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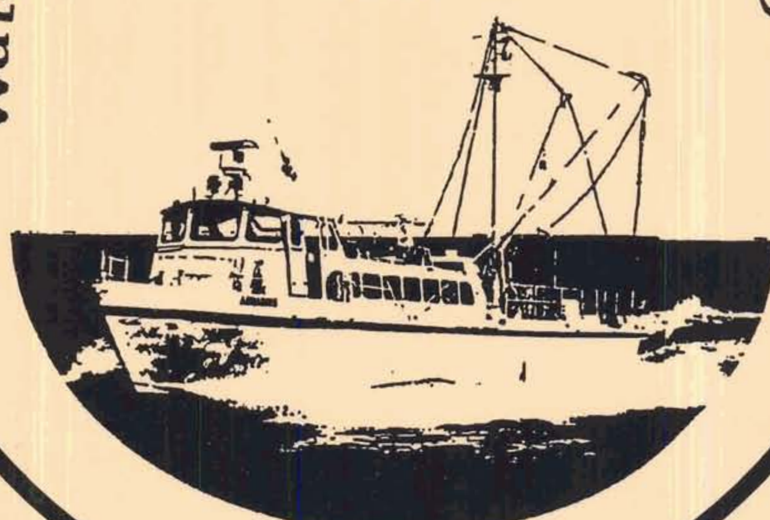
Chesapeake Bay Water Quality Monitoring Program

ECOSYSTEMS PROCESSES COMPONENT (EPC)



LEVEL ONE REPORT # 14
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. 14

INTERPRETIVE REPORT

(July 1984 - December 1996)

PREPARED FOR:

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Resource Assessment Administration
Tide Water Ecosystem Assessment Division
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PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in DNR Contract RAT-6-96-010 between the Maryland Department of Natural Resources (DNR), Resource Assessment Administration, Tidal Water Ecosystems Assessment Division and the University of Maryland System, Center for Environmental and Estuarine Studies (CEES).

This report contains a brief description of sampling procedures employed by the Ecosystems Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program and a complete hard copy listing of all data collected by the EPC during the period January 1, 1996 through December 31, 1996.

The Sediment Oxygen and Nutrient Exchanges (SONE) tables in Appendix B, reflect efforts begun in August, 1990 to verify and standardize all EPC files. Station code names used in data tables can be found in Table 3-1.1. Detailed location and descriptive information for all stations is in Tables 3-1.2. and 3-1.3. A copy of the Ecosystem Processes Component Data Dictionary, Sediment Oxygen and Nutrient Exchanges (SONE) variable and parameter list containing information relating to SONE data tables is attached as Appendix A. The listing contains SONE variable names and the matching CHESSEE (Chesie) variable used in the public information base of the Chesapeake Bay Program, along with a full description of the variables and units presently used. Entries are arranged alphabetically using the MDE/EPC table names. A copy of the Ecosystem Processes Component Data Dictionary is available on request from Dr. Bruce Michael (Maryland Department of Natural Resources) or from Dr. F.M. Rohland (Chesapeake Biological Laboratory). Any specific questions related to these data or 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 (status) relative to sediment-water nutrient and oxygen exchanges (2) determine the long-term trends that develop in sediment-water exchanges in response to pollution control programs, and (3) integrate the information collected in this program with other elements of the monitoring program.

This program was initiated in July 1984, and the basic data collection scheme has been followed through December 1996 with some changes in the station configuration and number of variables measured. The long-term data set (12 years) collected from 1985 - 1996 is evaluated in order to determine both current status and establish the presence of trends. Measurements of sediment-water nutrient and oxygen exchanges were made four times between mid-June and mid-September during 1996 at two locations in the mainstem bay (Point No Point [PNPT] and R-64 [R-64]), at a single location in one tributary (Ragged Point [RGPT] in the lower mesohaline region of the Potomac River; measurements were not made at Horn Point [HNPT] in the lower Choptank River during 1996) and at four locations in the Patuxent River (St. Leonard Creek [STLC], Broomes Island [BRIS], Marsh Point [MRPT] and Buena Vista [BUVA]).

A new element involving sediment chlorophyll-a mapping and MINI-SONE measurement (an abbreviated SONE program) in the Patuxent River was added in 1996. The prime objective was to develop a simpler methodology for assessment of sediment responses to water quality changes. High frequency (daily) measurement of community metabolism in the Patuxent River at the Route 231 Bridge near Benedict, MD was also completed which examined and compared community-level metabolic (primary production and respiration) responses of the estuary to both increasing (1960 - 1991) and decreasing (1992 - 1996) nutrient loads.

During the winter-spring period of 1996, all four of the major systems monitored, Susquehanna (Maryland mainstem bay), Potomac, Patuxent and Choptank Rivers, experienced both freshwater (and probably diffuse source nutrient) inputs which were far above average and were the highest recorded in each basin since 1978 (except for 1979 in the Patuxent Basin). An unusually wet year was indicated and it is expected that diffuse source nutrient loads will also turn out to be elevated.

During the monitoring period temperature ranged from 17.2 - 27.5 C and salinity conditions ranged between 3.9 - 18.8 ppt during 1996. Bottom water salinities were lower than usual at all seven stations in 1996.

Dissolved oxygen (DO) concentrations in 1996 were generally lower at the Potomac River station (RGPT) and at both stations in the mainstem bay (R-64 and PNPT). Hypoxia was severe at these sites in June - August. SONE locations in the Patuxent River were also prone to summer hypoxia during 1996, especially during the early summer period.

Rates of sediment-water fluxes of oxygen (SOC) in the Patuxent River during 1996 ranged from -0.14 g O_2 m^{-2} day^{-1} to -2.87 g O_2 m^{-2} day^{-1} while sediment oxygen consumption (SOC) at all other monitoring stations ranged from zero (0.0) g O_2 m^{-2} day^{-1} to -1.16 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. 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 high, possibly a response to improved oxygen conditions in bottom waters after a period of low DO conditions in June, 1996.

Ammonium (NH_4^+) fluxes at the two down river locations (St Leonard Creek [STLC] and Broomes Island [BRIS]) in the Patuxent River were similar to or slightly lower than those recorded in earlier years despite high river flow (and associated diffuse source nutrient load) which occurred in 1996. 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 main bay sites but this is probably caused by lower organic matter deposition during 1996 at these sites rather than persistent improvements in water quality. With few exceptions, fluxes of nitrate plus nitrite (NO_2^- + NO_3^-) were considerably less positive (*i.e.* directed from sediments to water column) than usual at most stations. Positive nitrate fluxes (or smaller fluxes directed into sediments) are a definite sign of sediment nitrification activity which is a microbial process converting ammonium to nitrate and requires that oxygen be present. Positive nitrate fluxes are a sign of improved sediment quality. The fact that this did not generally occur during a year of higher than normal nutrient loading rates is another indication that bay sediments are responsive to loading rates.

During 1996, inorganic phosphate (DIP or PO_4^-) fluxes were generally small in the lower Patuxent River and this most probably resulted from more oxidized sediment conditions at these sites. The reduction in phosphorus fluxes was most noticeable in the Patuxent River where reductions were large (up to a factor of 2). Measurements of silicate fluxes ($Si(OH)_4$) were discontinued after June, 1995. Rates of inorganic carbon (TCO_2) appear to be positively correlated with sediment organic matter content and with nutrient loading rates. This technique avoids the low dissolved oxygen problems associated with sediment oxygen consumption (SOC) rate measurements. A distinctive gradient of increasing TCO_2 fluxes was evident in the Patuxent with highest fluxes proximal to nutrient and organic matter sources in the upper estuary.

An analysis of sediment oxygen and nutrient exchanges (SONE) data for status and trends was completed for eight SONE stations. Indications of current status (average of fluxes during 1994, 1995 and 1996) were as expected; status was poor or fair in areas exposed to high rates of nutrient loading, status was poor or fair in areas with low DO levels during summer months and status was poor or fair at locations proximal to nutrient sources. At other locations status was fair to good for most flux variables. The high load years of 1994 and 1996 probably moved several status bars towards poorer conditions than would have been the case if recent river flows had been lower. There were few statistically significant trends evident at SONE stations. It can be concluded that nutrient load reductions have not yet been in place long enough and reductions have not been large enough to allow detection of trends in these variables.

Two approaches to monitoring impacts of nutrient and organic matter enrichment were also investigated during 1996. A method of increasing spatial resolution of the SONE program was introduced. This approach involves using sediment chlorophyll-a, sediment Eh (redox potential) and bottom water dissolved oxygen conditions as predictors of flux. These variables are mapped at fine spatial scales in spring and early summer and flux magnitude calculated based on these conditions; a statistical assessment of sediment chlorophyll-a and other variables are provided in this report. Results of sediment chlorophyll mapping in the Patuxent River indicated substantial month to month variability in the mass of deposited chlorophyll and in the spatial distribution of this material. During late winter chlorophyll mass was occasionally highest in shoal areas (possibly because of in-situ benthic diatom production) but was highest in deep waters during summer. Using sediment chlorophyll mass as a key variable, statistically significant regression (linear single and multiple variable models) analyses were developed for SOC, ammonium, phosphorus and nitrite plus nitrate fluxes. This analysis will be repeated during 1997 to confirm these relationships but the indication at this point is that these fluxes can be reasonably predicted based on a limited suite of readily measured variables. Secondly, a data time series (15 minute intervals) of temperature, salinity and dissolved oxygen was made at the lower end of the turbidity maximum zone of the Patuxent Rover during July through October 1996. The data set was analyzed for patterns of primary production and community respiration. Results indicated that production rates were higher than those measured during the mid-1960's but lower than rates observed in 1992. This procedure adds an additional sensitive monitoring tool for gauging the recovery of the Patuxent River in response to reduced nutrient loading rates.

Nutrient loading rates (total nitrogen [TN] and total phosphorus [TP]) were developed for the period 1960 - 1977 for the Patuxent River (fall line). These rates were estimated from historical rainfall and nutrient concentration data. During the decade of the 1960's TN and TP annual fall line loads averaged about 1300 kg N day^{-1} and 275 kg P day^{-1}, respectively; during the decade of the 1970's TN and TP loads averaged about 3000 kg N day^{-1} and 450 kg P day^{-1}, respectively; during the 1980's TN and TP loads averaged about 4500 kg N day^{-1} and 400 kg P day^{-1}, respectively; during the first half of the 1990's TN and TP loads were about 3300 kg N day^{-1} and 190 kg P day^{-1}, respectively.

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.*, 1995a). 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 sustains 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 was initiated and has continued since 1984. The working hypothesis is that if nutrient and organic matter loading to the bay decrease 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, include routine monitoring of sediment oxygen and nutrient exchanges (SONE) at locations in the mainstem bay and tributary rivers, investigations of techniques to increase the spatial coverage of SONE measurements based on sediment chlorophyll-a distributions and high frequency (daily) measurements of community metabolism. The latter two components are conducted in the Patuxent River estuary, an area of particular interest because of recently decreased nutrient loading rates. The EPC program discontinued measurements of organic matter deposition (Vertical Flux [VFX] study) in mid-1992 and SONE measurements at some stations due to fiscal constraints.

Although the Ecosystem Processes Component (EPC) has been modified since its inception in 1984, the overall objectives have remained the same and are consistent with those of the Monitoring Program, and are as follows:

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

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.

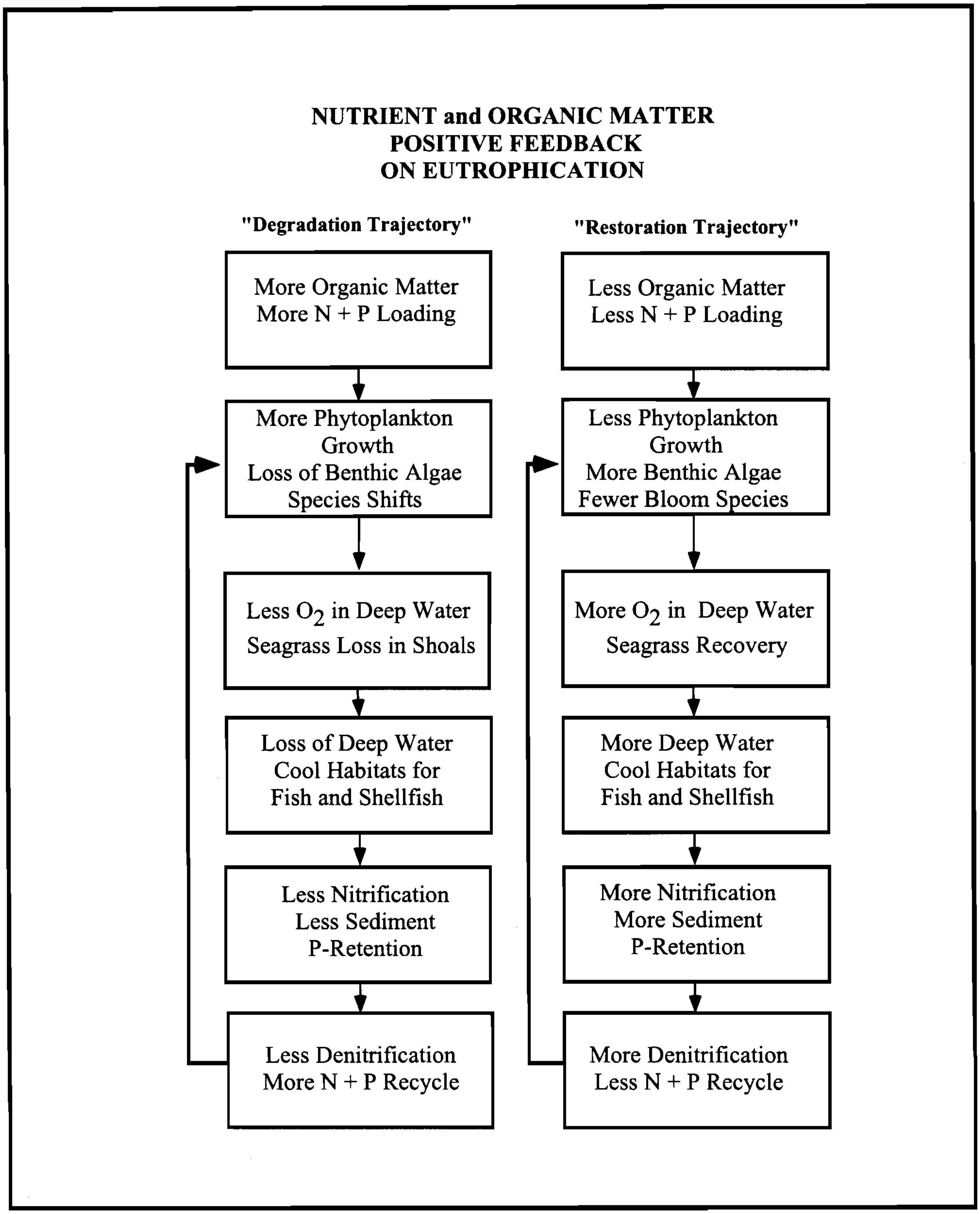

Figure 2-1. Nitrogen (N) and phosphorus (P) loads to the Chesapeake Bay affect coupled sediment nitrification-denitrification and sediment nitrogen and phosphorus cycling. High nitrogen and phosphorus inputs will ultimately result in less nitrogen and phosphorus removal from the benthos, while significant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

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).

The first phase of the study was undertaken over a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation, which were keys in the identification of problem areas. The EPC measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and the sediment surface. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of EPC monitoring have been summarized in a series of interpretive reports (Boynton *et al.*, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995b and 1996). The results of this characterization effort have largely confirmed the importance of deposition and sediment processes in determining water quality and habitat conditions.

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

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay was reevaluated. In this phase of the process, the monitoring program was 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.

During the latter part of 1997 the Chesapeake Bay Program will enter another phase of re-evaluation. Since the last evaluation, programs have developed further information, nutrient reduction strategies have been implanted and, in some areas, habitat improvements have been accomplished. The overall goal of the 1997 re-evaluation is to assess the progress of the program and make modifications where needed in the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay.

Ecosystem Processes Component (EPC) program data collected during 1996 are presented and interpreted in this report. Sediment-water fluxes are examined for trends using standardized statistical techniques; results of a sediment mapping technique are presented which indicate that sediment water and nutrient exchanges (SONE) measurements may well be extended to cover larger spatial scales at reduced costs; high frequency (daily) measurements of community metabolism in the Patuxent River are examined for controlling factors and compared to identical measurements made in the early 1990's and during the decade of the 1960's.

3. LOCATION OF STATIONS AND DESCRIPTION OF FIELD METHODS

Data collected during 1996 includes three major segments of the Ecosystem Processes Component program. The first, Sediment Oxygen and Nutrient Exchanges (SONE), has been in place for twelve years and during 1996 included measurements at seven stations during four summer months. This long-term data set was used to determine status and trends. The second is a new element and involves sediment chlorophyll-a mapping and MINI-SONE measurements (involving abbreviated SONE type measurements) in the Patuxent River which has as its goal the development of a simpler methodology for assessing sediment responses to water quality changes. The third element involves high frequency (daily) measurements of community metabolism in the Patuxent River (at the MD Route 231 Bridge) near Benedict, MD. Comparable measurements are available from the 1960's and early 1990's (Sweeney, 1995) providing an opportunity to examine the response of the estuary to both increasing (1960 - 1991) and decreasing (1992 - 1996) nutrient loads.

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

During 1996, measurements of sediment-water oxygen and nutrient exchanges (SONE) were made four times at seven locations; two stations in the mainstem bay and at least one station in two major tributary rivers (Patuxent and Potomac). The 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 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

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[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.

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 1996. Prior to July 1989, four of the ten SONE stations sampled were located along the salinity gradient in the mainstem bay between Point No Point (north of the mouth of the Potomac River) and Still Pond Neck (20 km south of the Susquehanna River mouth). Two stations were located in each of three tributary rivers (Patuxent River: Buena Vista [BUVA] and St. Leonard Creek [STLC], Choptank River: Windy Hill [WDHL] and Horn Point [HNPT] and Potomac River: Maryland Point [MDPT] and Ragged Point [RGPT]), 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 1996, two of the seven stations sampled as part of the SONE study are located in the mainstem bay adjacent to Point No Point (north of the mouth of the Potomac River) and Buoy R-64 (south of the Choptank River mouth). Four stations are located in the Patuxent River estuary and one station is located in the lower mesohaline region of the Potomac River. 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). The SONE station in the lower Choptank River (Horn Point [HNPT]) was not sampled during 1996.

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 nitrate 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.

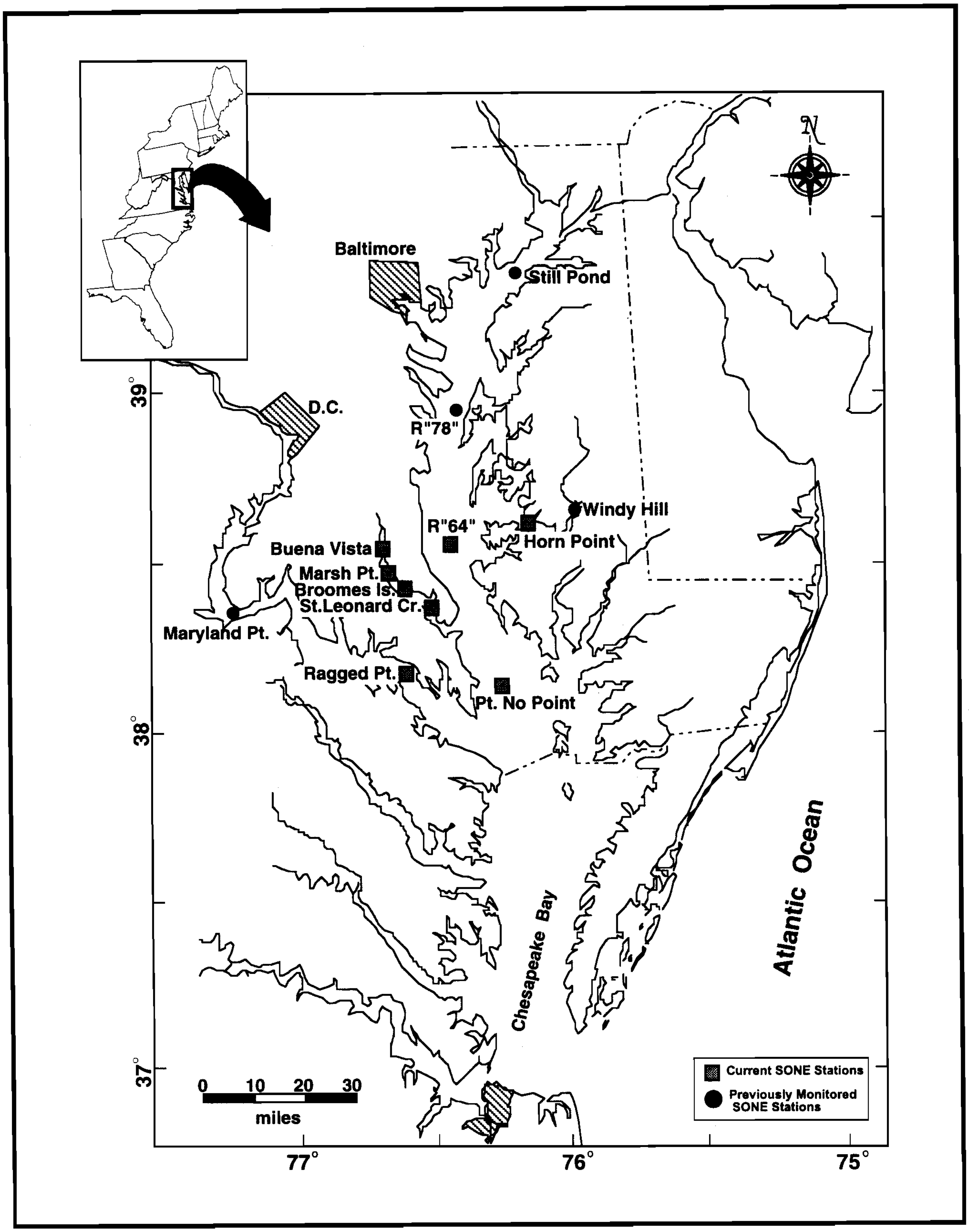


Figure 3-1. Location of Current and Previously sampled Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations in the Maryland portion of Chesapeake Bay (1984 - 1996).

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 they appear in the data tables.

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

* Prior to July 1, 1989, measurements at SONE stations were made four times per year (April or May, June, August and October or November). In 1989 and 1990, measurements were made five times per year (May, June, July, August and October). In 1991, 1992, 1993 and 1994, measurements were made six times per year (May, June, July, August, September and October). In 1995, measurements were made five times per year (May, June, July, August and September).

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

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

Table 3-1.3. SONE Station Code and Description

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

NOTES:

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

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

Table 3-2. Station Salinity

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

The Salinity Zone layer codes are as follows:

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

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.

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 four monthly measurements made between June and September, 1996 (SONE 58 through SONE 61). A complete listing giving the sampling dates of all SONE cruises (1984 - 1996) together with alpha-numeric cruise identification codes can be found in Table 3-3.

3.3 Field Methods for Sediment Oxygen and Nutrient Exchanges Program

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 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^-), particulate carbon (PC), particulate

[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 2	OCT 1984	15 OCT	18 OCT	Aquarius
SONE 3	MAY 1985	06 MAY	09 MAY	Aquarius
SONE 4	JUN 1985	24 JUN	27 JUN	Aquarius
SONE 5	AUG 1985	19 AUG	22 AUG	Aquarius
SONE 6	OCT 1985	14 OCT	17 OCT	Aquarius
SONE 7	MAY 1986	03 MAY	08 MAY	Aquarius
SONE 8	JUN 1986	23 JUN	26 JUN	Aquarius
SONE 9	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 AUG	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	01 MAY 08 MAY	03 MAY 08 MAY	Orion 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

Table 3-3. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 29	MAY 1991	06 MAY	09 MAY	Aquarius
SONE 30	JUN 1991	10 JUN	13 JUN	Aquarius
SONE 31	JUL 1991	22 JUL	25 JUL	Aquarius
SONE 32	AUG 1991	15 AUG 19 AUG	15 AUG 22 AUG	Aquarius
SONE 33	SEP 1991	16 SEP	18 SEP	Aquarius
SONE 34	OCT 1991	14 OCT 18 OCT	15 OCT 18 OCT	Aquarius
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 14 JUN	11 JUN 15 JUN	Orion
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 20 MAY	18 MAY 21 MAY	Aquarius
SONE 48	JUN 1994	13 JUN 20 JUN	17 JUN 20 JUN	Orion
SONE 49	JUL 1994	11 JUL 13 JUL	11 JUL 15 JUL	Orion
SONE 50	AUG 1994	8 AUG 15 AUG	11 AUG 15 AUG	Orion
SONE 51	SEP 1994	12 SEP	14 SEP	Orion

Table 3-3. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 52	OCT 1994	11 OCT 17 OCT	12 OCT 18 OCT	Orion
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
SONE 58	JUN 1996	14 JUN	17 JUN	Orion
MINI-SONE 1	JUN 1996	17 JUN	17 JUN	Orion
SONE 59	JUL 1996	15 JUL 23 JUL	16 JUL 24 JUL	Orion
MINI-SONE 2	JUL 1996	25 JUL	25 JUL	Orion
SONE 60	AUG 1996	12 AUG 19 AUG	12 AUG 21 AUG	Orion
MINI-SONE 3	AUG 1996	22 AUG	22 AUG	Orion
SONE 61	SEP 1996	9 SEP 12 SEP 16 SEP	9 SEP 13SEP 16 SEP	Orion
MINI-SONE 4	SEP 1996	13 SEP	13 SEP	Orion

NOTES:

See also: Boynton *et al.* (1997) for other Chesapeake Bay sediment flux measurements.

nitrogen (PN), particulate phosphorus (PP), and total and active chlorophyll-a concentrations. Measurements of silicious acid ($Si(OH)_4$) were discontinued beginning in June, 1996.

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. Near-surface samples were discontinued in July 1991 (SONE 31) as these measurements are not of particular importance in the interpretation of flux data.

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 for total and active sediment chlorophyll-a to a depth of 1 cm from 1985 through July 1989. In August 1989 measurements were made to a depth of 2 - 3 mm and in October, 1993, two measurements (2 mm and at 1 cm) were recorded. Particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), are sampled to a depth of 2 - 3 mm.

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 60 minutes over a 4 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 ($NO_2^- + NO_3^-$) and dissolved inorganic phosphorous (DIP or PO_4^-). 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

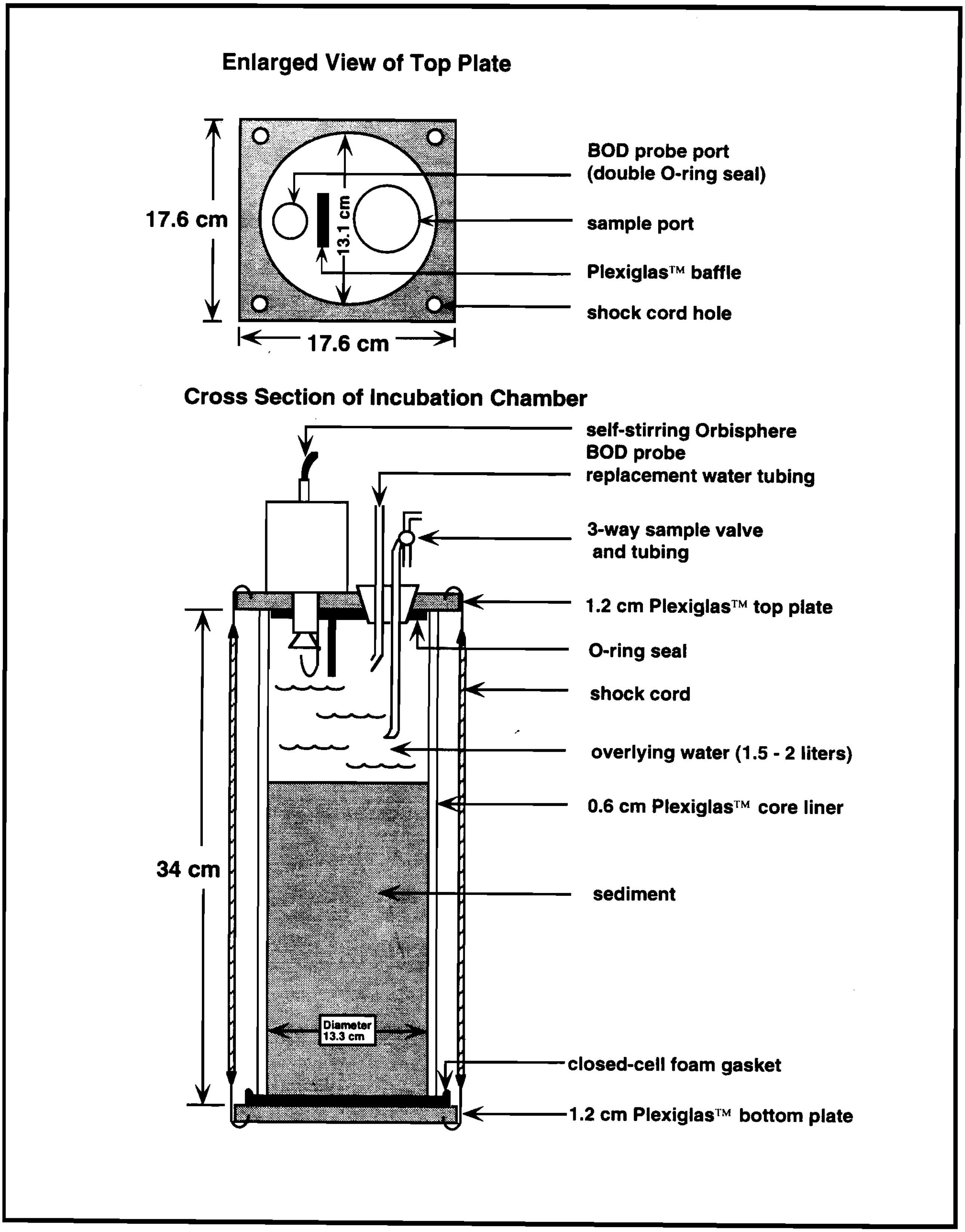


Figure 3-2. Schematic Diagram of the Incubation Chamber

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 beginning in 1995.

3.3.5 Dissolved Inorganic Carbon (TCO_2)

3.3.5.1 Field Method

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 as a free gas when 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 1996 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 through September, 1996 at a station in the mainstem bay (R-64), four stations in the Patuxent River (St. Leonard Creek [STLC], Broomes Island [BRIS], Marsh Point [MRPT] and Buena Vista [BUVA]) and one station in the lower Potomac River (Ragged Point [RGPT]).

3.3.6 Chemical Analyses used in Sediment Oxygen and Nutrient Exchanges Program

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 are as follows: 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); 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.

3.4 Location of Stations used in the Patuxent River Surficial Sediment Chlorophyll-a Mapping

These mapping activities were conducted to provide a quantitative index of the size and distribution of the spring phytoplankton bloom and potentially serve as a predictive index of sediment-water oxygen and nutrient exchanges.

In the Patuxent River tributary, thirty-seven (37) stations were sampled between the most upriver SONE Station (Buena Vista, [BUVA]) to Point Patience, several miles downstream of the St. Leonard Creek (STLC) station (Figure 3-3.). The stations represent both a salinity and depth gradient and were sampled once a month during March, April, and May, 1996. These months were chosen to document the settling of the spring bloom to the bottom sediments of the Patuxent River.

3.4.1 Chlorophyll-a measurements at Patuxent River Surficial Sediment Chlorophyll-a Mapping Stations

At each of thirty-seven (37) stations in the Patuxent River an intact sediment core is acquired using a modified Bouma box corer. The sediment sample is subcored to a depth of one centimeter. This subcore is placed in a 50 ml centrifuge tube, frozen on shipboard, and analyzed back at the laboratory for both total and active chlorophyll-a concentrations.

3.5 Location of Stations in the Patuxent River MINI-SONE Flux Study

The purpose of the MINI-SONE study in the Patuxent River is to increase the spatial resolution of SONE measurements in this targeted estuary and to develop a methodology designed to reduce costs of monitoring sediment effects on water quality.

After examining the station depth (Figure 3-4.) and the surficial sediment chlorophyll-a distribution in the mesohaline region of the Patuxent, oxygen and nutrient flux measurements (referred to as MINI-SONE measurements because only a single sediment core was obtained at each site and a limited number of nutrient analyses were conducted) were made at the following six sediment chlorophyll-a stations: PX07, PX15, PX21, PX23, PX25 and PX32.

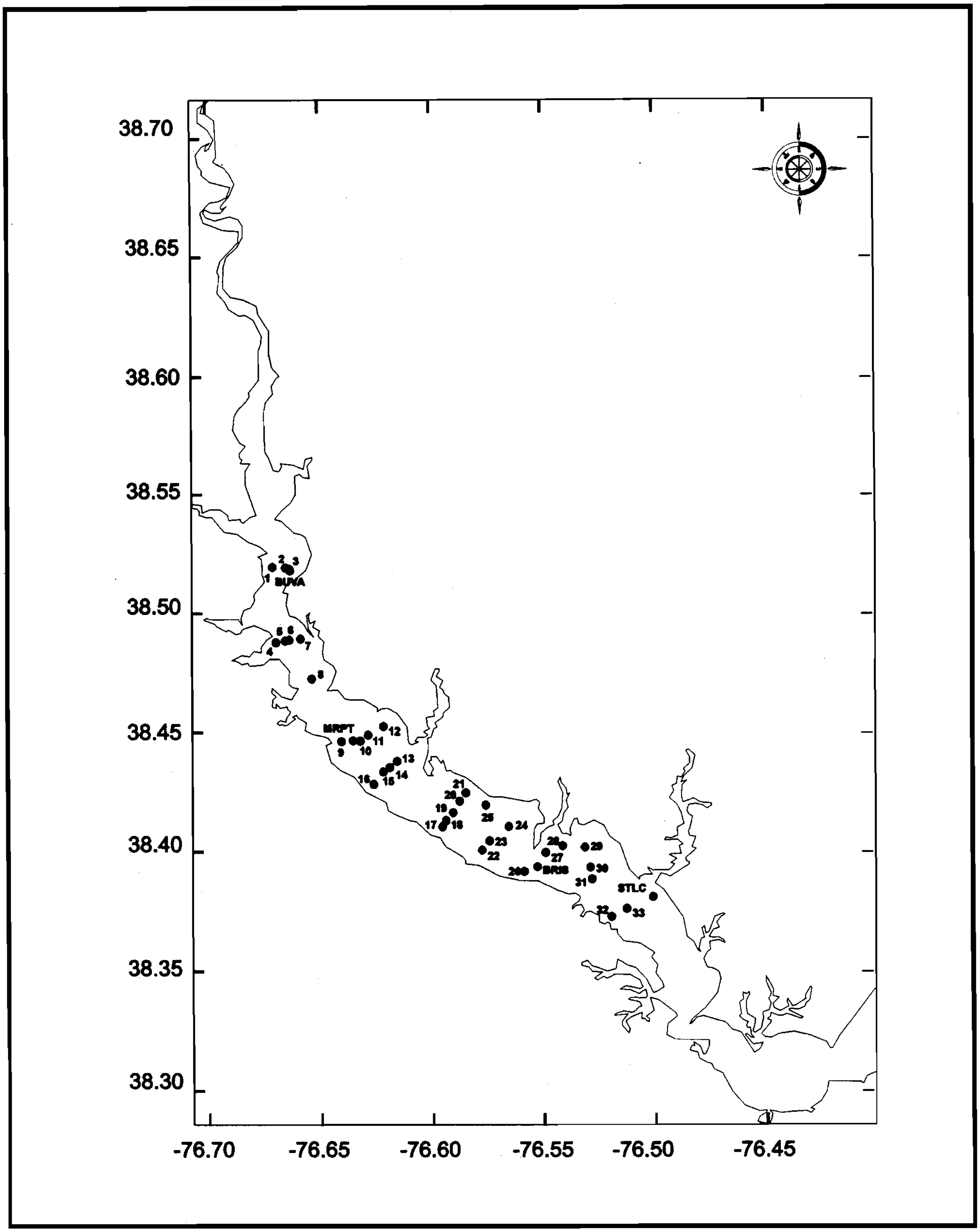


Figure 3-3. Location of thirty-seven (37) stations grouped in nine transects located in the Patuxent River used in the Sediment Chlorophyll-a Mapping Study.
** Stations PX08 and PX25 lie between transects and are grouped with stations in the nearest transect.*

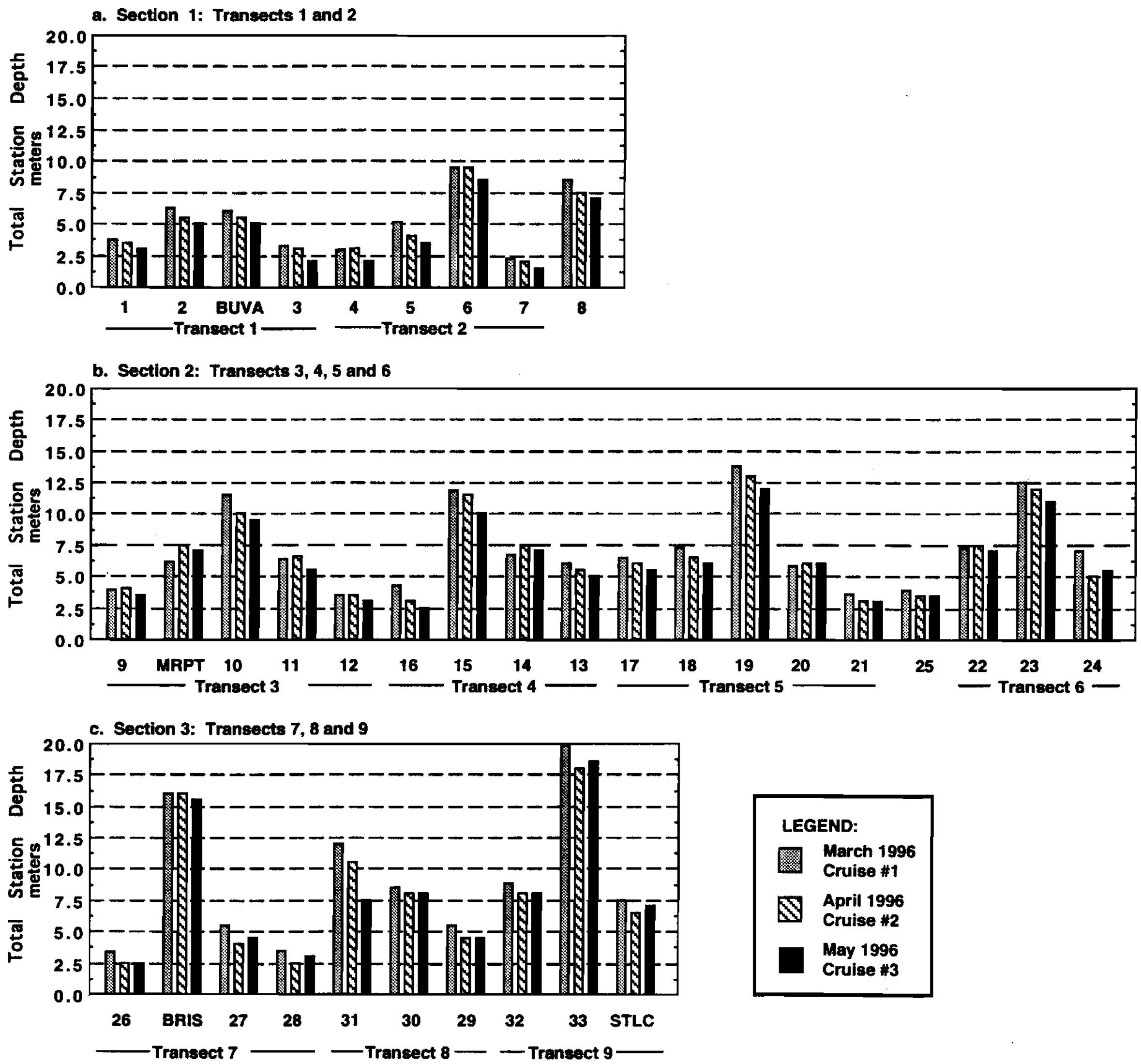


Figure 3-4. Total station depth measurements at thirty-seven (37) sediment chlorophyll-a mapping stations in the Patuxent River in March, April and May, 1996.

