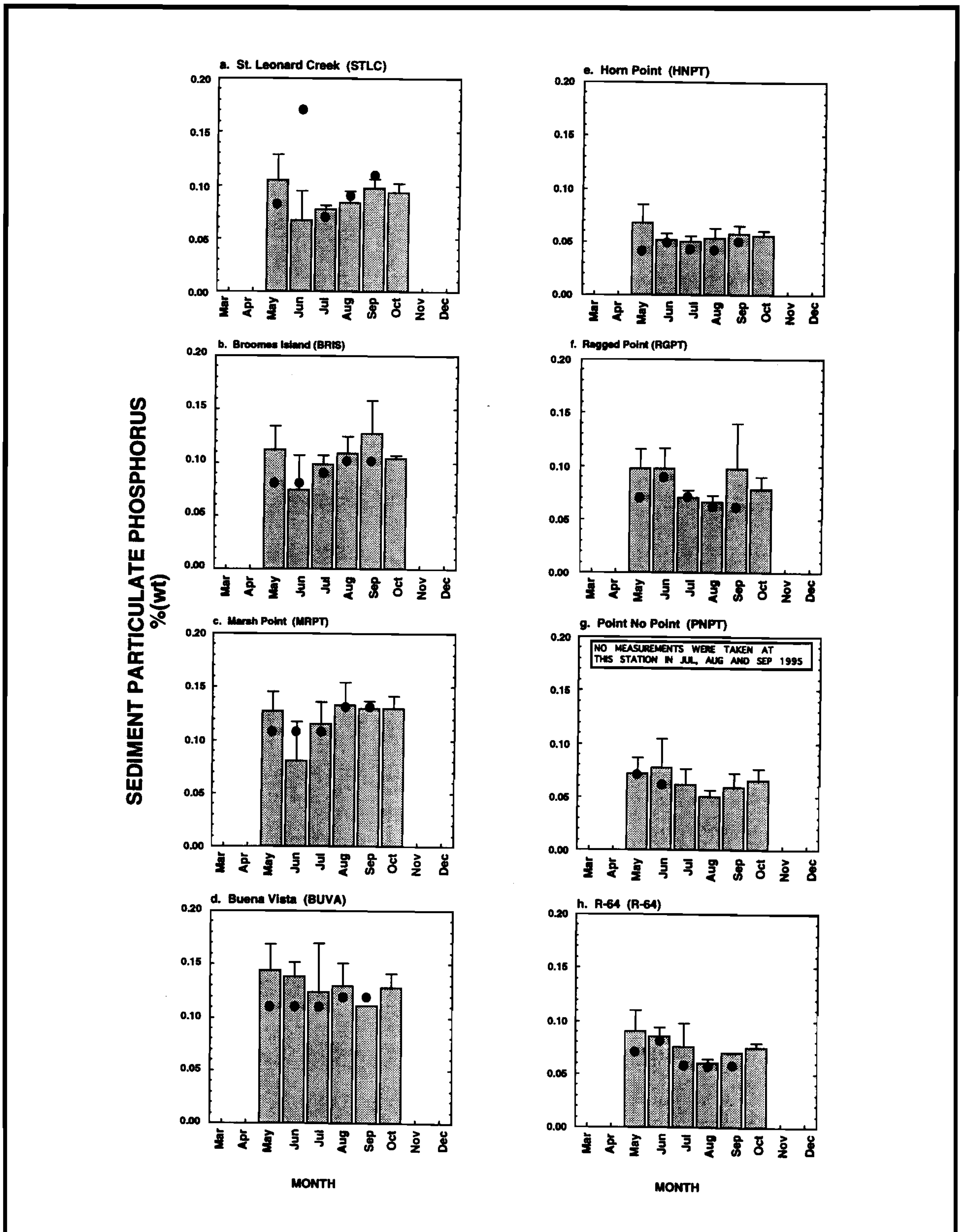

Figure 5-2.8 Mean monthly (April to November) sediment particulate phosphorus (PP) values at eight SONE stations located in the Maryland portion of Chesapeake Bay.
Monthly means and standard deviations were calculated using data for 1990 - 1994 for a specific month at each station during which period a standardized method was used. The bold dots indicate average monthly values for 1995. Station locations are shown in Figure 3-1.

6. MONITORING SEDIMENT METABOLISM UNDER ANOXIC AND OXIC CONDITIONS

6.1 Dissolved inorganic carbon (TCO_2) Flux Approach

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

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

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

Until recently this approach was the only way to obtain reasonable measurements of total sediment metabolism. However, new analytical technology has now made it possible to routinely measure total carbon dioxide (TCO_2) concentrations with great precision. The importance of this rests on the fact that carbon dioxide (CO_2) is the end product of both aerobic and anaerobic respiration (Boynton *et al.*, 1994). Prior to the development of this analytical technology it was not possible to confidently measure relatively small changes in carbon dioxide (CO_2) concentration in seawater against the huge background concentrations which are present.

Measurements of dissolved inorganic carbon (TCO_2) flux were made using the routine intact sediment core approach of the sediment oxygen and nutrient exchanges (SONE) program at six sediment SONE stations during 1995. The results are shown as a series of bar graphs in Figure 6-1.1. Seasonally averaged rates ranged from 2234 μM CO_2 m^{-2} hr^{-1} in the lower Patuxent River (St. Leonard Creek [STLC]) to 3358 μM CO_2 m^{-2} hr^{-1} at the up river station in the Patuxent (Marsh Point [MRPT]). Rates at other sediment oxygen nutrient exchanges (SONE) stations were intermediate between these values. There was not a strong seasonal signal generally associated with these data; rates at the Choptank

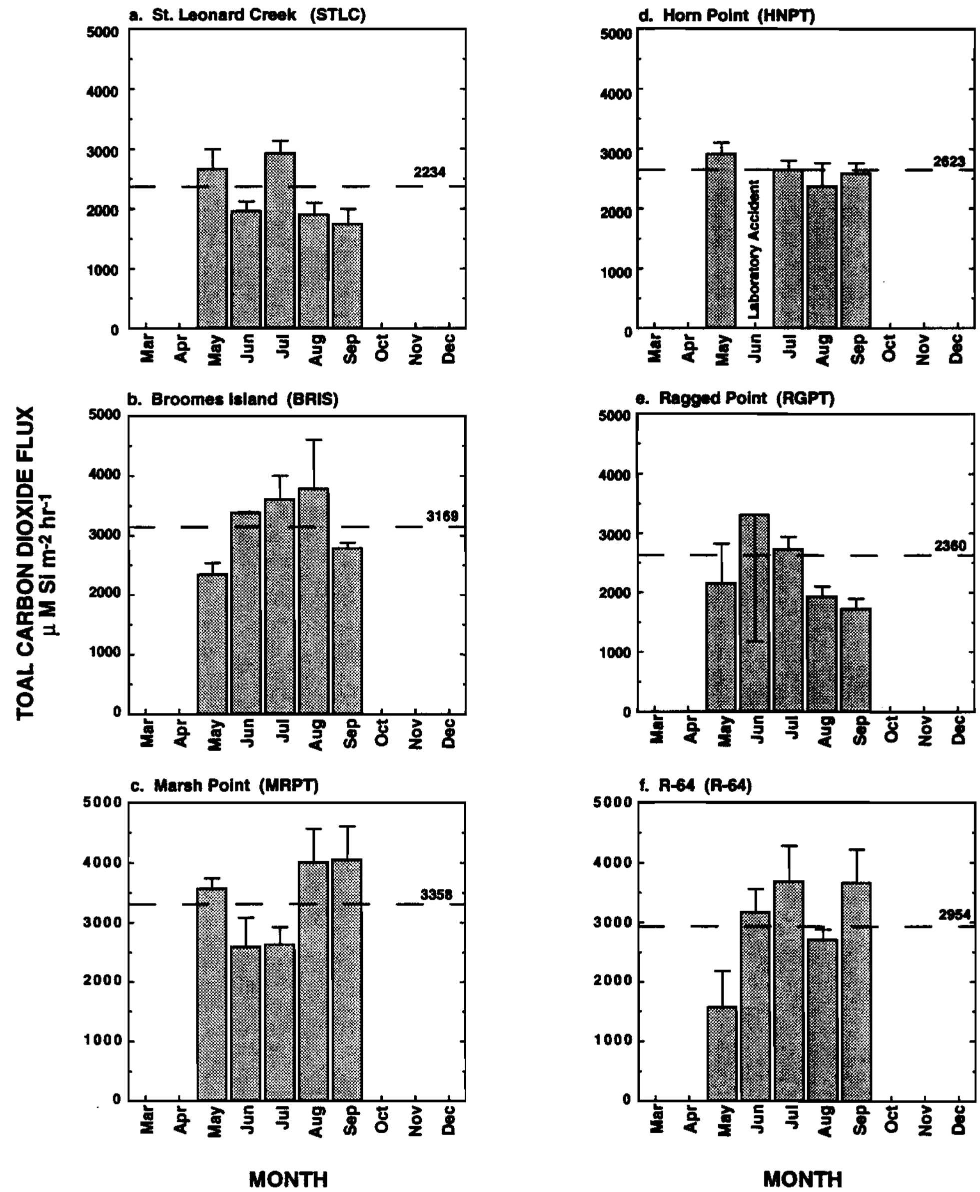

Figure 6-1. Mean monthly (± std. error) dissolved inorganic carbon (TCO_2) flux rates measured in 1995 for the months May through September at six SONE stations located in the Maryland portion of Chesapeake Bay.

River station (Horn Point [HNPT]) were relatively constant between May and September as were rates in the lower (St. Leonard Creek [STLC]) and upper Patuxent Rivers (Marsh Point [MRPT]). Rates at remaining stations exhibited some degree of seasonality with lower rates in spring and fall and highest rates in the June through August period. Further measurements will probably clarify patterns of seasonality.

These data can also be converted to organic carbon equivalents which provide a direct comparison of sediment metabolism with such things as primary production rates, deposition rates and water column and sediment POC stocks. To convert TCO_2 fluxes to units commonly used in these other measurements the TCO_2 fluxes are multiplied by 12 (to convert from molar to weight units), then multiplied by 24 (to convert hourly values to diel values) and the divided by 1,000,000 (to convert micrograms values to gram values). Conversion of the range of values given above to organic carbon equivalents yields values ranging from 0.6 g C m^{-2} day^{-1} to 1 g C m^{-2} day^{-1}. These rates constitute a large fraction (30 to 100 %) of primary production generally associated with the water column of these areas of the bay during summer periods. These dissolved inorganic carbon (TCO_2) values clearly indicate that benthic-pelagic coupling in the bay is a strong feature and as such will have significant impacts on sediment and water quality.

These data also indicate several points relevant to the Ecosystem Processes Component (ECP) program. First, rates are generally proportional to nutrient and organic matter loading rates (Figure 6-2.). For example, rates in the inner portion of the Patapsco River averaged almost 10 mM m^{-2} hr^{-1} during summer of 1994 (equivalent to about 3 g C m^{-2} day^{-1}). Lower rates were observed in the outer portions of the harbor and Back River as expected because loading rates are somewhat lower. Similarly, rates in the upper Potomac were higher than those farther downstream in the Potomac. Rates were similar in the Patuxent and Choptank Rivers but far lower than in the more enriched zones of the bay. It appears that CO_2 fluxes respond well to gradients of enrichment, as required of a monitoring tool.

Second, it appears that CO_2 fluxes provide reasonable estimates of sediment metabolism, even under anoxic conditions when sediment oxygen consumption (SOC) fluxes do not occur. At R-64 in the Maryland mainstem bay and at Ragged Point (RGPT) in the lower Potomac River sediment oxygen consumption (SOC) fluxes were near zero in July, 1995 while TCO_2 fluxes indicated moderate metabolic rates at these times amounting to about 1.0 g C m^{-2} day^{-1}. These rates are in the range estimated from budget calculations and represent a significant loss of organic matter (Kemp and Boynton, 1992). It should be noted that nutrient input conditions were low in 1995 in most areas of the bay. Measurement of dissolved inorganic carbon (TCO_2) fluxes have yet to be made at sediment oxygen and nutrient exchanges (SONE) stations under higher flow conditions. It is expected that higher values would be recorded under conditions of higher nutrient loading rates.

For monitoring purposes is useful to have good estimates of sediment total metabolism to gauge the effects of nutrient reductions on this important estuarine ecosystem component. It is recommended that dissolved inorganic carbon (TCO_2) fluxes be continued as a routine feature of the Ecosystem Processes Component (EPC) Program monitoring agenda.

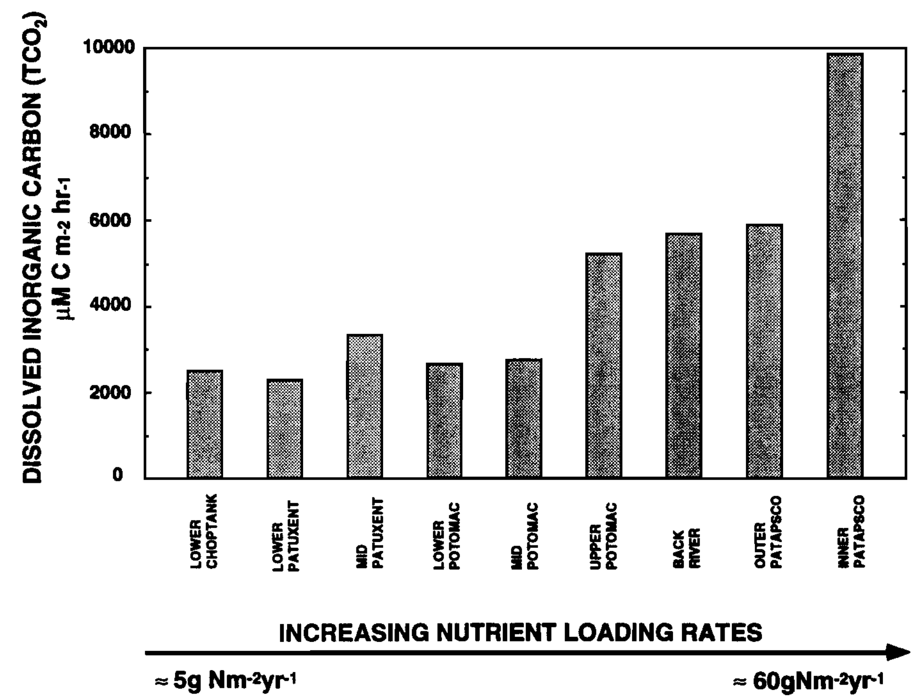

Figure 6-1.2. A bar graph showing a general relationship between dissolved inorganic carbon (TCO_2) flux and total nitrogen (TN) loading rates.
The values given at either extreme of the x-axis are from Boynton et al. (1995a). The remaining bars are arranged based on qualitative assessments of load. Refer to Boynton et al. (1995a) for information regarding station locations.

7. LOAD VERSUS PROCESS RELATIONSHIPS FOR THE PATUXENT RIVER ESTUARY

7.1 Background and Review

In the last few years there has been a growing literature which clearly indicates that nutrient loading rates (and/or freshwater inputs) are a very strong determinate of algal production, algal biomass, hypoxia in deep waters and sediment-water oxygen and nutrient exchanges in a variety of systems, including Chesapeake Bay.

One of the earliest such efforts was reported by Boynton *et al.* (1982a) regarding plankton production and nutrient loads, 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 DIN loading rates. In a previous report (Boynton *et al.*, 1995a) estimates of algal production from several areas of Chesapeake Bay were included and these fit the general relationship. 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 (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 indicted between 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. Finally, production rates from several Chesapeake Bay sites are particularly high indicating the importance of both the physically 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.*, 1988). 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-1970's 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 In a previous report (Boynton *et al.*, 1995a) a successful effort was initiated to produce a similar type of relationship for estuarine systems. An attempt was initially made to duplicate the Vollenweider 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. It was 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 biomass accumulation. Nitrogen was also used as the nutrient of interest and results improved. Additionally, sufficient data was obtained from the MERL eutrophication experiment (Nixon *et al.*, 1986) and portions of Tampa Bay (Johanson, *pers. comm.*) and these were added to the analysis. 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 this provides an opportunity to explore the robustness of this relationship and ultimately increases confidence in the conceptual model upon which it is based.

In this report this general line of synthesis is continued and data sets are explored sets for relationships between important external forcings and ecosystem responses. Specifically, this section focuses on an analysis of the influence of freshwater and nutrient loading rates on algal biomass levels, deep water hypoxia and sediment-water oxygen and nutrient exchanges in the Patuxent River estuary for the time period 1985-1995. The Patuxent River is a particularly good system to focus such an effort because the system has undergone significant nutrient management actions and the temporal and spatial data base is excellent.

7.2 Relationships of Algal Biomass and Hypoxia to Freshwater Inflow and Nutrient Loading Rates in the Patuxent River

One of the fundamental assumptions underlying the Chesapeake Bay nutrient reduction strategy is that nutrients (nitrogen, phosphorus) are indeed regulating some of the principal water quality characteristics and other ecosystem features of the bay system and that these features will respond to changes in nutrient loading rates. In this section, results of investigations of relationships between nutrient loads and freshwater inputs and algal biomass and hypoxia in the Patuxent River are presented.

In this analysis algal biomass data (chlorophyll-a) were assembled for the years 1985-1992 at all estuarine stations in the Patuxent River. A simple interpolator was used to generate volume weighted estimates of chlorophyll-a for each one mile segment of the estuary in the longitudinal direction and for one meter depth intervals in the vertical. Details of this extrapolation are given in Hagy (1996). These data were then grouped by region (*e.g.* upper estuary, transition zone, middle estuary and lower basin) and time weighted annual average chlorophyll-a concentrations were estimated for each region. These data were then regressed against various functions of river flow and nutrient loading rates.

A summary of the results of this analysis are given in Figure 7-1. In three of the four estuarine regions strong relationships emerged between flow or load and chlorophyll-a; however, not all were as expected. In the two lower regions of the estuary there were strong relationships between TN load and chlorophyll-a, a relationship which is of the type previously reported. This type of relationship suggests that algal stocks are proportional to TN loads and, if other factors do not change, that we should expect stocks to decline as loads decrease. However, results from the upper estuary (tidal freshwater zone) were not as expected; in this case algal biomass decreased as flow (well correlated with load in this case) increased. This somewhat counter intuitive finding results because in this sector of the estuary water residence times are very responsive to flow and are quite short (days), especially at high flow. In effect, the negative relationship between flow and algal biomass results because at high flow plankton are washed from the system at rates which exceed the growth rates, leading to smaller stocks. At low flow rates stocks increase because advective losses are smaller and because this zone of the river almost always has ample nutrients to support algal biomass accumulation. There were no obvious relationships between flow or load and plankton biomass in the transition (turbidity maximum) and perhaps this is not surprizing. In this region there may be simply too many time varying factors influencing biomass for any one of them to explain a substantial amount of interannual variability; in this zone nutrient concentrations are at times high (promoting plankton growth), turbidity

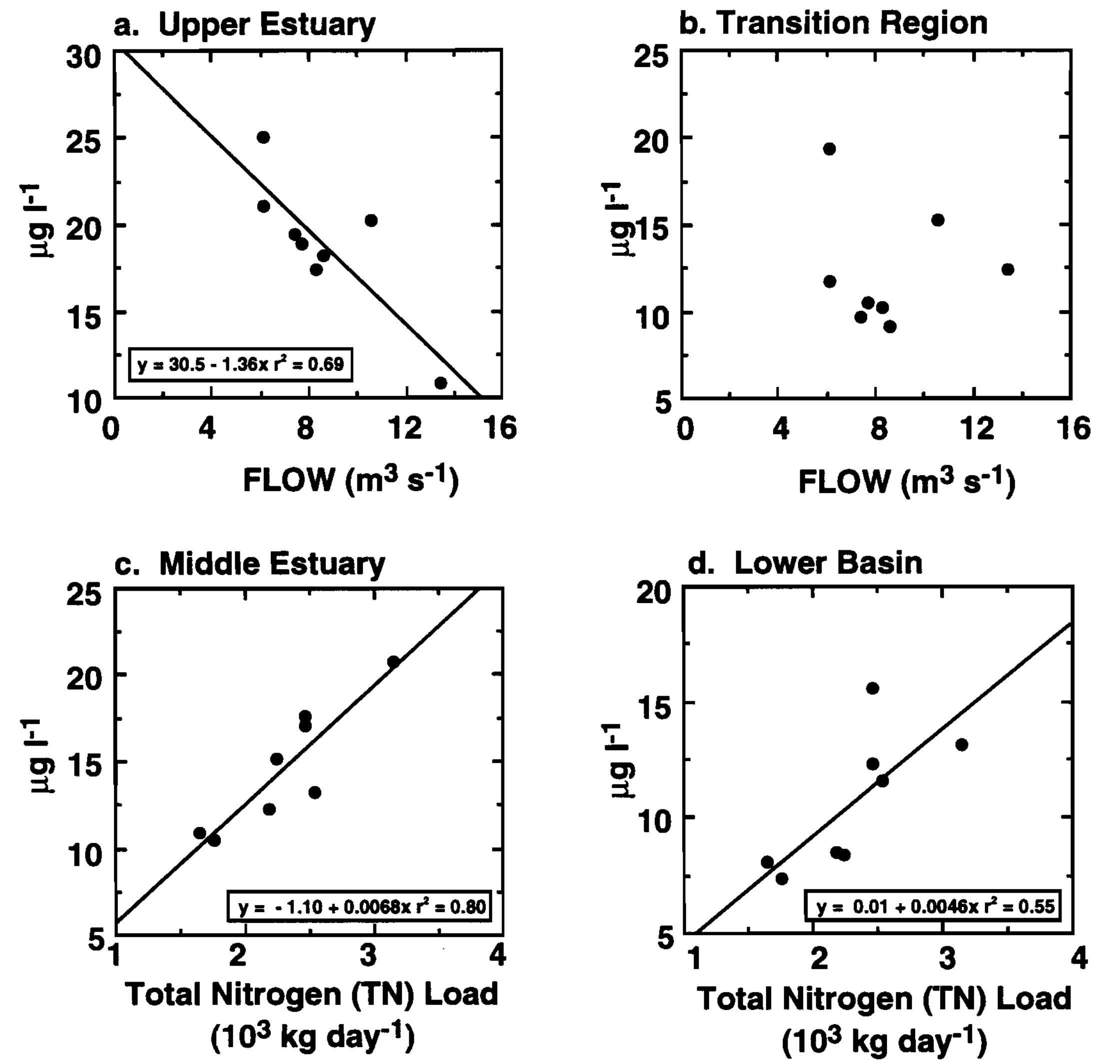

Figure 7-1. The upper panels show the relationships in the Patuxent River between annual mean fall line freshwater flow rate and annual mean surface (< 3 m) chlorophyll-a in the upper estuary (a.; 46 - 63 km from mouth) and transition regions (b.; 37 - 46 km) of the estuary.
The lower panels show the relationships between annual mean fall line total nitrogen (TN) loading and surface chlorophyll-a in the middle estuary (c.; 18 - 37 km) and lower basin (d.; 0 - 18 km).
The lines indicated are the least squares regression lines. No significant regression line can be drawn for the upper right panel, while all other regressions are significant ($p < 0.05$).
Figure is from Hagy (1996).

very high at times (limiting plankton growth) and residence times ranging from very short (depleting biomass) to relatively long (promoting biomass accumulation). Among the issues mentioned above, this analysis also clearly suggests that the relative importance of factors controlling plankton biomass vary spatially. In considering water quality conditions and response of those conditions to management actions, location must be an important part of the story.

A second major water quality factor of interest is the status of dissolved oxygen (DO) in deeper waters of the bay mainstem and tributary rivers. As indicated above, this analysis also focused on the Patuxent River, using the entire estuarine system as a study area and data collected between 1985 and 1992. Again, a simple interpolator was used to generate volume weighted estimates of DO for each one mile segment of the estuary in the longitudinal direction and for one meter depth intervals in the vertical. Details of this extrapolation are given in Hagy (1996). The volume of water in the river having dissolved oxygen (DO) concentrations less than 2 mg l^{-1} were computed for each monitoring cruise. The degree of hypoxia evident during each year is shown in Figure 7-2; integration of each annual curve yields an annual value with units of hypoxic volume-days. As indicated hypoxia was most prevalent in 1987, 1989 and 1990 and less prevalent in 1985, 1988 and 1992. If the full data set is considered, no temporal trends are evident; however, since 1989 there has been a steady decline in the magnitude of hypoxic volume-days. The conceptual model which we have used as a guide in the EPC program (Figure 2-1) suggests that as systems, such as the Patuxent River, become nutrient enriched, excessive organic matter production will lead to depleted dissolved oxygen (DO) conditions following oxidation of this material. However, biological respiration is generally not enough to deplete DO if the water column is well mixed because dissolved oxygen (DO) can diffuse from the atmosphere to the water at rates sufficient to maintain reasonable dissolved oxygen (DO) levels. However, if the water column is stratified, as it is during the warmer portion of the year in the Patuxent River, atmospheric reaeration of deep waters is much restricted and low DO conditions can result. This line of reasoning suggested that interannual variability in hypoxic volume-days might best be resolved by plotting this variable against freshwater inputs rather than nutrient loading rate. In the former, both the effects of stratification and nutrient enrichment are captured while nutrient loads by themselves do not include the stratification effect. Results are shown in Figure 7-3. for two cases; the first using inflow calculated on the basis of water year (October-September) and the second using inflows calculated just for the summer period (June-August). While both yield strong relationships, the water year analysis is considerably more predictive and suggests that inflow conditions prior to the summer period of hypoxia also plays a role. Several additional point should also be made. First, the data from 1987 diverge strongly from the general shape of the relationship. It appears that this resulted from an intrusion of water having very substantial oxygen demand into the lower Patuxent River from the mainstem bay during the summer period of 1987. This sort of event, which has been observed before in the Patuxent and Choptank Rivers (Sanford and Boicourt, 1990) reminds us that these systems are not disconnected one from the other. Said a different way, it is possible to improve water quality in one system but that improvement will be less persistent if water quality remains degraded in adjoining systems. Finally, as nutrient concentrations in freshwater inputs decrease we would expect that the magnitude of hypoxic volume-days to would also decrease; in effect, data points would begin to fall below the lines indicated in Figure 7-3. The reason for this is that lower nutrient loads would limit the amount of organic material would could be oxidized in deep waters and thereby lessen dissolved oxygen (DO) demand.

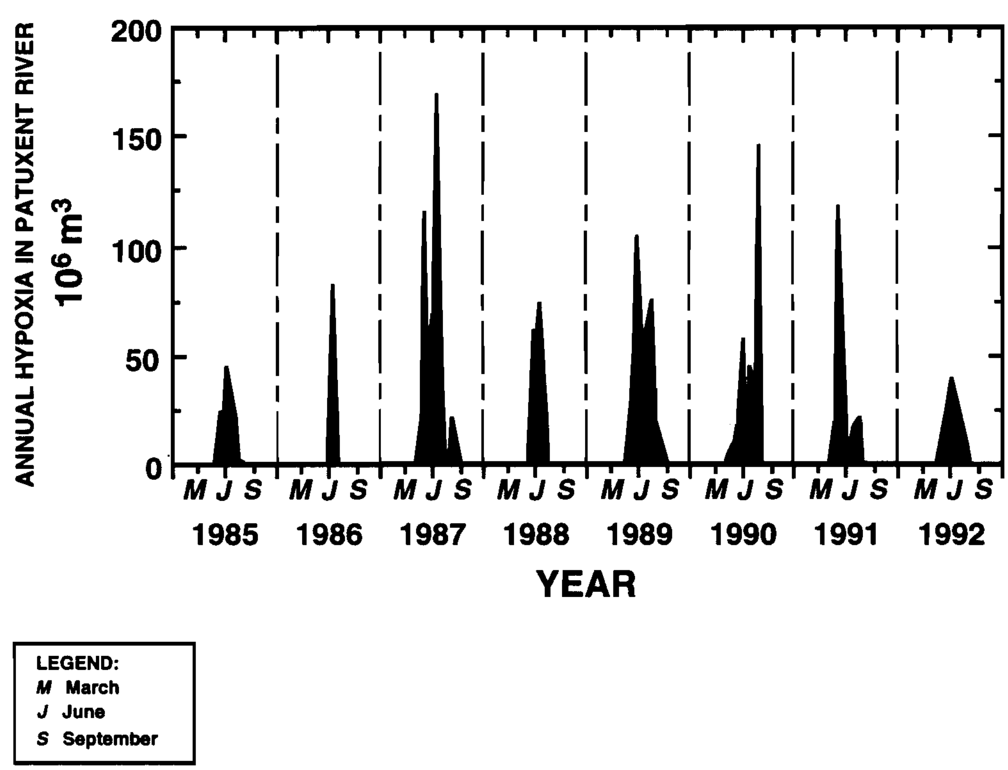

Figure 7-2. The volume of water in Patuxent River estuary with less than 2 mg l^{-1} dissolved oxygen during 1985 - 1992.

Integrated over one year, this yields 'hypoxic volume-days', a parameter used to describe annual hypoxia. Annual hypoxia was greatest during 1987 and smallest during 1986.
Figure is from Hagy (1996).

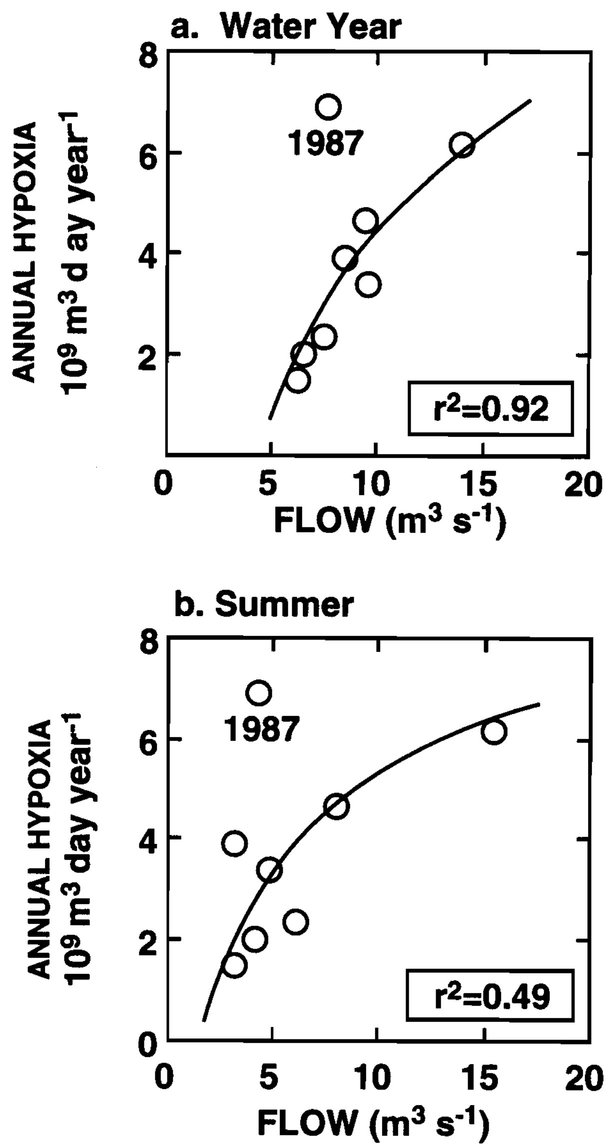

Figure 7-3. The relationships in the Patuxent River between water-year mean fall line river discharge and annual hypoxia (a.) and between summer (June through August) mean fall line river discharge and annual hypoxia (b.).
Correlation coefficients were calculated without the 1987 observation, and the curves were hand drawn. Figure is from Hagy (1996).