** Station locations are shown in Figure 3-3. (page 24). Stations PX08 and PX25 lie between transects and are grouped with stations in the nearest transect.*

These six stations cover the range of surficial sediment chlorophyll-a conditions measured at the thirty-seven (37) stations during March, April, and May, 1996.

Mapping winter-spring deposition of chlorophyll-a to bottom sediments in this estuary and relating this to sediment nutrient fluxes during the warmer months of the year will allow for very extensive spatial expansion of SONE coverage and a great reduction in SONE measurements if the sediment chlorophyll-a vs flux relationships are strong. A direct coupling between these has been demonstrated in other parts of the Bay (Cowan and Boynton, 1996). If this same coupling can be demonstrated in the Patuxent River, spring surficial sediment chlorophyll-a measurements may be used as a good and inexpensive predictor of summer nutrient fluxes from the sediments of this and other regions of the bay system.

3.5.1 Field Methods

3.5.1.2 Water Column Profiles

At each of the MINI-SONE stations a vertical water column profile of temperature, conductivity, salinity, and dissolved oxygen was measured at 2 meter intervals from the surface to one meter above the bottom. Water column turbidity was measured using a Secchi disc.

3.5.1.2 Sediment Profiles

At each MINI-SONE station an intact sediment core was used to measure the redox potential (Eh) of sediments at 1 cm intervals (starting with an overlying water, then a surface measurement) to 2 cm and at 2 cm intervals to 10 cm. Eh is determined using a platinum wire electrode referenced to a calomel electrode connected to a Corning Model 250 ion analyzer. The electrode response was calibrated using a standard Zobel's solution. Additionally, surface sediments were analyzed for total and active chlorophyll-a at the top 2 to 3 mm and the top 1 cm of the core.

3.5.1.3 Sediment - Water Fluxes

One intact sediment cores was obtained at each MINI-SONE station using a modified Bouma box corer. These sediment cores, each contained in a 15 cm x 30 cm Plexiglas microcosm (Figure 3-1.), constitute the basic system where changes in oxygen, nutrient, and other compound concentrations are determined. A decrease in these overlying water concentrations indicates uptake (either biologically or chemically) of the compounds by the sediments. Conversely, an increase in concentration indicates release by the sediments. Details of the technique are outlined in Section 3.3.4.

In most cases, incubations were conducted for four hours and five samples were collected from the MINI-SONE core. Every hour, oxygen concentrations are recorded and overlying water samples used to measure the various compound concentrations were extracted. (Note: as a water sample was extracted, an equal amount of bottom water from a reservoir was simultaneously pulled into the microcosm.) During June, 1996 a total of five samples were taken from the cores simply as a check on the future technique of reducing sampling frequency. The overlying water samples were immediately processed and frozen, then later analyzed for ammonium (NH_4^+), Nitrite (NO_2^-), and nitrite plus nitrate ($NO_2^- + NO_3^-$) and dissolved inorganic phosphorus (DIP or PO_4^{-3}) concentrations. Net sediment-water fluxes for oxygen and nutrients were estimated by: 1) calculating the rate of change in concentration in the overlying water during the four hour incubation period, and 2) converting the volumetric rate of change to an areal flux using the volume and area of the microcosm.

3.5.2 Chemical Analyses

Standard oceanographic and estuarine methods of chemical analysis were used for all determinations. Detailed reference material pertaining to all chemical analyses used can be found in section 3.4 and in the EPC Data Dictionary (Boynton and Rohland, 1990). In brief, methods for the determinations of dissolved nutrients are: ammonium (NH_4^+), nitrite (NO_2^-) and nitrite plus nitrate (NO_2^- + NO_3^-) and dissolved inorganic phosphorus (DIP or PO_4^{-3}), are measured using the automated method of EPA (1979); methods of Strickland and Parsons (1972) and Shoaf and Lium (1976) are followed for chlorophyll-a analysis.

3.6 High Frequency Monitoring near Benedict, MD

A Hydrolab DataSonde-3 was deployed at the high frequency monitoring site on the Route 231 bridge crossing the Patuxent River near Benedict, MD between 1 June, 1996 and 18 October, 1996. Parameters monitored were: time, temperature, specific conductance, salinity, dissolved oxygen percent saturation (DO % sat) and dissolved oxygen (DO). The DataSonde probes were maintained at a constant depth of one meter below the surface.

The major objectives of this effort are to: 1) examine dissolved oxygen data to determine if, at current loading regimes, dissolved oxygen habitat criteria are achieved and 2) to use the temperature, salinity and dissolved oxygen data to calculate daily water column production and respiration for this zone of the estuary and relate calculated rates to rates observed at this site when nutrient loads were considerably lower, as was the case in the mid-1960's.

The monitor operated continuously, logging measurements every 15 minutes for three to four days per week (*e.g.* Tuesday through Thursday) following the approach used by Sweeney (1995). The DataSonde is protected by a PVC tube and deployed at a constant depth of one meter below the water surface. The device was calibrated before deployment and the calibration checked after deployment in order that the data set could be corrected for drift if needed. The data stored in the memory of the DataSonde were down loaded to a computer at the end of each deployment. It was previously determined that during June through September intense biofouling occurs which restricts continuous monitoring to three days. When longer deployments (without maintenance of the sensor probes) are attempted, the data collected need considerable correction.

4. DATA MANAGEMENT AND QUALITY ASSURANCE AND QUALITY CONTROL (QA\QC) CHECKING

Data collected between 1984 and 1996 for the Sediment Oxygen and Nutrient Exchanges (SONE) Program has been organized into five major data sets and one small data set. Historical data for the Vertical Flux Program (VFX; now discontinued) have been organized into three data sets. Data from each of the two new additional studies (chlorophyll-a mapping and MINI-SONE program and high frequency oxygen measurements at the Benedict Bridge on the Patuxent River) are stored separately.

4.1. Sediment Oxygen and Nutrient Exchanges (SONE) Data Sets

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 were subsequently added to Volume III. Volume V was appended to Level 1, No 13 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 96-040 (Boynton *et al.*, 1996) and contained hard copy data table listings for 1993, 1994 and 1995.

Additionally Appendix B (Part II) of this report contains SONE data tables listings of variables measured during 1996. 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).

4.1.1. 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 in the water column.

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.

4.1.2 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.

4.1.3 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.

4.1.4 Statistical Analysis System (SAS) Files

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

A complete set of SAS data files for 1984 through 1996 as well as the ASCII and SAS program files used to create them 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 1997 to complete the existing Sediment Oxygen and Nutrient Exchanges database.

Table 4-1. 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., $PO_4F>TDP$), 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
YB	No blank measured for MINI-SONE fluxes
YY	Data not recorded

4.2 Sediment Chlorophyll-a Mapping Data Sets

Appendix C of this report contains data listings for variables measured in the chlorophyll-a mapping cruises in March, April and May, 1996. 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 mapping cruise (EPC Data Dictionary; Boynton and Rohland, 1990).

The data collected at each chlorophyll-a mapping station are organized into two data sets:

BOTTOM WATER PARAMETERS (Filename: **WTPBTMxx,** Table C-1) contain temperature, salinity and dissolved oxygen data measured in bottom water samples (~ 1 m from the bottom).

SEDIMENT CHLOROPHYLL-a PARAMETERS (Filename: **SEDCHLxx,** Table C-2) include measurements of total and active chlorophyll-a concentrations within the top 1 cm of sediment.

4.3 MINI-SONE data sets

Appendix D of this report contains data listings for variables measured in the MINI-SONE study conducted in June through September 1996. 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 MINI-SONE cruise (EPC Data Dictionary; Boynton and Rohland, 1990).

The data collected at each MINI-SONE station are organized into four data sets:

WATER COLUMN PROFILES (Filename: **MNHPRFxx,** Table D-1) contain temperature, salinity and dissolved oxygen data measured at two meter intervals in the water column.

SEDIMENT PROFILES (Filename: **MNSPRFxx,** Table D-2) include redox potential and sediment measurements of total and active chlorophyll-a concentrations.

CORE DATA (Filename: **MNCDATxx,** Table D-3) lists dissolved oxygen and nutrient measurements in MINI-SONE sediment-water flux chambers.

SEDIMENT-WATER FLUX (Filename: **MNFLUXxx,** Table D-4) is a summary table providing oxygen and nutrient flux data.

4.4 Benedict Bridge High Frequency Monitoring data set

Appendix E of this report contains data listings for variables measured in June through October, 1996 at the Benedict Bridge during the High Frequency Monitoring Program. Missing data have been identified and documented.

4.5. Quality Assurance/Quality Control (QA/QC) Checking

4.5.1 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 3-4) 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 MINI-SONE program have been added.

4.5.2 Preparation of Data Tables for SONE and MINI-SONE

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.

4.5.3 Preliminary Checking of Data Tables for SONE and MINI-SONE

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. The full data set is plotted and outlier values reevaluated. In the early years (1985 and 1986) some of the methods had not been perfected, so close scrutiny of outlier values was important. Values below detection limits are also indicated in the data tables.

4.5.4. 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 nutrient 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 nitrogen (ammonium [NH_4^+], nitrite [NO_2^-], nitrite plus nitrate [$NO_2^- + NO_3^-$] and dissolved inorganic phosphorus [DIP or PO_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).

4.5.4. Quality Assurance/Quality Control (QA/QC) of High Frequency Data collected at Benedict Bridge

The raw data set was plotted to show high frequency variations (Figure 9-2.1. - 9-2.5.). The graphics were examined and missing values where identified together with other values which were below the expected range and which were obviously in error. The log book was checked for notations with respect to faulty probes or unusual field conditions *e.g.* fouling. The formula which is used by the SONE program in the water profile data set to calculate percentage dissolved oxygen saturation (DO SAT [%]) was used as a check to determine the accuracy of the readings recorded by the probe. The probe was rigorously calibrated prior to deployment and on immediate return to the laboratory prior to the data dump. Since this program is to continue into 1997 it is envisaged that a computer program will be developed to assist with QA/QC checking especially to identify values below detection limits.

5. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) PROGRAM

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 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 been used as an indication of nutrient loading rates.

5.1 River Flow Characteristics in 1996

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 (Boynton *et al.*, 1995). Therefore, it is useful to consider river flow which is a good surrogate variable for diffuse source loading.

5.1.1 Average Annual River Flows

Annual average river flows for the period 1978 through 1996 are shown in Figure 5-1.1. The nineteen year average (1978 - 1996) flow to each system during this period is indicated by horizontal lines on this figure (James *et al.*, 1990; James, *pers. comm.*, 1994, 1995, 1996). The nineteen year average for the Susquehanna River was 40,251 cubic feet per second (cfs), the Potomac River 12,978 cfs, the Patuxent River 377 cfs and the Choptank River 139 cfs. 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 into all systems were above the nineteen 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 nineteen 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 nineteen 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 nineteen 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 Pattsuxent River 446 cfs). 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 nineteen year average value during the Ecosystem Processes Component monitoring period with a few exceptions (1989, 1993,1994 and 1996). 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.

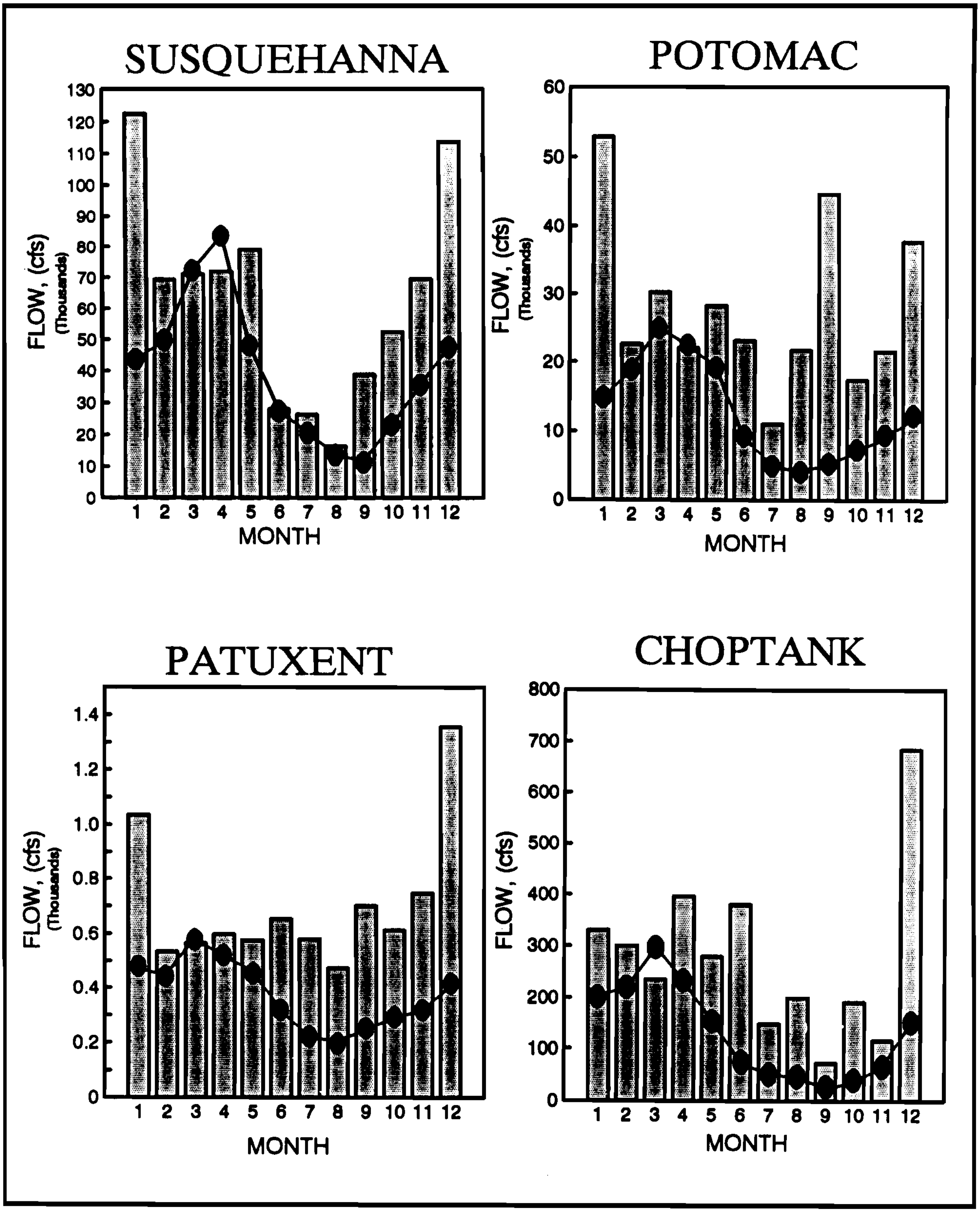


Figure 5-1.1. Bar graphs of average annual river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for the period 1978 through 1996 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers. comm.*, 1994, 1995 and 1996). Flows were measured at Conowingo, MD (01578310); Washington, D.C. (01646500); Bowie, MD (01594440) and Greensboro, MD (01491000) for the four systems, respectively.

Data for 1996 indicate that this was an unusually wet year; freshwater inputs (and probably diffuse source nutrient inputs) were far above average and were the highest annual flows recorded in each of the basins since 1978 (except for 1979 in the Patuxent basin).

5.1.2 Average Monthly River Flows

One of the more obvious characteristics of estuarine systems is the time and space variability associated with many parameters, 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 5-1.2.). In this figure the vertical bars represent average monthly flows for 1996 while the bold dots represent average monthly flows calculated over longer time periods (1978 - 1996).

Peak or seasonally high flows during 1996 were recorded between January and May in all of the rivers and through June in several. In some of the systems flows decreased as usual during summer months but flows increased sharply in the late summer and continued to be high or extremely high through the fall. The flood flows of January and December in all systems and the flood flows of September in the Potomac mark 1996 as a very unusual year. The Susquehanna had a flow rate of over 122,500 cfs (January), the Potomac 52,890 cfs (January), the Patuxent 1,035 cfs (January) and the Choptank 331 cfs (January; Figure 5-1.2.); all of these are well above average. In 1996, December flows in all rivers were very large compared with the nineteen year average (December flow rates: Susquehanna-113,700 cfs, Potomac 37,630 cfs, Patuxent 1,357 cfs and Choptank 685 cfs; Figure 5-1.2.). For example, flows during these months from the Susquehanna were more than a factor of two greater than the long term average; a similar situation was evident in the other rivers as well.

These data are presented to emphasize the need for careful consideration of temporal relationships between variables such as river flow or nutrient loading rates and ecosystem processes such as 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 rates 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.

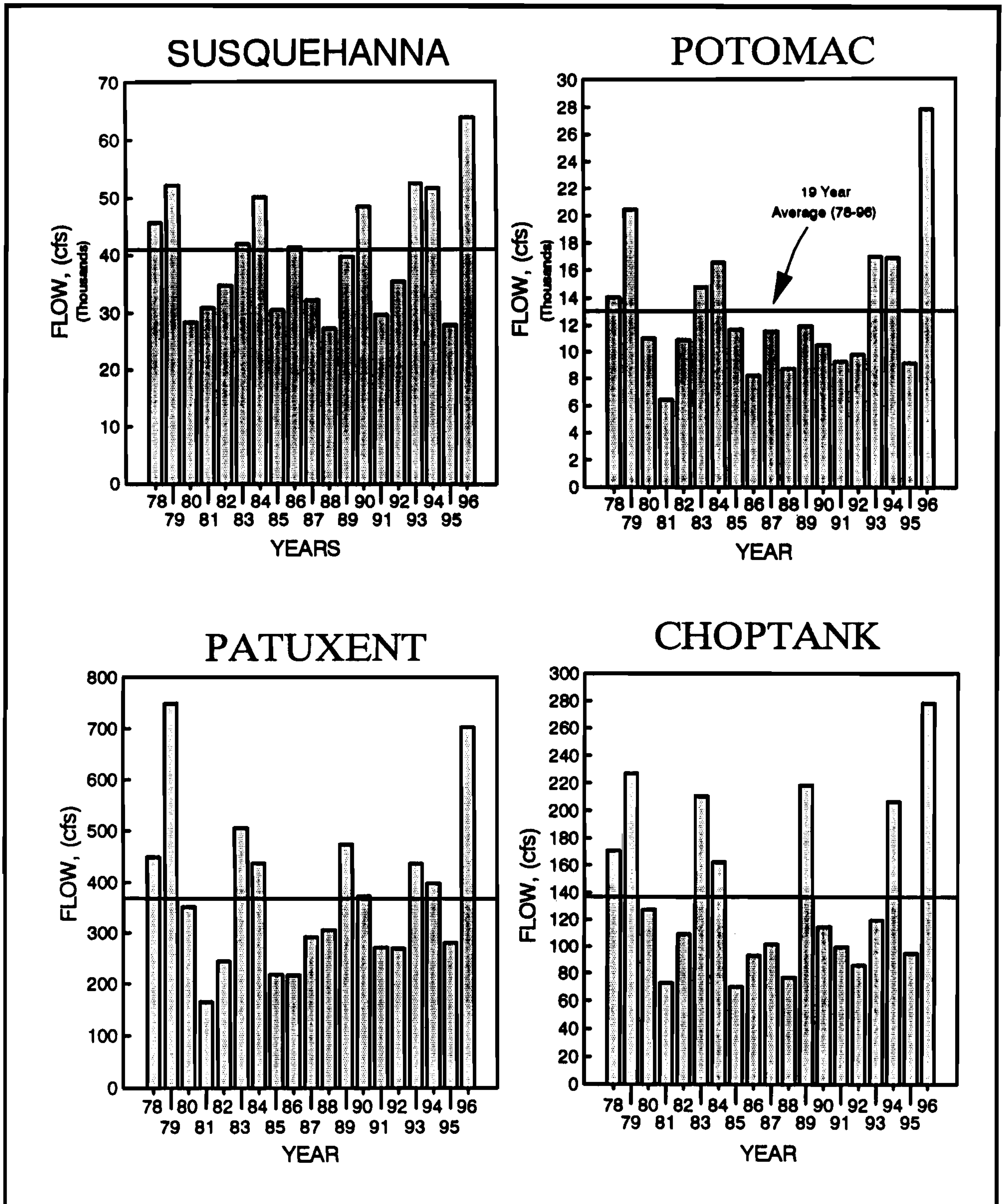


Figure 5-1.2. Bar graphs of average 1996 monthly river flows from the Susquehanna, Potomac, Patuxent and Choptank Rivers. The dot and line plots represent the long-term average flow for the period 1978 through 1996 (James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers comm.*, 1994, 1995 and 1996). Flows were measured at Conowingo, MD (01578310); Washington, D.C. (01646500); Bowie, MD (01594440) and Greensboro, MD (01491000) for the four systems, respectively.

5.2 Physical and Chemical Characteristics of Bottom Waters and Sediments: Sediment-water Fluxes and in situ Environmental Conditions

5.2.1 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 and sediment characteristics). The significance of these relationships (p values) has increased over the years as more observations have been added and as more has been learned about the mechanistic relationships between sediment fluxes and environmental conditions.

5.2.2 Bottom Water and Sediment Conditions

5.2.2.1 Temperature

Bottom water temperature conditions in the Patuxent River during 1996 ranged from 21.7 C at Broomes Island (BRIS) in June to 27.5 at Buena Vista (BUVA) in July. In the Potomac River bottom water temperatures at Ragged Point (RGPT) ranged from 17.9 C in June to 25.3 C in September. In the mainstem of the bay bottom water temperature conditions ranged from 17.5 C in June, 1996 to 25.1 C in August at Point No Point (PNPT) and at R-64 from 17.2 C in June to 25.4 C in September, 1996 (Tables B1-58. - B1-61.).

Temperature conditions followed the pattern observed in previous years and were comparable to 1995 temperature measurements despite the fact that freshwater inflows were appreciably higher in 1996 than in 1995.

5.2.2.2 Salinity

Bottom water salinity conditions during 1996 ranged from 3.9 ppt in July at Buena Vista (BUVA) to 12.2 ppt in September at three stations (St. Leonard Creek [STLC], Broomes Island [BRIS] and Marsh Point [MRPT]) in the Patuxent River, from 14.5 ppt in September, 1996 to 13.2 ppt in August, 1996 at Ragged Point (RGPT) in the Potomac River. In the mainstem bay salinity ranged from 14.6 ppt in July, 1996 to 18.8 ppt in August at Point No Point (PNPT) and from 14.1 ppt in September to 18.6 ppt in August, 1996 at R-64 (Tables B1-58. - B1-61.).

Salinity was noticeably lower at all seven stations in 1996 than in previous years characterized by low river inputs (such as 1995).

5.2.2.3 Dissolved Oxygen

Bottom water dissolved oxygen conditions during 1996 ranged from 0.48 mg l^{-1} in July at Marsh Point (MRPT) to 5.08 mg l^{-1} in May at Buena Vista (BUVA) in the Patuxent River, from 0.06 mg l^{-1} in June, 1996 to 0.99 mg l^{-1} in September, 1996 at Ragged Point (RGPT) in the Potomac River. In the mainstem bay, bottom water dissolved oxygen conditions ranged from 0.10 mg l^{-1}-1 in June, 1996 to 5.17 mg l^{-1} in September, 1996 at Point No Point (PNPT) and at R-64 from 0.09 mg l^{-1} in June, 1996 to 2.04 mg l^{-1} in September, 1996 (Tables B1-58. - B1-61.).

Dissolved oxygen values in 1996 were generally lower than the long-term average at the station in the Potomac River (RGPT) and at both stations in the mainstem bay (R-64 and PNPT). This pattern was particularly evident for the June-August period when hypoxia at these sites was quite severe. The pattern was not as severe in the Patuxent River and this may be a reflection of the progress made in reducing nutrient loading rates. For example, June bottom water dissolved oxygen values were depressed relative to the long-term mean values at the three Patuxent River sites prone to summer hypoxia (STLC, BRIS and MRPT) but the hypoxia was not generally as severe as at mainstem or Potomac locations. In July at the three Patuxent River sites dissolved oxygen conditions were higher than the long-term mean and higher than those observed during the low flow conditions of 1995. Values in August and September were depressed relative to the long-term mean but were not severely hypoxic.

During 1996 river flows to three portions of the Maryland bay monitored in the Chesapeake Bay Program were higher than the long term nineteen year average (Figure 4-1.1.). The conceptual model used to guide the Ecosystem Processes Component (EPC) Program indicates that nutrient loading (associated with river flow) stimulates phytoplankton production which leads to deposition of organic matter to deep waters and sediments. As this material decomposes, oxygen is consumed and nutrients are released from sediments, stimulating further phytoplanktonic production of organic matter and continued low dissolved oxygen conditions. 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 consistent with 1996 dissolved oxygen (DO) concentrations in deep waters which were expected to be lower than average in areas without significant nutrient reductions and not as low in areas such as the Patuxent where substantial nutrient reductions have been achieved

5.2.2.4 Total Sediment Chlorophyll-a

Surficial sediment (top 2-3 mm of the sediment column) total sediment chlorophyll-a mass during 1996 ranged from 26.8 mg m^{-2} in July at Marsh Point (MRPT) to 93.5 mg m^{-2} in August also at Marsh Point in the Patuxent River. In the Potomac River (Ragged Point [RGPT]) this value ranged between 29.6 mg m^{-2} in July, 1996 and 78.2 mg m^{-2} in September, 1996. In the mainstem bay, surficial sediment total sediment chlorophyll-a mass ranged from 56.2 mg m^{-2} in September, 1996 at R-64 to 123 mg m^{-2} in July, 1996 at station Point No Point ([PNPT]; Tables B3-58. - B3-61.). The main characteristic of sediment chlorophyll-a mass was that almost all the values measured were equal to or above long term averages at all stations. This is consistent with the conceptual model wherein high nutrient loads associated with a high flow year encourage the creation of a large spring bloom so that more organic material (*e.g.* phytoplanktonic debris) is deposited at the sediment surface where it is available for summer decomposition and excessive dissolved oxygen consumption.

5.2.2.5 Sediment Eh

Sediment Eh (corrected to the hydrogen electrode) values were measured at the sediment-water interface (sediment depth = 0 cm) at all sediment oxygen and nutrient exchanges (SONE) stations. The 1996 values ranged from 279 mV in June at Marsh Point (MRPT) to 373 mV in August at Broomes Island (BRIS) in the Patuxent River, and from 257 mV in

August, 1996 to 333 mV in July, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, sediment Eh values ranged from 120 mV in July, 1996 to 348 mV in September, 1996 at Point No Point (PNPT) and from 150 mV in August, 1996 to 299 in June, 1996 at R-64 (Tables B3-58. - B3-61). The 1996 values were quite similar to those observed in previous years in the Patuxent River. However, Eh values were higher, and at some Potomac and mainstem bay sites much higher, than those of previous years. This is unusual because low bottom water dissolved oxygen conditions, indicative of a reducing environment in sediments, were more prevalent in 1996 than in many other years. The reason for these relatively high values is not clear at the present time.

5.2.2.6 Bottom Water Nutrient Concentrations

Ammonium (NH_4^+) concentrations at SONE stations in June, 1996 ranged from 1.3 μM N (Buena Vista [BUVA], Patuxent River) to 23.6 μM N (at both Ragged Point [RGPT], Potomac River and R-64 [R-64], Mainstem Bay; Table B-2.1). Values in July, 1996 ranged from 11.6 μM N (Buena Vista [BUVA], Patuxent River) to 27.9 μM N (R-64 [R-64], Mainstem Bay; Table B-2.2). Values in August, 1996 ranged from 5.7 μM N (St. Leonard Creek [STLC], Patuxent River) to 27.0 μM N (Ragged Point [RGPT], Potomac River; Table B-2.3) while values for September, 1996 ranged from 6.9 μM N (Point No Point [PNPT], Mainstem Bay) to 16.9 μM N (R-64 [R-64]; Table B-2.4).

Nitrite (NO_2^-) concentrations at SONE stations in June, 1996 ranged from 0.22 μM N (Point No Point [PNPT], Mainstem Bay) to 3.83 μM N (Ragged Point [RGPT], Potomac River; Table B-2.1). Values in July, 1996 ranged from 0.04 μM N (R-64 [R-64], Mainstem Bay) to 1.06 μM N (Buena Vista [BUVA], Patuxent River; Table B-2.2). Values in August, 1996 ranged from 0.03 μM N (Point No Point [PNPT], Mainstem Bay) to 0.75 μM N (Broomes Island [BRIS], Patuxent River; Table B-2.3) while values for September, 1996 ranged from 0.14 μM N (R-64 [R-64], Mainstem Bay) to 4.59 μM N (Ragged Point [RGPT]; Table B-2.4).

Concentrations of nitrite plus nitrate ($NO_2^- + NO_3^-$) at SONE stations in 1996 ranged from 0.20 μM N (Point No Point [PNPT], Mainstem Bay) to 8.46 μM N (Broomes Island [BRIS], Patuxent River; Table B-2.1). Values in July, 1996 ranged from 0.22 μM N (R-64 [R-64], Mainstem Bay) to 14.90 μM N (Buena Vista [BUVA], Patuxent River; Table B-2.2). Values in August, 1996 ranged from 0.09 μM N (R-64 [R-64], Mainstem Bay) to 1.64 μM N (Broomes Island [BRIS], Patuxent River; Table B-2.3) while values for September, 1996 ranged from 0.24 μM N (R-64 [R-64], Mainstem Bay) to 4.87 μM N (Ragged Point [RGPT]; Table B-2.4).

Dissolved inorganic phosphorus (DIP) concentrations at SONE stations in June, 1996 ranged from 0.26 μM P (Broomes Island [BRIS], Patuxent River) to 1.49 μM P (Point No Point [PNPT], Mainstem Bay; Table B-2.1). Values in July, 1996 ranged from 0.31 μM P (Ragged Point [RGPT], Potomac River) to 1.94 μM P (Buena Vista [BUVA], Patuxent River; Table B-2.2). Values in August, 1996 ranged from 0.75 μM P (St. Leonard Creek [STLC], Patuxent River) to 2.20 μM P (Ragged Point [RGPT], Potomac River; Table B-2.3) while values for September, 1996 ranged from 0.50 μM P (Point No Point [PNPT], Mainstem Bay) to 2.66 μM P (Buena Vista [BUVA]; Table B-2.4). Values recorded in 1996 were higher than 1995 a low flow year.

5.2.2.7 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 2.41 percent dry weight in September, 1996 at Buena Vista (BUVA) to 3.88 percent dry weight in July, 1996 at Broomes Island (BRIS), from 2.92 percent dry weight in August, 1996 to 3.27 percent dry weight in June, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay at Point No Point (PNPT) values ranged from 2.32 percent dry weight in September, 1996 to 3.81 percent dry weight in July, 1996 and at R-64 from 2.95 percent dry weight in July, 1996 to 4.46 in September, 1996 (Tables B3-58. and B3-61.). Concentrations of PC in the Patuxent were similar to the long-term mean and were similar or slightly lower than the long-term mean at other sites.

(2) Particulate nitrogen (PN) ranged from 0.30 percent dry weight in September, 1996 at Buena Vista (BUVA) to 0.52 percent dry weight at Broomes Island (BRIS) in July, 1996, from 0.38 percent dry weight in August, 1996 to 0.46 percent dry weight in June and September, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay values at Point No Point (PNPT) ranged from 0.32 percent dry weight in September, 1996 to 0.54 percent dry weight in July, 1996 and at R-64 from 0.39 percent dry weight in July, 1996 to 0.60 percent dry weight in September, 1996 (Tables B3-58. and B3-61.). Concentrations of PN in the Patuxent were similar to the long-term mean and were generally similar or slightly lower than the long-term mean at other sites.

(3) Particulate phosphorus (PP) ranged from 0.070 percent dry weight in August, 1996 at St. Leonard Creek (STLC) and in June, 1996 at Broomes Island (BRIS) to 0.17 percent dry weight in August, 1995 at Marsh Point (MRPT), from 0.05 percent dry weight in August, 1996 to 0.070 percent dry weight in September, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay values at Point No Point (PNPT) ranged from 0.04 percent dry weight in September, 1996 to 0.07 percent dry weight in July, 1996 and at R-64 from 0.06 percent dry weight in July and August 1996 to 0.07 in June, 1996 (Tables B3-58. and B3-61.). Concentrations of PP in the Patuxent were similar or higher than the long-term mean and were generally similar or slightly lower than the long-term mean at other sites.

5.3 CHARACTERISTICS OF SEDIMENT-WATER OXYGEN AND NUTRIENT FLUXES

5.3.1. Overview

Monthly average sediment-water fluxes are summarized using box and whisker plots (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 at six stations over a period of twelve calendar years, 1985 through 1996, and at two Patuxent River stations, Broomes Island (BRIS) and Marsh Point (MRPT), over a period of eight years, 1989 through 1996, were used in the preparation of these graphics.

The box and whisker plot, a derivation of the original Tukey (1977) box graph, follows the method used in the SAS procedure (SAS, 1988; PROC UNIVARIATE PLOT). The bottom and top edges of the box are located at the sample 25th and 75th percentiles. The center horizontal line is drawn at the sample median and the central plus sign (+) is at the sample mean. The central vertical lines, "whiskers", extend from the box as far as the data extends or to a distance of at most 1.5 interquartile ranges, where an interquartile range is the distance between the 25th and the 75th sample percentiles. Any value more extreme than this is marked with a zero (**o**) if it is within three interquartile ranges of the box, or with an asterisk (*) if it is still more extreme. The width of each box is proportional to the total number of samples collected at each station and used in the analysis.
Data collected during 1996 (SONE 58 [June 1996] through SONE 61 [September 1996]; mean flux value of three replicates) are shown as bold dots superimposed on the box (Figures 5-1.1. through 5-1.5.). The Y axis represents the complete range of flux values derived from the complete flux data set for that parameter. The order of the eight stations in these figures reflects their spatial position in the Chesapeake Bay. The four stations on the left page 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 page 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:

(1) *no measurements were made at Horn Point (HNPT) during the 1996 program and silicate measurements were discontinued at all stations during 1996 so no current values are indicated on this figure and*

(2) *positive flux values indicate fluxes from sediment to water while negative flux values indicate fluxes from water to sediment.*

5.3.2 Sediment Oxygen Consumption (SOC)

Mean monthly sediment oxygen consumption (SOC) for 1996, ranged from -0.14 g O_2 m^{-2} day^{-1} in June, 1996 at Marsh Point (MRPT) to -2.87 g O_2 m^{-2} day^{-1} in July, 1996 at Buena Vista (BUVA) in the Patuxent River, from zero (0.00) in August, 1996 to -0.34 g O_2 m^{-2} day^{-1} in September, 1996 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 0.01 g O_2 m^{-2} day^{-1} in August to -1.16 g O_2 m^{-2} day^{-1} in September, 1996 and from 0.01 g O_2 m^{-2} day^{-1} in August, 1996 to -0.92 g O_2 m^{-2} day^{-1} at R-64 in September, 1996 (Figure 5-1.1.; Tables B6-58. - B6-61.). Values were generally larger in magnitude in the Patuxent and Choptank Rivers than at other sites. *Note that: larger negative sediment oxygen consumption (SOC) flux values indicate larger rates of oxygen loss to sediments.*

At most stations, 1996 observations showed markedly decreased rates of sediment oxygen consumption (SOC) early in the sampling period (June), depressed values in the summer (July and August) at stations where low dissolved oxygen (DO) conditions were prevalent (R-64, PNPT and RGPT) and slight increases in rates at the beginning of September when dissolved oxygen (DO) conditions were improving at these deep stations. The largest fluxes were recorded in June as is typical at Buena Vista (BUVA) in the upper Patuxent where bottom waters had ample dissolved oxygen (DO) concentrations; however, spring rates of sediment oxygen consumption (SOC) were considerably depressed at all other stations in the Patuxent as were bottom water dissolved oxygen (DO) levels. Bottom water dissolved oxygen levels were unusually low at these sites during 1996 and this was probably responsible for the low rates observed. In general sediment oxygen consumption (SOC) tends to be higher in low flow years when bottom water dissolved oxygen concentrations remain higher. As 1996 was such a high flow year, bottom water dissolved oxygen (DO) levels tended to become lower earlier in the year and this, in turn, depressed sediment oxygen consumption (SOC) rates.

Fluxes at hypoxic stations (where hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters) were depressed in summer 1996 in contrast to the summers of 1992 and 1995 when aerobic sediment metabolism persisted longer than in previous years because of higher dissolved oxygen (DO) concentrations in these bottom waters. In both 1992 and 1995, river flow to all sites was quite low (Figure 4-1.2.) and as a result diffuse source nutrient loads were probably lower than normal as was organic matter enrichment of bottom waters and sediments.