7.3 Analyses of Sediment-Water Flux Data in the Patuxent River Estuary

The main focus of the EPC studies has been monitoring sediment-water oxygen and nutrient 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.*, 1995b) 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 oxygen and nutrient 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). The differences in rates of organic matter deposition that determine spatial and seasonal variability in any one year also contribute to 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.

Data concerning organic matter deposition is not available for the sediment oxygen and nutrient exchanges (SONE) stations in the Patuxent River so direct comparisons of sediment flux with this process are not possible. However, the strong correlations indicated between freshwater inflow and nutrient loading rates with plankton biomass (previous section of this report) suggest that sediment-water fluxes may also be linked to these input variables because planktonic debris is the main source of organic matter reaching the sediment surface.

Measurements of sediment-water exchanges of dissolved oxygen (DO), ammonium (NH_4^+), nitrite plus nitrate ($NO_2^- + NO_3^-$) and phosphorus (PO_4^- or DIP) were organized as average values (May through October data) for the time period 1985 through 1995 for 3 stations in the Patuxent River (St. Leonard Creek [STLC], Broomes Island [BRIS] and Marsh Point [MRPT]). The same was done for sediment total chlorophyll-a mass, an indicator of labile organic matter. These data were then regressed with various functions of total nitrogen (TN) and total phosphorus (TP) load and freshwater inflow rates. Results are summarized in Table 7-1 and some representative scatter plots are shown in Figure 7-4.

Several points are immediately clear. First, there were a substantial number of significant relationships found indicating the importance of inputs on these sediment processes and stocks. In fact, it is a bit surprising that so many results were significant considering the low degrees of freedom in the analysis. Many more results were suggestive of patterns but one or more divergent points were sufficient to render the analysis non-significant at normal probability levels. Never the less, the patterns were indicative of some relationship between sediment processes and inputs. Second, there were more significant relationships related to flow than to nutrient loading rates. The exact reason for this is not clear but it seems reasonable to conclude that flow is a more "inclusive variable" regarding control of sediment-water exchanges. This seems to indicate that more of the processes which regulate sediment-water exchanges are related to flow than to nutrient load. Specifically, nutrient loads (diffuse loads) are correlated with flow; flow plays a role in water column stratification and hence dissolved oxygen (DO) conditions which certainly influence sediment-water fluxes; additionally flow plays a role in estuarine water residence times and hence the amounts of organic material transported (and deposited) in various regions of the estuary. Finally, the sediment responses to changes in flow or load were large rather than subtle. In the examples provided in Figure 7-4. the range in ammonium fluxes was about a factor of 2, for sediment oxygen consumption (SOC) a factor of 4 and for phosphorus (PO_4^- or DIP) fluxes a factor of 6. These sorts of ranges are large enough to make substantial differences in water quality conditions. It can be predicted that as nutrient loads decrease, so to will the magnitude of sediment processes, followed by improved water quality conditions.

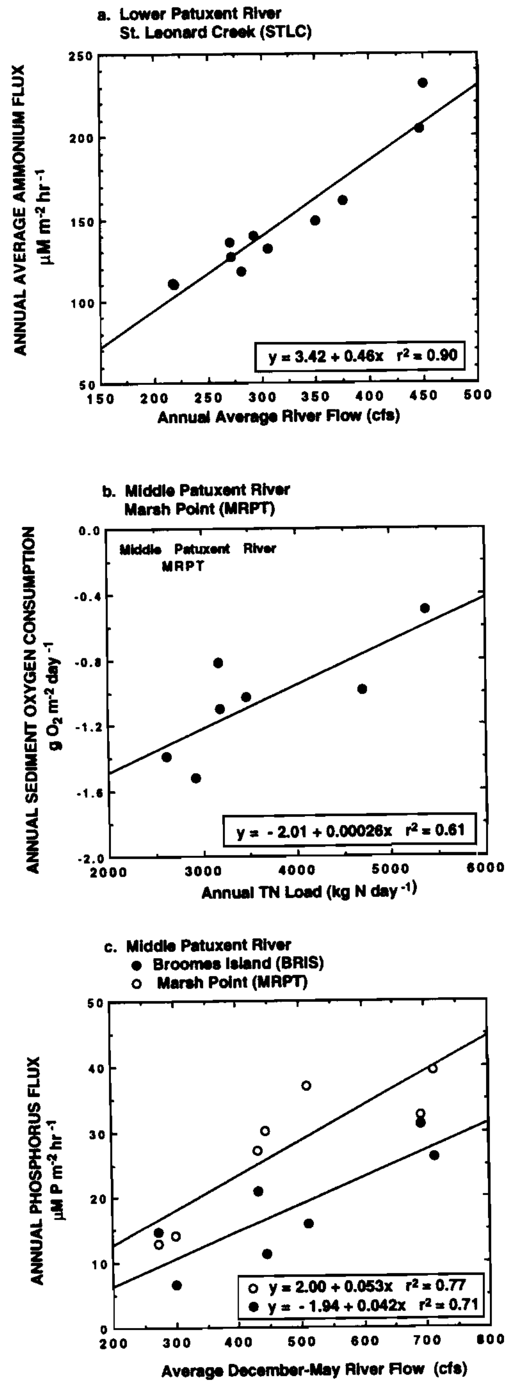

Figure 7-4. A series of scatter plots indicating relationships between various functions of river flow and nutrient loading rates and several sediment-water fluxes (ammonium [NH_4^+], sediment oxygen consumption [SOC] and phosphorus [DIP]).

River flow data were collected at the fall line near Bowie, MD. Nutrient loads include fall line loads plus below fall line point source loads.

Table 7-1. A summary of results of linear regression analyses relating various loads to sediment-water oxygen and nutrient fluxes and sediment total chlorophyll-a mass.
Fluxes and sediment total chlorophyll-a mass data were averaged for months, May through October, for each year. Averaging for loads are given in the body of the table. The blank entries in the table indicate that patterns were weak or not evident; a single asterisk indicates a pattern but with some divergent data; a double asterisk indicates a statistically significant result ($p < 0.05$).

TYPE OF LOAD	PATUXENT STATIONS	SOC $g\ O_2\ m^{-2}\ day^{-1}$	NH_4^+ FLUX $\mu M\ N\ m^{-2}\ h^{-1}$	NO_{23}^- FLUX $\mu M\ N\ m^{-2}\ h^{-1}$	PO_4^- FLUX $\mu M\ P\ m^{-2}\ h^{-1}$	SEDIMENT CHLOROPHYLL-a $mg\ m^{-2}$
Annual Average TN Load	STLC					
kg N day^{-1}	BRIS	*				*
	MRPT	**				*
Annual Average TP Load	STLC		**			
kg P day^{-1}	BRIS	*				
	MRPT	**				
Dec-Apr TN Load	STLC					
kg N day^{-1}	BRIS	*				*
	MRPT	*				*
Dec-Apr TP Load	STLC		**	*	*	
kg P day^{-1}	BRIS	*		*	**	*
	MRPT	*		*	*	*
Annual Average River Flow	STLC		**	*	*	
cfs	BRIS	*	*	*	**	*
	MRPT	*		*	*	
Dec-Apr River Flow	STLC		**	*	**	
cfs	BRIS		*	*	*	*
	MRPT			**	*	
Dec-May River Flow	STLC		**	*	**	**
cfs	BRIS	**	*	**	**	**
	MRPT	**		*	**	**

8. DISSOLVED OXYGEN THRESHOLDS FOR SEDIMENT QUALITY

8.1 Background

One of the central issues regarding water quality in the bay system concerns restoration of dissolved oxygen (DO) to reasonable levels in deeper waters during the warmer portions of the year. In the past few decades dissolved oxygen (DO) in deeper waters has been depleted and this situation effectively removes this portion of the bay as useful habitat for higher organisms. In addition to food web and habitat considerations, dissolved oxygen (DO) status plays a central role in regulation of some aspects of sediment-water nutrient exchanges which, in turn, impacts water quality conditions. In previous reports sediment oxygen and nutrient exchanges (SONE) and other data sets were examined for relationships between in-situ conditions and sediment-water fluxes (*e.g.* Boynton *et al.*, 1995a) and in this report the sediment oxygen and nutrient exchanges (SONE) data is examined for influences of dissolved oxygen (DO) conditions on phosphorus (PO_4^- or DIP) and nitrite plus nitrate (NO_2^- + NO_3^-) fluxes.

8.2 Dissolved Oxygen and Phosphorus Fluxes

Assuming that there is an adequate supply of phosphorus (PO_4^-) from overlying waters, phosphorus (PO_4^-) fluxes appear to be controlled largely by one of two mechanisms. In the case where dissolved oxygen (DO) levels are adequate and sediments support a macrofaunal community, phosphorus fluxes generally follow the annual temperature pattern. When temperatures are low then fluxes are low and fluxes are correspondingly higher when temperatures are higher during summer. The most likely mechanism is that flux is maintained by the burrowing and irrigation activities of the macrofaunal community. In cases where bottom sediments are exposed to oxygen, but the macrofaunal community is depleted or absent, phosphorus tends to be sequestered in sediments resulting in small fluxes to the water column (Jasinski, *pers. comm.*).

The second mechanism controlling phosphorus (PO_4^-) fluxes involves oxygen conditions in waters proximal to the sediment surface. Typically, much of the phosphorus in oxidized estuarine sediments is complexed as oxyhydroxides and is quite insoluble. However, under hypoxic conditions phosphorus becomes soluble and can diffuse from sediments to overlying waters. This pattern is generally evident at several sediment oxygen and nutrient (SONE) stations where water quality conditions vary between oxic and hypoxic (Figure 8-1.) and which typically have small macrofaunal communities. Conversely, at higher dissolved oxygen (DO) concentrations (> 2 mg l^{-1}) large phosphorus (PO_4^-) fluxes are not observed. A pattern of high release of phosphorus from sediments associated with a drop of bottom water dissolved oxygen concentration below about 2.0 mg l^{-1} is repeated throughout the sediment oxygen and nutrient exchanges (SONE) data record. An example of phosphorus flux versus dissolved oxygen (DO) conditions at three groupings of sediment oxygen and nutrient (SONE) stations (each having progressively lower dissolved oxygen (DO) concentrations during summer periods) is shown in Figure 8-2. Inspection of this plot again suggests that dissolved oxygen (DO) concentrations in bottom waters less than about 2 mg l^{-1} promote large sediment releases of phosphorus; large phosphorus releases are rare when bottom water dissolved oxygen (DO) concentrations are above this critical level. Once released this phosphorus is again available for phytoplanktonic uptake, algal growth, deposition and decomposition, reinforcing the downward water quality trajectory described earlier in this report (Figure 2-1.). While there are good biological reasons that discourage the maintenance of bottom water dissolved oxygen concentrations at only 2.0 mg l^{-1} (*i.e.* too low to support healthy infaunal communities), one benefit of at least achieving this goal would be to drastically reduce the flux of phosphorus from sediments to overlying waters.

In general nitrate fluxes do not constitute a large fraction of the nitrogen exchange between sediments and bottom waters. On occasion, large fluxes from water to sediments do occur, but these are almost always associated with high levels of nitrate in the water column and it is probable that this nitrate nitrogen is subsequently denitrified (converted to N_2) after diffusing into surface sediments. However, even small nitrate fluxes from sediments to overlying waters provide a useful indication of sediment conditions. Specifically, production and release of nitrate from sediments is a strong indication that sediment nitrification is occurring. This process requires at least low levels of dissolved oxygen and is hence an indication that surface sediments have been in contact with oxygenated waters. For example, during 1995, stations in the Patuxent River (with the exception of one measurement) exhibited relatively high rates of sediment nitrate release or much lower rates of nitrate uptake. In fact, at the St. Leonard Creek station (STLC) sediments released nitrate through the entire monitoring period, a pattern never before observed. A similar pattern was observed in the lower Potomac River (Ragged Point [RGPT]) and lower Choptank River (Horn Point [HNPT]) stations except during August when dissolved oxygen conditions were poor. These are the types of nitrate fluxes to be expected under reduced nutrient load conditions (as was the case in 1995) both because these conditions favor improved dissolved oxygen conditions in deep waters and sediments and lower concentrations of nitrate in overlying waters. Fluxes of nitrate from sediments to waters appear to serve quite well as an indicator of improved sediment quality. The specific examples referred to above appear to be generally observed at sediment oxygen and nutrient exchanges (SONE) stations. In Figure 8-3. summer nitrite plus nitrate (NO_2^- + NO_3^-) fluxes from three sediment oxygen and nutrient exchanges (SONE) station groups (each with successively lower dissolved oxygen [DO] conditions) are plotted versus bottom water dissolved oxygen (DO) concentrations at these stations. At all three station groups nitrite plus nitrate (NO_2^- + NO_3^-) fluxes from water to sediments were observed as expected because at all station groups high water column nitrite plus nitrate (NO_2^- + NO_3^-) concentrations occur during portions of the year. However, nitrite plus nitrate (NO_2^- + NO_3^-) fluxes from sediments to overlying waters occurs frequently only at the sites where bottom water dissolved oxygen (DO) conditions are elevated, in this case above about 4 mg l^{-1} during summer periods. Thus, while the absolute dissolved oxygen (DO) concentration at which nitrite plus nitrate (NO_2^- + NO_3^-) tends to diffuse from sediments is higher than the dissolved oxygen (DO) concentration required to prevent phosphorus (PO_4^- and DIP) fluxes, the concept remains the same, namely that there appear to be some minimum dissolved oxygen (DO) concentrations that promote good water quality by changing the nature of sediment-water nutrient exchanges.