5.3.3 Ammonium (NH_4^+) Fluxes

Average monthly ammonium (NH_4^+) fluxes in 1996, ranged from 123.6 μMN m^{-2} hr^{-1} in July, 1996 at St. Leonard Creek (STLC) to 706.6 μMN m^{-2} hr^{-1} in July, 1996 at Marsh Point (MRPT) in the Patuxent River. An additional high value of 620.2 μMN m^{-2} hr^{-1} was recorded at Buena Vista (BUVA) in August, 1996. Values ranged from 134.8 μMN m^{-2} hr^{-1} in August, 1996 to 220.6 μMN m^{-2} hr^{-1} in May, 1996 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 138.4 μMN m^{-2} hr^{-1} in August, 1996 to 193.1 μMN m^{-2} hr^{-1} in September, 1996 and at R-64 from 196.4 μMN m^{-2} hr^{-1} in July, 1996 to 597.9 μMN m^{-2} hr^{-1} in September, 1996 (Figure 5-1.2.; Tables B6-58. - B6-61.). The lack of high ammonium fluxes during some periods of summer, 1996 at the station in the lower Potomac (Ragged Point [RGPT] and at one of the mainstem bay stations (Point No Point [PNPT]) is surprising; high ammonium fluxes are generally associated with high river flow years at these sites.

The values recorded in 1996 generally followed temporal trends exhibited in previous years; fluxes tended to peak in early summer and decline during the latter portion of the summer. However, the magnitude of fluxes at the two stations in the lower Patuxent River (St. Leonard Creek [STLC] and Broomes Island [BRIS]) were comparable to the long-term mean or slightly below this level despite the fact that this was a high flow year. It is reasonable to suggest that reduced fluxes at these sites is evidence of the impact of nutrient reduction measures which have been instituted in this estuary. If this is the case, the effect was not evident at the two upper river stations in the Patuxent (Marsh Point [MRPT] and Broomes Island [BRIS]) where summer, 1996 ammonium fluxes were above average for at least portions of the summer. In a spatial context this also seems reasonable because these stations are more proximal to nutrient and organic matter sources which serve as either indirect or direct substrates supporting sediment-water fluxes of ammonium.

As indicated earlier, the magnitude of ammonium (NH_4^+) fluxes was below mean values for most months of 1996 at Ragged Point (RGPT) while in the mainstem bay fluxes at R-64 were higher than normal for only two of the four months sampled and at PNPT for only one of the months sampled (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. Neither of these conditions were evident at these deeper stations during 1996 and hence these patterns are unusual. The explanation may be that algal deposition (the fuel for sediment-water fluxes) was not as high as expected given the high flow conditions of 1996. As indicated in Figure 5-2.4 most sediment chlorophyll concentrations were average or below average at these sites during 1996. While there is little doubt that high nitrogen and phosphorus loads can create large algal biomass levels,

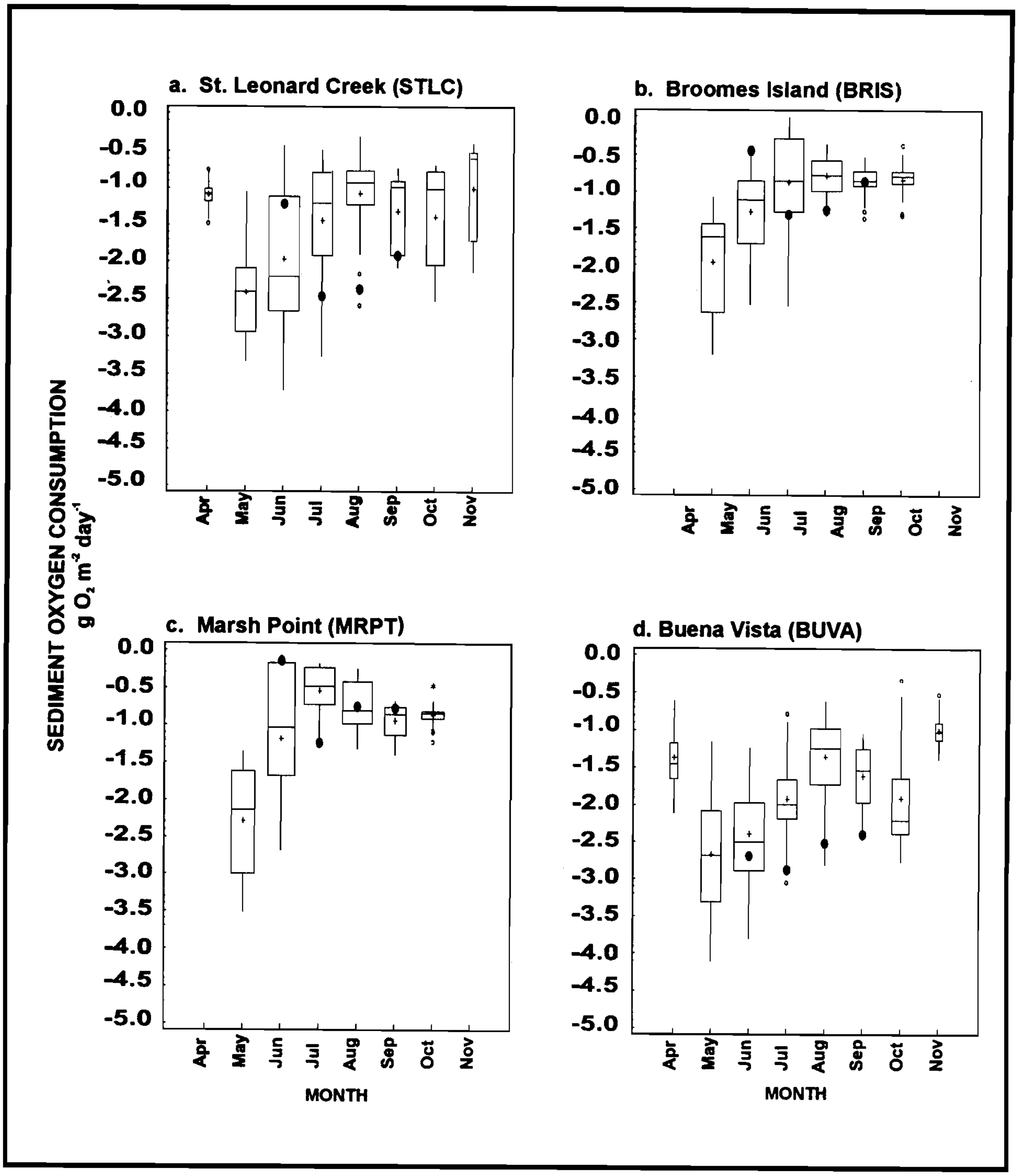


Figure 5-2.1. Box and whisker plots for sediment oxygen consumption (SOC) rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
a. St Leonard Creek (STLC); b. Broomes Island (BRIS);
c. Marsh Point (MRPT) and d. Buena Vista (BUVA)

The complete flux data set 1985 through 1996 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1996. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

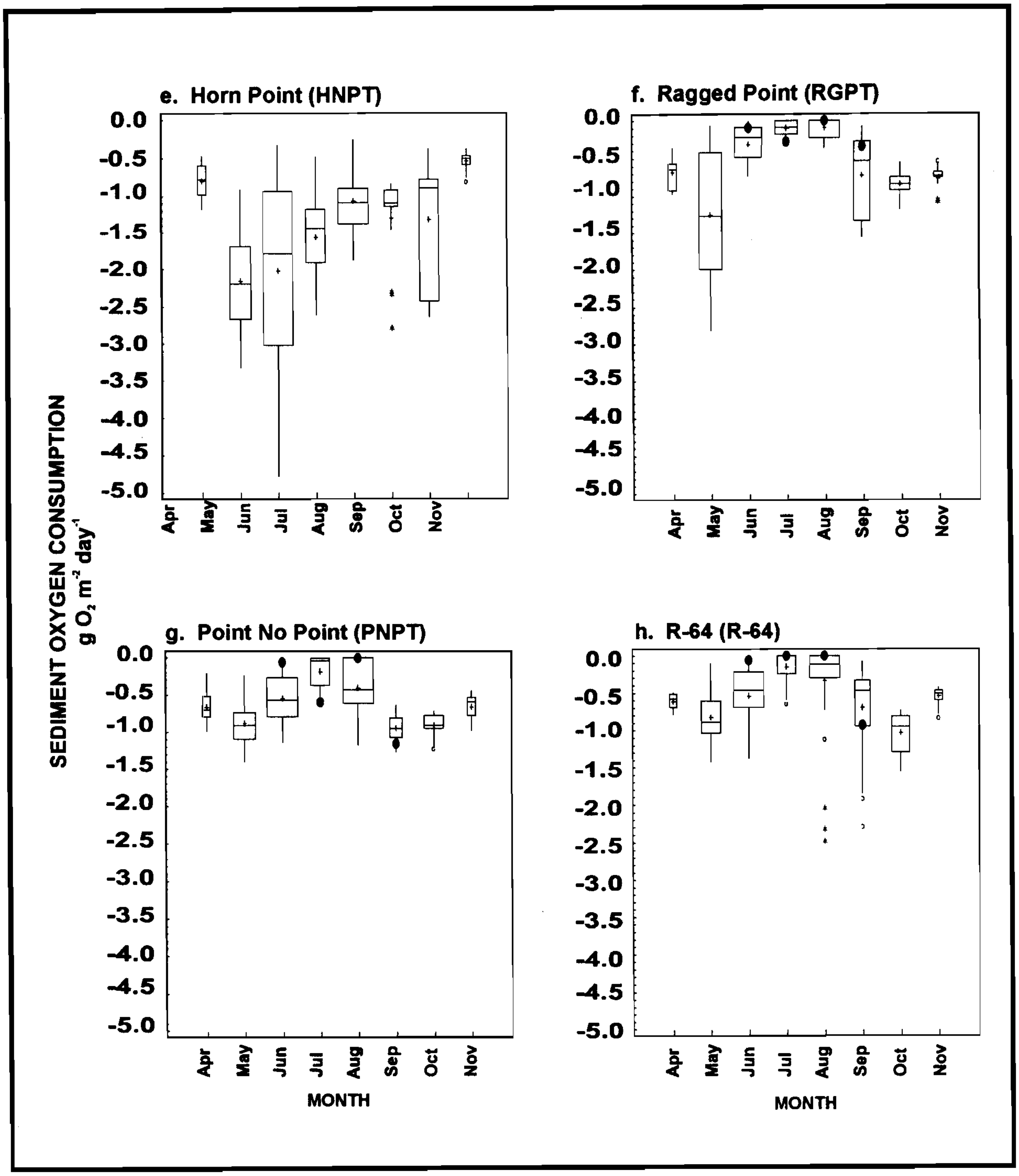


Figure 5-2.1. Box and whisker plots for sediment oxygen consumption (SOC) rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
e. Horn Point (HNPT); f. Ragged Point (RGPT);
g. Point No Point (PNPT) and h. R-64 (R-64)

The complete flux data set 1985 through 1996 was used to plot the graph. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. 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.

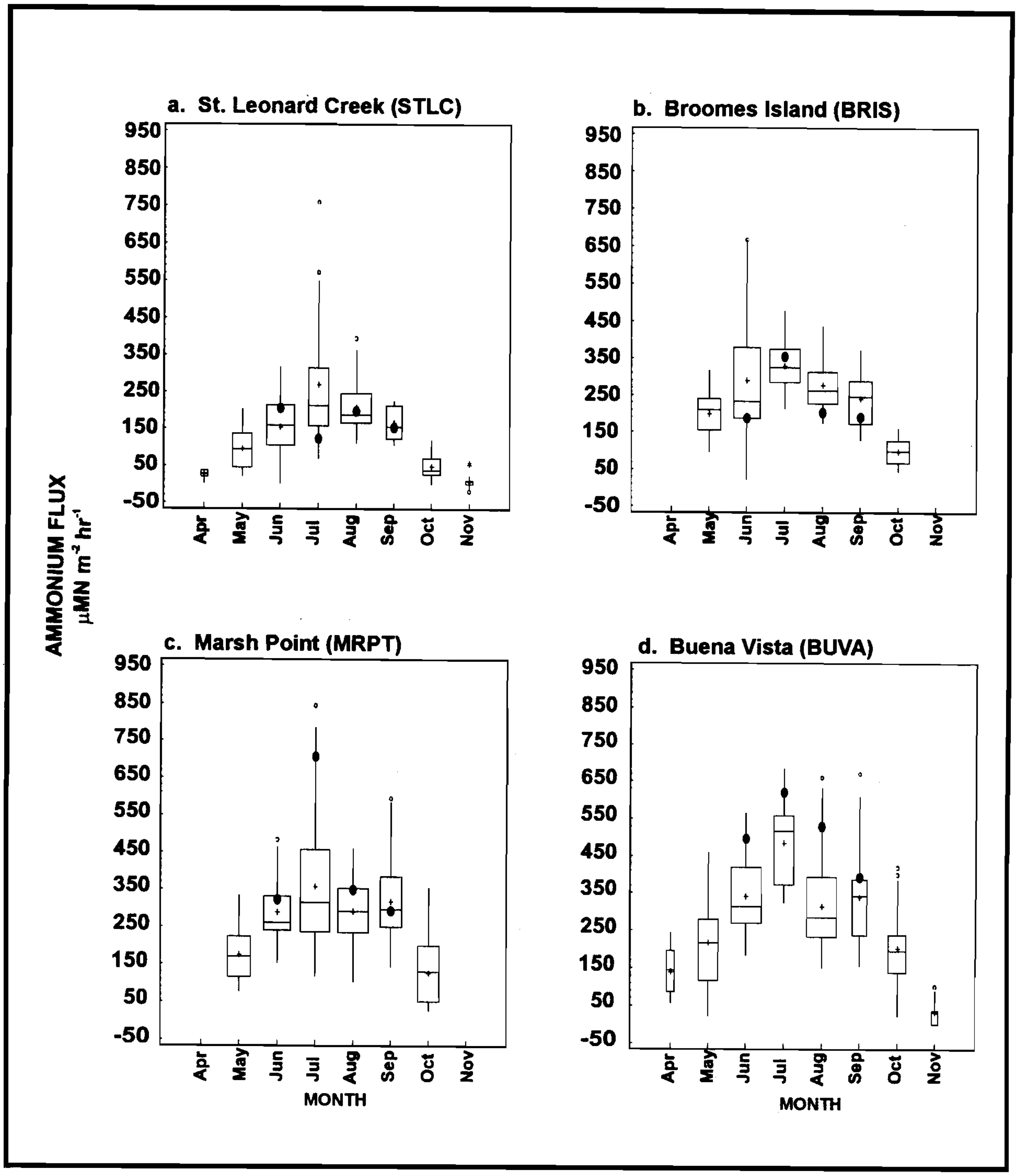


Figure 5-2.2. Box and whisker plots for ammonium (NH_4^+) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
a. St Leonard Creek (STLC); b. Broomes Island (BRIS);
c. Marsh Point (MRPT) and d. Buena Vista (BUVA)

The complete flux data set 1985 through 1996 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1996. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

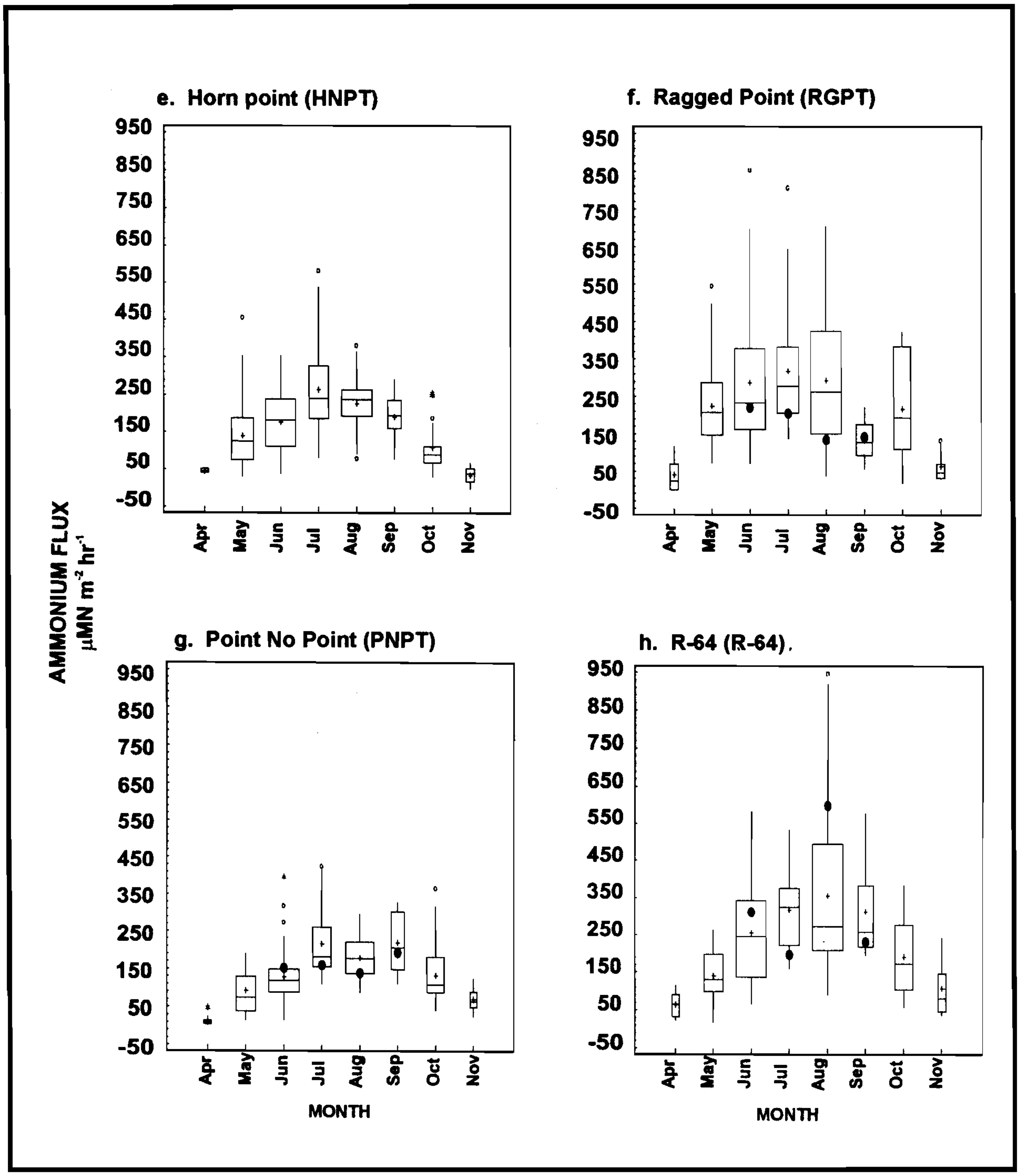


Figure 5-2.2. Box and whisker plots for ammonium (NH_4^+) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
e. Horn Point (HNPT); f. Ragged Point (RGPT);
g. Point No Point (PNPT) and h. R-64 (R-64)

The complete flux data set 1985 through 1996 was used to plot the graph. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. 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.

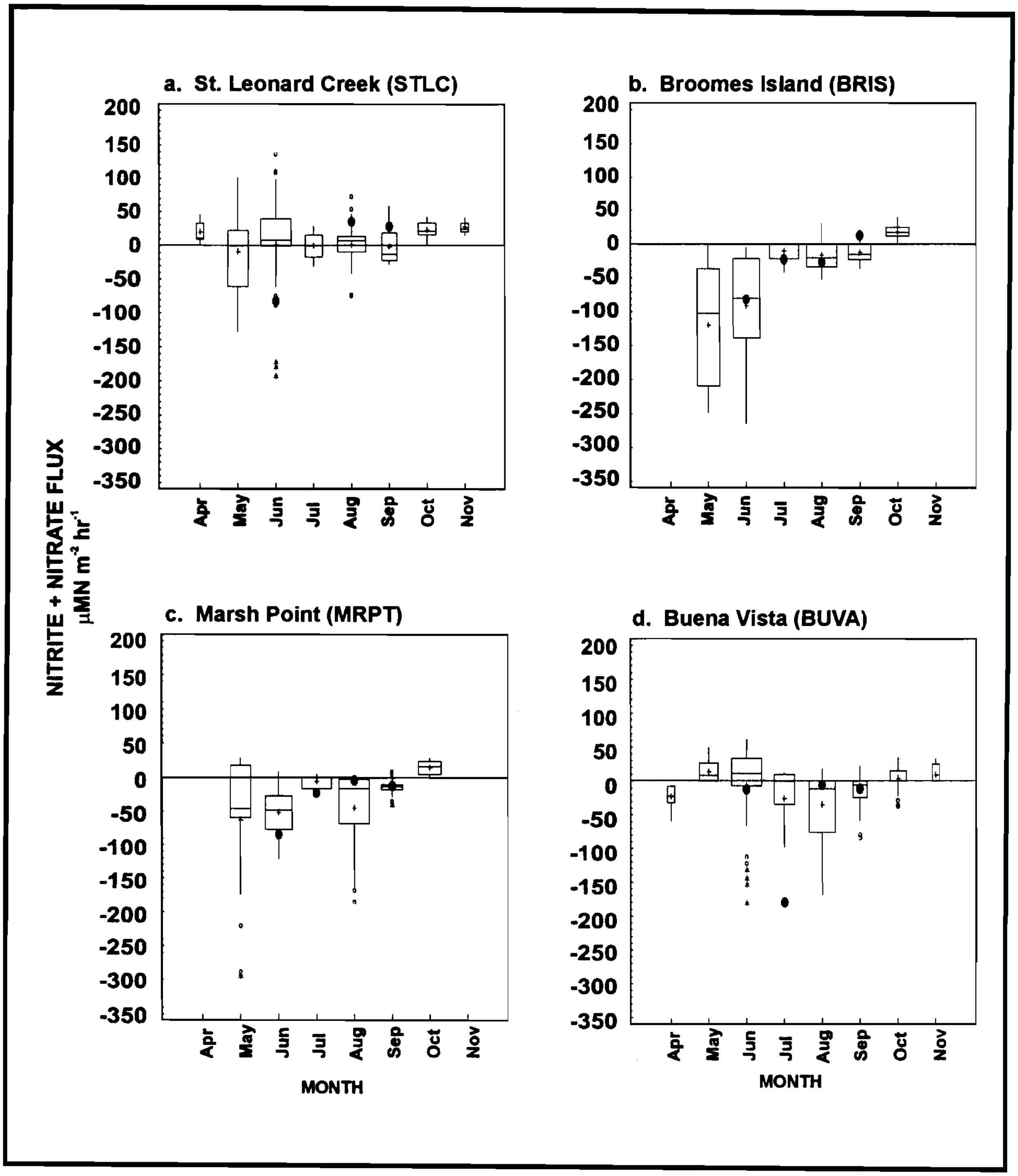


Figure 5-2.3. Box and whisker plots for nitrite plus nitrate (NO_2^- + NO_3^-) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
a. St Leonard Creek (STLC); b. Broomes Island (BRIS);
c. Marsh Point (MRPT) and d. Buena Vista (BUVA)

The complete flux data set 1985 through 1996 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1996. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

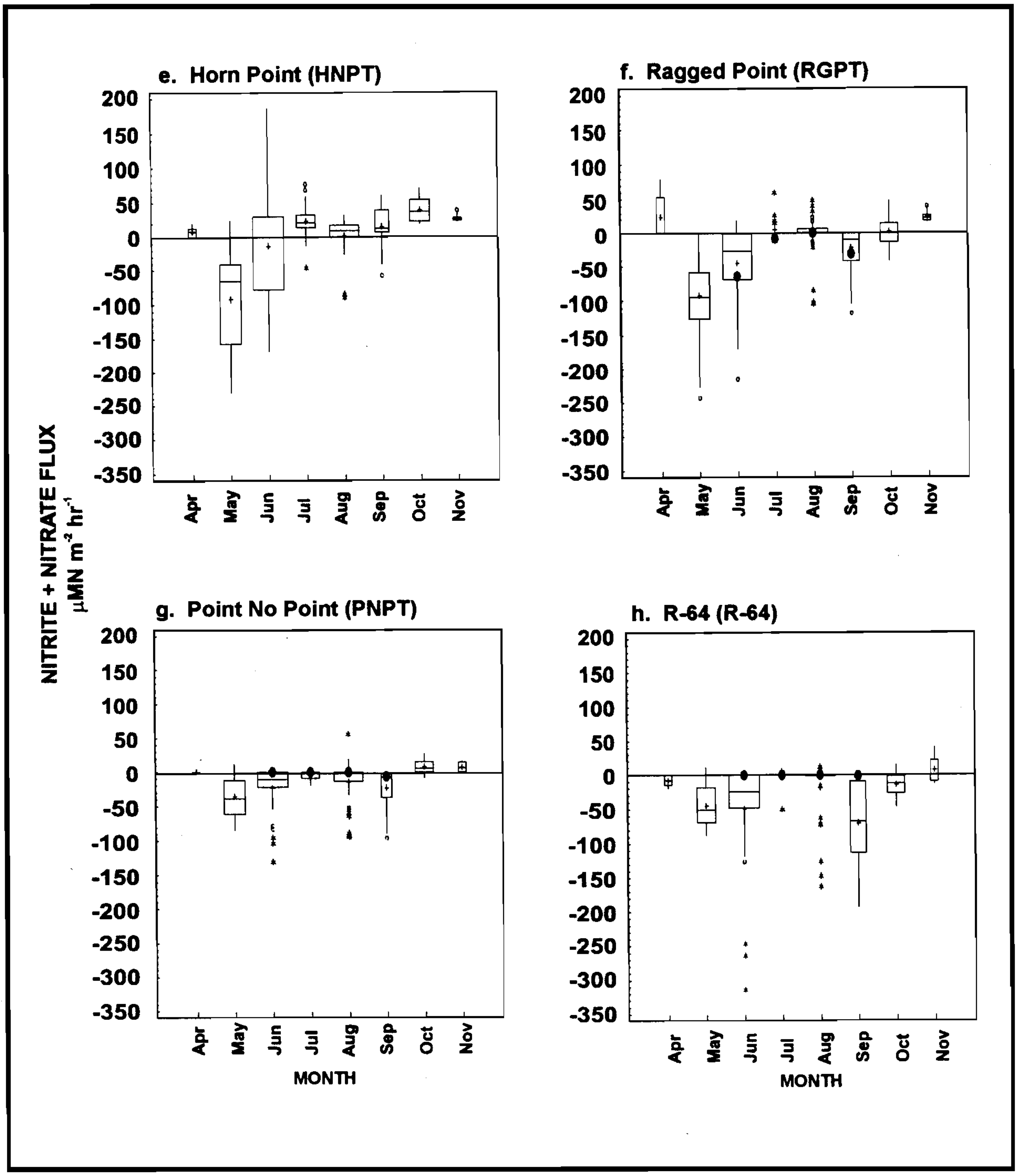


Figure 5-2.3. Box and whisker plots for nitrite plus nitrate (NO_2^- + NO_3^-) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
e. Horn Point (HNPT); f. Ragged Point (RGPT);
g. Point No Point (PNPT) and h. R-64 (R-64)

The complete flux data set 1985 through 1996 was used to plot the graph. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. 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.

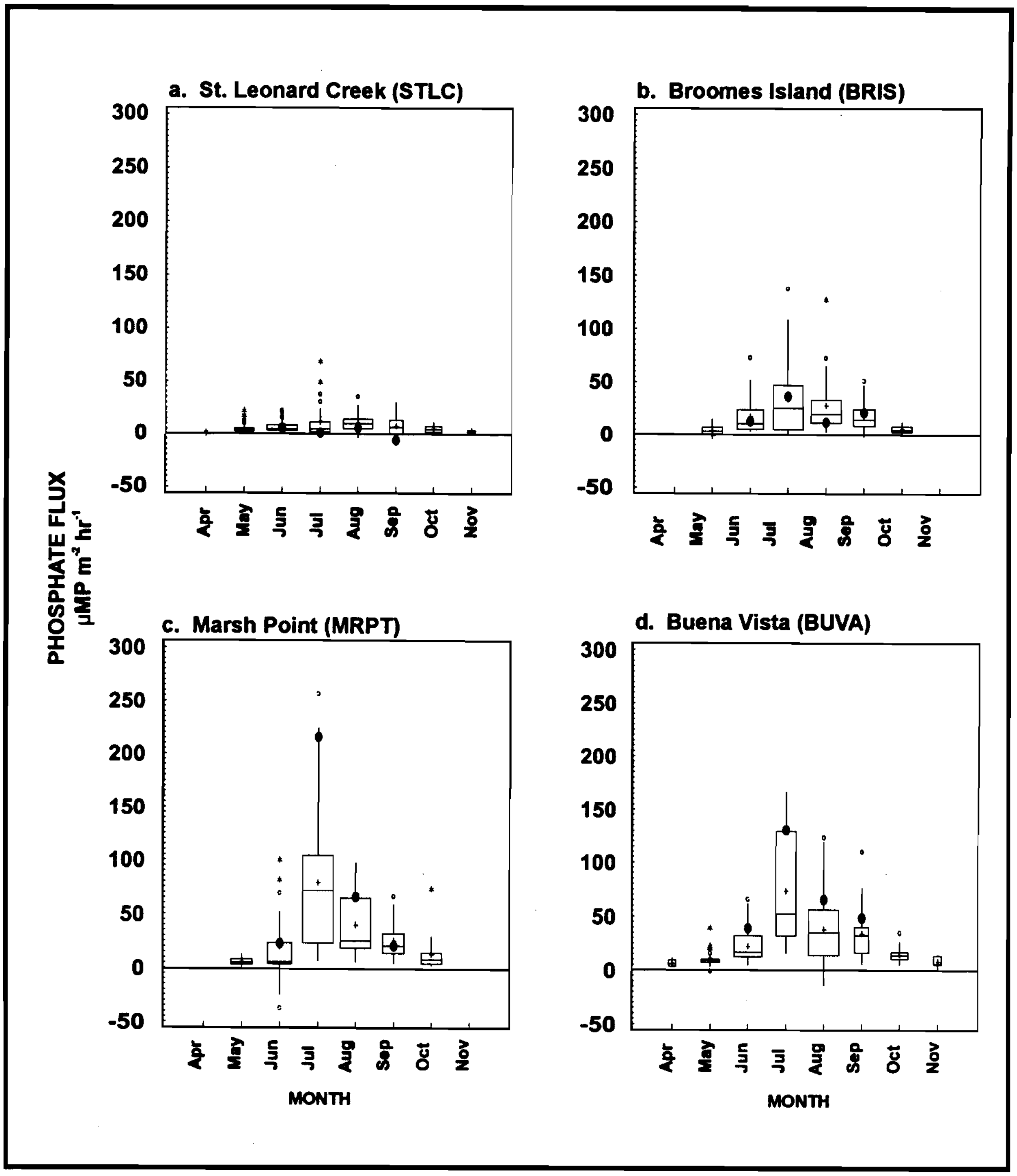


Figure 5-2.4. Box and whisker plots for phosphorus (PO_4^{-3} or DIP) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
a. St Leonard Creek (STLC); b. Broomes Island (BRIS);
c. Marsh Point (MRPT) and d. Buena Vista (BUVA)

The complete flux data set 1985 through 1996 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1996. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

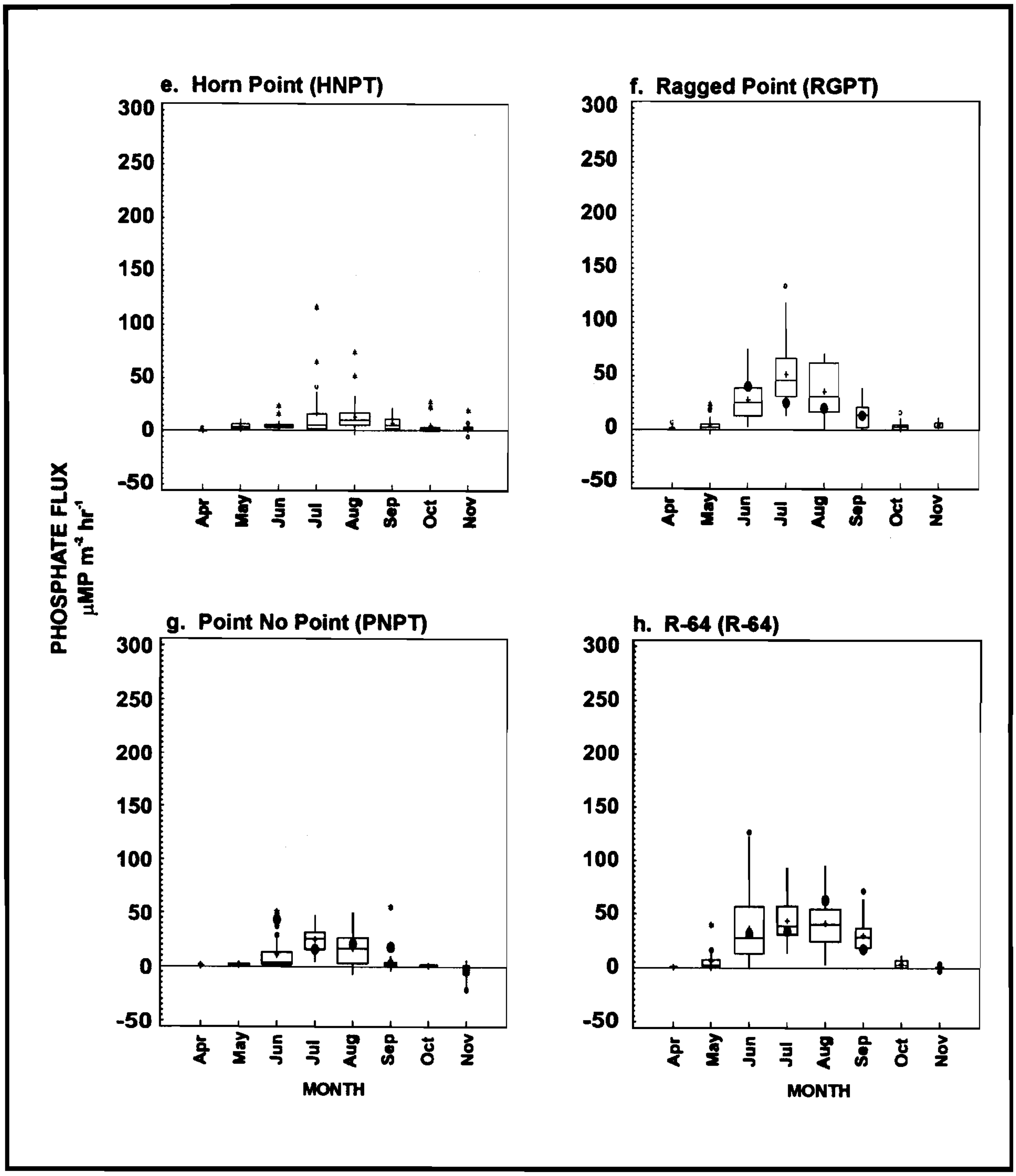


Figure 5-2.4. Box and whisker plots for phosphorus (PO_4^{-3} or DIP) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
e. Horn Point (HNPT); f. Ragged Point (RGPT);
g. Point No Point (PNPT) and h. R-64 (R-64)

The complete flux data set 1985 through 1996 was used to plot the graph. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. 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.