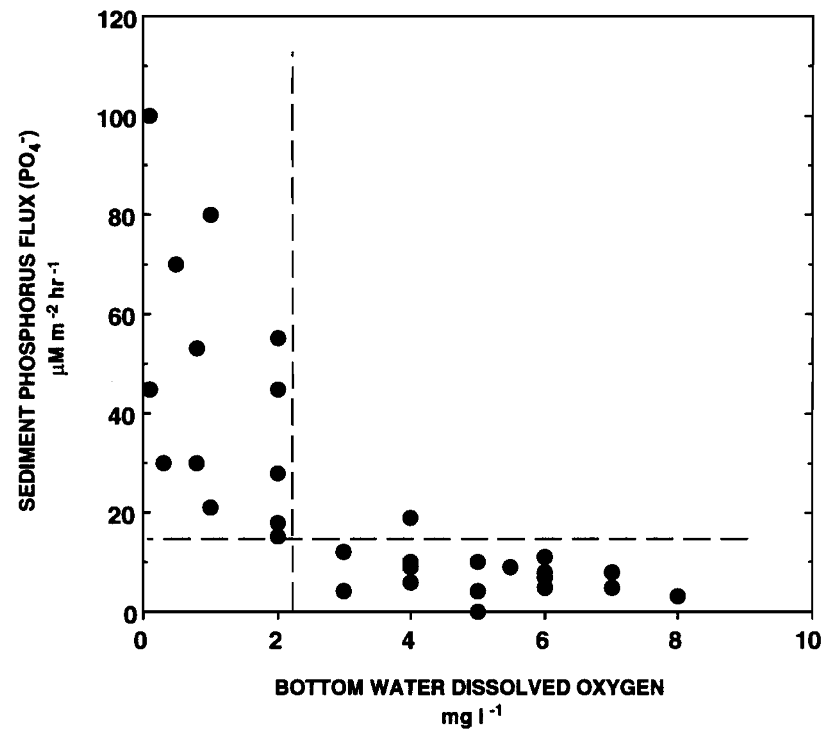

Figure 8-1. A scatter plot of bottom water dissolved oxygen concentration versus sediment phosphorus (PO_4^- or DIP) flux. Data are from sediment oxygen and nutrient exchanges (SONE) stations sampled between June, 1985 and September, 1995.
Vertical and horizontal dashed lines are just to indicate phosphorus fluxes at oxygen concentrations > 2 mg l^{-1} and < 2 mg l^{-1}.

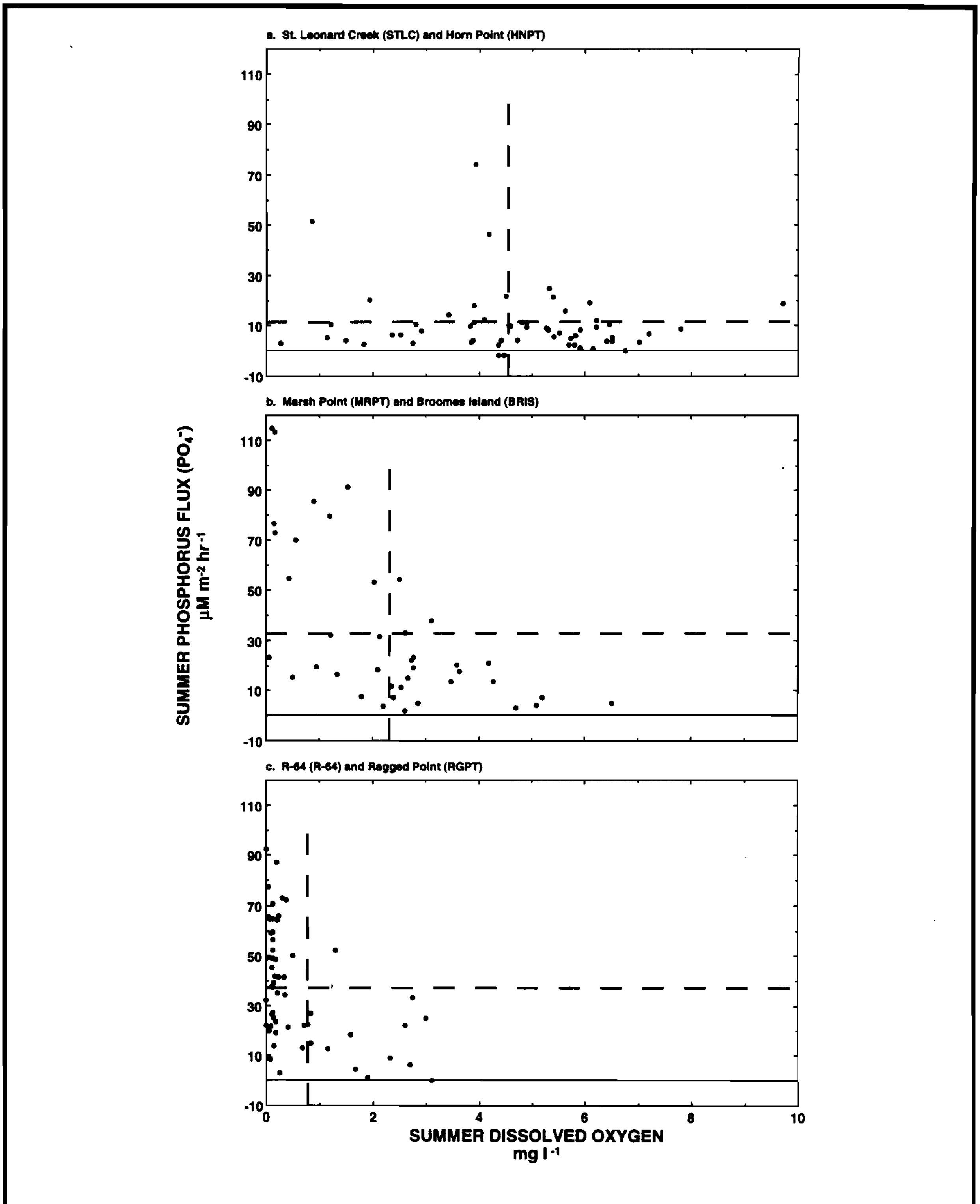

Figure 8-2. Scatter plots of average summer (June, July and August) sediment phosphorus (PO_4^- or DIP) flux versus average summer bottom water dissolved oxygen (DO) concentrations.
Vertical and horizontal dashed lines indicate average dissolved oxygen (DO) and phosphorus (PO_4^- or DIP) fluxes, respectively. Data are from the period 1985 - 1995 at St. Leonard Creek (STLC), Horn Point (HNPT), R-64 and Ragged Point (RGPT) and from 1989 - 1995 at Marsh Point (MRPT) and Broomes Island (BRIS).

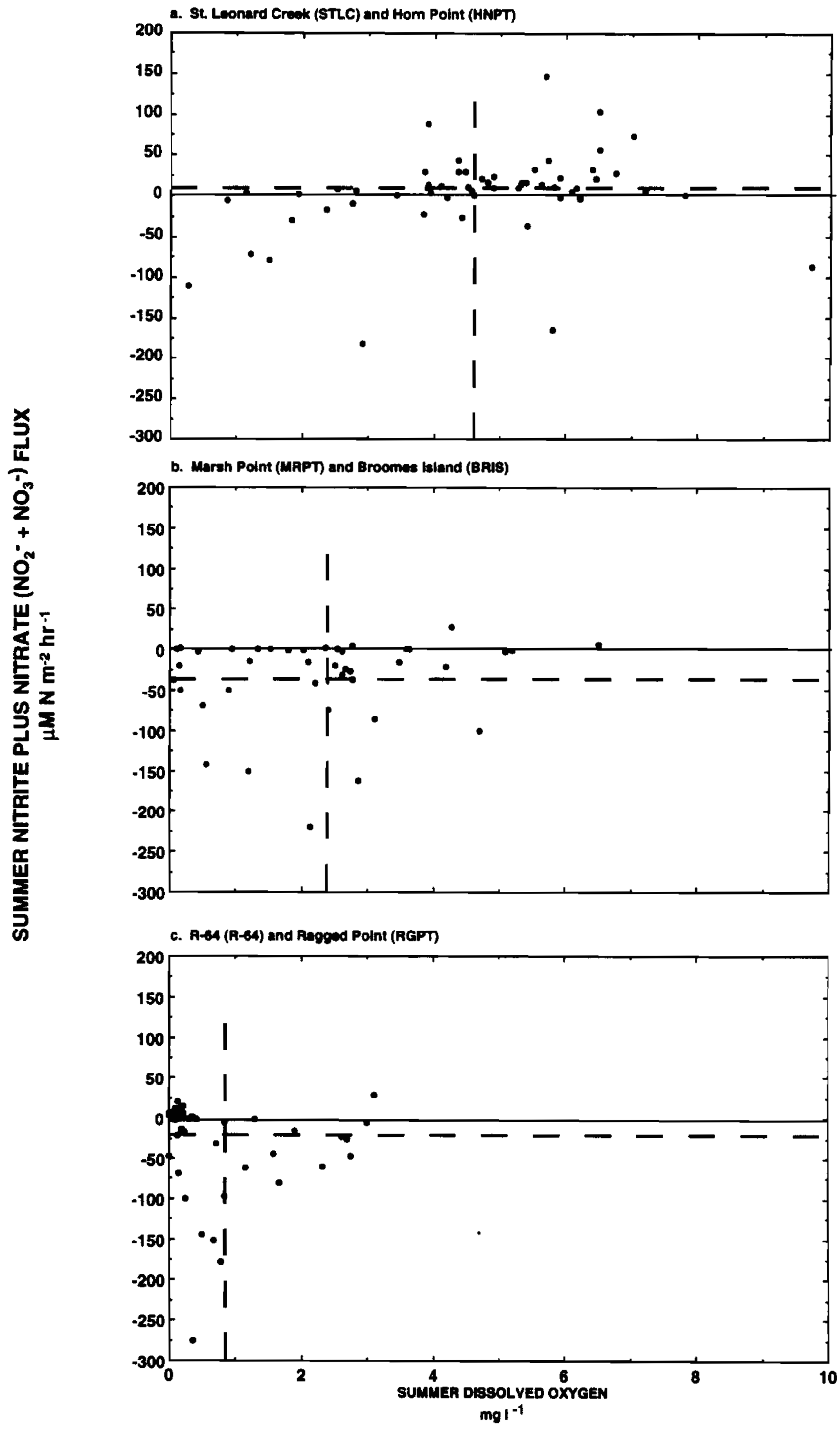

Figure 8-3. Scatter plots of average summer (June, July and August) sediment nitrite plus nitrate (NO_2^- + NO_3^-) flux versus average summer bottom water dissolved oxygen (DO) concentrations. *Vertical and horizontal dashed lines indicate average dissolved oxygen (DO) and nitrite plus nitrate (NO_2^- + NO_3^-) fluxes, respectively. Data are from the period 1985 - 1995 at St. Leonard Creek (STLC), Horn Point (HNPT), R-64 and Ragged Point (RGPT) and from 1989 - 1995 at Marsh Point (MRPT) and Broomes Island (BRIS).*

9. SELECTED TESTS FOR NUTRIENT LOADING, WATER QUALITY AND SEDIMENT-WATER FLUX TRENDS

9.1 Review of Previous Analyses

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 eleven complete years (1985 - 1995) of monitoring data have been accumulated.

A part of the Ecosystem Processes Component (EPC) Program was also designed to examine the sediment flux data in order to determine long-term trends in sediment-water nutrient and oxygen exchanges. In previous Interpretive Reports (Boynton *et al.*, 1993, 1994,) results of statistical testing for trends were presented and discussed. As an addition to this, a time series of important environmental variables (river flow, bottom water dissolved oxygen concentrations and key sediment-water fluxes) were presented in graphical format in the previous Interpretive Report (Boynton *et al.*, 1995a). These figures included monthly average data covering the complete ten year monitoring period (1985 - 1994) collected at six sediment oxygen and nutrient exchanges (SONE) stations. The specific purpose of these analyses was to explore the data to determine temporal trends and to provide a basis for discussion relating important environmental conditions to the characteristics of sediment fluxes. In the following sections the most important aspects of these earlier results are reviewed and results of a new set of trend analyses presented which focus on the Patuxent River, the site where extensive management actions have changed nutrient load characteristics.

9.2 Trends Indicated from Time-Series Plots

At all sediment oxygen and nutrient exchanges (SONE) stations there have been years with low average river flow and years with high average river flow during the monitoring period. These correspond to periods of relatively low and periods of high diffuse source nutrient loading rates, respectively. For example, in the Patuxent River, flows (loads) were high in 1984 (438 cfs) and then low until 1989 when large flows (475 cfs) again occurred. The years 1990 - 1992 were low flow years; 1993 and 1994 were high flow years, among the highest on record (438 and 440 cfs respectively). Corresponding to these periods of high and low flow were years of high and low ammonium fluxes. These patterns were particularly strong at St. Leonard Creek (STLC) and Ragged Point (RGPT). It is useful to note that such flux-load relationships were strongest during the 1990-1994 period when sediment oxygen and nutrient (SONE) measurements were of a higher frequency (six per year). At other sites patterns were not as consistent but years of large flow were associated with large fluxes. Some of the exceptions to the load-flux relationships are instructive in and of themselves. For example, fluxes were very high and sustained in the lower Potomac River (Ragged Point [RGPT]) during 1990 but river flow (nutrient load) was relatively small. One explanation of this is that there may have been an intrusion of phytoplanktonic debris into the Potomac

River from the bay during this period thereby suppling the organic matter needed to fuel large sediment fluxes. A similar phenomenon (but with very low dissolved oxygen conditions) was seen in the Patuxent River estuary during 1987 (Hagy, 1996). In the mainstem bay the load-flux relationship appears more complex than at other sites and seems to indicate spatial shifts in deposition related to river flow. It appears that during years of low to moderate flow, spring blooms are proportional to flow and so is the magnitude of deposition in the vicinity of SONE station R-64. Under these conditions the load-flux relationships appear to be robust (Boynton *et al.*, 1995a). However, during years of especially high flow (*e.g.* 1989, 1993 and 1994) it appears that the spring bloom is transported farther south prior to deposition. In these cases deposition at R-64 is less than expected as is also the case for sediment fluxes. Under the low to moderate flow regimes, sediment fluxes at the more southerly mainstem bay station (Point No Point [PNPT]) are lower than those at the more northerly station (R-64); however, under higher flow regimes (*e.g.* 1993 and 1994) the pattern is reversed. While more complex, these observations indicate that there can be substantial spatial shifts in ecological processes and this argues for adequate spatial coverage in monitoring programs.

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

The second mechanism controlling phosphorus fluxes involves oxygen conditions in deep waters proximal to the sediment surface. Typically, much of the phosphorus in estuarine sediments is complexed as oxyhydroxides and is quite insoluble. However, under anoxic conditions phosphorus becomes soluble and can diffuse from sediments to overlying waters. This pattern is particularly evident at several SONE stations. In the lower Choptank River (Horn Point [HNPT]) in 1985 through 1988 dissolved oxygen conditions in bottom waters were never measured below 4 mg l^{-1} and phosphorus fluxes were uniformly low. However, in August, 1989 bottom water dissolved oxygen concentrations dropped to about 1 mg l^{-1}, probably in response to the large freshet of 1989. Under these low dissolved oxygen conditions sediments responded quickly (same month) with the largest releases of phosphorus on record up to that time. This pattern was repeated again in 1993 and 1995 when low dissolved oxygen conditions again occurred probably in response to the very large freshet during 1994 and to intrusion of bay water into the Choptank River in 1995. A pattern of high release of phosphorus from sediments associated with a drop of bottom water dissolved oxygen concentration below about 2.0 mg l^{-1} is repeated throughout the sediment oxygen and nutrient (SONE) data record. Once released this phosphorus is again available for phytoplanktonic uptake, algal growth, deposition and decomposition, reinforcing the downward water quality trajectory described earlier in this report (Figure 2-1). While there are good biological reasons that discourage the maintenance of bottom water dissolved oxygen concentrations at 2.0 mg l^{-1} and indicate that this is too low a goal (*i.e.* too low to support healthy infaunal communities), one benefit of at least achieving this goal would be to drastically reduce the flux of phosphorus from sediments to overlying waters.

9.3 Statistical Analyses for Detection of Inter-Annual Trends

Statistical analyses have also been conducted to examine sediment oxygen and nutrient exchanges (SONE) flux data for temporal trends. Five different SONE flux variables, sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrate plus nitrite (NO_2^- + NO_3^-), phosphate (DIP or PO_4^-) and silicate ($Si(OH)_4$) fluxes were analyzed. The basic approach employed in examining Sediment-Water Oxygen and Nutrient Exchanges (SONE) flux data for long-term trends involved regressing flux data (*e.g.* ammonium (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 an analysis of variance (ANOVA) technique (SAS, GLM procedure). 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 $year^{-1}$. The ANOVA model included the sources of variation for location (4; Susquehanna, Potomac, Patuxent and Potomac Rivers), station or stations within a river system (8; regularly sampled SONE stations), month (7; April through November, omitting very limited 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 within rivers (Patuxent [PTX] and Susquehanna [SUS] Rivers only), between rivers within month (or between months within river). Tests were also done to determine if the change in flux per year was significantly different from zero overall or for any level of aggregation of river, station and month (t-test using MSE). The details of these analyses are given in Boynton *et al.* (1993) and should be referred to for a complete explanation of the methods. Findings, together with additional comments, relevant to achieving the goals of the monitoring program are summarized below.

There were no significant trends for SOC for any specific month in the Potomac River and Susquehanna River (Maryland Mainstem Bay). 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 and this was probably due to improving bottom water dissolved oxygen (DO) levels at this station.

Two ecologically significant trends were evident for ammonium (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 (NH_4^+) on an annual basis and this trend was significantly different from the other three rivers. The trend towards lower ammonium (NH_4^+) fluxes in the Potomac 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 ($\sim$1-2 mg l^{-1}) sediment oxygen consumption (SOC) rates would tend to increase. The reduction in ammonium (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, much of the resulting nitrate being denitrified and lost to the atmosphere as a biologically inert gas.

No significant trends for nitrite plus nitrate ($NO_2^- + NO_3^-$) 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 ($NO_2^- + NO_3^-$) 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 nitrate plus nitrite *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 nitrate plus nitrite ($NO_2^- + NO_3^-$) 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 waters to sediments. A different pattern may emerge for nitrate plus nitrite ($NO_2^- + NO_3^-$) fluxes as diffuse source nutrient controls become 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 sediments 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 1995) positive nitrate fluxes have been observed (Boynton *et al.*, 1995a).

Two significant decreasing trends of ecological importance were indicated for dissolved inorganic phosphorus (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 (PO_4^-) when data for all months is used. Again, the large decrease in phosphate flux observed in the Potomac 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 phosphate fluxes were not significant all indicated decreasing fluxes over the period of record (1985-1991) and this again is consistent with generally reduced phosphorus loading rates to many portions of the bay.

Overall, relatively few significant trends were detected in the Ecosystem Processes Component (EPC) Program sediment-water flux data (1985 through 1991) 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. 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.*, 1993). In earlier reports (Boynton *et al.*, 1995) 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 or freshwater input 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 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 (as they now appear to be in the Patuxent River) 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 (NH_4^+), phosphorus (PO_4^-) and nitrate plus nitrite ($NO_2^- + NO_3^-$) fluxes. These changes in flux are consistent with predictions associated with generally lower nutrient loading conditions which has been the case in the Potomac River, at least through 1991. Its 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 been generally decreasing during the last several years. As the relationships between nutrient loading rates and ecosystem responses such as sediment-water exchanges becomes clearer it may be possible to better 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.

9.4 Trends in the Patuxent River Estuary

Since completion of the analyses described above (1991 for statistical treatments and 1993 for time-series examinations) the bay system has experienced 2 years of exceptionally high flow (1993 and 1994) and one year of especially low flow (1995). Because of the problems of separating climatic variation from effects of management actions we chose not to simply repeat these analyses by including more recent data. However, in the Patuxent River very large reductions in total phosphorus (TP) loads have been achieved and more recently (1991) total nitrogen (TN) load reductions have become evident. Because of these changes and because sediment oxygen and nutrient exchanges (SONE) program has a number of sites in this tributary, the SONE and other data bases were examined again for trends, especially those associated with the period following 1989 (just prior to total nitrogen [TN] reductions). In these analyses the following variables were examined graphically and then exposed to linear regression analyses. In contrast to previous analyses, these yielded a great many significant trends suggesting that this tributary is in fact responding to nutrient load reductions. In the following section results of these analyses are summarized in a series of tables and figures.

Annual average Patuxent River discharge (at Bowie, MD [cfs]), total nitrogen (TN) and total phosphorus (TP) loads (calculated as fall line load plus below fall line point source load, kg N or P per day) are shown in Figure 9-1. River flow indicates years of both high (1984, 1989, 1993, 1994) and low (1985, 1986, 1991, 1992, 1995) flow. Given this normal climatic variability no longer term trends were expected and none emerged. However, this was not the case for TN and TP loads. In the former, loads varied between 4500-5600 kg day^{-1} between 1984 and 1989 and then began to decrease through 1995. The regression of TN load versus time is significant ($p < 0.01$) for both the full period of time and the post 1989 period with annual load decreases of about 230 kg day^{-1} $year^{-1}$. A similar pattern and level of significance was observed for total phosphorus (TP) loads but the largest decreases in loads occurred prior to 1986 but have still continued to generally decrease through the present time. It is especially important to note that while loads increased in 1993 and 1994 (years of strong river flow) the increases were small, barely larger than loads associated with recent dry year loads and much smaller than loads associated with wet years during the late 1980's. This strongly suggests that management actions associated with point and diffuse source load reductions are effective.

While decreases in nutrient loading rates are a very positive sign, it is equally important to link these changes to changes in water quality conditions. One of the central water quality features of interest is deep water dissolved oxygen (DO) concentrations. Summer (June-August) deep water dissolved oxygen (DO) concentrations at SONE stations in the Patuxent River are shown in Figure 9-2. for the years 1989-1995. As indicated, there have been sharp improvements in dissolved oxygen (DO) conditions at two of the stations (St. Leonard Creek [STLC] and Broomes Island [BRIS]; annual trend significant at $p < 0.01$) and less significant ($p < 0.05$) but still upward trends in dissolved Oxygen (DO) at the Marsh Point (MRPT) station. The improvements at Broomes Island (BRIS) are particularly important wherein at this site average summer conditions changed from poor (DO ~ 1 mg l^{-1}) in 1989 to good (DO ~ 4 mg l^{-1}) in 1995. Bottom dissolved oxygen (DO) conditions were lower during 1993 and 1994, years of high flow, but not nearly as depressed as in 1989, a year of similarly high flow. These trends should be viewed as important signals of improving water quality.

Another variable of interest is sediment chlorophyll-a which is used in the sediment oxygen and nutrient exchanges (SONE) program as an indicator of labile organic matter at the sediment-water interface which is available for rapid decomposition (Figure 9-3.). While at St. Leonard Creek (STLC) there is a downward trend, the mass versus time regression is not significant, nor is it significant at the other two stations. However, it is important to note that at two of the stations (St. Leonard Creek [STLC] and Broomes Island [BRIS]) 1995 concentrations are the lowest on record and that there is a significant decreasing trend if only years of similar and low flow are considered (1991, 1992 and 1995). These trends are not as crisp as those for dissolved oxygen (DO) but are still in the direction predicted based on the conceptual model used to guide this program (Figure 2-1.).

Finally, two series of linear regression analyses were conducted to examine sediment-water flux data collected in the Patuxent River for interannual trends. In the first series, flux data collected between 1985 and 1995 (1989 and 1995 at 2 stations) were grouped by month and fluxes collected during that month were plotted versus year. Sufficient data were available

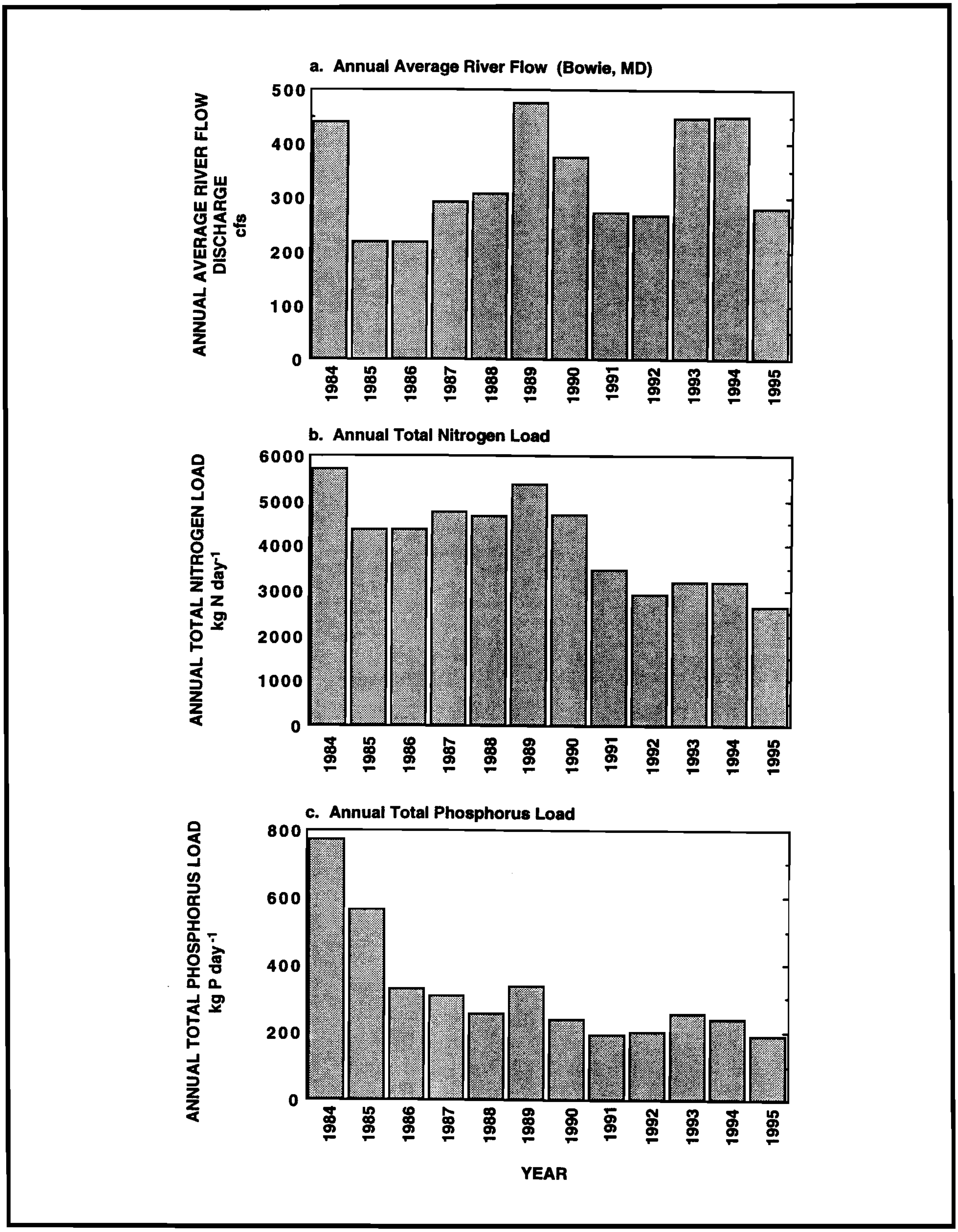

Figure 9-1. Bar graphs showing annual average river flow (measured at Bowie, MD) total nitrogen (TN) and total phosphorus (TP) loads (kg day^{-1} as N or P) for the Patuxent River estuary.
Total nitrogen (TN) and total phosphorus (TP) loads were calculated as the sum of fall line loads plus below fall line point source loads.

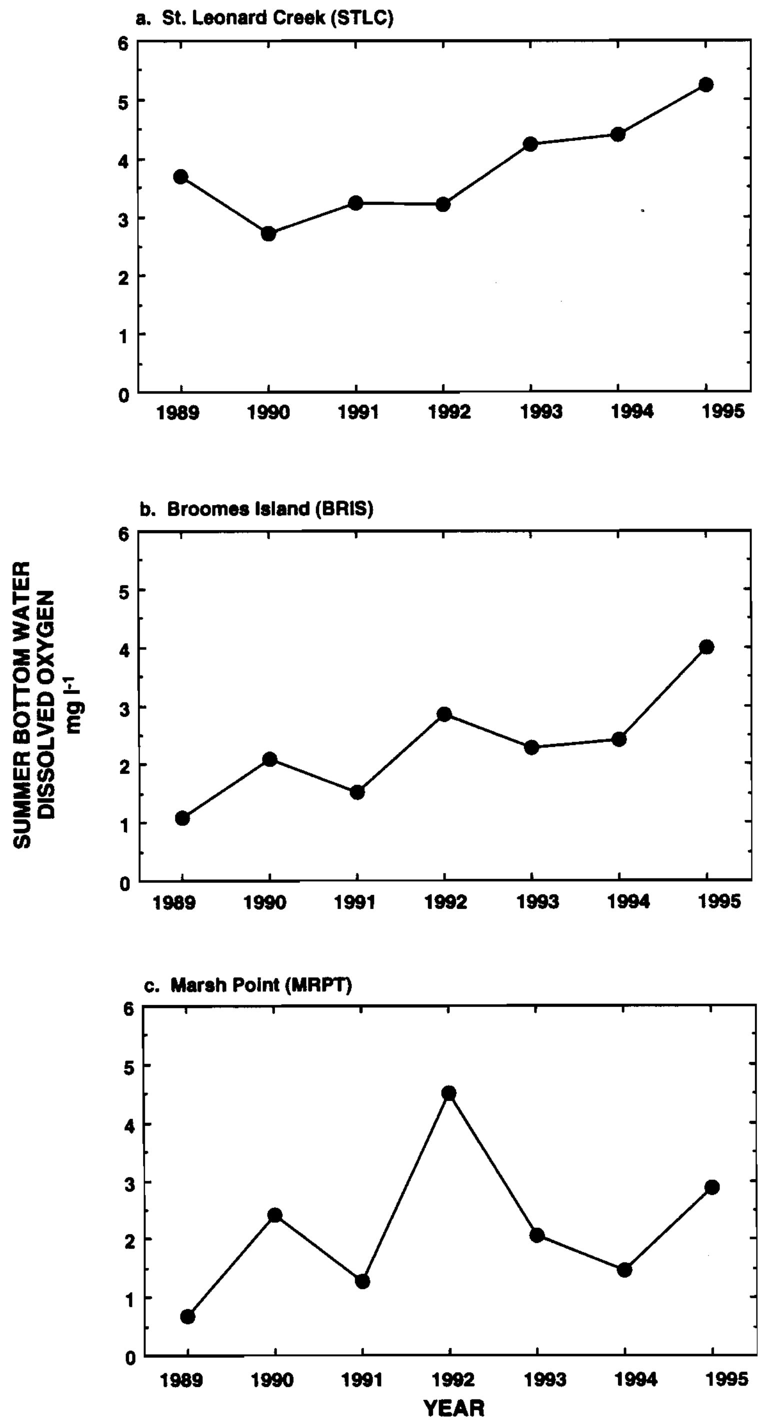

Figure 9-2. Summer average (June through August) bottom water dissolved oxygen (DO) concentrations at three sediment oxygen and nutrient exchanges (SONE) stations in the Patuxent River for the period 1989 through 1995.