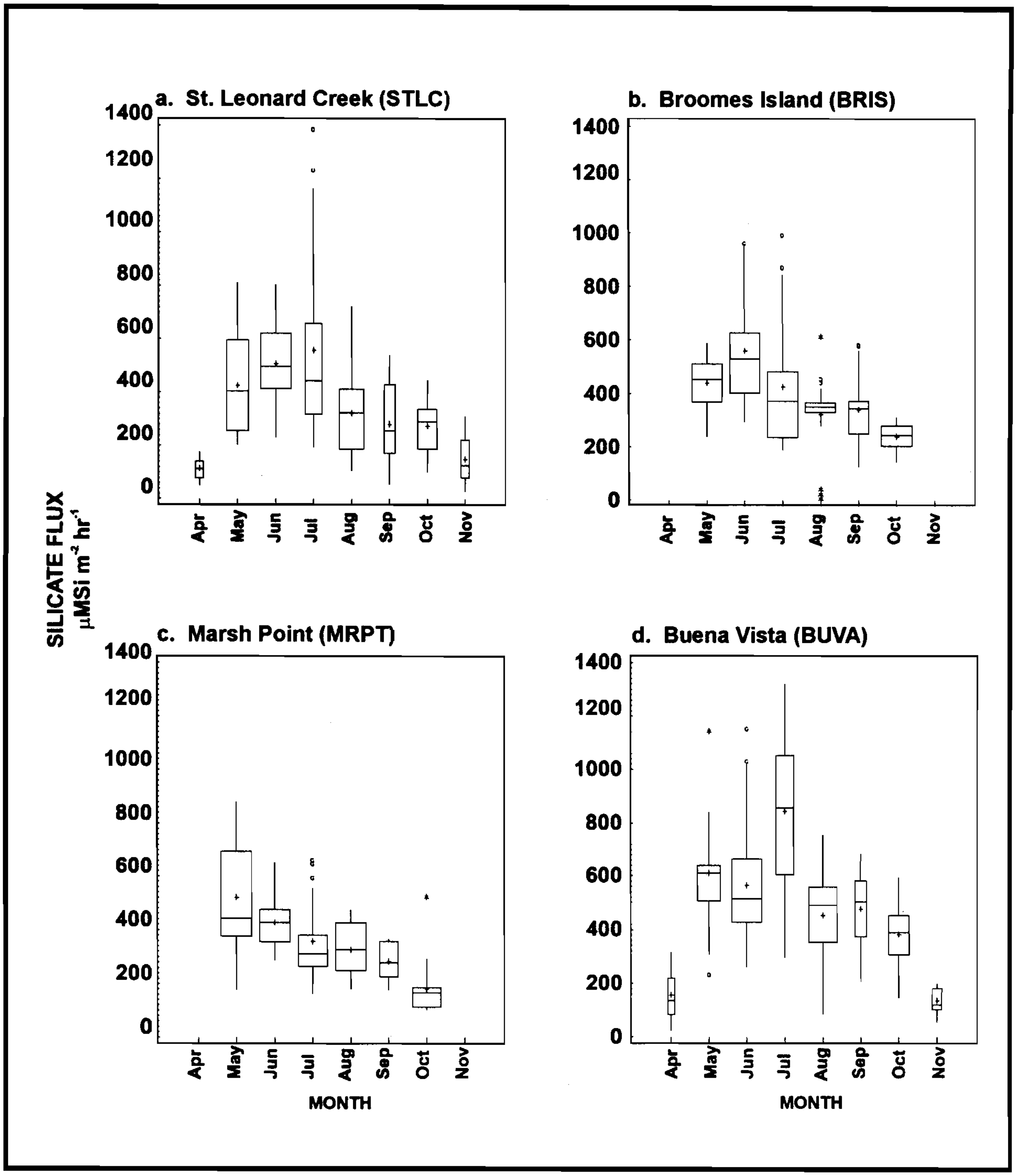


Figure 5-2.5. Box and whisker plots for silicate ($Si(OH)_4$) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
a. St Leonard Creek (STLC); b. Broomes Island (BRIS);
c. Marsh Point (MRPT) and d. Buena Vista (BUVA)

The complete flux data set 1985 through 1996 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1996. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

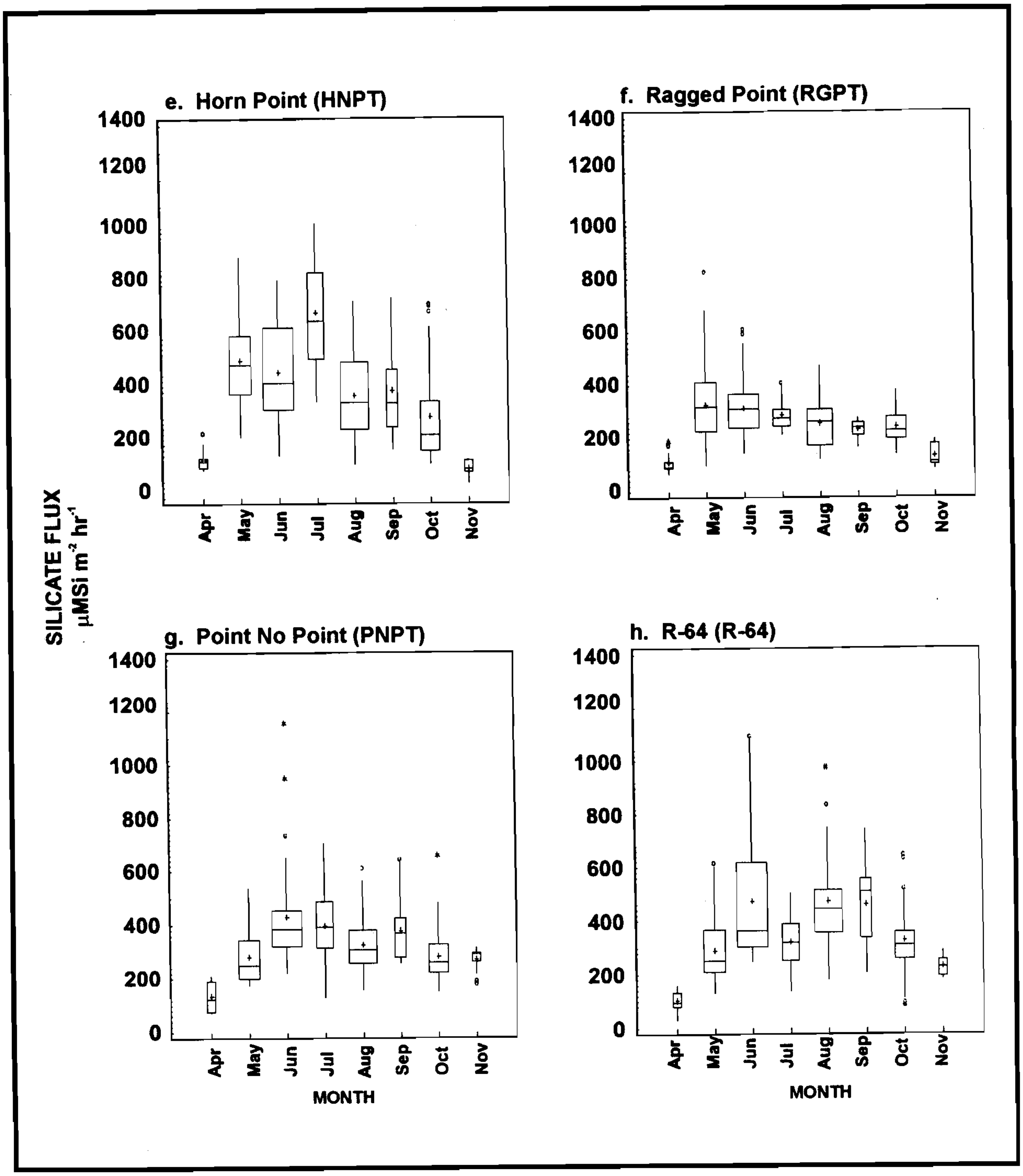


Figure 5-2.5. Box and whisker plots for silicate ($Si(OH)_4$) flux rates for April to November at eight SONE stations located in the Maryland portion of Chesapeake Bay.
e. Horn Point (HNPT); f. Ragged Point (RGPT);
g. Point No Point (PNPT) and h. R-64 (R-64)

The complete flux data set 1985 through 1996 was used to plot the graph. September values for all stations only include five years data, 1991 through 1996. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1996. Negative values indicate fluxes from water to sediment. 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.

there is more uncertainty about where this biomass will reach estuarine sediments. It is possible that enhanced estuarine circulation resulted in this material depositing farther down the bay during 1996, outside of the region sampled in this program.

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

Average monthly nitrite plus nitrate (NO_2^- + NO_3^-) fluxes for 1996 ranged from -180 μMN m^{-2} hr-1 in July at Buena Vista (BUVA) to 35.92 μMN m^{-2} hr^{-1} in August, 1996 at St. Leonard Creek (STLC) in the Patuxent River, from -64.38 μMN m^{-2} hr^{-1} in June, 1996 to 0 (zero) μMN m^{-2} hr^{-1} in July, 1996 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 -6.39 μMN m^{-2} hr^{-1} in September, 1996 (R-64) to zero (0) μMN m^{-2} hr^{-1} for the other three months and at R-64 from -1.14 μMN m^{-2} hr^{-1} in September, 1996 to 0 (zero) μMN m^{-2} hr^{-1} in the other three months (Figure 5-1.3.; Tables B6-58. - B6-61.). *Note that positive values indicate fluxes from sediment to water while negative values indicate fluxes from water to sediment.*

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 as was the case at the most up-river station in the Patuxent during 1996 (Buena Vista [BUVA]). 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 1996 the overwhelming pattern was nitrite plus nitrate flux (NO_2^- + NO_3^-) from water to sediments. At the deeper stations (R-64 [R-64], Point No Point [PNPT] and Ragged Point [RGPT]) there were no positive fluxes as was also the case at the most up-river station in the Patuxent (Buena Vista [BUVA]) where nitrate concentrations were unusually high throughout the 1996 monitoring period because of high river flow. However, there were positive nitrite plus nitrate (NO_2^- + NO_3^-) fluxes at two stations in the lower Patuxent (Broomes Island [BRIS] and St. Leonard Creek [STLC]) which would be expected as a result of relatively reduced nutrient loads. This suggests a pattern of sediment responses to load reductions starting first at locations removed from nutrient sources and grading back to poor conditions nearer to sources. In contrast to 1996 observations, during 1995, a very low flow year, stations in the Patuxent River exhibited relatively high rates of sediment nitrate release or much lower rates of nitrogen uptake. In fact, at the St. Leonard Creek (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 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.

5.3.5 Dissolved Inorganic Phosphorus (PO^{4-3} or DIP) Fluxes

Average monthly dissolved inorganic phosphorus (DIP) fluxes in 1996 ranged from -5.66 μMP m^{-2} hr^{-1} in September, 1996 at St. Leonard Creek (STLC) to 215 μMP m^{-2} hr^{-1} in July, 1996 at Marsh Point (MRPT) in the Patuxent River, from 13.18 μMP m^{-2} hr^{-1} in September, 1996 to 40.19 μMP m^{-2} hr^{-1} in May, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay, average monthly dissolved inorganic phosphorus (DIP) fluxes ranged from 15.54 μMP m^{-2} hr^{-1} in July, 1996 to 43.30 in June, 1996 at Point No Point (PNPT) and at R-64 from 17.03 μMP m^{-2} hr^{-1} in September, 1996 to 62.96 μMP m^{-2} hr^{-1} in August, 1996 (Figure 5-1.4.; Tables B6-58. - B6-61.).

Dissolved inorganic phosphorus (PO_4^{-3}) fluxes in 1996 at the deeper stations (R-64 [R-64], Point No Point [PNPT] and Ragged Point [RGPT]) followed a pattern similar to that observed for ammonium; fluxes were lower than expected during a high flow year. It is thought that this resulted for the same reason that ammonium fluxes were lower than expected; sediment stocks of labile organic matter (as indexed by total sediment chlorophyll-a) were not very high. It seems likely that the large algal stocks which did develop during 1996 (Harding, *pers. comm.*) deposited to sediments in more southern portions of the bay. The spatial pattern of phosphorus fluxes in the Patuxent River are consistent with those reported for both ammonium ($NH^4{}_+$) and nitrite plus nitrate ($NO_2^- + NO_3^-$); fluxes were small, and lower than average at times, at the down river stations and higher than average at the up-river sites more proximal to nutrient sources.

In some contrast to the 1996 observations, dissolved inorganic phosphorus (PO_4^{-3}) fluxes in 1995 were the most outstanding finding of the EPC-SONE program, especially in the Patuxent River. It is predicted that phosphorus (PO_4^{-3}) fluxes would be low during a low flow year because of both low loading rates and more oxidized sediments conditions, which tend to reduce phosphorus release from sediments via chemical reactions. 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.

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

No measurements of silicate flux ($Si(OH)_4$) were made in 1996. The data displayed in Figure 5-1.5 summarizes all silica flux information currently available and was described in the previous Interpretive Report (Boynton *et al.*, 1996).

5.4. Monitoring Sediment Metabolism under Anoxic and Oxic Conditions: 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 in the water 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 status and trends of 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 appeared 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 1996. Average monthly dissolved inorganic carbon (TCO_2) fluxes in 1996 ranged from 1437 μM CO_2 m^{-2} hr^{-1} in August, 1996 at Broomes Island (BRIS) to 7396 μM CO_2 m^{-2} hr^{-1} in July, 1996 at Buena Vista (BUVA) in the Patuxent River, from 900 μM CO_2 m^{-2} hr^{-1} in September, 1996 to 2223 μM CO_2 m^{-2} hr^{-1} in May, 1996 in the Potomac River (Ragged Point [RGPT]). In the mainstem bay at station R-64, average monthly dissolved inorganic carbon (TCO2) fluxes ranged from 1959 μM CO_2 m^{-2} hr^{-1} in July, 1996 to 5901 μM CO_2 m^{-2} hr^{-1} in August, 1996 (Figure 5-1.4.; Tables B6-58. - B6-61.).

Monthly average rates at stations in the Patuxent exhibited some particularly strong trends. First, rates were lower at the two down-river stations (St. Leonard Creek [STLC] and Broomes Island [BRIS]) than at the up-river sites (Marsh Point [MRPT] and Buena Vista [BUVA]). This is the same pattern observed for ammonium (NH_4^+) and phosphorus (PO_4^-) fluxes indicating the expected metabolic linkages among these fluxes. Second, fluxes at the two up-river stations exhibited a strong seasonal signal with highest fluxes in June and July and lower values in August and September. This pattern indicates that total sediment metabolism is most closely linked to organic matter supply during the present year rather

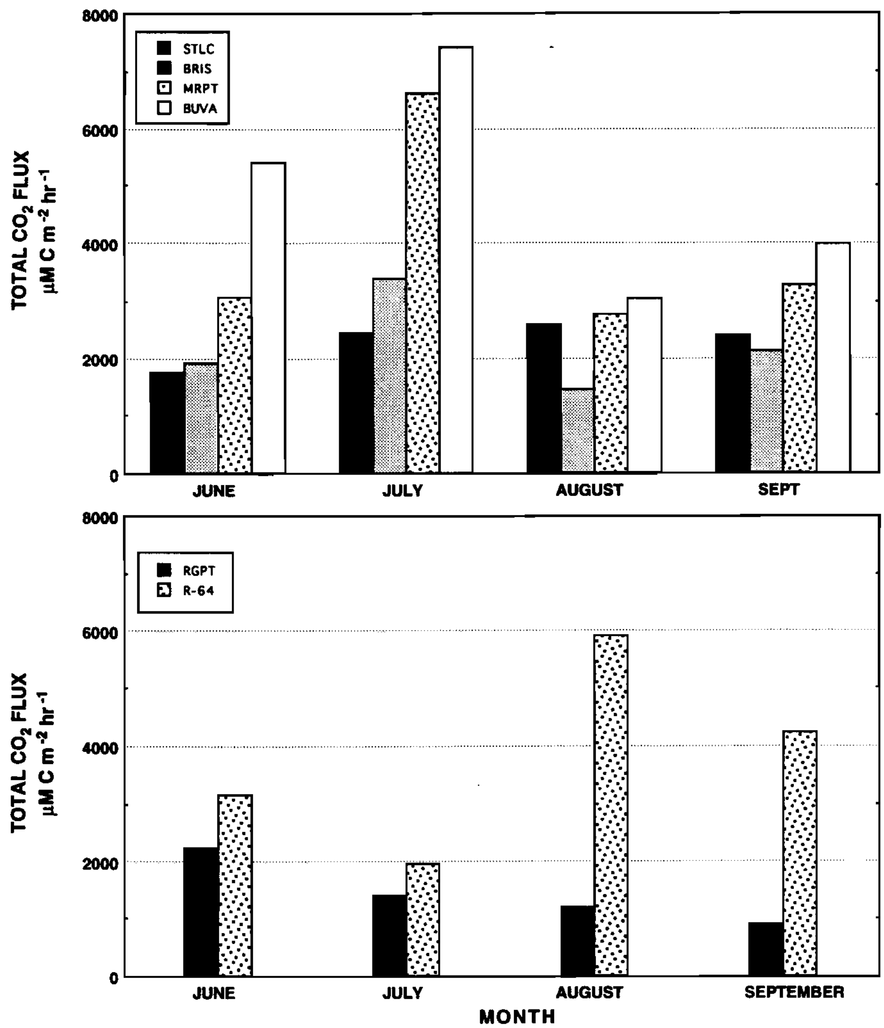


Figure 5-2. Mean monthly dissolved inorganic carbon (TCO_2) fluxes measured in 1996 for the months June through September at six SONE stations located in the Maryland portion of Chesapeake Bay.
a. Patuxent River stations;
b. Mainstem Bay stations.

than predominantly to organic matter which has accumulated in the sediment column over many years. This observation is important because it suggests a rapid (year) rather than slow (decade) time scale for water quality recovery.

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 then 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 0.3 g C m^{-2} day^{-1} to 2.0 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 program. First, it appears that TCO_2 fluxes are generally proportional to nutrient and organic matter loading rates (Figure 5-3.). 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.

Finally, 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 during summer 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).

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.

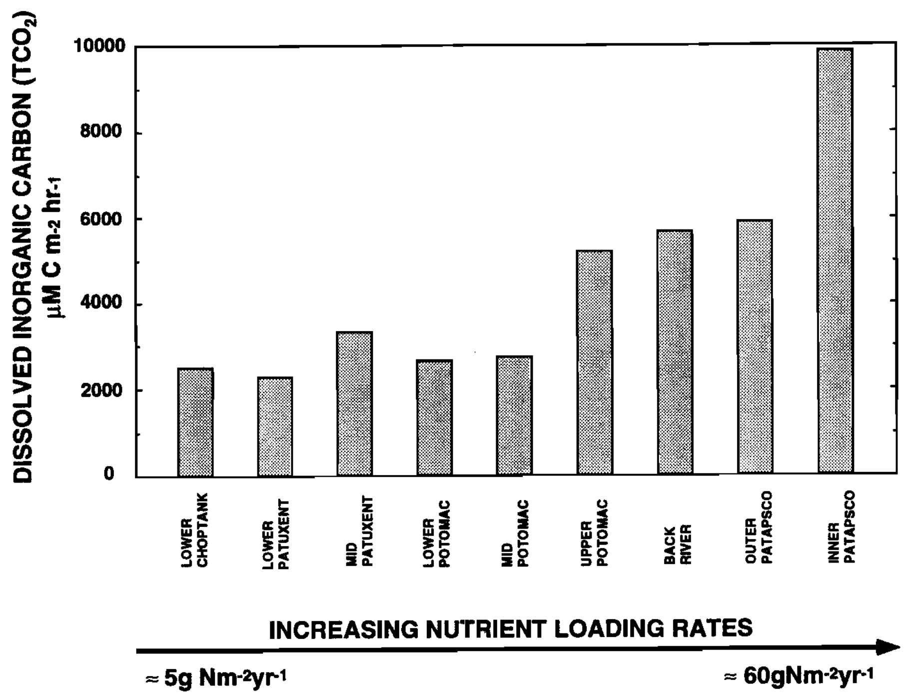


Figure 5-3. A bar graph showing a general relationship between dissolved inorganic carbon (TCO2) flux and total nitrogen (TN) loading rates based on 1995 data.
The values given at either extreme of the x-axis are from Boynton et al. (1995a). The remaining bars are arranged based on qualitative assessments of load. Refer to Boynton et al. (1995a) for information regarding station locations.

6. SEDIMENT-WATER FLUX STATUS AND TRENDS

6.1 Background and Goals

The development of management actions to implement the 40% nutrient load reduction strategy has been a 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 twelve complete years (1985 - 1996) 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 define current status of these processes and identify 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 Interpretive Report #12 (Boynton *et al.*, 1995b). These figures included monthly average data covering the first ten years of the monitoring program (1985 - 1994) collected at six sediment oxygen and nutrient exchanges (SONE) stations. The purpose of these analyses was to explore the data to determine temporal trends and to provide a basis for relating important environmental conditions to the characteristics of sediment fluxes.

The standardized protocol developed by the Monitoring Program is used in the following sections to characterize the current status of sediment-water exchange processes at SONE stations and to evaluate the SONE data set for interannual trends.

6.2 Sediment-Water Quality Status

A standardized protocol has been developed for scaling data in order to summarize the status of each parameter and evolving versions of this visual approach have been adopted by the Monitoring Program, including the EPC program (Alden and Perry, 1997). The status bar for each variable under consideration comprises a benchmark with a gradient scale and a pointer which indicates the current status or condition along that scale. This program has no counterpart in the Virginia section of the bay so these are the only data used in the determination of the status bar.

6.2.1 Development of the Status Bars

6.2.1.1 Development of the Benchmark

The complete SONE flux data set collected Bay-wide for 1985 through 1996 was used to create a status bar for each parameter (*i.e.* a specific SONE flux variable *e.g.* sediment oxygen consumption [SOC]) at each station. Four of the eight stations (St Leonard Creek

[STLC], Buena Vista [BUVA], Ragged Point [RGPT] and R-64 [R-64]) had complete data sets comprising twelve years (1985 - 1996); two data sets had eleven complete years of data, Point No Point ([PNPT]; 1985 - 1995; this station was not sampled in July, Aigust and September 1995) and Horn Point (HNPT; this station was not sampled during 1996). Two stations which were added to the SONE program in 1989, Broomes Island (BRIS) and Marsh Point (MRPT) had data sets comprising 8 years (1989 - 1996). This twelve year period includes the widest observable range of variability due to factors such as river flow and nutrient loading rates. The annual medians for each station for each parameter are calculated providing a benchmark data set which reduces the effects of extreme outliers. The 5th and the 95th percentile values are used to indicate the end points of the gradient scale. An additional two centiles, the 35th and 65th centiles in the benchmark median data set, are used to scale the final benchmark such that it is delineated into three categories: poor, fair and good. The extreme ends of the scale are determined by the parameter being considered, the 5th centile for sediment oxygen consumption fluxes is considered "poor" while the 5th centile for dissolved inorganic phosphorus it is considered "good" (Figure 6-1.). A linear quantitative (percentage) scale with "good" and "poor" end points is thus developed.

There are several differences in development of benchmark scales for the EPC-SONE program relative to other portions of the monitoring program. First, and most important, the stations were not segregated on the basis of salinity zones. In other words, every flux measurement made at all eight SONE stations was used to develop the benchmark for each SONE parameter. In other portions of the monitoring program separate benchmarks were developed for tidal fresh, oligohaline, mesohaline and polyhaline areas of the bay using only station data collected within those regions. The EPC-SONE program has seven of the eight annually monitored stations which can be classified as mesohaline while the eighth station (Buena Vista [BUVA] in the Patuxent River) can only be classified as oligohaline a small fraction of the time; on an annual average basis this station (Buena Vista [BUVA]) would also be classified as mesohaline. Therefore, a single benchmark is constructed for each of the six SONE variables; in effect, the SONE variable benchmark is synonymous with the mesohaline benchmark. Second, in most cases, twelve years of data were used to construct a benchmark rather than the first ten years as required of other portions of the monitoring program. The single reason for this is that the EPC-SONE program has no other counterpart in the Virginia portion of the bay. In effect, it is a stand alone data base. It is advantageous to include as many years of observations possible in the benchmark to capture temporal variability in a realistic fashion.

6.2.1.2 Determination of Current Status

A median value for the years 1994, 1995 and 1996 is added to the benchmark bar as a pointed arrow indicating the position on the benchmark of a particular SONE flux variable at which that particular station now resides. The use of the last three years of data provides an "indicator" value of the status of the parameter relative to all other years during which measurements was taken. The median value of the last three years data has the effect of eliminating the influence of extreme climatic conditions (*i.e.* very wet or very dry years) since such extremes do not usually occur several years in succession. Since river flow and nutrient loading rates are important variables which either directly or indirectly influence sediment-water exchanges, it is important to note that 1994 and 1996 were very wet years and 1995 was a dry year.

6.2.2 Evaluation of the Current Status

i Sediment Oxygen Consumption (SOC)

The current status (average of 1994, 1995 and 1996 data) of sediment oxygen consumption (SOC) fluxes at the eight SONE stations is indicated in Figure 6-1.a. It seems appropriate to judge higher values of SOC as good in the context of this evaluation for several reasons despite the fact that high SOC rates indicate that sediments are using dissolved oxygen. The main reason for adopting this approach is that SOC rates are responsive to DO concentrations in the water. When dissolved oxygen concentrations in the water are high, SOC rates can potentially be high. Conversely, when dissolved oxygen concentrations in the water are low, SOC rates also will be low. Since restoration of increased dissolved oxygen in bottom waters is a goal of the management program we have adopted the position of treating higher SOC rates as indicative of healthy sediments in aerobic environments. Among the SONE stations, three were considered to have SOC rates in the good range, four were in the fair range and one was in the poor range. The pattern of SOC fluxes in the Patuxent River is the most interesting and provides substantiation that the benchmark is appropriate. SOC fluxes progress from good down-river to almost poor at the head of the deep water channel at station Marsh Point (MRPT). This pattern would be expected based on proximity to nutrient sources. The station most upriver (and closest to nutrient sources) has a status of good (Buena Vista [BUVA]). This largely results because the water column is well mixed at this station and the propensity for low water column dissolved oxygen (DO) conditions is much reduced at this site.

ii. Ammonium (NH_4^+)

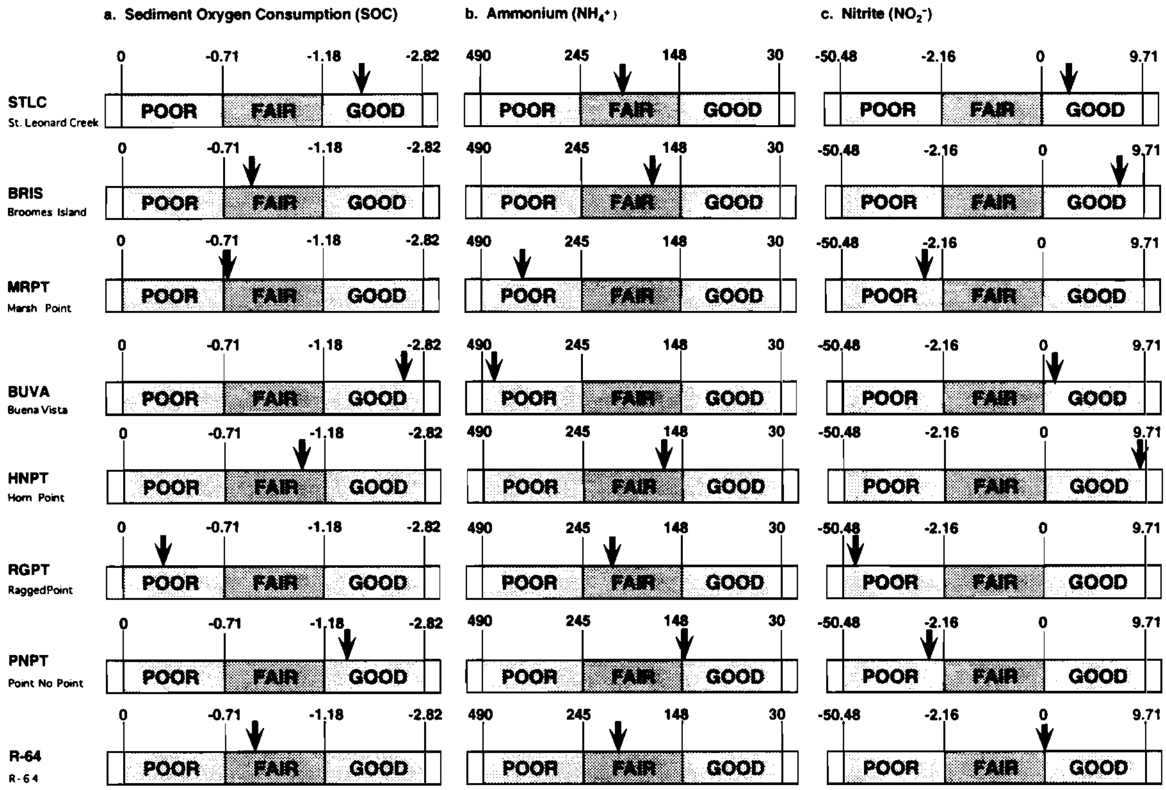
The current status (average of 1994, 1995 and 1996 data) of ammonium fluxes at the eight SONE stations is indicated in Figure 6-1.b. In the case of ammonium fluxes it appears appropriate to judge high values as poor because of the well established linkage between ammonium availability and excessive phytoplankton biomass accumulation. Among the SONE stations one was considered to have ammonium fluxes in the good range, five were in the fair range and two were in the poor range. It should be noted here that high river flow years have a particularly strong influence on ammonium fluxes (fluxes increase). Two of the three years considered here were high flow years and ammonium fluxes at several sites were enhanced enough to place them in the fair category (Horn Point [HNPT] and St. Leonard Creek [STLC]). These sites are expected to move towards the good category when river flows return to more normal levels.

iii. Nitrite (NO_2^-)

The current status (average of 1994, 1995 and 1996 data) of nitrite fluxes at the eight SONE stations is indicated in Figure 6-1.c. In the case of nitrite fluxes it appears appropriate to judge high values (positive values) as good because of the well established linkage between nitrite evolution from sediments and oxidized sediment conditions. Among the SONE stations three were considered to have nitrite fluxes in the good range, one in the fair range (borderline case between fair and good) and four were in the poor range. More stations are expected to move from poor to fair or fair to good when dissolved oxygen (DO) conditions in bottom waters improves, even if only enough to allow some nitrification activity to occur.

vi. Nitrite plus Nitrate ($NO_2^- + NO_3^-$)

The current status (average of 1994, 1995 and 1996 data) of nitrite plus nitrate fluxes at the eight SONE stations is indicated in Figure 6-1.d. In the case of nitrite plus nitrate fluxes it appears appropriate to judge high values (positive values) as good because of the well established linkage between nitrite plus nitrate evolution from sediments via complete nitrification and oxidized sediment conditions. Among the SONE stations three were



Sediment Oxygen Consumption (SOC):
High SOC rates are judged to be good because SOC rates are responsive to DO concentrations in the water. When dissolved oxygen concentrations are high SOC rates can be high; when dissolved oxygen concentrations are low, SOC rates will be low. Higher SOC rates are are judge to be indicative of healthy sediments in aerobic environments.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):

STLC: -2.03
BRIS: -0.84
MRPT: -0.72
BUVA: -2.34
HNPT: -0.93 No data for 1996
RGPT: -0.42
PNPT: -1.22 No data for Jul, Aug and Sep 1995
R-64: -0.87

Ammonium (NH_4^+):
High ammonium fluxes are judged to be poor because of the well established linkage between ammonium availability and excessive phytoplankton biomass accumulation.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):

STLC: 222.2
BRIS: 183.6
MRPT: 361.0
BUVA: 386.6
HNPT: 176.4 No data for 1996
RGPT: 224.5
PNPT: 147.7 No data for Jul, Aug and Sep 1995
R-64: 223.6

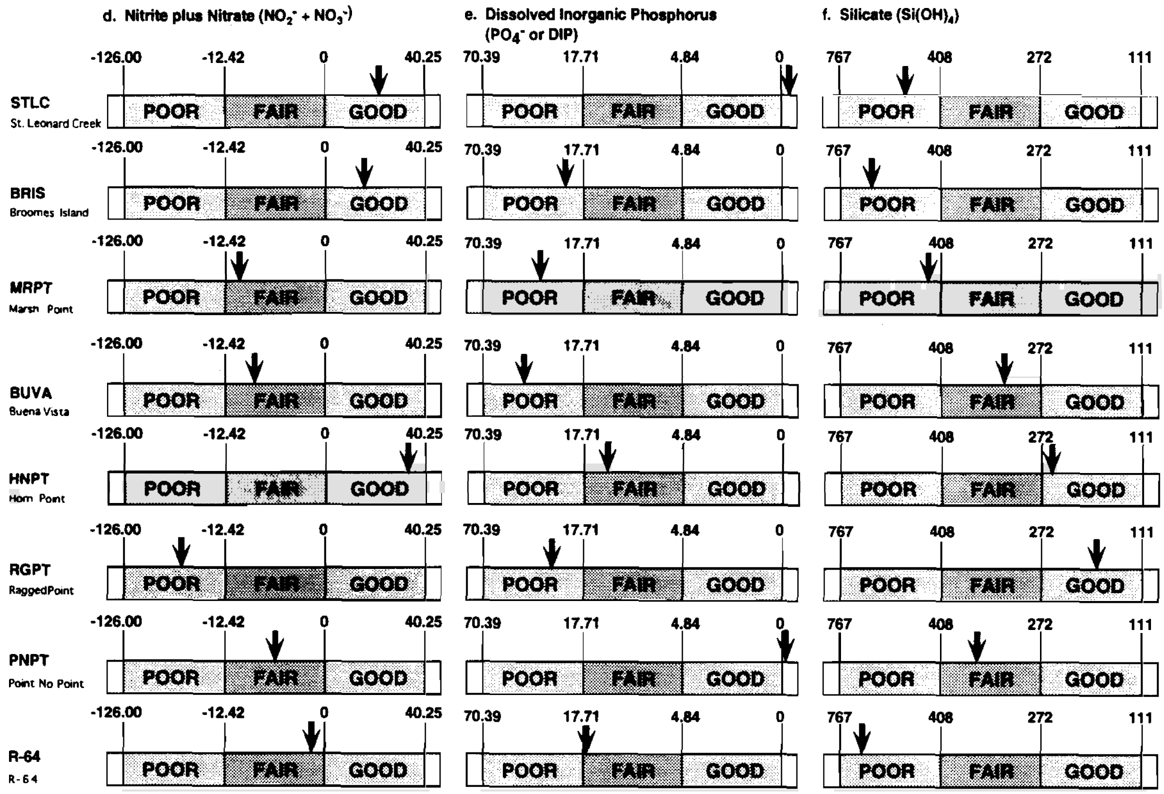
Nitrite (NO_2^-):
High nitrite plus fluxes (positive values) are judged to be good because of the well established linkage between nitrite plus nitrate evolution from sediments via nitrification and oxidized sediment conditions.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):

STLC: 3.74
BRIS: 7.23
MRPT: -4.89
BUVA: 1.26
HNPT: 9.12 No data for 1996
RGPT: -48.87
PNPT: -4.65 No data for Jul, Aug and Sep 1995
R-64: 0.00

Figure 6-1. A summary of the status of sediment oxygen and nutrient exchanges for each SONE station for three variables: a. Sediment Oxygen Consumption (SOC), b. Ammonium (NH_4^+), c. Nitrite (NO_2^-).

All flux data for each variable collected at each station between 1985 and 1996 (except for Horn Point and Point No Point) were combined and the 5th and 95th; 35th and 65th percentiles determined. Downward pointing arrows on each bar represent the current status of a sediment-water flux variable, the median of the fluxes observed during the period 1994, 1995 and 1996. The general criteria for judging the flux status as good, fair or poor is indicated below the figure.



Nitrite plus Nitrate ($NO_2^- + NO_3^-$):
High nitrite plus nitrate fluxes (positive values) are judged to be good because of the well established linkage between nitrite plus nitrate evolution from sediments via nitrification and oxidized sediment conditions.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):
STLC: 19.37
BRIS: 13.30
MRPT: -11.77
BUVA: -9.91
HNPT: 30.38 No data for 1996
RGPT: -42.27
PNPT: -6.39 No data for Jul, Aug and Sep 1995
R-64: -1.68

Dissolved Inorganic Phosphorus (PO_4^{-3} or DIP):
High phosphorus values are judged to be poor because of the well established linkage between phosphorus availability and excessive phytoplankton biomass accumulation.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):
STLC: -5.99
BRIS: 22.27
MRPT: 37.39
BUVA: 54.29
HNPT: 13.04 No data for 1996
RGPT: 23.92
PNPT: -1.33 No data for Jul, Aug and Sep 1995
R-64: 17.17

Silicate ($Si(OH)_4$):
High silicate values are judged to be poor because of the well established linkage between silicate availability and excessive phytoplankton biomass accumulation.

VALUE OF CURRENT STATUS
(Median for 1994, 1995 and 1996 indicated as arrows on bars):
STLC: 503
BRIS: 624
MRPT: 420
BUVA: 295
HNPT: 268 No data for 1996
RGPT: 186
PNPT: 321 No data for Jul, Aug and Sep 1995
R-64: 742

Figure 6-1. A summary of the status of sediment oxygen and nutrient exchanges for each SONE station for three variables: d. Nitrite plus Nitrate ($NO_2^- + NO_3^-$) e. Dissolved Inorganic Phosphorus (PO_4^{-3} or DIP) f. Silicate ($Si(OH)_4$).

All flux data for each variable collected at each station between 1985 and 1996 (except for Horn Point and Point No Point) were combined and the 5th and 95th; 35th and 65th percentiles determined. Downward pointing arrows on each bar represent the current status of a sediment-water flux variable, the median of the fluxes observed during the period 1994, 1995 and 1996. The general criteria for judging the flux status as good, fair or poor is indicated below the figure.

considered to have nitrite plus nitrate fluxes in the good range, four in the fair range and one was in the poor range. More stations are expected to move from poor to fair or fair to good when dissolved oxygen (DO) conditions in bottom waters improves, even if only enough to allow some nitrification activity to occur.

v. Dissolved Inorganic Phosphorus (PO_4^- or DIP)

The current status (average of 1994, 1995 and 1996 data) of dissolved inorganic phosphorus fluxes at the eight SONE stations is indicated in Figure 6-1.e. In the case of phosphorus fluxes it appears appropriate to judge high values as poor because of the well established linkage between phosphorus availability and excessive phytoplankton biomass accumulation. Among the SONE stations two were considered to have phosphorus fluxes in the good range, two were in the fair range and four were in the poor range. It should be noted here that high river flow years have a particularly strong influence on phosphorus fluxes (fluxes increase). Two of the three years considered here were high flow years and phosphorus fluxes at several sites were enhanced enough to place them deep within the fair category. We would expect these sites to move towards the fair and good categories when river flows return to more normal levels.

vi. Silicate ($Si(OH)_4$)

The current status (average of 1994, 1995 and 1996 data) of silicate fluxes at the eight SONE stations is indicated in Figure 6-1.f. In the case of silicate fluxes it appears appropriate to judge high values as poor because of the well established linkage between silicate availability and excessive phytoplankton biomass accumulation. In the case of silicate flux this characterization is more tenuous than it is for either ammonium or phosphorus fluxes because silicate can promote the growth of diatoms which are generally considered to be a good food source for estuarine food webs. However, even excessive diatom growth can cause water quality problems and it is for this reason that we categorize high silicate fluxes as poor. Among the SONE stations two were considered to have silicate fluxes in the good range, two were in the fair range and four were in the poor range.

6.3 Sediment Oxygen and Nutrient Exchanges (SONE) Trends

A standardized protocol was strongly recommended by the Monitoring Program for determining interannual trends of each parameter (Eskin *et al.*, 1993). This approach uses the non-parametric seasonal Kendall test. In results presented here, sediment oxygen and nutrient exchanges (SONE) flux data were corrected for river flow, as is the case for testing other variables for trends within the monitoring program. The following sections present summaries of earlier trend analyses (Boynton *et al*, 1993), the procedures used to perform the standardized Kendall test for trends and the resulting trends.

6.3.1 Highlights of Previous Trend Analyses: 1985 - 1992

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.*, 1995b). However, during years of especially high flow (*e.g.* 1989, 1993, 1994 and 1996) it appears that the spring bloom was 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, 1994 and 1996) 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 temperatures 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.

Statistical analyses have also been conducted to examine sediment oxygen and nutrient exchanges (SONE) flux data for temporal trends (1985 - 1992; Boynton *et al.*, 1993). 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 the period 1985 through 1992 for SOC for any specific month in the Potomac River and Susquehanna River (Maryland Mainstem Bay; [Boynton *et al.*, 1993]). 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 the period 1985 through 1992 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 (~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.*, 1996).

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 this earlier examination of 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 have 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.

6.3.2 Current Testing (Seasonal Kendall Test) for Seasonal Trends: 1985 - 1996

Trend analysis is one method which can be use to assess the changes within the Bay system and the effectiveness of the program's design to restore optimum conditions in the Bay as well as preventing further deterioration of present conditions. The Seasonal Kendall test is recommended by the Monitoring Program as the preferred statistical procedure for trend assessments. The seasonal Kendall test is non-parametric and is a generalization of the Mann-Kendall test. It is applied to data sets exhibiting seasonality. The test does not assume a specific parametric form. Details of the statistical method are given in Gilbert (1987).