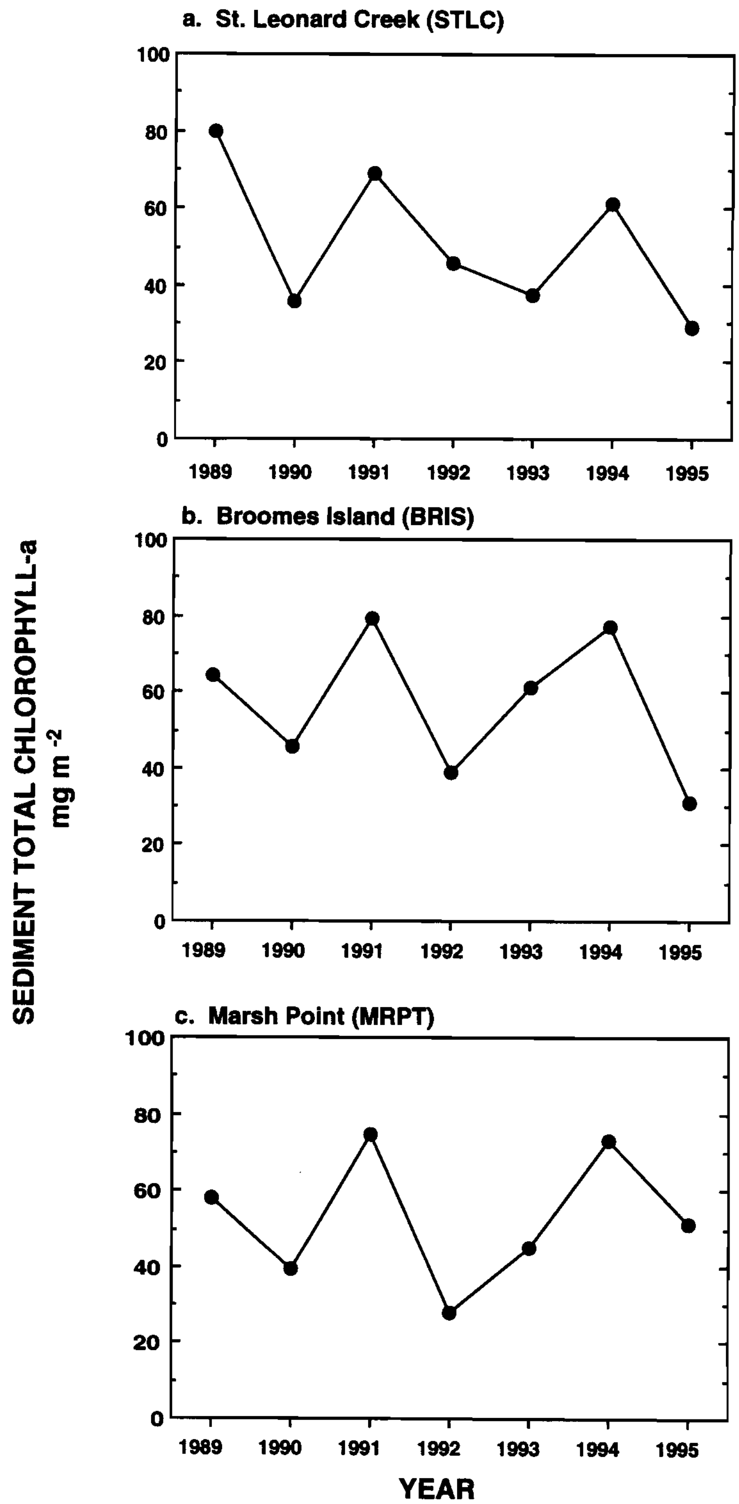

Figure 9-3. Summer average (June through August) surficial sediment chlorophyll-a mass at three sediment oxygen and nutrient exchanges (SONE) stations in the Patuxent River for the period 1989 through 1995.
Chlorophyll-a mass was determined based on surface scrape samples.

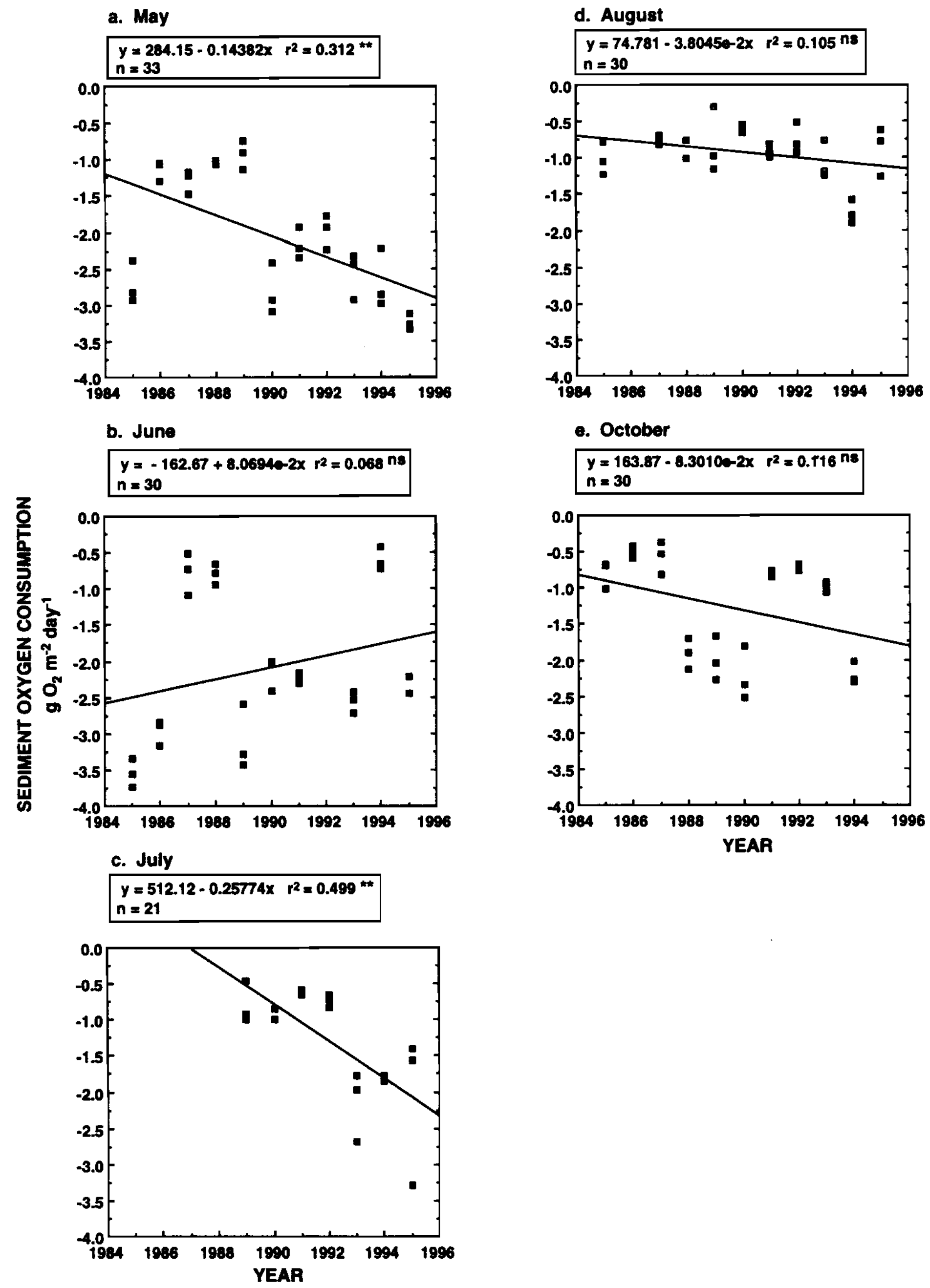

Figure 9-4.a. Linear regressions (monthly average flux versus year) for St. Leonard Creek (STLC). Flux is sediment oxygen consumption (SOC), months are May, June, July, August and October and the complete eleven year data record, 1985 through 1995, is used.

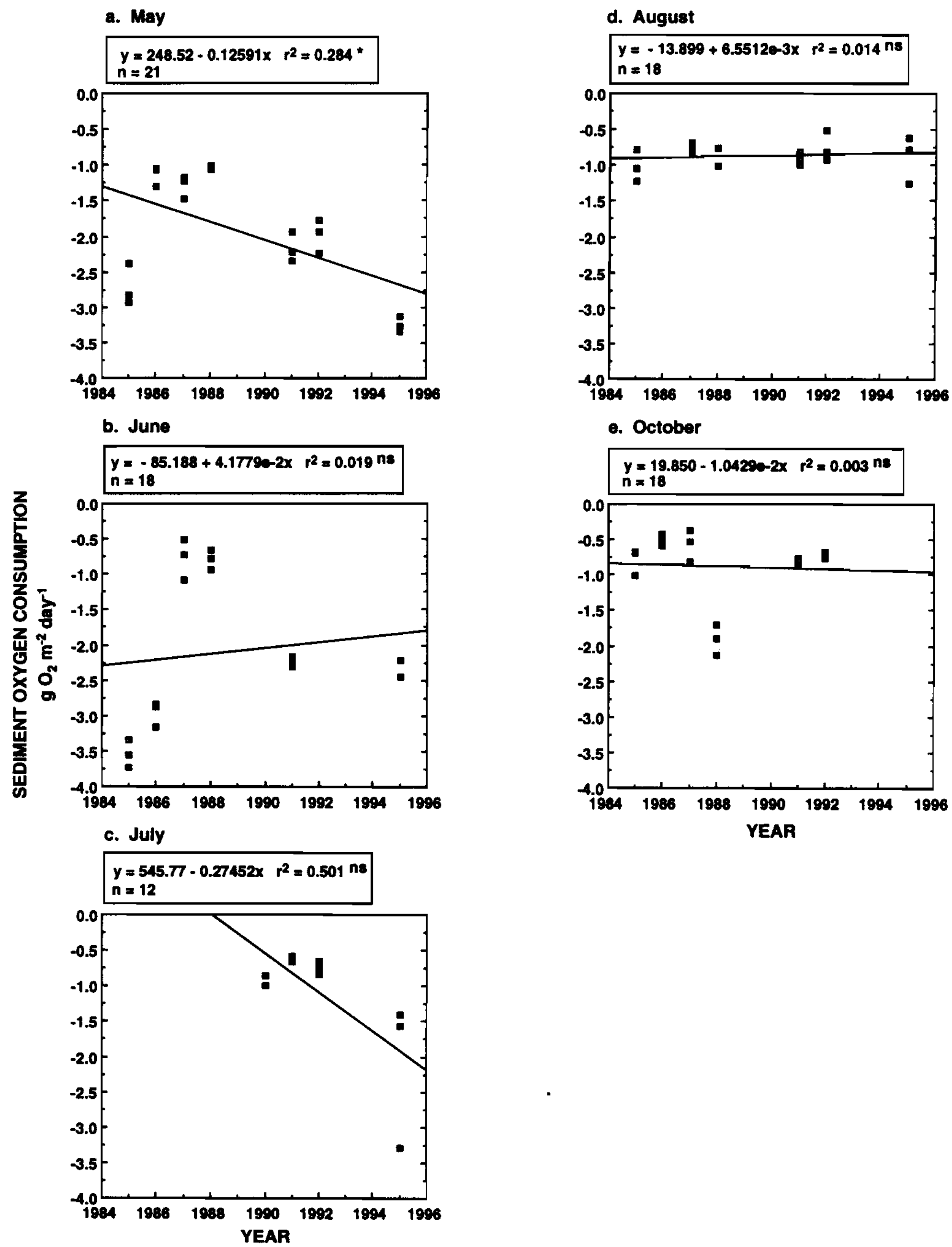

Figure 9-4.b. Linear regressions (monthly average flux versus year) for St. Leonard Creek (STLC). Flux is sediment oxygen consumption (SOC), months are May, June, July, August and October while selected years (parsed data set), 1985, 1986, 1987, 1988, 1991, 1992 and 1993, are used.

Table [illegible]-1. A summary of results (slope, r and p) of linear regression analyses (monthly average flux versus year). Data used were for the complete eleven years, 1985 through 1995.
Tests were conducted for sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate (NO_2^- + NO_3^-) and phosphate (PO_4^- or DIP) fluxes for the months of May, June, July, August and October.

	ALL YEARS														
	MAY Slope	r	p	JUNE Slope	r	p	JULY Slope	r	p	AUGUST Slope	r	p	OCTOBER Slope	r	p
SEDIMENT OXYGEN CONSUMPTION (SOC)															
STLC	284.15	0.56	**	-162.67	0.26	ns	512.12	0.71	**	74.78	0.32	ns	163.87	0.34	ns
BRIS	-21.70	0.03	ns	419.85	0.60	**	331.38	0.52	*	190.65	0.86	**	236.86	0.80	**
MRPT	322.02	0.40	ns	-461.91	0.51	*	114.09	0.49	*	231.43	0.69	**	20.20	0.12	ns
BUVA	269.53	0.48	**	98.40	0.24	ns	195.76	0.48	*	122.91	0.50	**	282.96	0.58	**
AMMONIUM (NH_4^+)															
STLC	5901.30	0.17	ns	9719.90	0.18	ns	48451.00	0.30	ns	-11479.00	0.28	ns	-7531.10	0.33	ns
BRIS	22531.00	0.31	ns	-31622.00	0.17	ns	-43971.00	0.63	**	13982.00	0.22	ns	-4279.70	0.11	ns
MRPT	-62736.00	0.76	**	23061.00	0.32	ns	-8160.80	0.07	ns	-54510.00	0.58	**	-59084.00	0.57	*
BUVA	-37001.00	0.53	**	-8623.30	0.18	ns	-9895.30	0.10	ns	-18105.00	0.28	ns	-34121.00	0.43	*
NITRITE + NITRATE (NO_2^- + NO_3^-)															
STLC	1055.80	0.03	ns	20077.00	0.43	*	11739.00	0.63	**	4824.80	0.26	ns	-1044.20	0.13	ns
BRIS	15853.00	0.14	ns	-15620.00	0.17	ns	-5328.20	0.39	ns	-14427.00	0.58	**	-179.43	0.00	ns
MRPT	82331.00	0.62	*	-15675.00	0.38	ns	-4914.80	0.66	**	-25760.00	0.41	ns	-4570.20	0.40	ns
BUVA	1703.40	0.12	ns	-994.44	0.03	ns	-13039.00	0.67	**	13540.00	0.40	*	3109.40	0.25	ns
DISSOLVED PHOSPHORUS (PO_4^- or DIP)															
STLC	-1310.50	0.41	*	255.50	0.07	ns	-6992.30	0.39	ns	-856.01	0.16	ns	-54.67	0.03	ns
BRIS	-2695.00	0.41	ns	-3908.10	0.19	ns	-8508.50	0.23	ns	8622.20	0.31	ns	528.28	0.14	ns
MRPT	-807.37	0.19	ns	-1847.00	0.56	*	2647.30	0.06	ns	13402.00	0.49	*	-6217.50	0.33	ns
BUVA	-815.60	0.17	ns	4960.50	0.55	**	16360.00	0.35	ns	-7206.60	0.41	*	605.63	0.12	ns

Table 9-2. A summary of results (slope, r and p) of linear regression analyses (monthly average flux versus year). Data were for the selected years (parsed data set), 1985, 1986, 1987, 1988, 1991, 1992 and 1995.
Tests were conducted for sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate ($NO_2^- + NO_3^-$) and phosphate (PO_4^- or DIP) fluxes for the months of May, June, July, August and October.

	PARSED YEARS														
	MAY Slope	r	p	JUNE Slope	r	p	JULY Slope	r	p	AUGUST Slope	r	p	OCTOBER Slope	r	p
SEDIMENT OXYGEN CONSUMPTION (SOC)															
STLC	248.52	0.53	*	85.19	0.14	ns	545.77	0.71	ns	-13.90	0.12	ns	19.85	0.05	ns
BRIS	109.89	0.15	ns	756.27	0.90	**	665.00	0.91	**	285.58	0.91	**			
MRPT	328.98	0.65	ns	120.34	0.15	ns	208.14	0.69	*	36.17	0.11	ns			
BUVA	286.93	0.51	*	55.58	0.14	ns	-16.59	0.05	ns	169.64	0.83	**	307.32	0.64	**
AMMONIUM (NH_4^+)															
STLC	0.00	0.21	ns	31604.00	0.61	*	23745.00	0.39	ns	1880.00	0.06	ns	2535.60	0.10	ns
BRIS	31526.00	0.38	ns	42842.00	0.33	ns	-38515.00	0.49	ns	-23360.00	0.40	ns			
MRPT	-68105.00	0.81	**	-57483.00	0.77	*	426.98	0.00	ns	17389.00	0.18	ns			
BUVA	-30641.00	0.56	**	-8466.70	0.19	ns	4473.50	0.03	ns	-8183.50	0.17	*	-31947.00	0.43	ns
NITRITE + NITRATE ($NO_2^- + NO_3^-$)															
STLC	16503.00	0.72	*	-345.85	0.00	ns	-9742.20	0.52	ns	6039.30	0.48	*	-932.62	0.11	ns
BRIS	-71970.00	0.66	ns	-2.68	0.81	**	1371.50	0.48	ns	79676.00	0.64	ns			
MRPT	-17840.00	0.34	ns	-2011.80	0.08	ns	-1425.40	0.39	ns	-46891.00	0.60	ns			
BUVA	4555.00	0.37	ns	4641.60	0.35	ns	-950.62	0.23	ns	21399.00	0.78	**	3126.80	0.28	ns
DISSOLVED PHOSPHORUS (PO_4^- or DIP)															
STLC	-1244.90	0.46	*	720.26	0.18	ns	1592.00	0.39	ns	-354.96	0.06	ns	-127.13	0.07	ns
BRIS	239.75	0.03	ns	5740.80	0.58	ns	7091.40	0.54	ns	3499.20	0.33	ns			
MRPT	125.39	0.03	ns	-5895.00	0.93	**	11623.00	0.44	ns	20353.00	0.52	ns			
BUVA	-1223.10	0.23	ns	6650.10	0.67	**	25271.00	0.76	*	-1968.70	0.19	ns	-52.07	0.00	ns

to conduct analyses for the months of May, June, July, August and October. In the second series of analyses the same procedure was used except that data were used only from years of low to moderate freshwater input. In this case, data were used from 1985, 1986, 1987, 1988, 1991, 1992 and 1995). By using this approach (parsed data record) the climatic influence of wet or very wet years (*e.g.* 1993, 1994) in detecting trends is removed. It is assumed that fluxes recorded in each year are independent of the previous year, but this appears to be a good assumption as has been shown in an earlier report (Boynton *et al.*, 1990).

The results of these analyses are shown in Tables 9-1 (full data record) and Table 9-2 (parsed data record) and an example plot is shown in Figure 9-4.a., complete record and Figure 9-4.b., parsed record. These results contrast sharply with earlier analyses in that there were many significant trends indicating improving sediment quality. Approximately 40% of tests using the full data record were significant while about 25% of the tests based on the parsed record were significant, all of this despite a relatively small sample size ($n = 21$ or $n = 33$). The lower percentage of significant tests from the parsed record initially seemed counter intuitive because some years which would have contributed to interannual variability had been excluded. However, the reduced degrees of freedom associated with the parsed data record played a role in reducing the number of significant analyses. Furthermore, the sediment-water flux responses to wet years late in the data record (1993, 1994) were not nearly as pronounced as they were in earlier in the record, presumably because recent wet years yielded lower nutrient loads than in the mid-late 1980's. Thus, some trends emerged from the full data set which had not been expected.

It is important to note that July and August exhibited the most significant trends. These are the months with the highest nutrient fluxes and thus adjustments during these months have the largest water quality impacts. Trends were least evident for October data.

All but two of the significant trends for sediment oxygen consumption (SOC) were towards increasing rates and significant trends were most common in July and August at all but one station in the Patuxent River. Increasing sediment oxygen consumption (SOC) rates most probably result from increased dissolved oxygen (DO) concentrations at the sediment-water interface. It is interesting to note that in the early stages of the sediment oxygen and nutrient (SONE) program, sediment oxygen consumption (SOC) rates in tributary rivers were generally higher than in the mainstem. This was and still is related to the fact that dissolved oxygen (DO) conditions are generally better at SONE stations in tributary rivers than at SONE stations in the mainstem bay. Another way to interpret the sediment oxygen consumption (SOC) trend is that these sediments are becoming more aerobic, expressing this as increased sediment oxygen consumption (SOC).

There were relatively few significant ammonium (NH_4^+) trends but all were towards decreasing fluxes, a good sign from a sediment and water quality viewpoint. While most analyses did not yield significant results at traditional probability levels, most trends were towards decreasing sediment-water exchanges of ammonium. A similar pattern was evident for phosphate (PO_4^- or DIP) fluxes, although not as strong. Finally, nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes exhibited significant trends during summer months (June, July and August) and all but one of these were towards larger releases of nitrite plus nitrate from sediments to overlying waters. The importance of this is that releases of these compounds from sediments is a clear indication that sediment nitrification was occurring and this process requires the presence of oxygen. In a sense, nitrite plus nitrate releases are an indicator of sediment oxygen status and if releases occur, it is an indication of improving sediment quality.

Overall, these analyses, which focused on the Patuxent River, identified a number of significant trends. Nutrient loads, bottom water dissolved oxygen (DO) concentrations and, to a lesser extent, sediment chlorophyll-a all indicated trends which indicate improving water quality. Additionally, about 40% sediment-water fluxes exhibited trends indicative of improving sediment conditions.

10. THE ROLE OF DISSOLVED OXYGEN IN SEDIMENT PHOSPHORUS FLUXES: RESULTS OF A LABORATORY EXPERIMENT

This chapter authored by: D.A. Jasinski

The relative importance of "new" and "recycled" nutrients to water quality is an important area of concern within managed systems. New nutrients refers to nitrogen and phosphorous imported to a water system either from natural or anthropogenic sources while recycled nutrients are those that have been released from organic matter that has undergone microbial degradation within the system.

The difference in importance between "new" and "recycled" nutrients appears to be of a temporal nature. In Chesapeake Bay, new nutrients are important during the winter-spring period when river flows are generally high; the nutrients which enter the system from riverine sources support the spring diatom bloom. Recycled nutrients are more important in supporting summer and fall production (Boynton ***et al.***, 1991b) and a significant portion of recycled nutrients during the summer and fall periods is based on organic matter produced during the spring and fall blooms which eventually decomposed after reaching estuarine sediments.

The partitioning of total nitrogen (TN) and total phosphorous (TP) stock between the water column, biota and sediments in four areas of Chesapeake Bay is summarized in Table 10-1. Of the three partitions, the sediments contain by far the largest amounts of total nitrogen (TN) and total phosphorus (TP). This is due, in part, to the fact that the residence time of water within Chesapeake Bay is less that one year and hence it is not possible for the water column to accumulate multi-year nutrient stocks as it is in some other estuarine systems (*e.g.* Baltic Sea). We are aware of no systems where most of the nutrient stock is contained within the living biota and at the current time only a few percent of total nitrogen (TN) and total phosphorus (TP) are partitioned in this compartment in Chesapeake Bay. The sediments of the bay represent the only significant long term storage site of nutrients. Organic matter that is not consumed in the water column or flushed from the system is deposited on the sediments. Here, nutrients within the organic matter are released through microbial degradation. Biogeochemical processes can act either to release these nutrients back to the water column or retain them within the sediments depending on a number of environmental conditions. Overall, the relatively huge amounts of total nitrogen (TN) and total phosphorus (TP) in sediments suggests that these systems would have ample nutrient reserves to sustain recycling processes for multi-year periods even if external nutrient sources were much reduced.

In oxidized sediments, a portion of the ammonium (NH_4^+) released by degradation processes can be transformed to NO_3- by nitrifying bacteria ($\sim$25-50%; Seitzinger, 1988). This NO_3^- can then diffuse into the sediments to the anoxic zone where denitrifying bacteria can either reduce it to N_2 (whereupon it is lost from the system) or to ammonium (NH_4^+) which can then diffuse back to the oxic zone and be again transformed to NO_3^-. This represents a storage mechanism for nitrogen within the sediments for, although nitrogen is cycled, it remains within the sediments. This breaks down under anoxic conditions as the lack of oxygen inhibits nitrifying bacteria, allowing ammonium to be released to the overlying water.

Phosphorous chemistry is similarly affected by redox conditions. In oxic sediments, phosphate is normally bound to Fe_3^+ (ferric iron) which is abundant in Chesapeake Bay sediments. As conditions become reducing, ferric iron is reduced to ferrous iron (Fe_2^+) which does not bind phosphate as readily. Phosphate becomes dissolved in the interstitial water as Fe_2^+ is bound to sulfide. Sulfide is a end product of sulfate reduction, an anaerobic metabolic pathway. As long as the oxidized sediment layer remains intact, phosphate diffusing from deeper in the sediments towards the sediment surface will be bound by Fe^{3+} and phosphate will be stored within the sediments. Should the oxic layer become reduced, phosphate can be released from the sediments to the overlying water.

The bottom waters of certain areas of the bay are periodically anoxic or hypoxic causing nitrogen and phosphorous periodically to be released from the sediments in these areas at enhanced rates. An important question from a management perspective is "*What is the response time of the system to changed nutrient inputs?*" Another way of stating the question is "*How long after nutrient input reductions are made will the system respond? What is the nutrient memory of the bay?*". Given the large nutrient storages in estuarine sediments, it is important to know how long nutrients can be released from sediments after inputs of new nutrients have been reduced. In other words, how much of the nitrogen (N) and phosphorus (P) that has been loaded into the Bay as "new" nutrients and is being retained within the sediments via the above storage mechanisms can be eventually released? Of this large quantity, how much is available for further biological utilization. Insight into this question may be gained if the quantity of biologically available nutrients contained within the sediments is known.

An experiment was recently conducted with the intention of determining how much biologically available phosphate is contained within the sediments (*i.e.* an estimate of the sediment phosphorus memory was made) of Chesapeake Bay. In this experiment eight sediment cores were obtained from station R-64 in the mesohaline region of Chesapeake Bay. Once in the laboratory, the cores were attached to a flow-through (chemostatic) irrigation system and maintained in the dark at 20 C. The cores were allowed to equilibrate for three days before four of the cores and a water blank were switched to a hypoxic (0.10 - 0.35 mg l^{-1}) flow-through irrigation system and maintained under these conditions for the duration of the experiment.

Water for the hypoxic system was obtained from a reservoir isolated from the surrounding atmosphere and bubbled with N_2 to remove the oxygen. A peristaltic pump then pumped the water from the reservoir to the cores. The same type of system was used for the four cores that were left oxic. Flow rates from the reservoir through the cores were maintained at a rate of 8 - 10 ml min^{-1}. This rate was fast enough to replenish oxygen consumed and maintain a phosphorous concentration gradient between the sediment and overlying water comparable to that found in-situ. Samples for analyses were taken by placing the outflow line from a core into an amber glass BOD bottle. Samples were analyzed for dissolved inorganic phosphorus (DIP) colorimetrically (Murphy and Riley, 1962). Fluxes were calculated as function of the difference between in flowing concentration and outflowing concentration and the flow rate. Oxic and hypoxic cores were sacrificed to determine depth profiles of pore water dissolved inorganic phosphorus (DIP) concentrations in the sediment; one of each mid-way through the experiment and two of each at the end of the experiment.

The theory behind this experiment is that by inducing hypoxia in the sediment cores, phosphate will be released from the sediment via the geochemical processes described above. By maintaining this hypoxia, a measure of the mass and duration of this phosphorus release is obtained. Comparison of the depth concentration profiles allows the determination of changes over time and differences between treatment cores related to hypoxia.

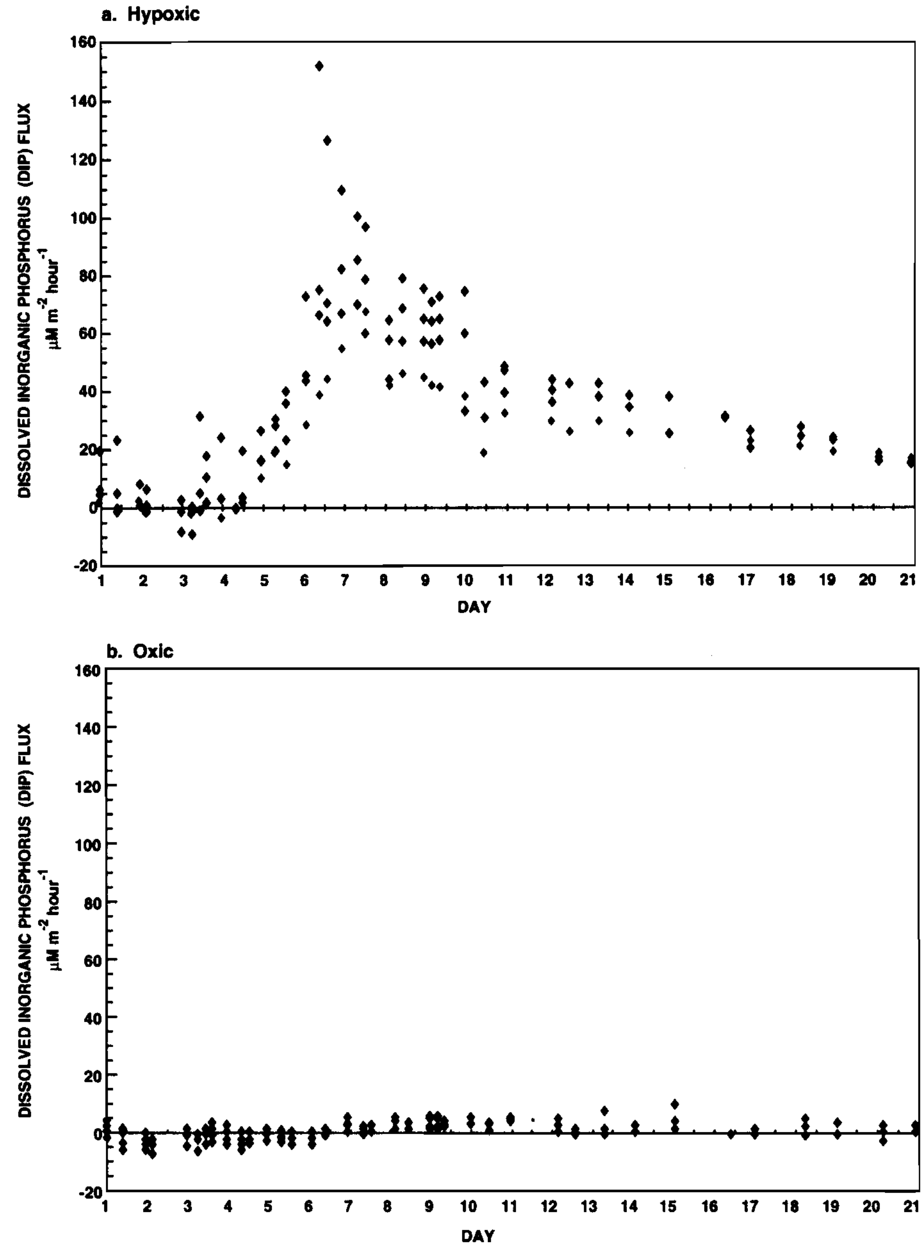

Figure 10-1. Phosphate (PO_4^- or DIP) fluxes measured during a twenty one (21) day experiment in which one set of sediment cores (triplicates) were initially incubated with oxygenated overlying waters and then exposed to hypoxic waters (a. Hypoxic) and a set of cores (triplicates) which were continually exposed to oxygenated overlying waters (b. Oxic).