6.3.2.1. Sediment Oxygen Nutrient and Exchanges (SONE) Flux Data Set

Flux data is collected over a period of twelve years (1985 - 1996) during seven months, April through November, at 8 stations: two in the Maryland Mainstem (R-64 and Point No Point [PNPT]), four in the Patuxent River (Buena Vista [BUVA]. Broomes Island [BRIS], Marsh Point [MRPT] and St. Leonard Creek [STLC]), one in the Potomac River (Ragged Point [RGPT] and one in the Choptank River (Horn Point [HNPT]). Flux data typically exhibit strong seasonality which may increase the variance of the data. In order to characterize the data initially, manual QA/QC checks are completed. A plot of the complete data set for each fluxvariable was prepared, an example for ammonium (NH_4^+) values at Buena Vista (BUVA) is included (Figure 6-2.). Extreme outliers were examined

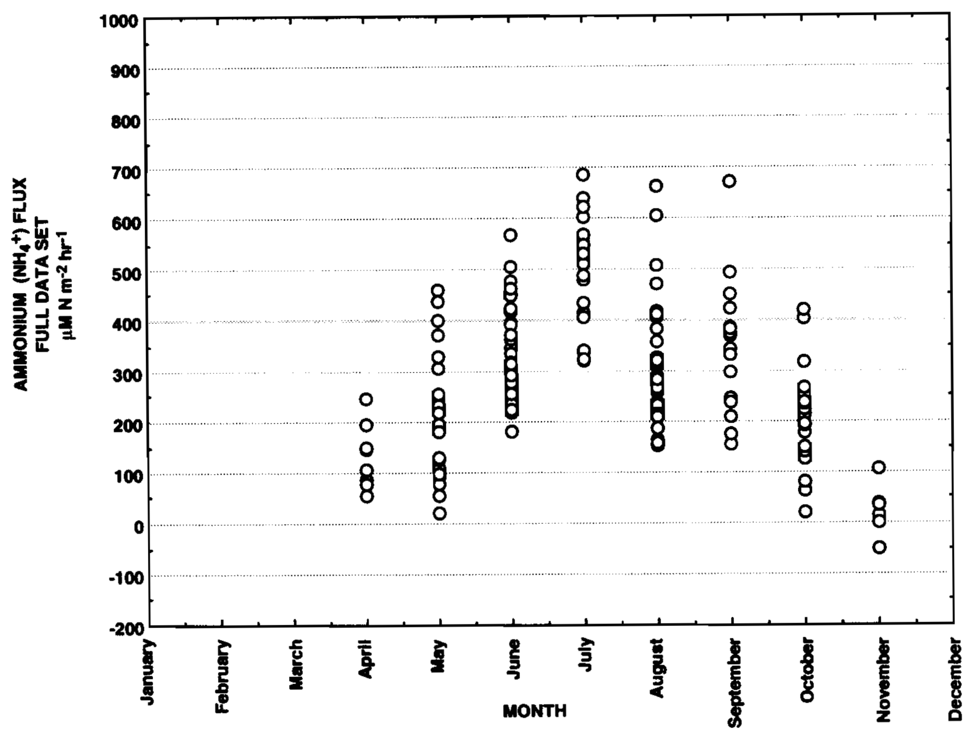


Figure 6-2. Plot of full flux data set for ammonium (NH_4^+) at Buena Vista (BUVA) for Quality Assurance and Quality Control (QA/QC) checking.

and in certain cases these data were discarded. Monthly variation and distribution of flux data are presented using box and whisker plots (Section 5.3). It has been recommended that for water quality data the median (rather than the mean) be used to determine the center point of the data set, particularly since it is well known that environmental quality data is usually positively skewed (Helsel, 1990). Separate analyses were performed for each sediment oxygen and nutrient exchanges (SONE) variable. A probability level of **0.01** was used to assess the significance of the results using observed data.

6.3.2.2. Flow adjustment

River discharge rates often influence concentrations of nutrients and other materials in estuarine systems. For example, heavy rains may cause a dilution effect or, in some systems, may have the net result of increasing total nutrient loads. The use of flow adjusted concentrations (or some other variable) is an attempt to remove the influence of flow *per sae* from the inspection of a data set for interannual trends. So, for example, if nitrate concentration in a mesohaline zone of an estuary was a partial correlate of flow, flow correction would remove the influence of flow from the data set. In effect, the trend analysis is done on the residuals of the flow vs variable relationship. In the monitoring program this is important because it is effects other than flow (*e.g.* managed nutrient concentration reductions) that are being sought, if they exist. In the case of SONE variables an appropriate river flow (or river flow period) needed to be selected. In other portions of the monitoring program flow lags of 7 -14 days appeared appropriate and were adopted. However, SONE variables are influenced by river flow through a chain of events which taken together argue for a longer lag averaged over a substantial time period. Analyses presented in previous reports (Boynton *et al.*, 1994; Cowan and Boynton, 1996) suggest using river flow values averaged for December through February and applied to data collected between May and October is a reasonable solution.

The flux data were "flow detrended" or adjusted to standardize the effects of flow using a linear regression model. The independent variable of this model was the average of flow for the three winter months (December, January, and February) preceding the flux collections. The regression model was designed such that data for each month had a separate slope that described the flux as a function of flow. In the results, it was clear that flux rates for some months were more strongly influenced by flow than flux rates for other months.

A flow adjusted flux datum was computed as the sum of the overall mean flux and the difference between the original datum and the regression prediction. Using terms commonly employed in regression analysis, a flow adjusted datum is the overall mean plus the regression model. Geometrically, envision a scatter plot of flux versus flow on which is superimposed a line fitted by least squares. If each point of the scatter plot is moved parallel to the regression line to a new point just above mean flow, the new points would represent the flow adjusted data. The flow adjusted data therefor are our best estimate of what the flux would have been if flow had been constant at the mean level for the study period. Bear in mind that in this analysis, the data for each month were described by a different slope and therefore a different line.

The residuals were used to assess the data set for long-term trends using the seasonal Kendall test. Separate analyses were performed for each sediment oxygen and nutrient exchanges (SONE) variable. A probability level of **0.05** was used to assess the significance of the results using flow adjusted data.

6.3.3 Results of Kendall Tests for Detection of Inter-Annual Trends

A set of graphic representations were used to summarize results of the annual Kendall testing for trends (with flow corrections; Figures 6-3. and 6.4.). Flow detrended annual values and seasonal combination values are presented in Table 6-3 while the same values for observed data are presented in Table 6.2. An overview of the significance of trends is presented in Table 6-1. The figures include results for a total of six sediment-water flux variables, including sediment oxygen consumption (SOC), silicate, ammonium, dissolved inorganic phosphorus, nitrite and nitrite plus nitrate. The first three graphics, Figures 6-3.1. - 6-3.3., summarize results of the six flux variables measured at four sites (Buena Vista [BUVA], Broomes Island [BRIS], Marsh Point [MRPT] and St. Leonard Creek [STLC]) in the Patuxent River estuary and the remaining three graphics, Figures 6-4.1. - 6-4.3., summarize results found at SONE stations in the Potomac (Ragged Point [RGPT]), Choptank (Horn Point [HNPT]) and mainstem bay (Point No Point [PNPT] and R-64 [R-64]).

Testing for trends at the annual time scale resulted in few statistically significant results ($p < 0.05$). In the Patuxent River estuary sediment oxygen consumption (SOC) fluxes have been increasing in magnitude at the most up river station (Buena Vista [BUVA]) and at one station in the lower estuary (Broomes Island [BRIS]). It is important to note that increasing values of sediment oxygen consumption (SOC) indicate that sediments are consuming more dissolved oxygen over the study period. As indicated above, this is an indication of improving conditions because there must be adequate dissolved oxygen in bottom waters to support sediment oxygen consumption (SOC) fluxes. Two significant trends were indicated for nitrite (NO_2^-) in the Patuxent River estuary, one at the most upriver station (Buena Vista [BUVA] and the other at the station closest to the mouth of the estuary (St. Leonard Creek [STLC]). Again, it is important to note that these upward trends are considered positive because they indicate that sediments have been exposed to more oxidized conditions.

There were no significant annual trends for silicate, ammonium, dissolved inorganic phosphorus or nitrite plus nitrate fluxes in the Patuxent River estuary. Despite a first-order correction for effects of river flow on these variables, it appears that there is sufficient interannual variability to obscure trends if they exist. During the last 12 years both wet and dry years have been recorded (relatively high and low diffuse source loading years) which tend to produce high and low sediment fluxes. Since high/low load years have occurred without pattern, trends due either to climatic variability or management actions (reduced nutrient load) have not yet become apparent.

Testing for trends at the annual time scale at SONE stations in the mainstem bay and two other tributaries also resulted in very few statistically significant results ($p < 0.05$). There were no significant trends for sediment oxygen consumption (SOC) at these sites and only silicate ($Si(OH)_4$) fluxes were decreasing (from very high levels) at SONE station R-64 in the mainstem bay. There were no significant ammonium, dissolved inorganic phosphorus, nitrite or nitrite plus nitrate flux trends. These results are expected because substantial reductions in nitrogen loads (a particularly important nutrient in mesohaline regions of the bay system) have not been realized in these sectors of the bay.

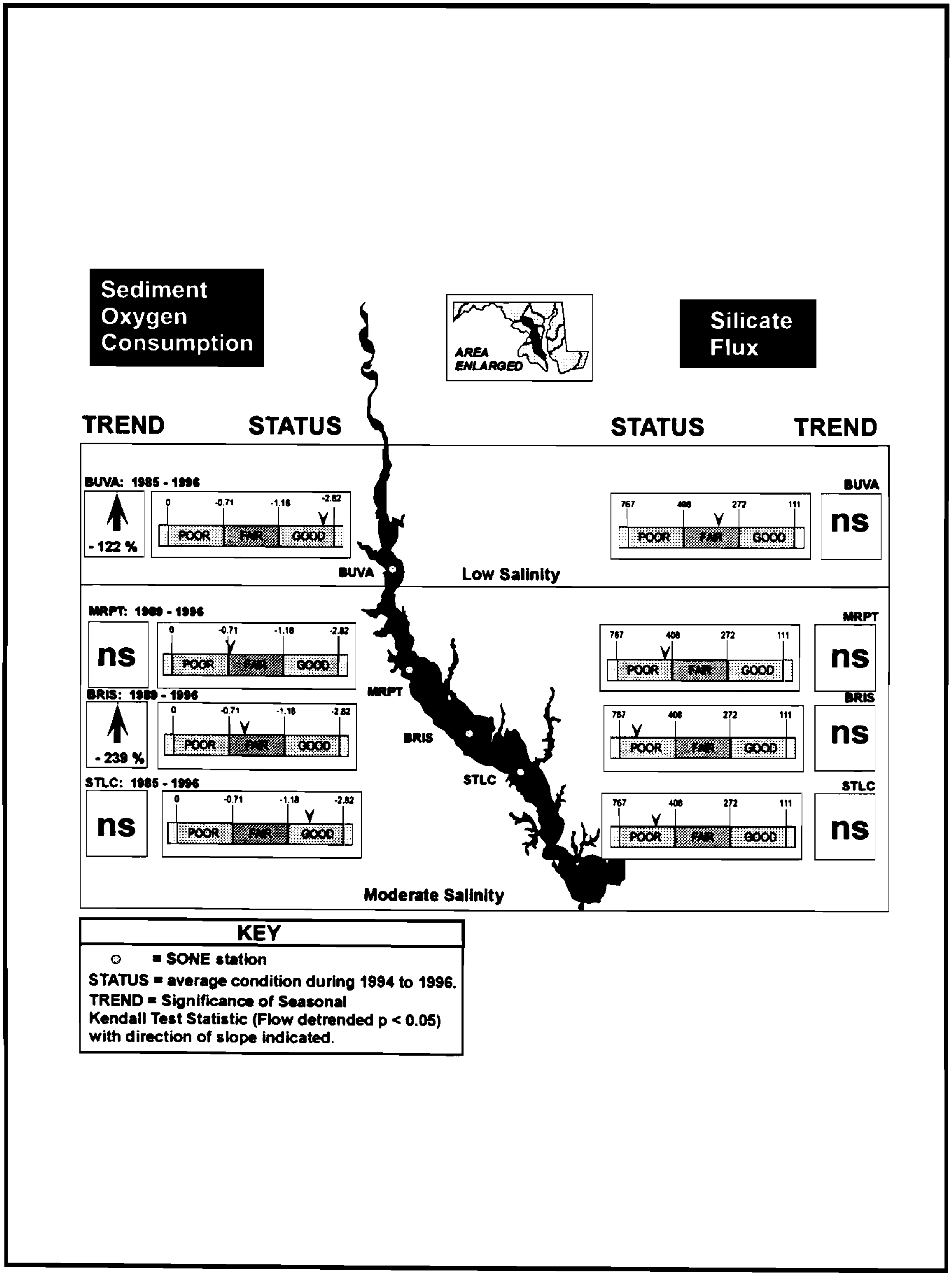


Figure 6-3.1 Map showing status and trends in the Lower Patuxent River for two flux variables (flow detrended), sediment oxygen consumption (SOC) and silicate fluxes ($Si(OH)_4$).

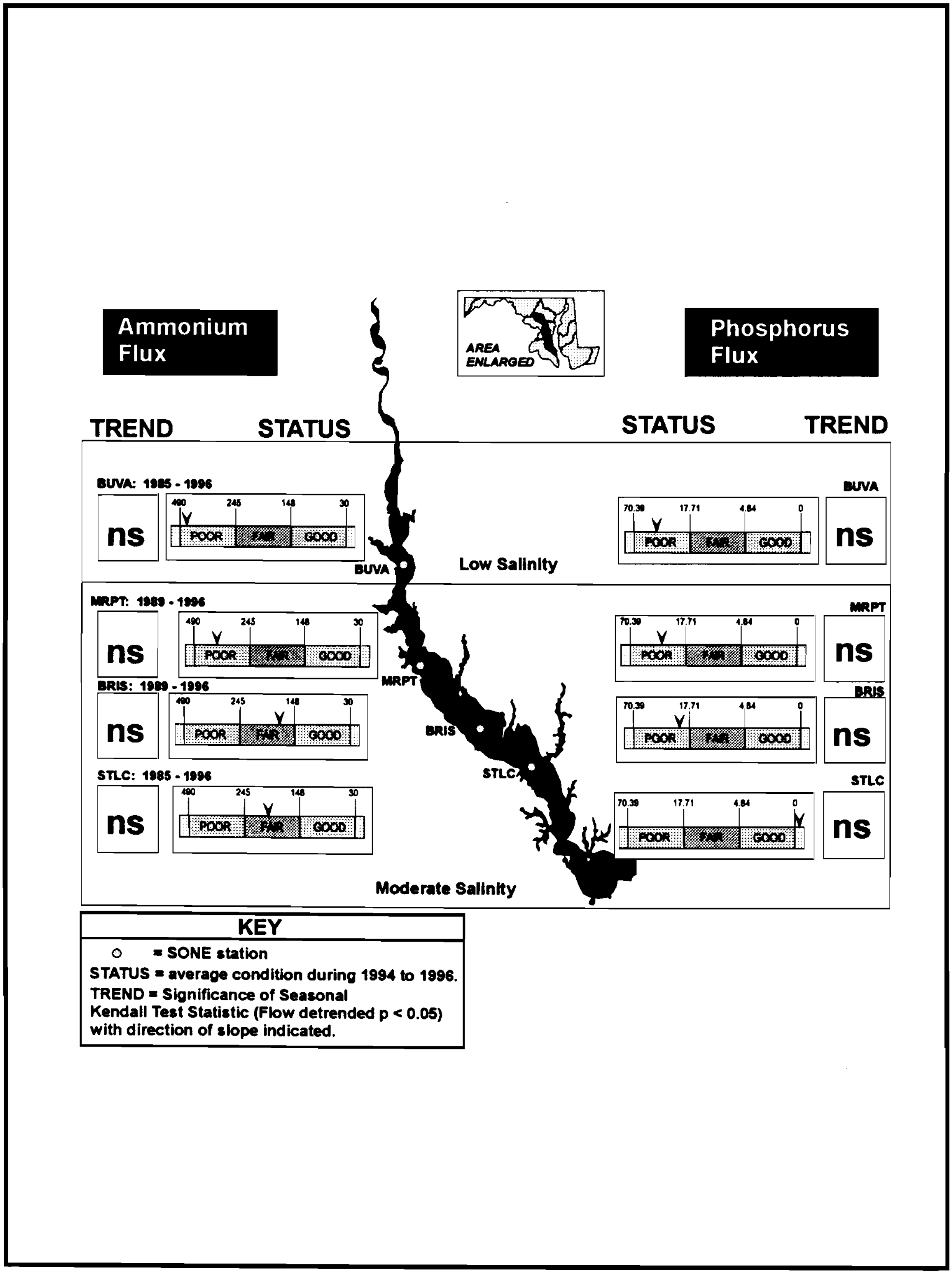


Figure 6-3.2. Map showing status and trends in the Lower Patuxent River for two flux variables (flow detrended), ammonium (NH_4^+) and phosphorus fluxes (PO_4^{-3}).

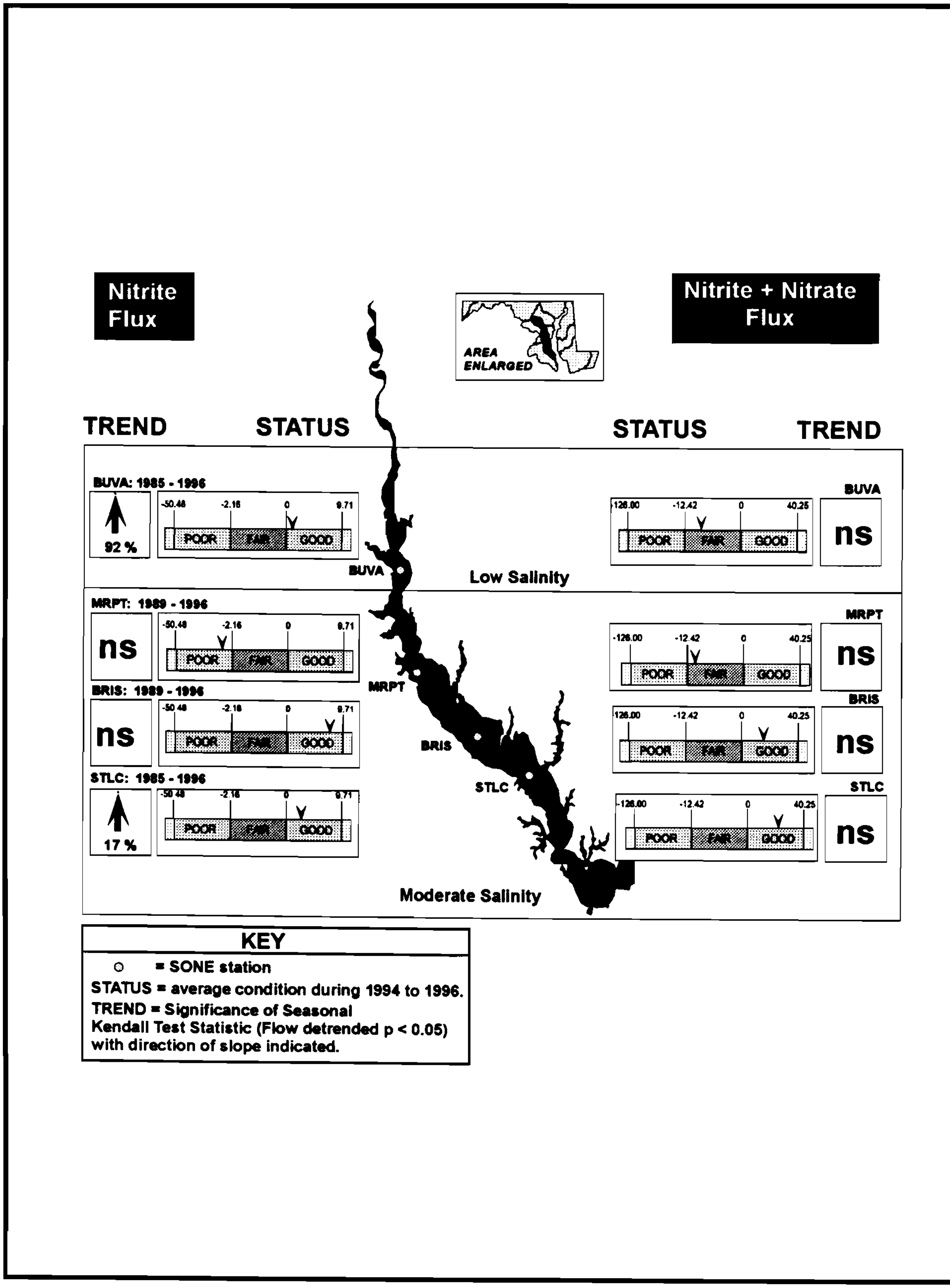


Figure 6-3.3 Map showing status and trends in the Lower Patuxent River for two flux variables (flow detrended), nitrite (NO_2^-) and nitrite plus nitrate ($NO_2^- + NO_3^-$).

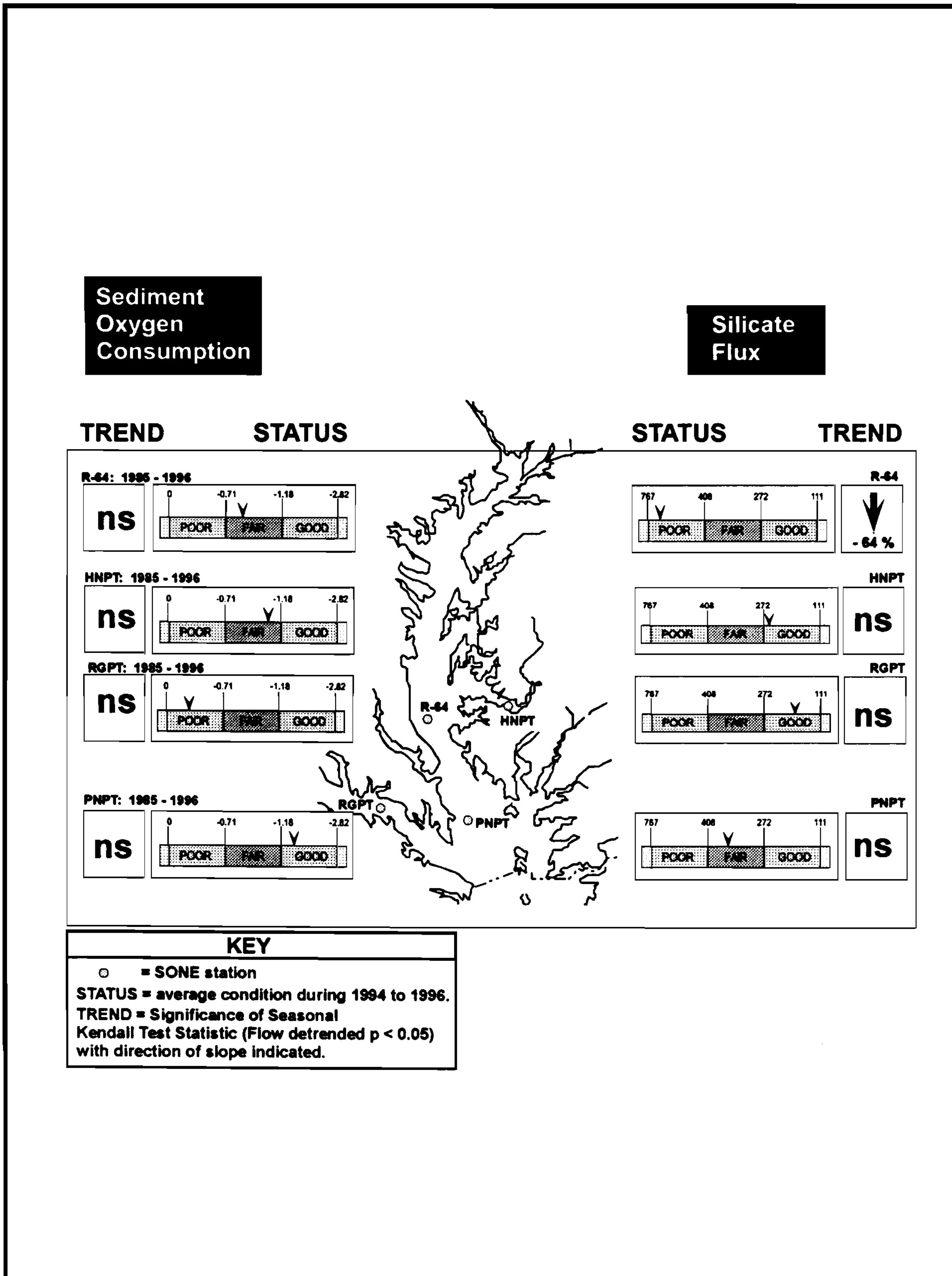
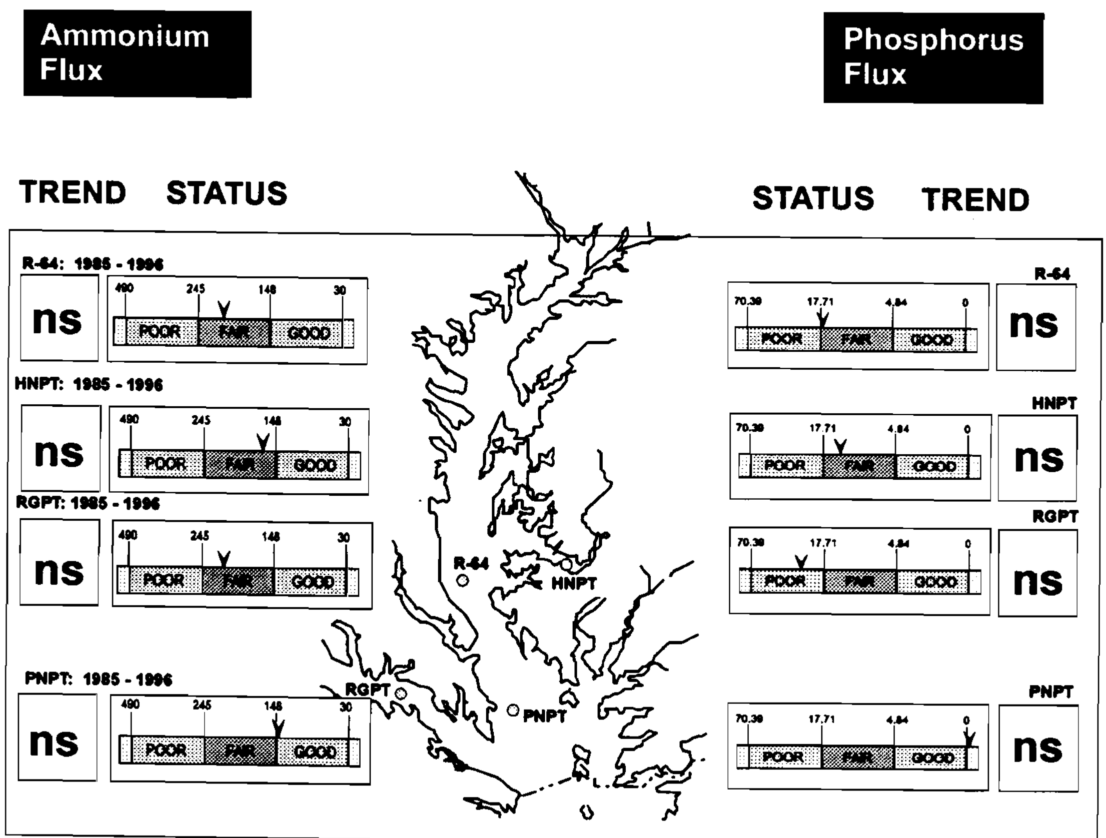


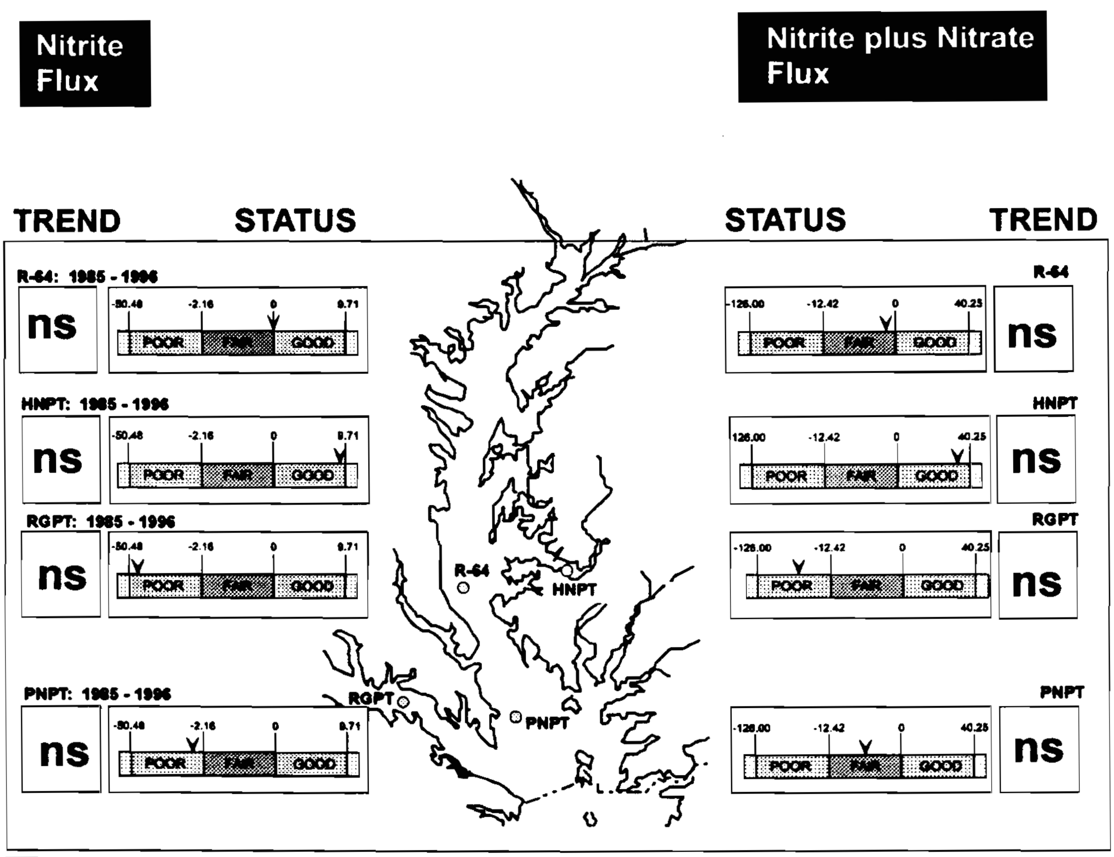
Figure 6-4.1 Map showing status and trends in Two Tributaries and Mainstem Bay for two flux variables (flow detrended), sediment oxygen consumption (SOC) and silicate fluxes ($Si(OH)_4$).



KEY

○ = SONE station
STATUS = average condition during 1994 to 1996.
TREND = Significance of Seasonal Kendall Test Statistic (Flow detrended $p < 0.05$) with direction of slope indicated.

Figure 6-4.2. Map showing status and trends in Two Tributaries and Mainstem Bay for two flux variables (flow detrended), ammonium (NH_4^+) and phosphorus (PO_4^{-3}).



KEY
○ = SONE station
STATUS = average condition during 1994 to 1996.
TREND = Significance of Seasonal Kendall Test Statistic (Flow detrended $p < 0.05$) with direction of slope indicated.

Figure 6-4.3 Map showing status and trends in Two Tributaries and Mainstem Bay for two flux variables (flow detrended), nitrite (NO_2^-) and nitrite plus nitrate ($NO_2^- + NO_3^-$).

Table 6-1. A condensed summary of significant trends detected for sediment-water exchange data using seasonal Kendall Test statistic.
a. Observed data ($p = 0.01$; $p = 0.001$)
b. Flow detrended data ($p = 0.05$; $p = 0.01$; $p = 0.001$).
*Significance: * $p = 0.05$;** $p = 0.01$; *** $p = 0.001$*

a. Observed data

Station	Month								Season Combination			
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Ann	Jun-Sep	Jun-Aug	Jul-Aug
a. Sediment Oxygen Consumption (SOC; g O^2 m^{-2} day^{-1} yr^{-1})												
BRIS					**				**	**	**	***
BUVA									**	**	**	**
b. Ammonium (NH_4^+; µM N m^{-2} hr^{-1})												
BUVA									**	**	**	**
c. Nitrite (NO_2^-; µM N m^{-2} hr^{-1})												
STLC				**								
R-64										**	**	**
d. Nitrite plus nitrate (NO_2^- + NO_3^-; µM N m^{-2} hr^{-1})												
HNPT			**									
RGPT											**	
e. Dissolved Phosphorus (PO_4^-; µM P m^{-2} hr^{-1})												
MRPT			**									
f. Silicate ($Si(OH)_4$; µM Si m^{-2} hr^{-1})												
BRIS									**			
RGPT					**							
R-64									**			

b. Flow detrended

Station	Month								Season Combination			
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Ann	Jun-Sep	Jun-Aug	Jul-Aug
a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})												
BRIS					**				***	***	**	**
BUVA									**	*	*	*
b. Ammonium (NH_4^+; µM N m^{-2} hr^{-1} yr^{-1})												
BUVA										*	*	
MRPT		**										
HNPT			**									
c. Nitrite (NO_2^-; µM N m^{-2} hr^{-1} yr^{-1})												
									*	*	*	
BUVA		*							*			
d. Nitrite plus nitrate (NO_2^- + NO_3^-; µM N m^{-2} hr^{-1} yr^{-1})												
HNPT			**									
RGPT										*	**	
e. Dissolved Phosphorus (PO_4^{-3}; µM P m^{-2} hr^{-1} yr^{-1}])												
PNPT					*							*
f. Silicate ($Si(OH)_4$; µM Si m^{-2} hr^{-1} yr^{-1})												
MRPT		*										
RGPT					*							
R-64					*				**	*	*	

Table 6-2.a. Table of Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
St Leonards Creek (STLC): 1985 - 1996				
Sign	-41	-30	-19	-35
p value	0.10	0.18	0.39	0.03*
Slope	-0.049	-0.048	-0.038	-0.105
Broomes Island (BRIS): 1989 - 1996				
Sign	-47	-40	-37	-38
p value	0.004**	0.006**	0.007**	0.001***
Slope	-0.111	-0.115	-0.124	-0.128
Marsh Point (MRPT): 1989 - 1996				
Sign	-17	-9	-12	-23
p value	0.32	0.57	0.40	0.05*
Slope	-0.034	-0.013	-0.055	-0.091
Buena Vista (BUVA): 1985 - 1996				
Sign	-80	-59	-58	-46
p value	0.002**	0.011**	0.010**	0.007**
Slope	-0.093	-0.091	-0.092	-0.112
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	5	9	11	0
p value	0.86	0.69	0.61	1.00
Slope	0.009	0.016	0.020	-0.003
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	-37	-42	-44	-35
p value	0.11	0.04*	0.03*	0.02*
Slope	-0.006	-0.010	-0.012	-0.013
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	33	12	14	7
p value	0.15	0.58	0.50	0.68
Slope	0.021	0.015	0.018	0.020
R-64 (R-64): 1985 -1996				
Sign	37	37	38	26
p value	0.14	0.11	0.09	0.12
Slope	0.010	0.010	0.010	0.005

Table 6-2.b. Table of Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

b. Ammonium (NH_4^+; µM N m^{-2} hr^{-1} yr^{-1})

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION	St Leonards Creek (STLC): 1985 - 1996			
Sign	11	16	13	14
p value	0.69	0.51	0.59	0.44
Slope	1.448	2.300	2.206	2.945
	Broomes Island (BRIS): 1989 - 1996			
Sign	0	4	1	2
p value	1.00	0.83	1.00	0.93
Slope	-0.325	2.417	0.850	1.225
	Marsh Point (MRPT): 1989 - 1996			
Sign	38	20	23	18
p value	0.03*	0.18	0.10	0.14
Slope	24.587	21.864	26.267	29.867
	Buena Vista (BUVA): 1985 - 1996			
Sign	68	63	64	46
p value	0.008**	0.006**	0.005**	0.007**
Slope	11.147	11.693	12.299	13.908
CHOPTANK RIVER:				
	Horn Point (HNPT): 1985 - 1995			
Sign	-26	-23	-23	8
p value	0.27	0.27	0.26	0.63
Slope	-4.142	-8.694	-9.305	3.677
POTOMAC RIVER:				
	Ragged Point (RGPT): 1985 - 1996			
Sign	-26	-17	-22	-20
p value	0.32	0.48	0.34	0.25
Slope	-8.767	-6.083	-11.499	-22.518
MAINSTEM BAY:				
	Point No Point (PNPT): 1985 - 1994, 1996			
Sign	-15	-8	-8	-4
p value	0.55	0.74	0.73	0.84
Slope	-1.138	-0.890	-0.890	-0.469
	R-64 (R-64): 1985 -1996			
Sign	-36	-43	-40	-30
p value	0.17	0.07	0.08	0.08
Slope	-9.107	-18.233	-19.005	-22.423

Table 6-2.c. Table of Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

c. Nitrite (NO_2^-; μM N m^{-2} hr^{-1} yr^{-1})

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION	St Leonards Creek (STLC): 1985 - 1996			
Sign	36	34	25	25
p value	0.04*	0.03*	0.09	0.04*
Slope	1.079	1.169	1.067	1.343
	Broomes Island (BRIS): 1989 - 1996			
Sign	3	2	-7	-8
p value	0.90	0.94	0.65	0.54
Slope	0.056	0.241	-0.311	-0.924
	Marsh Point (MRPT): 1989 - 1996			
Sign	9	-5	-4	2
p value	0.62	0.78	0.82	0.93
Slope	0.117	-0.173	-0.177	0.075
	Buena Vista (BUVA): 1985 - 1996			
Sign	42	27	18	8
p value	0.02*	0.10	0.25	0.58
Slope	1.230	1.056	0.561	0.545
CHOPTANK RIVER:				
	Horn Point (HNPT): 1985 - 1995			
Sign	-2	0	-6	3
p value	0.95	1.00	0.69	0.85
Slope	-0.115	0.056	-0.334	0.458
POTOMAC RIVER:				
	Ragged Point (RGPT): 1985 - 1996			
Sign	4	4	3	9
p value	0.86	0.84	0.89	0.48
Slope	0.102	0.102	0.051	0.282
MAINSTEM BAY:				
	Point No Point (PNPT): 1985 - 1994, 1996			
Sign	-11	-19	-21	-10
p value	0.52	0.18	0.12	0.37
Slope	-0.024	-0.290	-0.302	-0.050
	R-64 (R-64): 1985 -1996			
Sign	-39	-44	-43	-31
p value	0.02*	0.003**	0.002**	0.006**
Slope	-0.399	-0.664	-0.637	-0.395