Methods used to measure fluxes are described in the text.

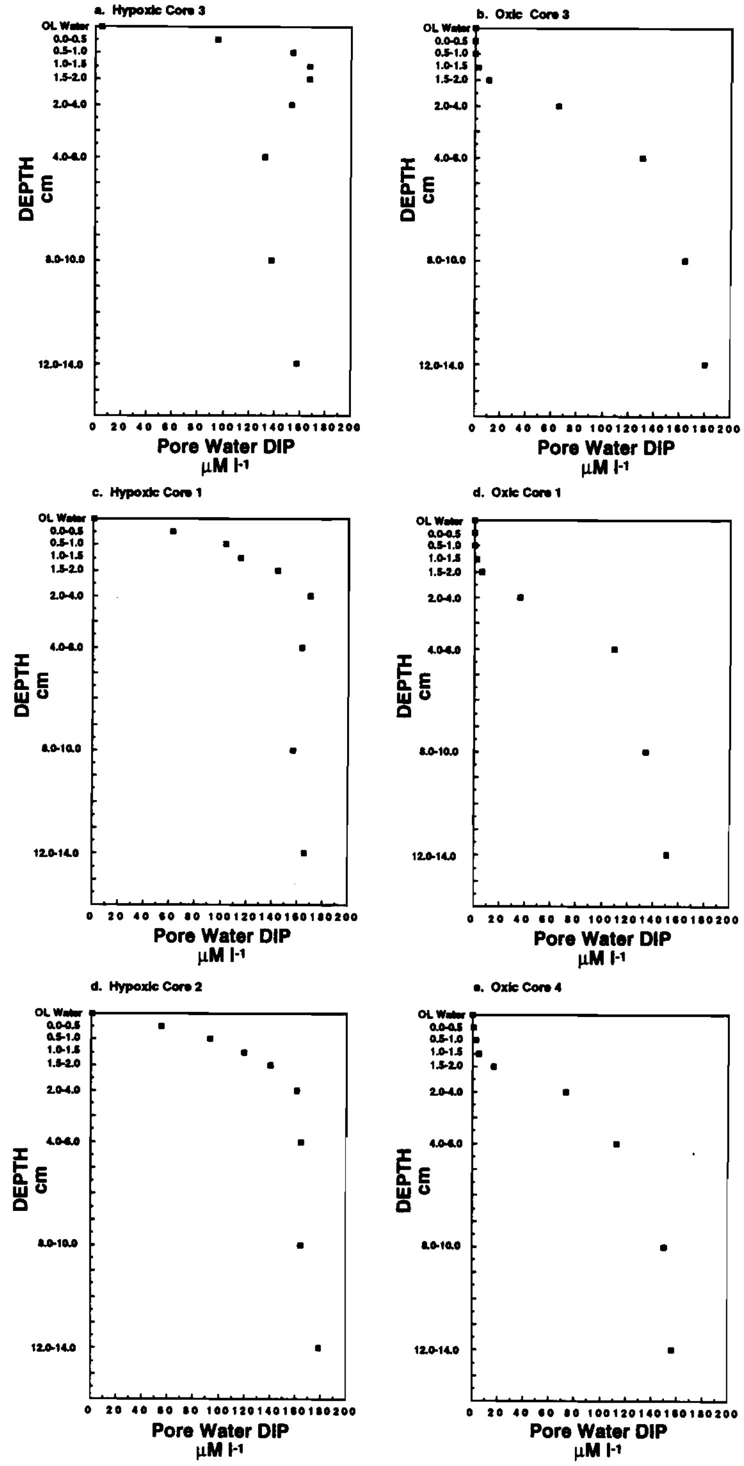

Figure 10-2. A series of phosphate (PO_4^- or DIP) concentration-sediment depth plots. *Measurements were made from samples taken from hypoxic and oxic sediment cores at the mid-point (hypoxic and oxic core 3) and end (hypoxic cores 1 and 2; oxic cores 1 and 4) of the experiment period. Note: that concentrations are very low in near surface sediments in oxic cores and enhanced in hypoxic cores.*

Table 10-1. A summary of the partitioning of total nitrogen (TN) and total phosphorus (TP) in various regions of Chesapeake Bay.
Units in the table are kg x 10^6 of nitrogen (N) or phosphorus (P) and are annual averages based on data collected in the late 1980's

	Maryland Mainstem Bay		Potomac River		Patuxent River		Choptank River	
	TN	TP	TN	TP	TN	TP	TN	TP
Water Column	19.73	1.098	6.63	0.655	0.055	0.073	1.21	0.117
Sediment	214.5	36.38	58.27	1.834	7.39	2.123	18.84	3.676
Biota	3.51	0.426	0.71	0.086	0.1	0.013	0.12	0.012
% in Sediments	**90.2**	**96.0**	**88.8**	**71.2**	**97.9**	**96.1**	**93.4**	**96.6**

Data from Boynton *et al.,* (1995a)

Table 10-2. Mean fluxes and total mass of phosphorus (P) released from each core over the duration of the experiment.
Means for each treatment are also displayed.

Core	Mean Flux Rate µM P m^{-2} h^{-1}	Total Mass mg m^{-2}	Mean Treatment Rate µM P m^{-2} h^{-1}	Mean Treatment Total Mass mg m^{-2}
Oxic #1	-0.52	-8.1	1.1	19.8
Oxic #2	1.20	23.5		
Oxic #4	2.69	44.0		
Hypoxic #1	39.30	509.1	38.6	476.9
Hypoxic #2	48.90	589.5		
Hypoxic#4	27.65	332.1		

Figure 10-1. shows the dissolved inorganic phosphorus (DIP) flux over time in both the oxic and hypoxic cores. Mean dissolved oxygen concentration within the oxic cores over the duration of the experiment was 5.62 mg O_2 l^{-1}. Mean dissolved oxygen concentration within the hypoxic reservoir was 0.27 mg O_2 l^{-1}. Dissolved oxygen concentrations within the hypoxic cores may have been lower due to consumptive processes but dissolved oxygen in these cores were not directly measured. Upon examination of Figure 10-1., two things are immediately apparent about the dynamics of the phosphorus (P) flux in the hypoxic treatment. First, the sediment response to the onset of hypoxia is rapid; phosphorus (DIP) fluxes increased rapidly from a mean of -2.7 M P m^{-2} h^{-1} at the onset of hypoxia to a mean peak level of 95.8 M P m^{-2} h^{-1} in three days. Second, the duration of the elevated phosphorus (DIP) efflux was short lived; approximately 18 days after peak efflux (end of experiment), the mean flux rate dropped to 16.2 M P m^{-2} h^{-1}. Fluxes of phosphorus (DIP) in the oxic cores remained small (mean = 1.16 M P m^{-2} h^{-1} and were directed both into and out of the sediment over the duration of the experiment. These changes in flux direction were most likely in response to changes in the DIP concentration in the overlying water versus surficial sediments. Table 10-2. shows the differences in mean flux rates and mean mass of DIP released for each core.

Sediment pore water profiles of phosphorus (DIP) from the sacrificed cores are displayed in Figure 10-2. The profiles labeled hypoxic 3 and oxic 3 are from the two cores sacrificed on day 12 of the experiment while the other four profiles are from cores sacrificed on day 21 at the end of the experiment. The most notable difference between the oxic and hypoxic cores is the low dissolved inorganic phosphorus (DIP) concentration in the first cm of sediment of the oxic cores whereas dissolved inorganic phosphorus (DIP) concentrations in the surface 0.5 cm of the hypoxic cores are equivalent to those 3 - 5 cm below the surface in the oxic cores. Also, a decrease in the dissolved inorganic phosphorus (DIP) concentration in the top two cm of the hypoxic cores is apparent between mid experiment and the end of the experiment. This change is most likely the result of efflux to the overlying water.

The results of this experiment have important implications for management. First, results indicate that dissolved oxygen concentration in the water overlying the sediment is very important in controlling the dissolved inorganic phosphorus (DIP) flux between sediments and water column. Taking management actions to ensure that dissolved oxygen (DO) concentrations of bottom waters within Chesapeake Bay remain elevated will help to maintain dissolved inorganic phosphorus (DIP) efflux from the sediments at low levels. However, should bottom waters become hypoxic, either naturally or through anthropogenic influence, these results indicate that the sediment dissolved inorganic phosphorus (DIP) response will be large but probably not of long duration. There is a large efflux of dissolved inorganic phosphorus (DIP) shortly after the onset of hypoxia ($\sim$36 hours) which quickly diminishes to levels approaching pre-hypoxic levels after several weeks. Apparently, even though there is a large amount of phosphorous stored within the sediments, there is only short "blast" of dissolved inorganic phosphorus (DIP) efflux even under conditions of a controlled laboratory experiment designed to promote efflux. The sediment phosphorus memory, from a biological standpoint, appears to be relatively short.

11. MANAGEMENT SUMMARY

Based on a review of previous Ecosystem Processes Component (EPC) Sediment Oxygen and Nutrient Exchanges (SONE) Reports (Boynton *et al.*, 1989, 1990, 1991a, 1992, 1993b, 1994 and 1995a) and the analyses summarized in this report the following observations are provided which have relevance to water quality management.

- Nutrient loading data (monthly fall line load of TN and TP and both above and below fall line point source loads of TN and TP) for the Patuxent River were reviewed for the period 1984-1995. Fall line loads of TP (which include above fall line point source inputs) have decreased dramatically between 1984 and 1995 (4-5 fold); recent loads would be even lower except for very high inputs associated with flood events (*e.g.* May, 1989, March, 1993 and March, 1994). Fall line loads of TN have also decreased over this period but not to nearly as great a degree as for TP; the same increased loads of TN were evident associated with flood events. Both TN and TP loads during 1995 were, or were close to, the lowest on record since 1984.

- Dissolved oxygen conditions at SONE locations in the Patuxent River were generally very good. At both the Broomes Island (BRIS) and St. Leonard Creek (STLC) locations summer dissolved oxygen conditions were considerably improved compared to previous years. Dissolved oxygen concentrations at the Choptank River location are typically high (> 4 mg l^{-1}) during summer. However, in August, 1995 dissolved oxygen concentrations dropped to very low levels. Inspection of salinity measurements indicated that this low dissolved oxygen condition was most probably due to intrusion of deep water from the bay into the Choptank rather than low dissolved oxygen conditions developing due to local processes. This event, while not usual at this location, reminds us that these systems are all connected and can influence one another.

- Ammonium (NH_4^+) fluxes at the two down river locations (STLC and BRIS) in the Patuxent River were lower than those recorded in earlier years probably as a response to the small spring river flow (and associated diffuse source nutrient load) which occurred in 1995. The reduced ammonium fluxes and improved dissolved oxygen conditions are both positive improvements in sediment quality. Ammonium fluxes were also reduced at the lower Potomac River location (Ragged Point [RGPT]) and in the Choptank River (Horn Point [HNPT]) except in August when low dissolved oxygen conditions were present.

- With few exceptions, fluxes of nitrate plus nitrite (NO_2^- + NO_3^-) were considerably more positive (*i.e.* directed from sediments to water column) than usual at most stations. Positive nitrate fluxes (or smaller fluxes directed into sediments) is a definite sign of sediment nitrification activity which is a microbial process which converts ammonium to nitrate and which requires that oxygen be present. Positive nitrate fluxes are a sign of improved sediment quality. The fact that this occurred during a year of lower than normal nutrient loading rates is another indication that bay sediments are responsive to reduced loading rates and improved DO conditions. Even relatively low DO conditions in deep waters can improve water quality by decreasing sediment-water nutrient exchange rates.

- During 1995, inorganic phosphate (PO_4^- or DIP) fluxes were more reduced than ammonium (NH_4^+) fluxes and this most probably resulted from more oxidized sediment conditions. The reduction in phosphorus fluxes was most noticeable in the Patuxent River where reductions were large (up to a factor of 2) and, in this case, both improved DO conditions and decreased phosphorus loading rates were probably responsible for this positive trend. Experimental studies involving phosphorus (PO_4^-) flux and dissolved oxygen (DO) conditions also indicated a tight coupling between flux and DO status and further indicated that the time needed for estuarine sediments to respond to decreased loading rates is probably quite short (weeks to months) despite large storages of particulate nutrients in sediments.

- Selected environmental variables (river flow, nutrient loads and bottom water dissolved oxygen concentrations) and key sediment nutrient fluxes (ammonium [NH_4^+], phosphate [PO_4^- or DIP] and nitrite plus nitrate [NO_2^- + NO_3^-]) were examined for portions of the monitoring period. Strong relationships of flux to river flow and nutrient loads were found and the importance of low dissolved oxygen concentrations on sediment phosphorus and nitrate fluxes further confirmed from both field and laboratory measurements.

- A method for measuring total sediment metabolism, which is consistent with the needs of a monitoring program, has been implemented. Recently developed and reliable technology was used to detect changes in dissolved inorganic carbon flux (TCO_2 flux) at a reasonable cost. Data based on TCO_2 fluxes were compared with sediment oxygen consumption (SOC) rates and were found to be appreciably larger, as expected. The technique completely avoids the low dissolved oxygen problems associated with sediment oxygen consumption (SOC) rate measurements. The general magnitude of TCO_2 fluxes were consistent with sediment enrichment and nutrient loading rates.

- A focused review of sediment oxygen and nutrient exchanges (SONE) data for trends was completed for stations in the Patuxent River. Significant reductions in total nitrogen (TN) and total phosphorus (TP) loading rates were found; bottom water dissolved oxygen (DO) concentrations have been increasing since 1990; sediment chlorophyll-a mass appears to be declining although trends were not highly significant; sediment oxygen consumption (SOC) fluxes are increasing in response to better dissolved oxygen (DO) conditions in deep waters; ammonium (NH_4^+) and phosphate (PO_4^- or DIP) fluxes are generally decreasing and trends were significant for some summer months; nitrite plus nitrate (NO_2^- + NO_3^-) fluxes have also responded to improved dissolved oxygen (DO) conditions in deep waters. All of these trends indicate improving water and sediment quality conditions in response to reduced nutrient loading rates in the Patuxent River system.

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