Table 6-2.d. Table of Seasonal Kendall Test Statistics (Observed data) at eight SONE stations four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

d. Nitrite plus Nitrate ($NO_2^- + NO_3^-$; $\mu M\ N\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	-5	-10	-23	3
p value	0.87	0.69	0.31	0.90
Slope	-0.287	-0.450	-0.884	1.554
Broomes Island (BRIS): 1989 - 1996				
Sign	11	13	6	3
p value	0.53	0.40	0.70	0.86
Slope	1.687	2.085	1.053	0.263
Marsh Point (MRPT): 1989 - 1996				
Sign	12	16	13	12
p value	0.50	0.29	0.36	0.34
Slope	0.768	1.192	1.221	1.022
Buena Vista (BUVA): 1985 - 1996				
Sign	-30	-8	-13	-7
p value	0.23	0.75	0.57	0.69
Slope	-1.781	-0.772	-1.541	-1.781
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	-42	-33	-41	-8
p value	0.07	0.11	0.04*	0.63
Slope	-2.695	-3.276	-4.643	-0.676
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	-52	-51	-59	-31
p value	0.04*	0.03*	0.008**	0.07
Slope	-1.582	-1.708	-2.141	-1.202
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-26	-26	-24	-5
p value	0.28	0.23	0.26	0.78
Slope	-0.565	-0.790	-0.790	0.000
R-64 (R-64): 1985 -1996				
Sign	-1	6	1	6
p value	1.00	0.82	1.00	0.75
Slope	0.000	0.000	0.000	0.000

Table 6-2.e. Table of Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

e. Dissolved Phosphorus (PO_4^{-3}; $\mu M\ P\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	5	-1	6	-4
p value	0.87	1.00	0.82	0.86
Slope	0.015	-0.048	0.034	-0.154
Broomes Island (BRIS): 1989 - 1996				
Sign	-6	-8	-11	-10
p value	0.76	0.62	0.45	0.43
Slope	-0.088	-0.435	-0.773	-1.355
Marsh Point (MRPT): 1989 - 1996				
Sign	22	14	21	4
p value	0.19	0.36	0.13	0.79
Slope	1.476	1.615	2.865	1.668
Buena Vista (BUVA): 1985 - 1996				
Sign	15	20	15	30
p value	0.56	0.38	0.51	0.08
Slope	0.395	1.169	1.085	3.372
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	-6	-5	-5	0
p value	0.82	0.84	0.84	1.00
Slope	-0.119	-0.137	-0.137	0.045
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	4	-3	-10	-14
p value	0.91	0.93	0.68	0.44
Slope	0.033	-0.044	-0.275	-0.622
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	33	32	28	30
p value	0.17	0.14	0.19	**0.05***
Slope	0.370	1.001	0.923	2.612
R-64 (R-64): 1985 -1996				
Sign	3	-13	-18	0
p value	0.94	0.60	0.44	1.00
Slope	0.117	-0.589	-0.817	0.051

Table 6-2.f. Table of Seasonal Kendall Test Statistics (Observed datapo) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

f. Silicate ($Si(OH)_4$; μM Si m^{-2} hr^{-1} yr^{-1})

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	1	2	2	17
p value	1.00	0.95	0.95	0.14
Slope	0.533	2.211	2.211	35.933
Broomes Island (BRIS): 1989 - 1996				
Sign	35	17	19	16
p value	0.006**	0.10	0.05*	0.50*
Slope	26.000	29.333	31.667	30.833
Marsh Point (MRPT): 1989 - 1996				
Sign	3	-11	-9	-8
p value	0.87	0.30	0.39	0.35
Slope	2.334	-25.667	-25.667	-29.033
Buena Vista (BUVA): 1985 - 1996				
Sign	44	37	39	26
p value	0.03*	0.03*	0.02*	0.04*
Slope	20.869	32.000	34.533	36.778
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	-12	-7	-9	4
p value	0.60	0.74	0.65	0.81
Slope	-1.633	-1.584	-1.600	7.083
POTOMAC Ragged Point (RGPT): 1985 - 1996				
Sign	24	35	33	26
p value	0.28	0.06	0.07	0.04*
Slope	6.095	10.778	10.778	15.142
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-18	-7	-5	10
p value	0.42	0.74	0.82	0.47
Slope	-6.945	-6.084	-4.600	8.786
R-64 (R-64): 1985 -1996				
Sign	-54	-37	-35	-26
p value	0.01**	0.05*	0.06	0.04*
Slope	-15.678	-18.056	-16.625	-17.340

Table 6-3.a. Table of Seasonal Kendall Test Statistics (Flow detrended) at eight SONE stations for four seasonal and an annual variable.
Significance: * $p = 0.05$; ** $p = 0.01$; *** $p = 0.001$

a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
St Leonards Creek (STLC): 1985 - 1996				
Sign	-45	-34	-23	-27
p value	0.07	0.13	0.30	0.09
Slope	-0.038	-0.037	-0.034	-0.049
Broomes Island (BRIS): 1989 - 1996				
Sign	-54	-50	-43	-32
p value	0.001***	0.001***	0.002**	0.007**
Slope	-0.087	-0.101	-0.112	-0.104
Marsh Point (MRPT): 1989 - 1996				
Sign	-16	-6	-9	-20
p value	0.35	0.73	0.55	0.10
Slope	-0.033	-0.018	-0.030	-0.085
Buena Vista (BUVA): 1985 - 1996				
Sign	-70	-55	-54	-40
p value	0.006**	0.02*	0.02*	0.02*
Slope	-0.072	-0.072	-0.072	-0.081
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	4	15	15	2
p value	0.89	0.48	0.47	0.94
Slope	0.006	0.033	0.034	0.002
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	-27	-30	-37	-28
p value	0.26	0.16	0.07	0.07
Slope	-0.006	-0.009	-0.014	-0.013
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	21	14	16	10
p value	0.37	0.51	0.44	0.53
Slope	0.013	0.014	0.015	0.018
R-64 (R-64): 1985 -1996				
Sign	13	12	13	3
p value	0.63	0.63	0.59	0.90
Slope	0.006	0.007	0.010	0.004

Table 6-3.b. Table of Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

b. Ammonium (NH_4^+; μM N m $^{-2}$ hr $^{-1}$ yr $^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	-16	-7	-10	-2
p value	0.55	0.79	0.68	0.95
Slope	-1.239	-0.960	-1.257	-0.092
Broomes Island (BRIS): 1989 - 1996				
Sign	-8	-2	-3	0
p value	0.66	0.94	0.88	1.00
Slope	-1.698	-0.715	-1.673	1.095
Marsh Point (MRPT): 1989 - 1996				
Sign	28	10	13	10
p value	0.09	0.53	0.36	0.43
Slope	17.558	8.672	9.813	11.048
Buena Vista (BUVA): 1985 - 1996				
Sign	46	45	44	30
p value	0.07	0.05*	0.05*	0.08
Slope	5.899	7.202	7.250	9.239
CHOPTANK RIVER:				
Horn Point (HNPT): 1985 - 1995				
Sign	-34	-33	-33	4
p value	0.14	0.11	0.10	0.84
Slope	-4.270	-7.292	-8.511	1.077
POTOMAC RIVER:				
Ragged Point (RGPT): 1985 - 1996				
Sign	-34	-23	-32	-20
p value	0.19	0.33	0.16	0.25
Slope	-9.470	-8.724	-11.517	-11.517
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-17	-14	-14	-4
p value	0.50	0.53	0.53	0.84
Slope	-1.368	-1.351	-1.351	-0.816
R-64 (R-64): 1985 -1996				
Sign	-40	-41	-40	-26
p value	0.12	0.08	0.08	0.13
Slope	-9.117	-16.506	-17.474	-18.027

Table 6-3.c. Table of Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

c. Nitrite (NO_2^-; $\mu M\ N\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	40	36	29	23
p value	0.02*	0.02*	0.05*	0.06
Slope	0.918	0.967	0.837	1.185
Broomes Island (BRIS): 1989 - 1996				
Sign	12	12	5	0
p value	0.50	0.44	0.76	1.00
Slope	0.838	0.856	0.545	0.009
Marsh Point (MRPT): 1989 - 1996				
Sign	-4	-8	-7	2
p value	0.85	0.62	0.65	0.93
Slope	-0.119	-0.375	-0.276	0.056
Buena Vista (BUVA): 1985 - 1996				
Sign	38	21	12	6
p value	0.03*	0.21	0.46	0.69
Slope	0.967	0.643	0.561	0.523
CHOPTANK RIVER:				
Horn Point (HNPT): 1985 - 1995				
Sign	-2	-4	-12	-1
p value	0.95	0.82	0.38	1.00
Slope	-0.028	-0.133	-0.561	-0.209
POTOMAC RIVER:				
Ragged Point (RGPT): 1985 - 1996				
Sign	-17	-5	-2	-4
p value	0.34	0.79	0.94	0.79
Slope	-0.405	-0.086	-0.048	-0.070
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-7	-9	-9	1
p value	0.70	0.56	0.55	1.00
Slope	-0.233	-0.406	-0.409	0.050
R-64 (R-64): 1985 -1996				
Sign	3	1	4	10
p value	0.91	1.00	0.83	0.43
Slope	0.106	0.053	0.120	0.625

Table 6-3.d. Table of Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

d. Nitrite plus Nitrate ($NO_2^- + NO_3^-$; $\mu M\ N\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	5	0	-11	1
p value	0.87	1.00	0.64	1.00
Slope	0.105	-0.063	-1.171	0.105
Broomes Island (BRIS): 1989 - 1996				
Sign	22	22	17	8
p value	0.19	0.14	0.23	0.54
Slope	2.988	4.936	4.136	2.450
Marsh Point (MRPT): 1989 - 1996				
Sign	6	14	13	12
p value	0.76	0.36	0.36	0.34
Slope	0.481	1.501	1.402	1.191
Buena Vista (BUVA): 1985 - 1996				
Sign	-31	-14	-19	-7
p value	0.22	0.55	0.39	0.69
Slope	-2.045	-2.683	-3.219	-2.151
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	-28	-23	-31	4
p value	0.23	0.27	0.12	0.84
Slope	-2.817	-3.358	-4.163	0.314
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	-46	-47	-56	-32
p value	0.07	0.04*	0.01**	0.06
Slope	-1.572	-2.045	-2.537	-1.540
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-36	-32	-32	-8
p value	0.14	0.14	0.13	0.63
Slope	-0.869	-1.254	-1.254	0.711
R-64 (R-64): 1985 -1996				
Sign	-30	-11	-16	-6
p value	0.25	0.66	0.50	0.76
Slope	-1.136	-0.474	-0.675	-0.433

Table 6-3.e. Table of Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

e. Dissolved Phosphorus (PO_4^{-3}; $\mu M\ P\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	-12	-19	-12	-10
p value	0.66	0.43	0.62	0.59
Slope	-0.115	-0.243	-0.154	-0.301
Broomes Island (BRIS): 1989 - 1996				
Sign	-6	-12	-13	-12
p value	0.76	0.44	0.36	0.34
Slope	-0.171	-0.867	-0.935	-1.053
Marsh Point (MRPT): 1989 - 1996				
Sign	-2	-10	-1	-4
p value	0.95	0.53	1.00	0.79
Slope	-0.119	-2.087	-1.414	-3.058
Buena Vista (BUVA): 1985 - 1996				
Sign	-3	-4	-7	10
p value	0.93	0.89	0.78	0.59
Slope	-0.208	-0.221	-0.241	1.457
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	1	-7	-7	0
p value	1.00	0.76	0.76	1.00
Slope	0.004	-0.052	-0.052	0.062
POTOMAC RIVER				
Ragged Point (RGPT): 1985 - 1996				
Sign	2	1	-8	-4
p value	0.97	1.00	0.75	0.86
Slope	0.026	0.004	-0.101	-0.101
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	34	34	28	34
p value	0.16	0.12	0.19	0.02*
Slope	0.385	1.509	1.335	2.643
R-64 (R-64): 1985 -1996				
Sign	0	-17	-22	-2
p value	1.00	0.48	0.34	0.95
Slope	0.018	-0.871	-1.186	-0.107

Table 6-3.f. Table of Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for four seasonal and an annual variable.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

f. Silicate ($Si(OH)_4$; $\mu M\ Si\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
STATION St Leonards Creek (STLC): 1985 - 1996				
Sign	-9	-10	-10	5
p value	0.69	0.60	0.59	0.72
Slope	-3.467	-3.971	-3.971	6.373
Broomes Island (BRIS): 1989 - 1996				
Sign	17	1	5	-2
p value	0.19	1.00	0.66	0.89
Slope	17.640	6.108	8.745	-7.605
Marsh Point (MRPT): 1989 - 1996				
Sign	5	-15	-11	-6
p value	0.74	0.15	0.28	0.51
Slope	4.769	-20.764	-18.003	-19.016
Buena Vista (BUVA): 1985 - 1996				
Sign	28	19	21	20
p value	0.18	0.29	0.23	0.12
Slope	11.821	12.944	16.869	27.767
CHOPTANK RIVER				
Horn Point (HNPT): 1985 - 1995				
Sign	-14	-5	-7	0
p value	0.54	0.82	0.74	1.00
Slope	-2.317	-1.360	-1.365	1.179
POTOMAC Ragged Point (RGPT): 1985 - 1996				
Sign	20	29	27	22
p value	0.37	0.12	0.15	0.09
Slope	5.842	9.896	9.896	11.442
MAINSTEM BAY:				
Point No Point (PNPT): 1985 - 1994, 1996				
Sign	-26	-11	-9	8
p value	0.24	0.58	0.65	0.57
Slope	-6.661	-4.228	-4.228	7.695
R-64 (R-64): 1985 -1996				
Sign	-56	-45	-43	-24
p value	0.009**	0.02*	0.02*	0.06
Slope	-15.887	-17.836	-17.836	-16.816

6.3.3 Results of Seasonal Kendall Tests for Detection of Monthly Trends

The results from the monthly Seasonal Kendall test are presented as two tables. The first contains values for observed data (without correction for river flow) using the Kendall test (Table 6-4) and the second contains values after the flow correction has been applied (Table 6-5). In these tables the values for each month at each station are given together with the annual value for the station. The Seasonal Kendall Test Statistic value indicates the direction of slope ("+" indicate a positive or increasing slope while "-" indicates a negative or decreasing slope). Different probability levels for significance are indicated in Table 6-4 and 6-5. The n value indicates the number of observations used in the analysis.

i. Sediment Oxygen Consumption (SOC)

In the Patuxent River a significant SOC trend was found for August at Broomes Island ([BRIS]; Table 6-4.a). No significant trends were indicated at $p < 0.01$ for the remaining seven stations. After the flow correction was applied, significance ($p < 0.05$) was once again indicated at Broomes Island (BRIS) in August (Table 6-5.a). In both cases, negative slopes representing an increasing value of sediment oxygen consumption by sediments was indicated. This was considered as an improving trend because higher sediment oxygen consumption (SOC) fluxes require higher dissolved oxygen (DO) concentrations in bottom waters.

ii. Ammonium (NH_4^+)

No significant trends were indicated for ammonium (NH_4^+) fluxes at $p < 0.01$ for trends without flow correction (observed values). After the flow correction was applied, a positive trend was found at Marsh Point (MRPT) for May and a negative trend was found in June at Horn Point (HNPT) in the Choptank River (Table 6-5.b). The improving conditions during June at Horn Point (HNPT) were of sufficient magnitude to be of importance.

iii. Nitrite (NO_2^-)

A positive significant trend was indicated for nitrite (NO_{2^-}) fluxes in the Patuxent River at St. Leonard Creek (STLC) in July (Table 6-4.c). The trend in the Patuxent River at Buena Vista (BUVA) was significant after applying the flow correction (Table 6-5.c). This positive trend is considered to be good since nitrite fluxes from sediments to water is an indication of nitrification activity which requires dissolved oxygen (DO) in bottom waters.

iv. Nitrite plus Nitrate ($NO_2^- + NO_3^-$)

Only one significant positive trend was found in the Choptank River for Horn Point (HNPT) in June (Table 6-4.d). This trend was still significant after the flow correction was applied.

v. Dissolved Inorganic Phosphorus (PO_4^- or DIP)

Two significant positive trends were found for phosphorus (PO_4^-) in the Patuxent River, in June at Marsh Point ([MRPT]; Table 6-4.e). After the flow correction was applied an additional significant positive trend was indicated at Point No Point (PNPT) for August (Table 6-5.e). Both of these trends are considered bad because positive fluxes indicate increasing phosphorus fluxes from sediments to overlying waters.

vi. Silicate ($Si(OH)_4$)

A positive trend was found in the Potomac River (Ragged Point [RGPT]) in August (Table 6-4.f). After the flow correction was applied, this positive trend was slightly less significant ($p < 0.05$). Another significant positive trend was found in May at Marsh Point (MRPT) in the Patuxent River and a significant negative trend was found in August at R-64 (Table 6-4.f). Positive trends for silicate are considered bad from a water quality perspective.

Table 6-4.a. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	3	-8	16	-16	-19	-11	-3	-3
p value	.	0.40	0.30	0.06	0.16	0.06	0.77	.
n	3	8	12	8	11	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		5	1	-14	-24	-3	-12	
p value		0.47	1.00	0.11	0.002**	0.72	.	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		-5	11	-15	-8	3	-3	
p value		0.47	0.14	.	0.40	0.72	0.72	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	1	-12	-12	-12	-34	-1	-9	-1
p value	.	0.18	0.45	0.18	0.02*	1.00	0.24	.
n	3	8	12	8	12	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	3	-2	11	-7	7	-2	-4	-1
p value	.	0.90	0.44	0.38	0.64	0.82	.	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	1	6	-9	-13	-22	2	-3	1
p value	.	0.55	0.53	.	0.08	.	0.77	.
n	3	8	11	8	11	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	3	10	7	-9	16	-2	5	3
p value	.	0.28	0.64	0.24	0.24	0.82	0.56	.
n	3	8	11	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	-1	0	12	4	22	-1	0	1
p value	.	1.00	0.45	0.72	0.14	1.00	.	.
n	3	8	12	8	12	6	7	3

Table 6-4.b. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

b. Ammonium (NH_4^+; µM N $m^{-2} hr^{-1} yr^{-1}$)

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	1	-10	-1	-4	18	3	3	1
p value	.	0.28	1.00	0.72	0.24	0.72	0.77	.
n	3	8	12	8	12	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		-5	-1	18	-16	3	1	
p value		0.47	1.00	0.03	0.06	0.72	1.00	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		9	5	6	12	-3	9	
p value		0.14	0.56	0.55	0.18	0.72	0.14	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-3	8	18	12	34	-1	1	-1
p value	.	0.40	0.24	0.18	0.02*	1.00	1.00	.
n	3	8	12	8	12	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-1	0	-31	5	3	0	-3	1
p value	.	1.00	0.02*	0.56	0.88	1.00	0.77	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-1	-4	-2	-8	-12	5	-1	-3
p value	.	0.72	0.95	0.40	0.45	0.47	1.00	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	3	-10	-4	-1	-3	0	-1	1
p value	.	0.28	0.84	1.00	0.88	1.00	1.00	.
n	3	8	12	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	3	-2	-10	-14	-16	-3	5	1
p value	.	0.90	0.54	0.11	0.30	0.72	0.56	.
n	3	8	12	8	12	6	7	3

Table 6-4.c. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

c. Nitrite (NO_2^-; $\mu M\ N\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	0	1	0	17	8	9	1	0
p value	.	1.00	1.00	0.01**	0.48	0.14	1.00	.
n	1	6	8	7	9	6	6	1
Broomes Island (BRIS): 1989 - 1996								
Sign		-5	1	-10	2	9	6	
p value		0.47	1.00	0.28	0.90	0.14	.	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		3	-6	0	2	-1	11	
p value		0.72	.	1.00	0.90	1.00	0.06	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	0	11	10	6	2	9	4	0
p value	.	0.06	0.28	0.55	0.92	0.14	0.48	.
n	1	6	8	8	9	6	5	1
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	0	3	-9	1	2	6	-5	0
p value	.	0.72	0.24	1.00	0.90	0.23	0.47	.
n	1	6	7	7	8	5	6	1
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	0	-5	-6	10	-1	1	5	0
p value	.	0.47	0.55	0.28	.	1.00	0.47	.
n	1	6	8	8	8	6	6	1
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	0	3	-11	-1	-9	2	5	0
p value	.	0.72	.	1.00	.	0.82	0.47	.
n	1	6	8	7	8	5	6	1
R-64 (R-64): 1985 -1996								
Sign	0	1	-12	-14	-17	-1	4	0
p value	.	1.00	0.18	0.11	.	1.00	.	.
n	1	6	8	8	8	6	6	1

Table 6-4.d. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

d. Nitrite plus nitrate ($NO_2^- + NO_3^-$; μM N m^{-2} hr^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	-1	2	-26	9	-6	13	5	1
p value	.	0.90	0.09	0.24	0.73	0.02*	0.56	.
n	3	8	12	7	12	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		-3	3	-5	8	7	1	
p value		0.72	0.77	.	0.40	0.27	1.00	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		-7	1	6	6	3	3	
p value		0.27	1.00	0.55	0.55	0.72	0.72	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-3	-11	-6	2	-9	5	-8	0
p value	.	.	0.73	0.9	0.53	0.47	.	.
n	3	8	12	8	11	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	1	-8	-33	5	-13	8	-5	3
p value	.	0.40	0.01**	0.56	0.35	0.08	0.56	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-3	2	-28	-10	-21	8	1	-1
p value	.	0.90	0.06	0.28	0.17	.	1.00	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	0	0	-19	6	-11	-2	3	-3
p value	.	1.00	0.22	.	0.42	0.82	0.77	.
n	3	8	12	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	1	-4	-5	12	-6	5	-3	-1
p value	.	0.72	0.78	0.18	0.73	0.47	0.77	.
n	3	8	12	8	12	6	7	3

Table 6-4.e. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

e. Dissolved Phosphorus (PO_4^{-3}; $\mu M\ P\ m^{-2}\ hr^{-1}\ yr^{-1}$)

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
	St Leonards Creek (STLC): 1985 - 1996							
Sign	-2	10	10	0	-4	-7	-3	1
p value	.	0.28	0.54	1.00	0.84	0.27	0.77	.
n	3	8	12	8	12	6	7	3
	Broomes Island (BRIS): 1989 - 1996							
Sign		3	-1	2	-12	3	-1	
p value		0.72	1.00	0.90	0.18	0.72	1.00	
n		6	7	8	8	6	6	
	Marsh Point (MRPT): 1989 - 1996							
Sign		1	17	6	-2	-7	7	
p value		1.00	0.01**	0.55	0.90	0.27	0.27	
n		6	7	8	8	6	6	
	Buena Vista (BUVA): 1985 - 1996							
Sign	-3	4	-15	0	30	5	-7	1
p value	.	0.72	0.28	1.00	0.05	0.47	0.38	.
n	3	8	11	8	12	6	7	3
CHOPTANK RIVER								
	Horn Point (HNPT): 1985 - 1995							
Sign	-3	6	-5	-7	7	0	-3	-1
p value	.	0.55	0.76	0.38	0.64	1.00	0.77	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
	Ragged Point (RGPT): 1985 - 1996							
Sign	3	-6	4	-8	-6	7	11	-1
p value	.	0.55	0.84	0.40	0.73	0.27	0.14	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
	Point No Point (PNPT): 1985 - 1994, 1996							
Sign	-2	9	-2	7	23	4	-5	-1
p value	.	.	0.95	0.38	0.09	0.48	0.56	.
Slope	3	8	12	7	11	5	7	2
n								
	R-64 (R-64): 1985 -1996							
Sign	-1	16	-18	-2	2	5	2	-1
p value	.	0.06	0.24	0.90	0.95	0.47	.	.
n	3	8	12	8	12	6	7	3

Table 6-4.f. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

f. Silicate($Si(OH)_4$; µM Si m^{-2} hr^{-1} yr^{-1})

	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
STATION St Leonards Creek (STLC): 1985 - 1996								
Sign	-3	-2	-15	7	10	0	1	3
p value	.	0.90	0.28	0.27	0.36	1.00	1.00	.
n	3	8	11	6	9	4	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		11	3	9	7	-2	7	
p value		0.06	0.72	0.14	0.27	0.75	0.27	
n		6	6	6	6	4	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		9	-1	1	-9	-2	5	
p value		0.14	1.00	1.00	0.14	0.75	0.47	
n		6	6	6	6	4	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-1	8	13	-1	27	-2	1	-1
p value	.	0.40	0.29	1.00	0.02*	0.75	1.00	.
n	3	8	10	6	10	4	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-3	0	-13	3	1	2	1	-3
p value	.	1.00	0.35	0.72	1.00	0.75	1.00	.
n	3	8	11	6	10	4	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-3	-2	7	-5	31	2	-3	-3
p value	.	0.90	0.64	0.47	0.005**	0.75	0.77	.
n	3	8	11	6	10	4	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	-3	2	-15	11	-1	-2	-9	-1
p value	.	0.90	0.28	0.06	1.00	0.75	0.24	.
n	3	8	11	6	10	4	7	3
R-64 (R-64): 1985 -1996								
Sign	-1	-6	-9	1	-27	-2	-9	-1
p value	.	0.55	0.53	1.00	0.02*	0.75	0.24	.
n	3	8	11	6	10	4	7	3

Table 6-5.a. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	1	-8	4	-14	-13	-11	-3	-1
p value	.	0.40	0.84	0.11	0.35	0.06	0.77	.
n	3	8	12	8	11	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		-1	-11	-12	-20	-7	-3	
p value		1.00	0.14	0.18	0.01**	0.27	0.72	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		-7	11	-12	-8	3	-3	
p value		0.27	0.14	0.18	0.40	0.72	0.72	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-1	-10	-14	-12	-28	-1	-3	-1
p value	.	0.28	0.37	0.18	0.06	1.00	0.77	.
n	8	12	8	12	6	7	3	
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	1	-14	13	-3	5	0	5	-3
p value	.	0.11	0.35	0.77	0.76	1.00	0.56	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-1	8	-9	-12	-16	7	-3	-1
p value	.	0.40	0.53	0.18	0.24	0.27	0.77	.
n	3	8	11	8	11	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	1	8	6	-7	17	-2	-3	1
p value	.	0.40	0.70	0.38	0.21	0.82	0.77	.
n	3	8	11	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	1	0	10	-7	10	-1	1	-1
p value	.	1.00	0.54	.	0.54	1.00	1.00	.
n	3	8	12	8	12	6	7	3

Table 6-5.b. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

b. Ammonium (NH_4^+; µM N m^{-2} hr^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	-1	-10	-8	-4	-13	-11	-3	-1
p value	.	0.28	0.63	0.72	0.95	0.72	0.77	.
n	3	8	12	8	12	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		-7	-3	14	-14	1	1	
p value		0.27	0.77	0.11	0.11	1.00	1.00	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		13	3	2	8	-3	5	
p value		0.02*	0.77	0.90	0.40	0.72	0.47	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-1	8	14	6	24	1	-5	-1
p value	.	0.40	0.37	0.55	0.11	1.00	0.56	.
n	3	8	12	8	12	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-1	6	-37	3	1	0	-3	-3
p value	.	0.55	0.005**	0.77	1.00	1.00	0.77	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-1	-8	-12	-8	-12	9	-1	-1
p value	.	0.40	0.45	0.40	0.45	0.14	1.00	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	1	-10	-10	-3	-1	0	5	1
p value	.	0.28	0.54	0.77	1.00	1.00	0.56	.
n	3	8	12	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	1	-4	-14	-10	-16	-1	3	1
p value	.	0.72	0.37	0.28	0.30	1.00	0.77	.
n	3	8	12	8	12	6	7	3

Table 6-5.c. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

c. Nitrite (NO_2^-; µM N m^{-2} hr^{-1} y^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	0	3	6	13	10	7	1	0
p value	.	0.72	0.55	0.07	0.36	0.27	1.00	.
n	1	6	8	7	9	6	6	1
Broomes Island (BRIS): 1989 - 1996								
Sign		-5	5	-10	10	7	5	
p value		0.47	0.56	0.28	0.28	0.27	0.47	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		-1	-9	0	2	-1	5	
p value		1.00	0.24	1.00	0.90	1.00	0.47	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	0	13	6	6	0	9	4	0
p value	.	0.02*	0.55	0.55	1.00	0.14	0.48	.
n	1	6	8	8	9	6	5	1
% Change		92%						
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	0	5	-11	-1	0	8	-3	0
p value	.	0.47	0.14	1.00	1.00	0.08	0.72	.
n	1	6	7	7	8	5	6	1
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	0	-3	2	4	-8	-3	-9	0
p value	.	0.72	0.90	0.72	0.40	0.72	0.14	.
n	1	6	8	8	8	6	6	1
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	0	1	-10	-1	2	0	1	0
p value	.	1.00	0.28	1.00	0.90	1.00	1.00	.
n	1	6	8	7	8	5	6	1
R-64 (R-64): 1985 -1996								
Sign	0	5	-6	6	4	-3	-3	0
p value	.	0.47	0.55	0.55	0.72	0.72	0.72	.
n	1	6	8	8	8	6	6	1

Table 6-5.d. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

d. Nitrite plus nitrate ($NO_2^- + NO_3^-$; μM N m⁻² hr⁻¹ yr⁻¹)

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	-1	6	-12	9	-8	11	1	-1
p value	.	0.55	0.45	0.24	0.63	0.06	1.00	.
n	3	8	12	7	12	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		1	9	-6	14	5	-1	
p value		1.00	0.24	0.55	0.11	0.47	1.00	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		-11	1	6	6	1	3	
p value		0.06	1.00	0.55	0.55	1.00	0.72	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-1	-10	-12	2	-9	5	-5	-1
p value	.	0.28	0.45	0.90	0.53	0.47	0.56	.
n	3	8	12	8	11	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-1	0	-35	7	-3	8	-7	3
p value	.	1.00	0.008**	0.38	0.88	0.08	0.38	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-1	6	-24	-6	-26	9	-3	-1
p value	.	0.55	0.11	0.55	0.09	0.14	0.77	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	0	0	-24	-3	-5	0	-3	-1
p value	.	1.00	0.11	0.77	0.76	1.00	0.77	.
n	3	8	12	7	11	5	7	3
R-64 (R-64): 1985 -1996								
Sign	1	-8	-10	-8	2	5	-11	-1
p value	.	0.40	0.54	0.40	0.95	0.47	0.14	.
n	3	8	12	8	12	6	7	3

Table 6-5.e. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

e. Dissolved Phosphorus (PO_4^{-3}; µM P m^{-2} hr^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
St Leonards Creek (STLC): 1985 - 1996								
Sign	-1	10	-2	-2	-8	-7	-1	-1
p value	.	0.28	0.95	0.90	0.63	0.27	1.00	.
n	3	8	12	8	12	6	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		3	-1	-4	-8	1	3	
p value		0.72	1.00	0.72	0.40	1.00	0.72	
n		6	7	8	8	6	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		1	3	0	-4	-9	7	
p value		1.00	0.77	1.00	0.72	0.14	0.27	
n		6	7	8	8	6	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	-1	6	-17	-10	20	3	-3	-1
p value	.	0.55	0.21	0.28	0.19	0.72	0.77	.
n	3	8	11	8	12	6	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-1	8	-7	-7	7	0	-1	2
p value	.	0.40	0.64	0.38	0.64	1.00	1.00	.
n	3	8	11	7	11	5	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	1	-8	-4	-2	-2	9	9	-1
p value	.	0.40	0.84	0.90	0.95	0.14	0.24	.
n	3	8	12	8	12	6	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	-1	6	-6	7	27	6	-5	0
p value	.	0.55	0.73	0.38	0.04*	0.23	0.56	.
Slope	3	8	12	7	11	5	7	2
n								
R-64 (R-64): 1985 -1996								
Sign	-1	16	-20	-2	0	5	1	1
p value	.	0.06	0.19	0.90	1.00	0.47	1.00	.
n	3	8	12	8	12	6	7	3

Table 6-5.f. Table of Monthly Seasonal Kendall Test Statistics (Flow Detrended) at eight SONE stations for six SONE variables.
*Significance: * p = 0.05; ** p = 0.01; *** p = 0.001*

f. Silicate(Si(OH)$_4$; [μM Si m^{-2} hr^{-1} yr^{-1})

	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
STATION St Leonards Creek (STLC): 1985 - 1996								
Sign	-1	0	-15	3	2	0	1	1
p value	.	1.00	0.28	0.72	0.92	1.00	1.00	.
n	3	8	11	6	9	4	7	3
Broomes Island (BRIS): 1989 - 1996								
Sign		11	7	-1	-1	-4	5	
p value		0.06	0.27	1.00	1.00	0.33	0.47	
n		6	6	6	6	4	6	
Marsh Point (MRPT): 1989 - 1996								
Sign		13	-5	1	-7	-4	7	
p value		0.02*	0.47	1.00	0.27	0.33	0.27	
n		6	6	6	6	4	6	
Buena Vista (BUVA): 1985 - 1996								
Sign	1	4	1	-1	21	-2	3	1
p value	.	0.72	1.00	1.00	0.07	0.75	0.77	.
n	3	8	10	6	10	4	7	3
CHOPTANK RIVER								
Horn Point (HNPT): 1985 - 1995								
Sign	-1	0	-7	-3	3	2	-5	-3
p value	.	1.00	0.64	0.72	0.86	0.75	0.77	.
n	3	8	11	6	10	4	7	3
POTOMAC RIVER								
Ragged Point (RGPT): 1985 - 1996								
Sign	-1	-4	5	-5	27	2	-3	-1
p value	.	0.72	0.76	0.47	0.02*	0.75	0.77	.
n	3	8	11	6	10	4	7	3
MAINSTEM BAY:								
Point No Point (PNPT): 1985 - 1994, 1996								
Sign	-1	0	-17	11	-3	-2	-13	-1
p value	.	1.00	0.21	0.06	0.86	0.75	0.07	.
n	3	8	11	6	10	4	7	3
R-64 (R-64): 1985 -1996								
Sign	1	-4	-19	-1	-23	-2	-9	1
p value	.	0.72	0.16	1.00	0.05*	0.75	0.24	.
n	3	8	11	6	10	4	7	3

7. SEDIMENT CHLOROPHYLL-a MAPPING IN THE PATUXENT RIVER

Thirty-seven (37) stations in the Patuxent River between Benedict and Point Patience were sampled during March, April and May, 1996. These mapping activities provide a quantitative index of the size and distribution of the spring phytoplankton bloom and potentially serve as an index of the role sediments play in water quality during summer periods of the year.

In a previous report (Boynton *et al.*, 1993) it was proposed that sediment mapping could prove to be a valuable tool which should be included in the SONE program. The advantages of sediment mapping include the following:

(1) it provides a synoptic evaluation of an index of labile organic material which is delivered to sediments following the spring bloom each year

(2) it need only be done several times per year following the sinking of the spring bloom because it has been shown that much of the annual organic matter deposition is associated with the spring bloom

(3) the mapping, assuming that stations are properly located, could provide a quantitative estimate of labile sediment organic matter biomass on a bay-wide basis or on the basis of specific sectors of particular tributaries

(4) interannual differences in nutrient loading rates and loading rate reduction might then be directly related to the amount of algal biomass which is delivered to sediment and is a primary cause of water quality problems. Hagy (1996) has established that there is a strong relationship between reduction in nutrient load and reduced chlorophyll-a concentrations and hypoxic water volumes in the Patuxent River;

(5) finally, sediment chlorophyll concentrations might be used, along with a few other simply measured environmental variables, as predictors of sediment-water exchanges which would greatly enhance the spatial coverage of sediment responses to water quality conditions.

The following sections report the results of sediment chlorophyll-a mapping cruises and the environmental conditions at mapping stations. Chapter 8 addresses the linkage between sediment chlorophyll-a mapping and sediment water fluxes.

7.1. Physical and Chemical Characteristics of Bottom Waters and Sediments

Temperature at all stations in the Patuxent River showed very little variation within months sampled but showed an increasing trend between months following the well established pattern of the SONE program. There was a slight down river gradient pattern observed with higher temperature the upper reaches of the river and lower temperature near the mouth of the river. In March 1996, temperature ranged between 5.57 C and 7.63 C; station PX33 near the mouth of the Patuxent River had the lowest temperature recorded (3.66 C). In April 1996, temperature ranged between 11.73 C and 15.02 C while in May 1996, temperature ranged between 15.53 C and 17.40 C and there was a less marked down river gradient (Figure 7-1.; Tables C-1.1. - C-1.3.).

Secchi depth at mapping stations in the Patuxent River exhibited a strong down river gradient of increasing water clarity towards the mouth of the Patuxent River, particularly during the March period (Figure 7-2.; Tables C-1.1. - C-1.3.). In general, secchi depths decreased as the spring progressed.

Salinity at mapping stations in the Patuxent River showed little spatial pattern with the exception of up-river stations during May which exhibited sharply reduced salinities. The especially high flows of 1996 apparently reduced salinities throughout the system. There was a down river gradient observed with lower salinity values in the upper reaches of the river and higher values near the mouth of the river but this gradient was not as strong as expected. In March 1996, salinity values ranged between 7.0 ppt and 9.5 ppt, while station PX33 near the mouth of the Patuxent River had the highest salinity value recorded (13.8 ppt). In April 1996, salinity values ranged between 5.3 ppt and 10.4 ppt while in May 1996, values ranged between 1.7 ppt and 8.4 ppt and there was a less marked down river gradient (Figure 7-3.; Tables C-1.1 - C-1.3).

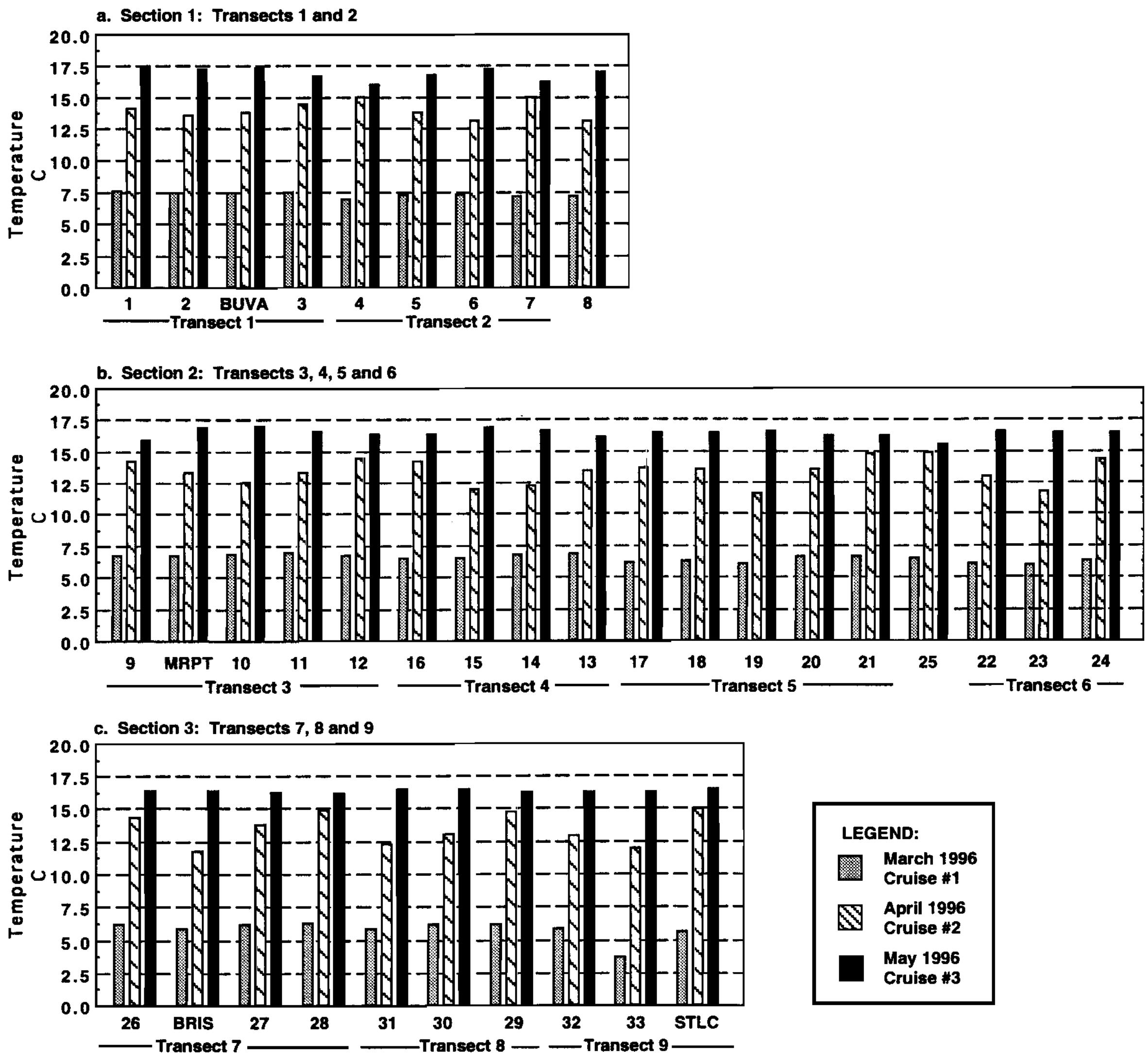


Figure 7-1. Bottom water temperature measured at thirty-seven (37) sediment chlorophyll-a mapping stations in the Patuxent River in March, April and May, 1996.

** Station locations are shown in Figure 3-3. (page 24). Stations PX08 and PX25 lie between transects and are grouped with stations in the nearest transect.*

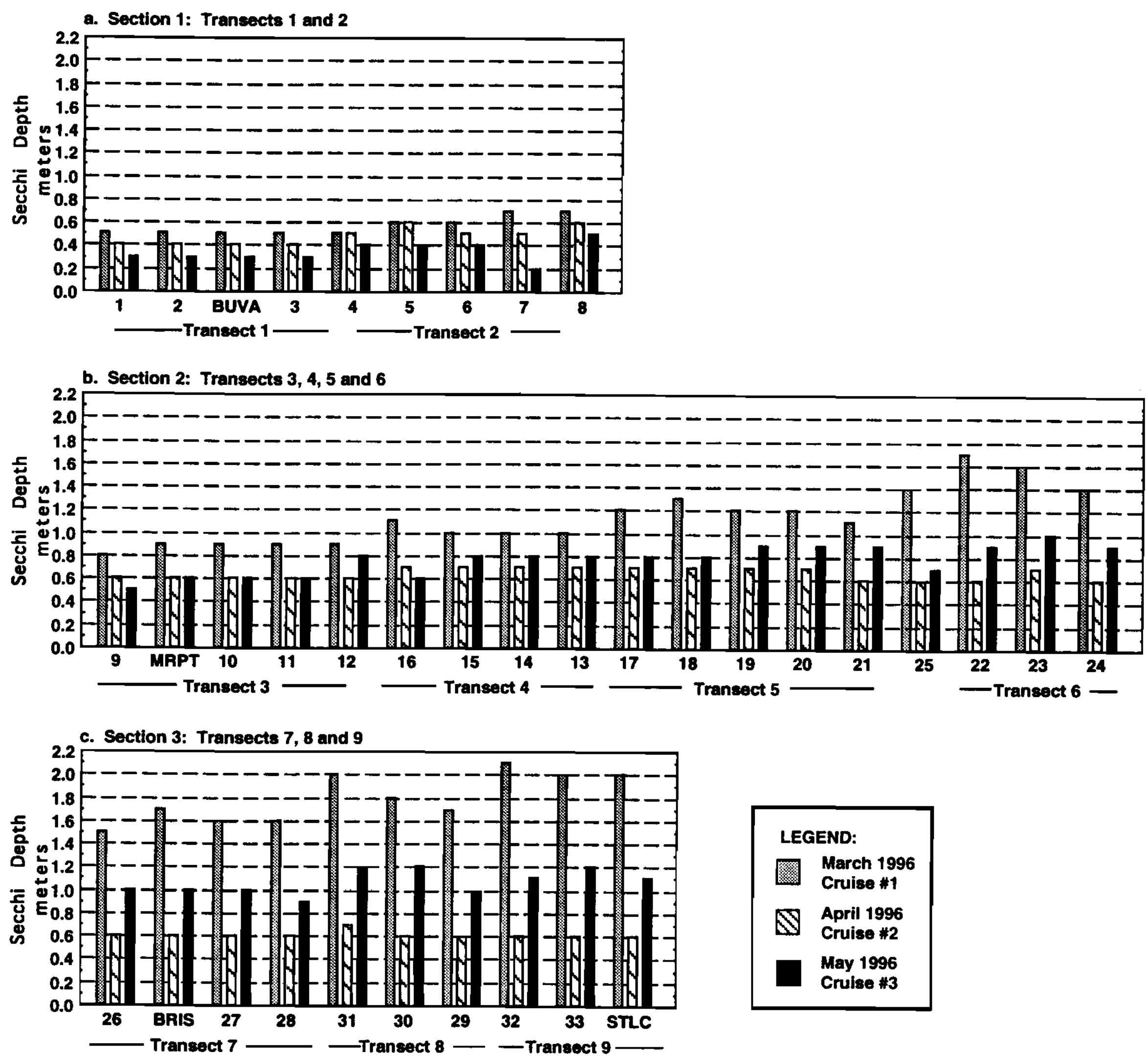


Figure 7-2. Secchi depth measured at thirty-seven (37) sediment chlorophyll-a mapping stations in the Patuxent River in March, April and May, 1996.
** Station locations are shown in Figure 3-3. (page 24). Stations PX08 and PX25 lie between transects and are grouped with stations in the nearest transect.*

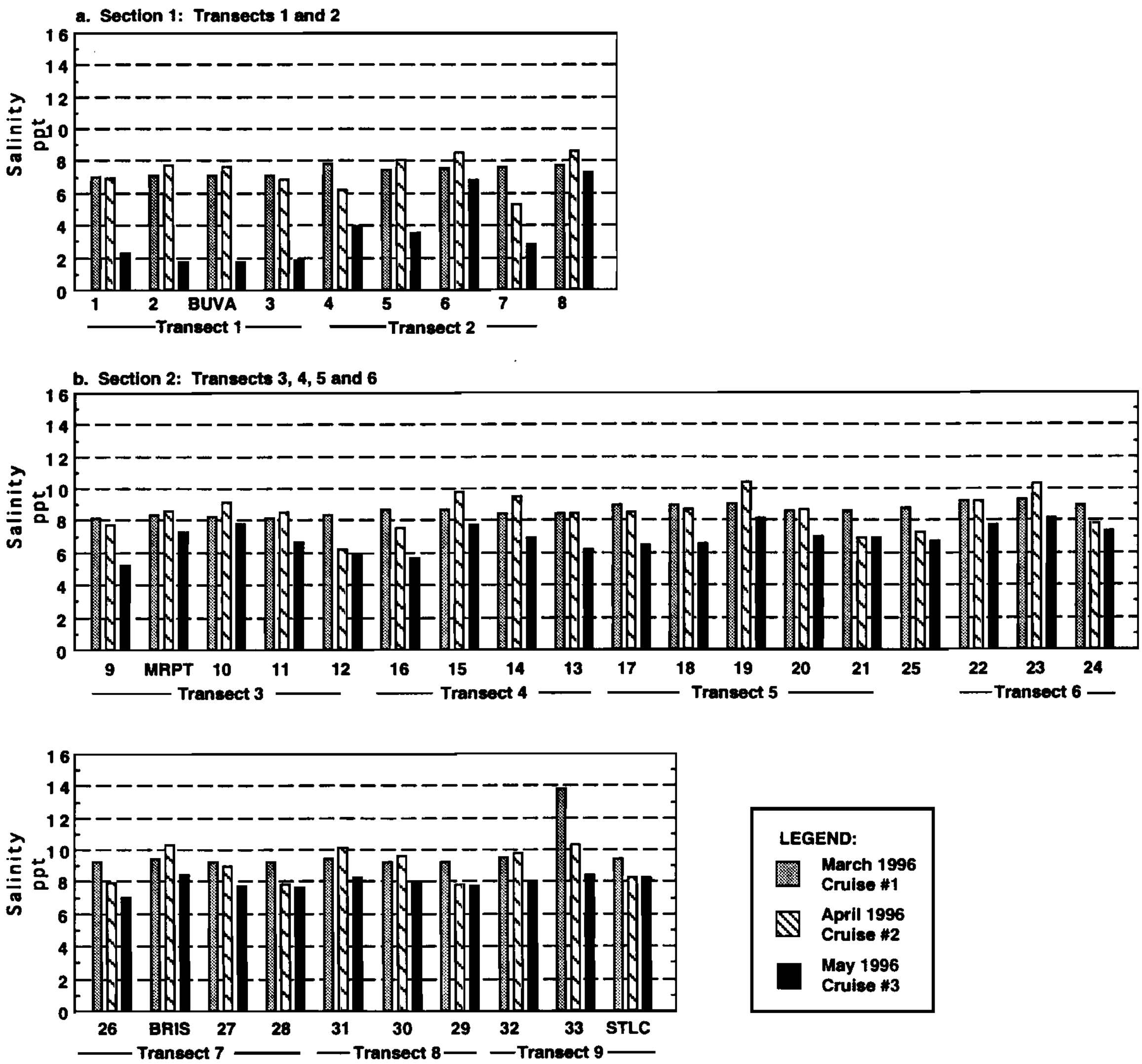


Figure 7-3. Bottom water salinity measurements at thirty-seven (37) sediment chlorophyll-a mapping stations in the Patuxent River in March, April and May, 1996.

** Station locations are shown in Figure 3-3. (page 24). Stations PX08 and PX25 lie between transects and are grouped with stations in the nearest transect.*

7.2. Total Sediment Chlorophyll-a Maps

Maps of both total sediment chlorophyll-a and active sediment chlorophyll-a were produced for each cruise by interpolating using kriging to a uniform grid of 0.002 degrees latitude and longitude, then using automated contouring software. The original data were posted on the contour plots to visually verify that an acceptable interpolation had been achieved. To calculate summary statistics for total chlorophyll-a, the regularly gridded chlorophyll-a values resulting from interpolation were exported from the interpolation software. Only values for the main portion of Patuxent River (*i.e.* side creeks were excluded) were included in the analysis. Interpolated data were used for calculating summary statistics because the locations of the stations were arranged in transects rather than random. This approach assured a reasonable weighting of values in the overall mean, but precludes estimation of variance. For this reason, statistical testing of effects due to depth, location in the estuary and cruise were conducted on the original data.

The weighted average total sediment chlorophyll-a concentrations resulting from the interpolations are summarized in Table 7-1 for the estuary as a whole, for the channel areas (>8 m) and for the shoal areas (<8 m). Total sediment chlorophyll-a averaged 109 mg m^{-2} in March, 102 mg m^{-2} in April and 132 mg m_{-2} in May. On each cruise, the channel average was higher than the shoal average, although it will be shown below that these differences are not statistically significant. Although the average chlorophyll-a concentration over the estuary did not change by a large amount from 20 March, 1996 through 25 April, 1996, redistribution resulted in concentration changes from -97 to 95 mg m^{-2}. Between 25 April, 1996 and 13 May, 1996, the average concentration increased, but changes in concentration ranged from a decrease of 42 mg m^{-2} to an increase of 89 mg m^{-2}, again indicating dynamics due to deposition and degradation, physical redistribution, or both.

7.2.1 Patterns in Chlorophyll-a Distributions in Time and Space

An analysis of covariance (ANCOVA) model was constructed to test for significant trends in the distribution of active and total sediment chlorophyll-a in time and space. Since the data were collected on discrete cruises and transects, these variables were modeled as discrete variables, while depth was modeled as a continuous variable. The only significant differences were among cruises. Average total chlorophyll-a during the April and March cruises was found to be 28 and 15 mg m_{-2} less than during the May cruise, respectively. There were no significant differences among transects or along the gradient of depth. Similar results were found for active sediment chlorophyll-a, except that the average active chlorophyll-a was highest during the March cruise (57.9 mg m^{-2}), lowest during the April cruise (39.2 mg m^{-2}), and intermediate in May (48.1 mg m^{-2}). No significant differences in active chlorophyll-a concentration were found among transects or along gradients of depth.

Mapping winter-spring deposition of chlorophyll-a to bottom sediments in this estuary and relating this to sediment nutrient fluxes during the warmer months of the year will allow for very extensive spatial expansion of SONE coverage and a great reduction in SONE measurements if the sediment chlorophyll-a vs flux relationships are strong. A direct coupling between these events has been demonstrated in other parts of the Bay (Cowan and Boynton, 1996) and are consistent with such relationships developed for Mobile Bay, AL (Cowan *et al.*, 1977). If this same coupling can be demonstrated in the Patuxent River, spring surficial sediment chlorophyll-a measurements may be used as a good and inexpensive predictor of summer nutrient fluxes from the sediments of this and other regions of the bay system. In addition, data collected from such mapping activities could be used to address the other questions posed at the beginning of this section.

Figures 7-4.1.a. through 7-4.1.c. show contoured total sediment chlorophyll-a concentrations in the Patuxent river based on March, April and May, 1996 sediment samples collected at 37 stations. These maps were generated with SURFER software from Golden Software which is an interpolation and contouring software package.

Table 7-1. The average total sediment chlorophyll-a concentration in Patuxent River on three cruises during spring 1996.
The channel was defined as areas deeper than 8 meters, while the shoals are the remaining areas.

Date	Average Concentration (mg m^{-2})	Channel Concentration (mg m^{-2})	Shoal Concentration (mg m^{-2})
3/20/96	109	119	106
4/25/96	102	111	100
5/13/96	132	145	129

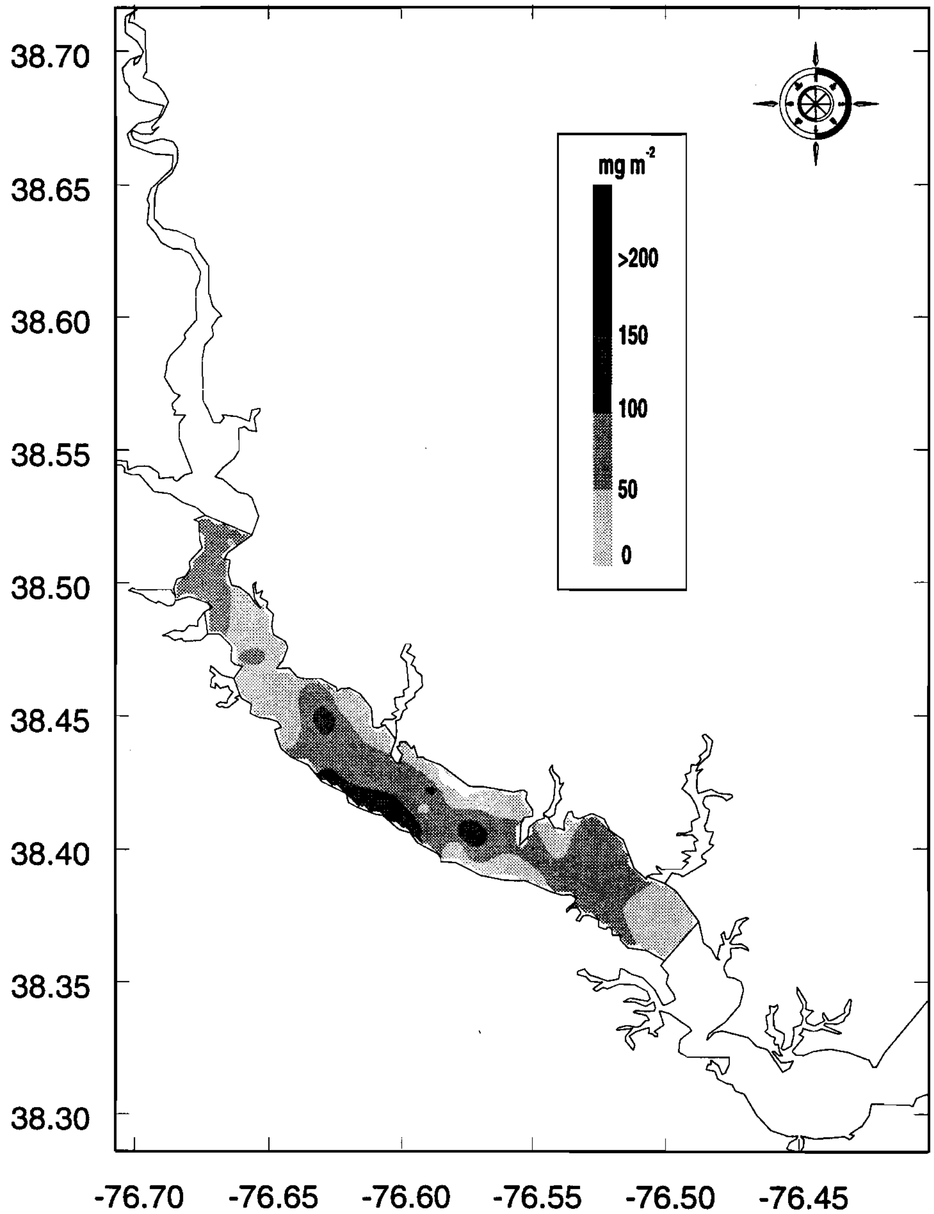


Figure 7-4.1.a. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during March, 1996 (sediment chlorophyll-a mapping cruise #1; Table C-2.1). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

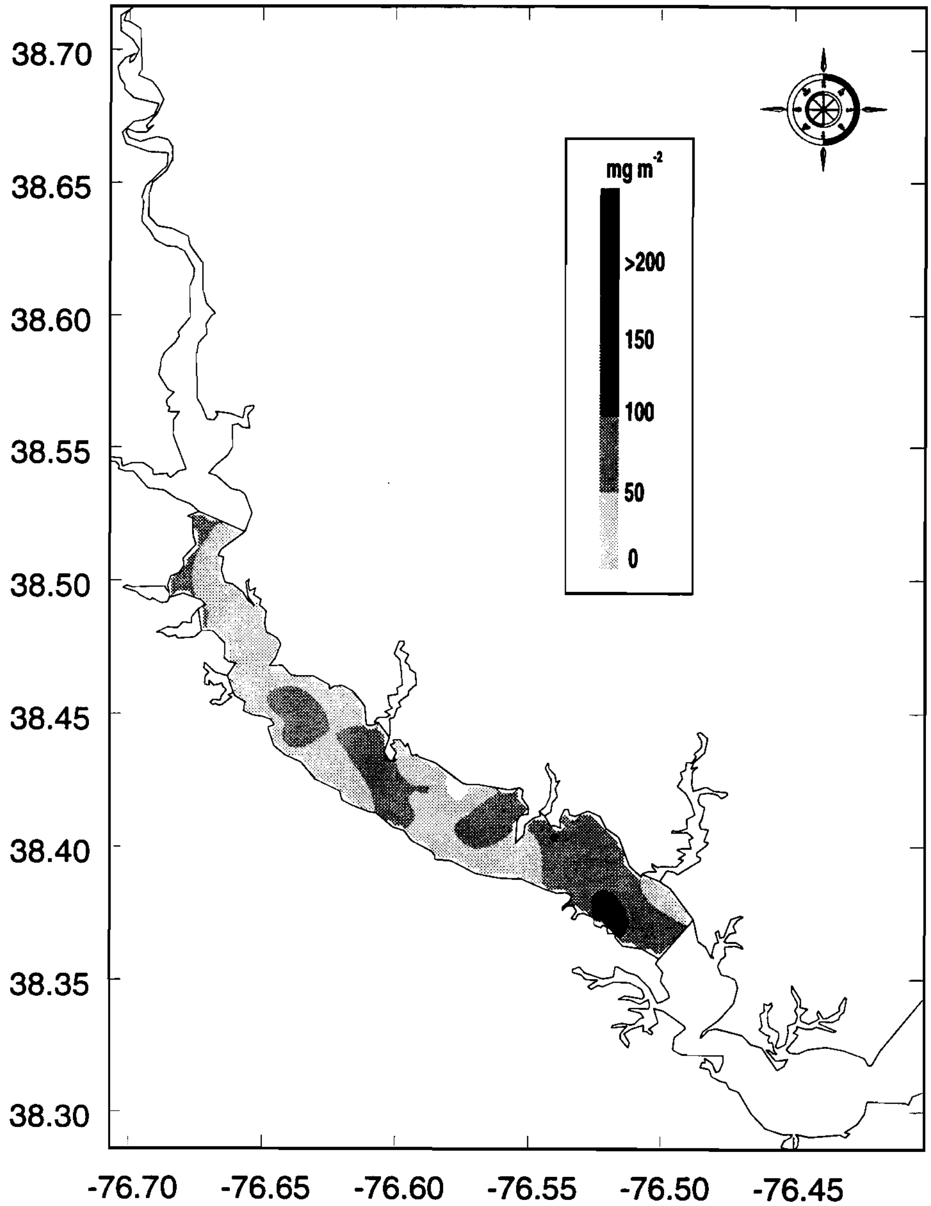


Figure 7-4.1.b. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during April, 1996 (sediment chlorophyll-a mapping cruise #1; Table C-2.2). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

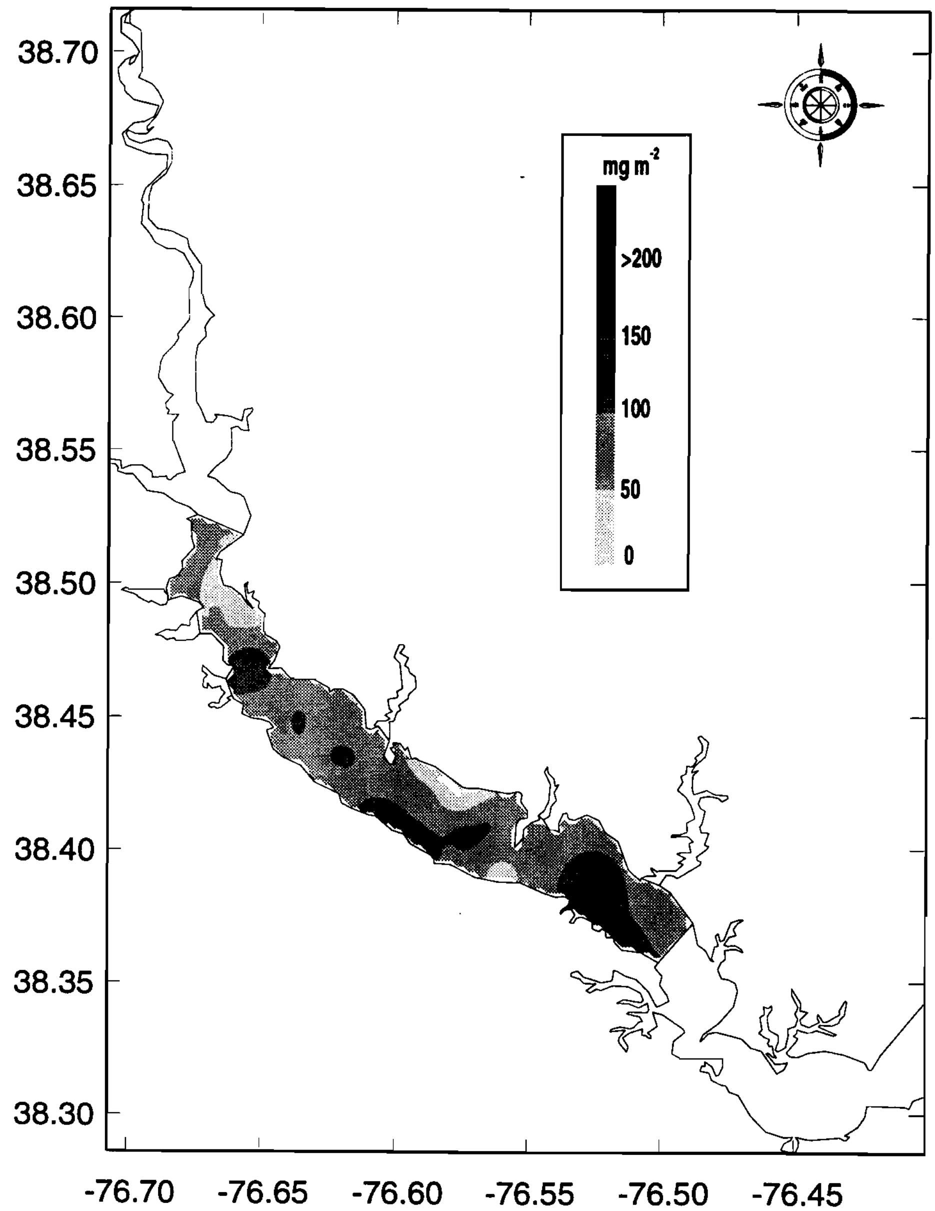


Figure 7-4.1.c. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during May, 1996 (sediment chlorophyll-a mapping cruise #1; Table C-2.3). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

8. MINI-SONE MEASUREMENTS

An abbreviated SONE study referred to as MINI-SONE was conducted in the Patuxent River during 1996. The purpose of the study was twofold. First it increased the spatial resolution of SONE measurements in this targeted estuary as the SONE program has traditionally been a low spatial resolution study. Second, it is envisaged that a methodology will be developed which would be reduce costs of monitoring sediment effects on water quality. Visual observations of sediment conditions at MINI-SONE stations are listed in Table 8-1.

8.1 MINI-SONE measurements: Physical characteristics of bottom waters

8.1.1 Temperature

Bottom water temperature conditions in June, 1996 ranged from 21.7 C at Broomes Island (BRIS) to 27.3 C at PX2 (Table D-1.1); in July, 1996 from 25.4 C at Broomes Island (BRIS) to 27.5 C at Buena Vista ([BUVA]; Table D-1.2); from 25.8 C at Broomes Island (BRIS) to 27.0 C at PX21 (Table D-1.3) and from 27.0 C at Buena Vista (BUVA) to 25.6 C at PX21 (Table D-1.1). Temperature showed minor monthly differences (on the order of 5 C) at each of the ten MINI-SONE stations.

8.1.2 Salinity

Bottom water salinity conditions in June, 1996 ranged from 5.0 ppt at Buena Vista (BUVA) one of the furthermost upstream stations located in the oligohaline reaches of the Patuxent River to 8.5 ppt at two stations, PX32 and St. Leonard Creek (STLC), located near the mouth of the Patuxent River in the mesohaline area of the Patuxent River (Table D-1.1). In July, 1996, salinity values ranged from 3.9 ppt at Buena Vista (BUVA) to 9.5 ppt at PX23 (Table D-1.2), while in August the salinity range was 7.0 ppt at Buena Vista (BUVA) to 11.1 ppt at PX23 (Table D-1.3). In September, 1996, salinity values ranged from 6.1 ppt at Buena Vista (BUVA) to 12.3 ppt at PX23 (Table D-1.4). Salinity exhibited a down river gradient with lowest salinity values occurring furthermost upstream (Buena Vista [BUVA]) and increasing toward the mouth of the estuary. In September, 1996 salinity values in excess of 12 ppt were recorded at 5 stations: Marsh Point (MRPT), PX15, PX32, Broomes Island (BRIS) and St. Leonard Creek (STLC).

8.1.3 Dissolved Oxygen

Dissolved oxygen concentrations ranged from 0.12 mg l^{-1} (1.4% saturated) at PX15 located in mid-estuary to 7.44 mg l^{-1} (97.9% saturated) at PX21 also located in this region in June, 1996 (Table D-1.1). In July, 1996, concentrations ranged from 1.20 mg l^{-1} (15.5% saturated) at PX15 to 9.5 mg l^{-1} (17.9% saturated) at PX21 (Table D-1.2), while in August, 1996, concentrations ranged from 0.87 mg l^{-1} (11.4% saturated) at PX32 located near the mount of the estuary to 7.29 mg l^{-1} (95.6% saturated) at PX25 (Table D-1.3). In September, 1996, concentrations ranged from 1.41 mg l^{-1} (18.6% saturated) at PX15 to 9.03 mg l^{-1} (116.5% saturated) at PX21 (Table D-1.4). Moderate dissolved oxygen values were recorded at two of the upper most stations in the estuary, Buena Vista [BUVA] and PX07 while the highest dissolved oxygen values were recorded at two mid estuary stations, PX21 and PX25.

8.1.4 Total Sediment Chlorophyll-a

Total sediment chlorophyll-a values ranged from 35.9 mg m^{-2} at PX25 to 198.1 mg m^{-2} at Broomes Island (BRIS) in June, 1996 (Table D-2.1). In July, 1996 values ranged from 19.2 mg m^{-2} at PX21 to 174.2 mg m^{-2} at PX23 (Table D-2.2). In August values ranged from 40.5 mg m^{-2} at PX21 to 223.5 mg m^{-2} at PX15 (Table D-2.3) while in September, 1996 values ranged from 35.0 mg m^{-2} at PX21 to 188.8 mg m^{-2} at Broomes Island ([BRIS]; Table D-2.4).

8.1.5 Sediment Eh

Eh values were positive throughout the sediment column to a depth of 10 cm for all four months during which measurements were taken. In June, 1996 Eh values ranged from 279 mV (at 0 cm) at Marsh Point (MRPT) to 346 mV at St. Leonard Creek ([STLC]; Table D-2.1), in July, 1996 Eh values ranged from 304 mV at Marsh Point (MRPT) to 385 mV at PX21 (Table D-2.2), in August, 1996 Eh values ranged from 312 mV at Marsh Point (MRPT) to 373 mV at Broomes Island ([BRIS]; Table D-2.3) and in September, 1996 Eh values ranged from 306 mV at PX23 to 373 mV at PX21 (Table D-2.4).

8.2 Characteristics of Sediment-Water Oxygen and Nutrient Exchanges

Sediment oxygen consumption (SOC) flux values for MINI-SONE in June 1996 ranged from -2.69 g O_2 m^{-2} day^{-1} at Buena Vista (BUVA) to -0.14 g O_2 m^{-2} day^{-1} at PX15 in the Patuxent River (Table 6-4.1) In July, 1996, SOC values ranged from -2.87 g O_2 m^{-2} day^{-1} at Buena Vista (BUVA) to -0.65 g O_2 m^{-2} day^{-1} at PX23 (Table D-4.2). In August, 1996 SOC values ranged from -2.52 g O_2 m^{-2} day^{-1} at Buena Vista (BUVA) to -0.17 g O_2 m^{-2} day^{-1} at PX15 (Table D-4.3), while in September, 1996 values ranged from -2.17 g O_2 m^{-2} day^{-1} at Buena Vista (BUVA) to -0.70 g O_2 m^{-2} day^{-1} at Broomes Island ([BRIS]; Table D-4.4).

Ammonium values (NH_4^+) recorded in June, 1996 ranged from 497.1 μMN m^{-2} hr^{-1} at Buena Vista (BUVA) to 63.7 μMN m^{-2} hr^{-1} at PX21 (Table D-4.1). In July, 1996, ammonium values (NH_4^+) ranged from zero (0.0) at PX25 to 705.8 μMN m^{-2} hr^{-1} at Marsh Point ([MRPT]; Table D-4.2.). In August, 1996, ammonium values (NH_4^+) ranged from 13.1 μMN m^{-2} hr^{-1} at PX25 to 528.9 μMN m^{-2} hr^{-1} at Buena Vista ([BUVA]; Table D-4.3), while in September, 1996 values ranged from zero (0.0) at PX 21 to 336.8 μMN m^{-2} hr^{-1} at Buena Vista ([BUVA], Table D-4.4).

The overwhelming pattern indicated a net flux of dissolved inorganic phosphorus (PO_4^{-3}) from sediments to the overlying waters (*note that positive values indicate fluxes from sediments to water while negative values indicate fluxes from water to sediment*) in all four months with the exception of one value measured at PX32 in September, 1996. The dissolved inorganic phosphorus values recorded in June, 1996 ranged from 1.24 μMP m^{-2} hr^{-1} at PX25 to 87.96 μMP m^{-2} hr^{-1} at PX23 (Table D-4.1). In July, 1996 values ranged from zero (0.0) at PX32 near the mouth of the Patuxent River to 215.62 μMP m^{-2} hr^{-1} at Marsh Point ([MRPT]; Table D-4.2). In August, 1996 dissolved inorganic phosphorus (DIP) values ranged from zero (0.0) at PX32 to 186.02 μMP m^{-2} hr^{-1} at 186.02 μMP m^{-2} hr^{-1} at PX15 (Table D-4.3). In September, 1996 values ranged from -7.75 μMP m^{-2} hr^{-1} at PX32 to 44.82 μMP m^{-2} hr^{-1} at PX21 (Table D-4.4).

Table 8-1. Visual observations of sediment conditions at MINI-SONE stations in June, 1996.

MINI-SONE STATION	DESCRIPTION
DEEP STATIONS	
PX-15	Very fine silty sediment throughout Beggiatoa mat of surface 2 cm brown surface sediment, black sulfidic sediment below No shell obvious No sulfide smell in water No methane observed
PX23	Fine, silty sediment No Beggiatoa Surface sediment consisted of easily disturbed greenish brown flocs Oxidized layer (i.e. brown) approximately 1.0 cm thick Black sediment beneath No methane observed Abundance of clams and worms
PX32	3.5 cm light fluffy brown surface sediment No Beggiatoa Few worm tubes Medium gray clay Old oyster shell at 12 cm
SHALLOW STATIONS	
PX-7	Fine grained oxidized, muddy sand down to 8-9 cm Abundance of worm tubes, small clams, small pieces of shell Reduced muddy sand below 8-9 cm Fluff on surface Methane bubbles noticed when coring but not in core at surface
PX25	Coarser sand, lots of amphipodes and isopods Small pieces of clam shell, occasional old oyster shell Abundance of Mullinea clams Worms, worm tubes down through sediments are dark brown No fluff on surface Pockets of reduced sediment throughout 12 cm oxidized surface Methane bubbles present Slightly reduced area 7 cm below surface, coarse sand runs full depth

Table 8-1. Visual observation of sediment conditions at MINI-SONE stations (Continued).

MINI-SONE STATION	DESCRIPTION
SHALLOW STATIONS	
PX21	Finer sand than at PX25 Pockets of reduced sediment throughout Worms, amphipods, Mullinea clams Worm tubes down through sediments are dark brown No fluff on sediment surface No methane bubbles evident 10 cm oxidized sediment

8.3 Analysis of MINI-SONE flux data from the Patuxent River Estuary

8.3.1 Background

It has long been recognized that there are strong relationships between sediment-water oxygen and nutrient fluxes and external nutrient loading to estuarine systems (*e.g.*, Boynton *et.al.*, 1982a; Nixon,1988). Seasonal variations in the magnitude of nutrient fluxes and strong correlations with river flow also have been well documented (*e.g.*, Boynton *et al.*, 1995) These relationships have led to the understanding that the amount of labile organic matter deposited on the sediment surface, modified by parameters such as temperature, salinity as well as infaunal activity, ultimately control the magnitude of these fluxes (Kelly and Nixon, 1984; Kemp and Boynton, 1984; Jensen *et al.*, 1990).

The magnitude and direction (either into or out of sediments) of these fluxes are often powerful indicators of the general health of the benthic habitat. For example, fluxes of nitrite or nitrite plus nitrate are indicative of existing or recently existing oxic bottom waters; large fluxes of phosphorus are indicative of hypoxic bottom waters and anoxic sediments. However, measurement of these fluxes is difficult, expensive and time consuming. Since the regeneration of nutrients in estuarine sediments is linked chemically and physiologically to a suite of bottom water and sediment parameters, the goal of this data analysis is to define specific linear regression models that will sufficiently explain nutrient flux variability using a few easily measured water quality or sediment parameters.

While this approach is not new, it was our contention that, based on MINI-SONE measurements, a statistical tool could be generated to predict sediment-water oxygen and nutrient fluxes using easily collected field data. The use of surficial sediment chlorophyll-a has been shown in several cases to be an excellent predictor of seasonal ammonium, phosphate, and silica flux (Cowan and Boynton, 1996; Cowan *et al.*, 1996). However, the relationships observed by Cowan were based on data collected over large estuarine gradients and the strength of the gradient (*i.e.* salinity, DO, organic matter supply rate and probably others) favored finding statistically significant results. The Patuxent is very small compared to the mainstem Chesapeake and it is possible that spatial gradients in important environmental features influencing sediment-water exchanges are not large enough to produce a measurable response in fluxes. Previously collected sediment-water flux data from the Patuxent River did show some strong spatial differences and there were also reasonably strong gradients observed in water column chlorophyll-a and deep water dissolved oxygen concentrations (Hagy, 1996) to suggest that this approach might be successful. The motivation to undertake this analysis was that these models can be used to construct a spatial map of seasonal nutrient and oxygen fluxes throughout an estuary with minimal time and effort thereby more accurately assessing the condition and role of sediments in water quality processes.

8.3.2 Data Sources

The statistical models presented here were constructed using sediment-water flux and water quality data from six MINI-SONE and four regular SONE stations on the Patuxent River Estuary as well as the corresponding sediment chlorophyll-a data from those stations. The techniques for sediment-water flux and chlorophyll collection and a description of station locations are found in Section 3 of this report. The flux values for ammonium (NH_4^+), nitrite and nitrate (NO_2^- + NO_3^-), dissolved inorganic phosphorus (DIP), as well as sediment oxygen consumption (SOC) were collected monthly from June through September of 1996. Various water quality parameters such as bottom water dissolved oxygen (DO), temperature, salinity, and redox potential (Eh) were also collected concurrently with the fluxes. Total sediment chlorophyll-a collected to a depth of 1 cm was also used in this analysis and was collected monthly from March through September 1996. Surficial sediment chlorophyll-a (surface scrapes approximately 2-3 mm in depth) collected during this time were not used in the analysis since preliminary results were highly variable. Ammonium fluxes (NH_4^+), collected from the Buena Vista station (BUVA) were exceptionally high relative to the other MINI-SONE stations during all sampling dates. This may have been due to elevated sediment irrigation rates resulting from infaunal biomass more than an order of magnitude higher than at other stations. For this reason, the Buena Vista data were excluded from the ammonium flux analysis.

8.3.3 Statistical Analyses

Potential relationships among sediment-water fluxes and selected water and sediment variables were examined using two approaches. The first approach used individual flux values at each station along with the corresponding water or sediment quality parameters collected on each census date. The second approach used four-month (June-September) station means for both flux values and water or sediment quality parameters. Since total sediment chlorophyll-a was collected over a longer time interval than sediment flux values, analyses with a time differential (lag) between total sediment chlorophyll-a collection and flux measurements were also performed.

Each analysis consisted of a series of simple and multiple linear regression models similar to a stepwise regression procedure in which explanatory variables are eliminated from the model until the most robust combination of variables is found. Several models from each analysis are presented in tabular format while the preferred models are shown as scatter plots of sediment flux versus predicted flux. Regression equations and 95% confidence intervals for individual observations (data points) are also shown. The goal of this effort was to determine if highly significant relationships based upon known chemical and physiological mechanisms emerged from the data set. As this was an explanatory analysis, rather than a curve-fitting exercise, the preferred models have been limited to two or three independent variables.

8.3.4 Results

Ammonium (NH_4^+) fluxes were poorly correlated (r^2 = 0.39) with total sediment chlorophyll-a using individual concurrent station values, but well correlated (r^2 = 0.73) with concurrent seasonal mean values (Table 8-2; Figure 8-1.). However, when total s*ediment chlorophyll-a values were temporally-shifted by one month, using May through August values, the correlation coefficient for individual values increased to r^2 = 0.43, while the station means correlation coefficient increased to r^2 = 0.78. When a two month shift in the total sediment chlorophyll-a values was used, correlation coefficients decreased relative to the one month shift models for both individual and station mean approaches (Table 8-2). By adding sediment Eh as another explanatory variable, an r-squared value of 0.48 was achieved for the individual station observations, and an r-squared of 0.86 was achieved for the station means (Figure 8-2.). All ammonium (NH_4^+) regression models were significant at $p < 0.05$ and for each flux model, the correlation coefficient (r-squared) was higher for the mean station approach than the individual value approach (Table 8-2).

Results of the nitrite plus nitrate combined flux ($NO_2^- + NO_3^-$) analyses were similar to that for ammonium except that differences in correlation strength between the individual station value models and the station mean models were very small (Table 8-3). Very high correlations (r^2 = 0.85 [individual values] and r^2 = 0.84 [mean values]) were found for

Table 8-2. Summary of regression models evaluated for summer ammonium (NH_4^+) flux at Patuxent River MINI-SONE stations.
a. Models with individual station observations;
b. Model with four month averages per station.
All model regressions were significant at $p < 0.05$.

a. Individual Summer Ammonium Flux Values (Buena Vista [BUVA] station excluded)

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Simple Linear	Total Chlorophyll-a to 1cm June - September	No shift	0.39
Simple Linear	Total Chlorophyll-a to 1cm May - August	1 month	0.43
Simple Linear	Total Chlorophyll-a to 1cm April - July	2 month	0.25
Multiple Linear	Total Chlorophyll-a to 1cm May - August Sediment Eh@1cm	1 month	0.48
Simple Linear	Sediment Eh@1cm	N/A	0.38

b. Mean Summer Ammonium Flux Values (Buena Vista [BUVA] station excluded)

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Simple Linear	Total Chlorophyll-a to 1cm June - September	No shift	0.73
Simple Linear	Total Chlorophyll-a to 1cm May - August	1 month	0.78
Simple Linear	Total Chlorophyll-a to 1cm April - July	2 month	0.63
Multiple Linear	Total Chlorophyll-a to 1cm May - August Sediment Eh@1cm	1 month	0.86
Simple Linear	Sediment Eh@1cm	N/A	0.79

Table 8-3. Summary of regression models evaluated for summer nitrite plus nitrate (NO_2^- + NO_3^-) flux at Patuxent River MINI-SONE stations.
a. Models with individual station observations;
b. Model with four month averages per station.
All model regressions were significant at $p < 0.05$.

a. Individual Summer Nitrite and Nitrate Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Bottom water, NO_{23} Total Chlorophyll-a to 1cm June - September	No shift	0.79
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm May - August	1 month	0.85
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm April - July	2 month	0.76
Simple Linear	Bottom water NO_{23}	No shift	0.69
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm June - September Summer Temperature (C)	No shift	0.79

b. Mean Summer Nitrite and Nitrate Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Bottom water, NO_{23} Total Chlorophyll-a to 1cm June - September	No shift	0.83
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm May - August	1 month	0.84
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm April - July	2 month	0.75
Simple Linear	Bottom water NO_{23}	No shift	0.43
Multiple Linear	Bottom water NO_{23} Total Chlorophyll-a to 1cm June - September Summer Temperature (C)	No shift	0.88

Table 8-4. Summary of regression models evaluated for summer dissolved oxygen phosphorus (PO_4^{-3} or DIP) flux at Patuxent River MINI-SONE stations.
a. Models with individual station observations;
b. Model with four month averages per station.
All model regressions were significant at $p < 0.05$.

a. Individual Summer Dissolved Inorganic Phosphorus (DIP) Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Sediment Eh @ 1cm Total Chlorophyll-a to 1cm June - September	No shift	0.21
Multiple Linear	Sediment Eh @ 1 cm Total Chlorophyll-a to 1cm May - August	1 month	0.21
Multiple Linear	Bottom water PO_4^{-3} Sediment Eh @ 1 cm	2 month	0.48
Simple Linear	Bottom water PO_4^{-3}	No shift	0.44
Simple Linear	Sediment Eh @ 1 cm	N/A	0.19

b. Mean Summer Dissolved Inorganic Phosphorus (DIP) Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Sediment Eh @ 1 cm Total Chlorophyll-a to 1cm June - September	No shift	0.67
Multiple Linear	Sediment Eh @ 1 cm Total Chlorophyll-a to 1cm May - August	1 month	0.67
Multiple Linear	Bottom water PO_4^{-3} Sediment Eh @ 1 cm	N/A	0.87
Simple Linear	Bottom water PO_4^{-3}	N/A	0.77
Simple Linear	Sediment Eh @ 1 cm	N/A	0.67

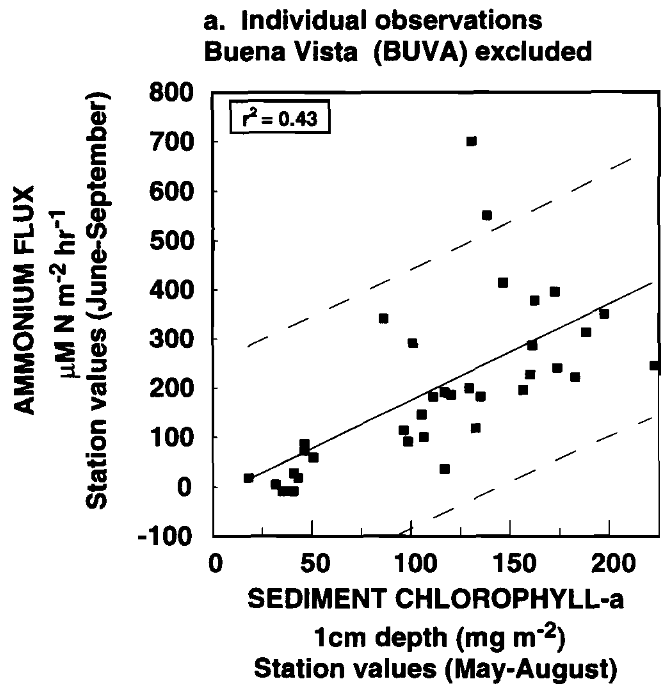
Table 8-5. Summary of regression models evaluated for sediment oxygen consumption (SOC) flux at Patuxent River MINI-SONE stations.
a. Models with individual station observations;
b. Model with four month averages per station.
All model regressions were significant at $p < 0.05$.

a. Individual Summer Sediment Oxygen Consumption (SOC) Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Total Chlorophyll-a to 1cm June - September DO mg l^{-1} Temperature (C)	No shift	0.36
Multiple Linear	Total Chlorophyll a to 1cm May - August DO mg l^{-1} Temperature (C)	1 month	0.34
Multiple Linear	Total Chlorophyll-a to 1cm May - August Temperature (C)	1 month	0.30
Multiple Linear	Total Chlorophyll-a to 1cm May - August DO mg l^{-1}	1 month	0.27
Multiple Linear	DO mg l^{-1} Temperature (C)	N/A	0.33

b. Mean Summer Sediment Oxygen Consumption (SOC) Flux Values

Model Type	INPUT (Explanatory variables)	Temporal shift Total Chla 1cm	Correlation Coefficient (r^2)
Multiple Linear	Total Chlorophyll-a to 1cm June - September DO mg l^{-1} Temperature (C)	No shift	0.64
Multiple Linear	Total Chlorophyll-a to 1cm May - August DO mg l^{-1} Temperature (C)	1 month	0.65
Multiple Linear	Total Chlorophyll-a to 1cm May - August Temperature (C)	1 month	0.64
Multiple Linear	Total Chlorophyll-a to 1cm May - August DO mg l^{-1}	1 month	0.51
Multiple Linear	DO mg l^{-1} Temperature (C)	N/A	0.64



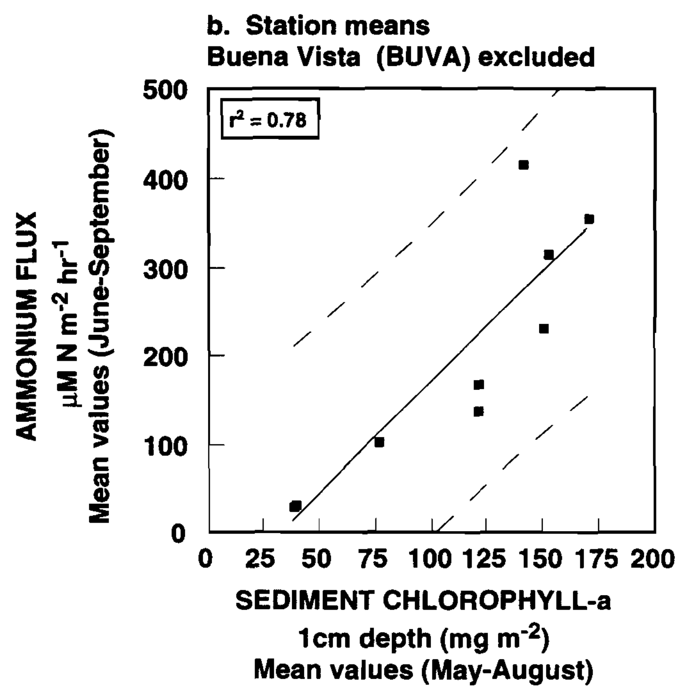


Figure 8-1.a. Simple linear regression plot of individual sediment ammonium (NH_4^+) flux values for the Patuxent River MINI-SONE stations (June - September) versus total sediment chlorophyll-a to 1 cm (May - August);
b. Simple linear regression plot of mean ammonium (NH_4^+) flux (June - September) by Patuxent River MINI-SONE stations versus mean total sediment chlorophyll-a values (May - August).
Dashed lines represent 95% confidence intervals for individual observations.

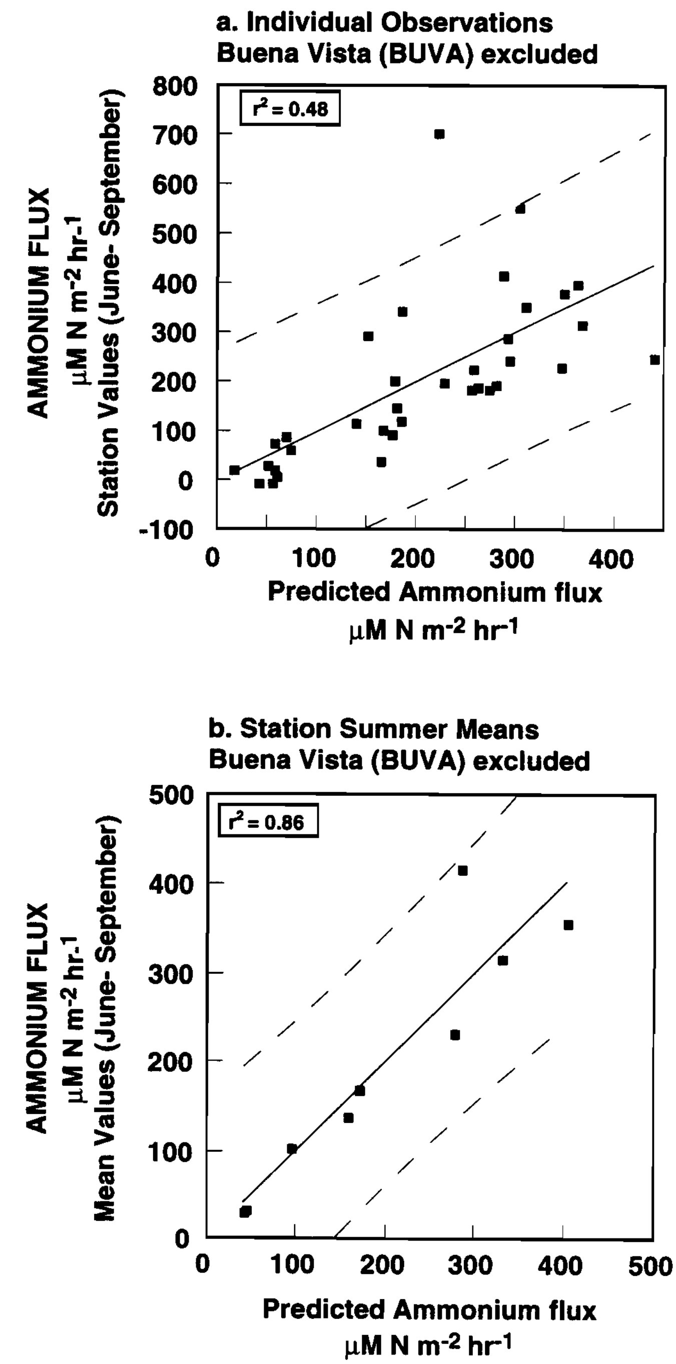


Figure 8-2. Patuxent River 1996 summer ammonium (NH_4^+) flux at MINI-SONE stations versus predicted values from the best fit multivariate linear relationships.
a. Observed station values with best fit, $z = 1.43x - 0.42y + 144.80$;
b. Station 4 month summer means with best fit, $z = 1.2x - 0.67y + 231.53$;
z = summer ammonium flux, x = total sediment chlorophyll-a to 1 cm (May - August mean), y = sediment eH at 1 cm
Dashed lines indicate 95% confidence intervals for individual values.

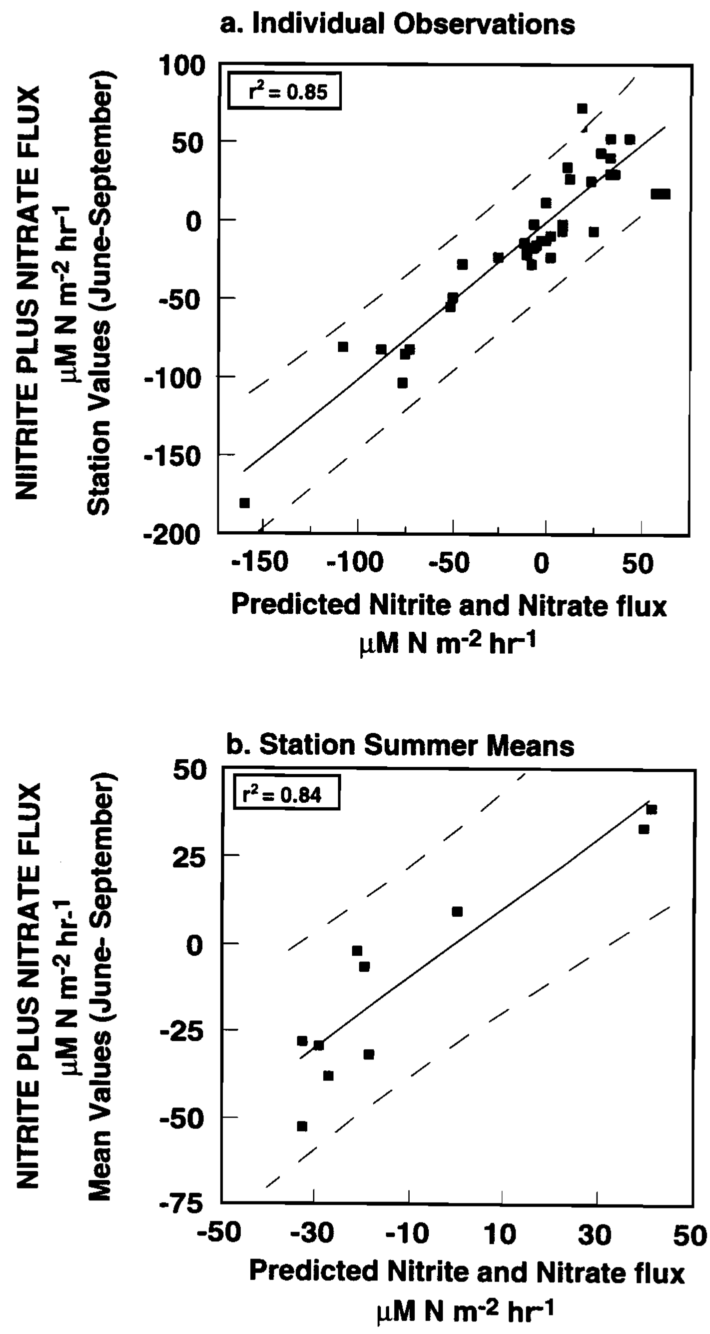


Figure 8-3. Patuxent River 1996 summer nitrite plus nitrate (NO_2^- + NO_3^-) flux at MINI-SONE stations versus predicted values from the best fit multivariate linear relationships.
a. Observed station values with best fit, $z = -13.09x - 0.44y + 77.7$;
b. Station 4 month summer means with best fit, $z = -12.9x - 0.4y + 71.0$;
z = summer nitrite plus nitrate (NO_2^- + NO_3^-), x = bottom water summer NO_2^- + NO_3^-, y = sediment total chlorophyll-a to 1 cm
Dashed lines indicate 95% confidence intervals for individual values.

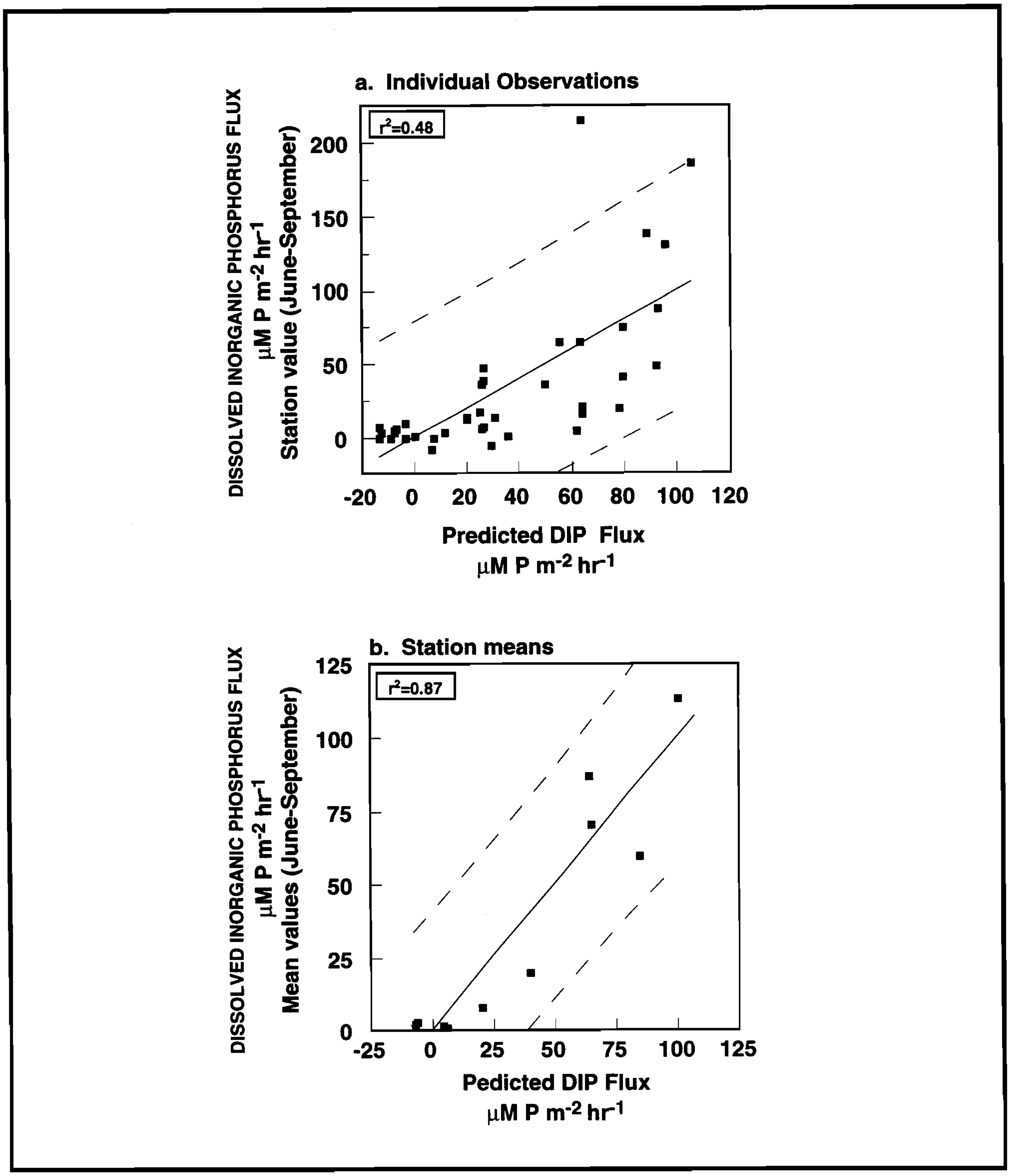


Figure 8-4. Patuxent River 1996 summer dissolved inorganic phosphorus (DIP or PO_4^-) flux at MINI-SONE stations versus predicted values from the best fit multivariate linear relationships.
a. Observed station values with best fit, $z = -0.11x + 38.74y + 25.77$;
b. Station 4 month summer means with best fit, $z = -0.18x + 38.76y + 44.47$;
z = summer DIP flux, x = sediment eH at 1 cm, y = bottom water PO_4^- concentration
Dashed lines indicate 95% confidence intervals for individual values.

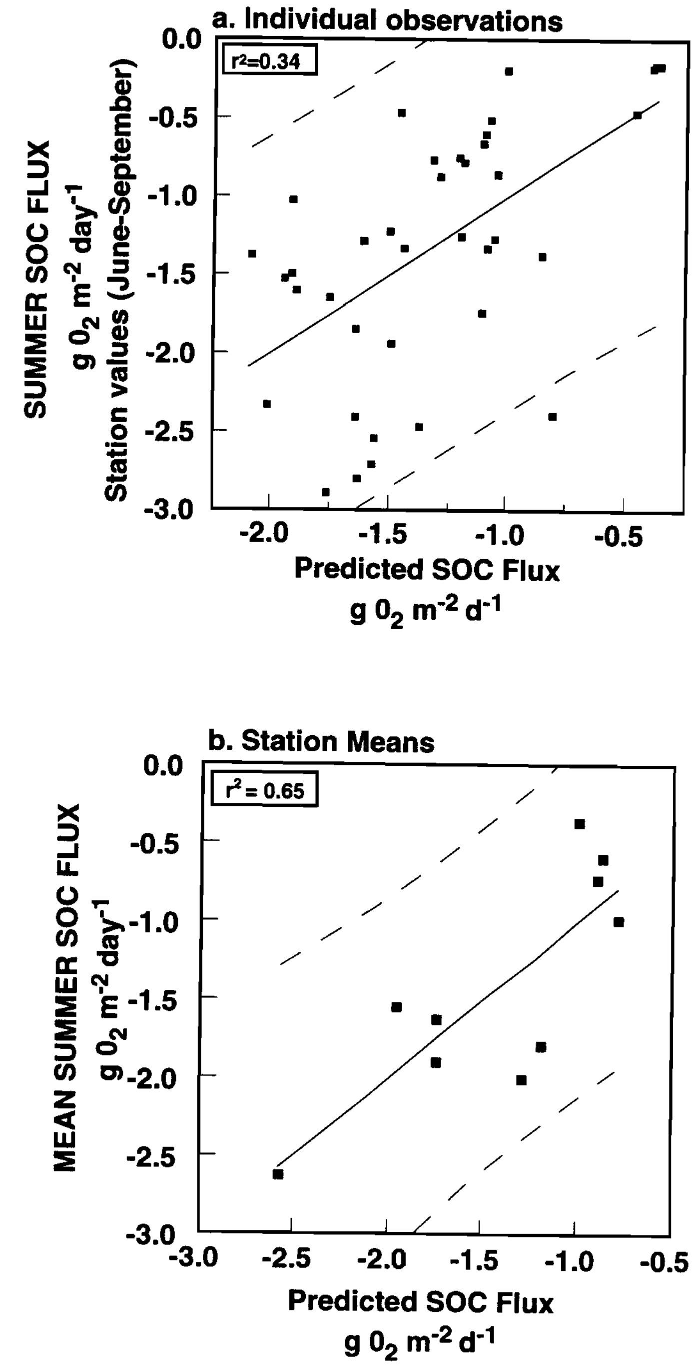


Figure 8-5. Patuxent River 1996 summer sediment oxygen consumption (SOC) at MINI-SONE stations versus predicted values from the best fit multivariate linear relationships.
a. Observed station values with best fit, F= 0.001x - 0.15y - 0.10z + 2.85;
b. Station 4 month summer means with best fit, F = -0.01x - 0.84y - 0.14z + 21.93;
F = summer SOC, x = total sediment chlorophyll-a at 1 cm (May - August), y = temperature C, z = dissolved oxygen
Dashed lines indicate 95% confidence intervals for individual values.

models using bottom water ($NO_2^- + NO_3^-$) and temporally-shifted total sediment chlorophyll-a as explanatory variables (Figure 8-3.).

Models using concurrent total chlorophyll-a data were less well correlated than those with temporally-shifted total sediment chlorophyll-a values (Table 8-3). All nitrite plus nitrate regression models were significant at $p < 0.05$.

Models for dissolved inorganic phosphorus (DIP) flux were most highly correlated with bottom water phosphate (PO_4^-) and sediment Eh (Table 8-4, Figure 8-4.) with $r^2 = 0.48$ for individual values, and $r^2 = 0.87$ for the seasonal mean values. Bottom water PO_4^- concentration alone was responsible for explaining most of the variation in phosphate flux. Total sediment chlorophyll-a did not enter this analysis as an important explanatory variable. However, high sediment Eh can be indicative of abundant surficial organic material. All phosphate (PO_4^-) regression models were significant at $p < 0.05$. For each dissolved inorganic phosphorus (DIP) flux model, the correlation coefficient (r-squared) was higher for the mean station approach than the individual value approach (Table 8-4).

The preferred model chosen for prediction of sediment oxygen consumption (SOC) rates involved use of three explanatory variables ($r^2 = 0.65$), including total sediment chlorophyll-a, bottom water dissolved oxygen, and temperature (Table 8-5; Figure 8-5.). Although many of the individual based models were not very predictive, all SOC regression models were significant at $p < 0.05$. For each sediment oxygen consumption (SOC) flux model, the correlation coefficient (r-squared) was higher for the mean station approach than the individual value approach (Table 8-5).

8.3.5 Discussion and Conclusions

For those models using sediment chlorophyll-a, higher correlations were found using a one month time shift compared to models using concurrent values. These results agree well with similar studies by Cowan *et al.* (1996) and Cowan and Boynton, (1996) who found that including a 40 day temporal shift in the sediment chlorophyll values created an exceptionally predictive model. Models using early spring (March - April) chlorophyll-a were less well correlated compared to models using either one month or concurrent chlorophyll-a values. This result is not surprising since the time required to regenerate this labile material depends on a variety of factors and may often be quite variable. The relative decrease in predictive power of models using either two or three month temporally-shifted chlorophyll-a are likely the result of physical or biological processes taking place during the interval between total sediment chlorophyll-a deposition and sediment flux measurement. These observations are reasonable if one considers that a time interval is required to convert labile organic matter into a sediment-water flux. However, as this time interval increases, processes such as sediment transport and bioturbation can increase the noise to signal ratio, rendering this relationship less accurate. Since this analysis is based upon 1996 data only, the inclusion of inter-annual variation may lead to models that perform best with time shifts of greater or lesser extent. It is therefore recommended that total sediment chlorophyll-a information be collected from the early spring (as is currently planned) until early fall (which would need to be added to the sampling schedule) until this variation can be assessed. Overall these models provide some powerful tools for examining possible spatial components to summer season fluxes in the Patuxent River Estuary.

While these results are promising, more data from different locations are needed to verify the generality of this approach. An example of this is demonstrated in a regression ($r^2 = 0.88$) shown in Figure 8-6. in which ammonium flux data from Mobile Bay and the mainstem of the Chesapeake (Cowan *et al.*, 1996 and Cowan and Boynton, 1996) is combined with the

1996 MINI-SONE data. The high correlation is truly compelling since all three systems differ substantially in a variety of ways. While more of this type of comparison is needed, early results are very promising.

Several prudent courses of action are suggested which would have as an ultimate goal the adoption of regression models for routine prediction of sediment-water fluxes in the Maryland portion of Chesapeake Bay and tributary rivers. First, complete both spring (March, April and May) and summer (June, July, August and September) sediment chlorophyll-a mapping activities in the Patuxent during 1997. The spring cruises are already planned. The summer cruises should be extended slightly so as to allow for sediment chlorophyll-a mapping and sampling of selected variables in deep waters. The analyses reported above should be re-examined using both the 1996 and 1997 data sets and conclusions reached regarding the generality and predictive power of the statistical models. Second, portions of the sediment oxygen and nutrient exchanges (SONE) data base have variables measured in temporal sequences such that this data could be examined using the models indicated above; they may indeed suggest modifications to the models we now have. Finally, if the above activities are successful we should begin to consider ways in which we could obtain sediment chlorophyll-a maps of other portions of the Bay for appropriate times of the year; some mix of samples collected from small boats in tributaries and from regularly scheduled research vessel cruises in exposed areas of the mainstem bay may be an effective approach.

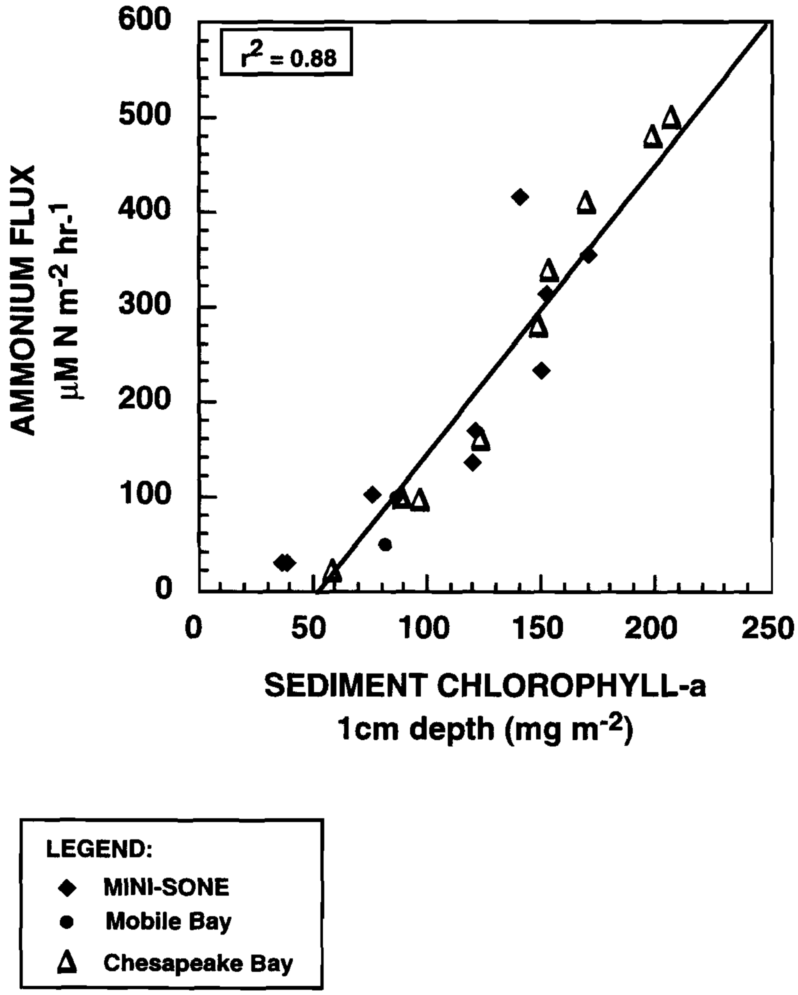


Figure 8-6. Scatter plot of ammonium (NH_4^+) flux versus average total sediment chlorophyll-a from Patuxent River MINI-SONE stations, Mobile Bay and Chesapeake mainstem.
Sediment chlorophyll-a for Mobile Bay and Chesapeake mainstem is the mean from day 80 to 220. Sediment total chlorophyll-a for MINI-SONE stations is the mean from day 130 to 220.

9. PATUXENT RIVER HIGH FREQUENCY MONITORING

9.1. Open Water Metabolism Measurements in the Patuxent River: Some preliminary findings from the high frequency monitoring data

One of the central concepts in estuarine ecology concerns the relationship between nutrient supply rate and phytoplanktonic responses. Nixon (1986) has referred to this as the agricultural paradigm wherein addition of fertilizer to agricultural crops leads to a larger yield. In a similar, but certainly less tested fashion, nutrient additions to estuarine waters result in modest increases in cell growth rates (D'Elia *et al.*, 1986) but large increases in standing stocks of planktonic algae (Boynton *et al.*, 1982a; Nixon, 1986). It is this algal response to "fertilization" which is one of the root causes of estuarine eutrophication. In recognition of this, the monitoring program routinely measures nutrient inputs to the system and phytoplanktonic responses in terms of speciation, production and standing crop. The Ecosystem Processes Component (EPC) Program and others have shown that there are strong relationships between loading rate and algal responses (Boynton *et al.*, 1994; Hagy, 1996).

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

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

9.2. Historical eutrophication evidence from the Patuxent River

Deterioration of water quality in the Patuxent River has been documented since 1936 (Mirhursky and Boynton, 1978). A pattern of nutrient enrichment emerged which was related to increase in nutrient inputs from upstream point and diffuse sources with associated increases in phytoplankton biomass and decreases in dissolved oxygen in the bottom waters of the lower estuary, decreased water column transparency and the resultant loss of submerged aquatic vegetation (SAV). The eutrophication process in the Patuxent River was particularly evident in 1978 when dissolved oxygen concentrations below 5 mg l^{-1}

were recorded (Domotor *et al.*, 1989). Intensive research and legislation in recent years (1982 - 1992), in particular the Patuxent Nutrient Reduction Strategy, has contributed to the recovery of the tributary through reduction of loading of nitrogen and phosphorus from point sources into the river.

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

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

Both the Cory data set and the 1992 data set were analyzed by Sweeney (1995). Figure 9-1. shows the estimates of production and respiration (weekly averages and standard deviations) from 1964 and 1992. Average rates during 1992 were much larger than in the past. Rates of daytime net community production (Pa*) in 1992 exceeded those in 1964 by a factor of three (300%) while estimates of community night respiration (Rn) in 1992 were greater than those in 1964 by a factor of two (200%). Preliminary analyses by Sweeney (1995) indicate a statistically significant trend towards higher values for both daytime net community production (Pa*) and community night respiration (Rn) between 1964 and 1969 and significant differences between the data collected in the 1960's and 1992. Furthermore, there have been changes in the seasonal pattern of metabolism between the 1960's and 1992. In the 1960's, daytime net community production (Pa*) exhibited very low values during late winter and then increased sharply at the beginning of May (week 17). With one exception this was the highest value of daytime net community production (Pa*) recorded during the year and probably represents enhanced production associated with the spring algal bloom. By 1992 this pattern had been substantially altered; production was already enhanced by May and rates continued to climb through September generally following the temperature cycle. This change in pattern was probably caused by increased nutrient loading rates and the positive feedback effects associated with increased loads (Figure 2-1.). Rates of oxygen consumption (Rn) also increased and during 1992 exhibited a longer period of enhanced rates. Sweeney (1995) suggests that the increased variability in the 1992 data occurs because increased nutrient availability allows for extremely high rates whenever sufficient light is available; in earlier years nutrient limitation prohibited very high rates.

Examination of the Cory and 1992 data sets strongly suggests that use of the dial oxygen technique for measuring community production and respiration would be a powerful and cost effective addition to monitoring efforts in the Patuxent River estuary and possibly other sites as well. It appears that the technique is sensitive to temporal changes in these rates which are known to be strongly impacted by nutrient supply rates. Current technology makes continuous measurements convenient to make, at least relative to older approaches. Finally, the Patuxent River in particular is undergoing intensive management programs aimed at nutrient reduction. It seems prudent to utilize some measurements having fine-scale temporal resolution from which several rate processes which are central to estuarine eutrophication can be inferred and which may also resolve further the issue of time lags related to fall-line nutrient loading and estuarine biological responses. A modern weather station making continuously recording measurements of wind speed, wind direction, precipitation and solar radiation is now available and these data would be useful for interpretation of the community metabolism data collected.

9.3. Additional High Frequency Monitoring during 1996

A Hydrolab DataSonde-3 was deployed at the high frequency monitoring site on the Route 231 bridge crossing the Patuxent River near Benedict, MD from 1 June, 1996 through 18 October, 1996. Parameters monitored were: time, temperature, specific conductance, salinity, pH, dissolved oxygen percent saturation (DO % sat) and dissolved oxygen (DO). The DataSonde probes were maintained at a constant depth of one meter below the surface.

The major objectives of this effort are:

> *1. to examine dissolved oxygen data to determine if at current loading regimes dissolved oxygen habitat criteria are achieved,*
>
> *2. to use the temperature, salinity and dissolved oxygen data to calculate daily water column production and respiration for this zone of the estuary and*
>
> *3. to relate calculated rates to rates observed at this site when nutrient loads were considerably lower as was the case in the mid 1960's.*

9.4. Examination of the 1996 Data

Data for June through October, 1996 were plotted for four water quality parameters: temperature (C), salinity (ppt), dissolved oxygen (DO; mg l^{-1}) and dissolved oxygen saturation (%) presenting a first overview of the data set. Some 11,000 values of each variable were graphed in these figures. In general the data record acquired is very pleasing and the equipment performance coupled with the level of effort needed to obtain the data set has met our expectations.

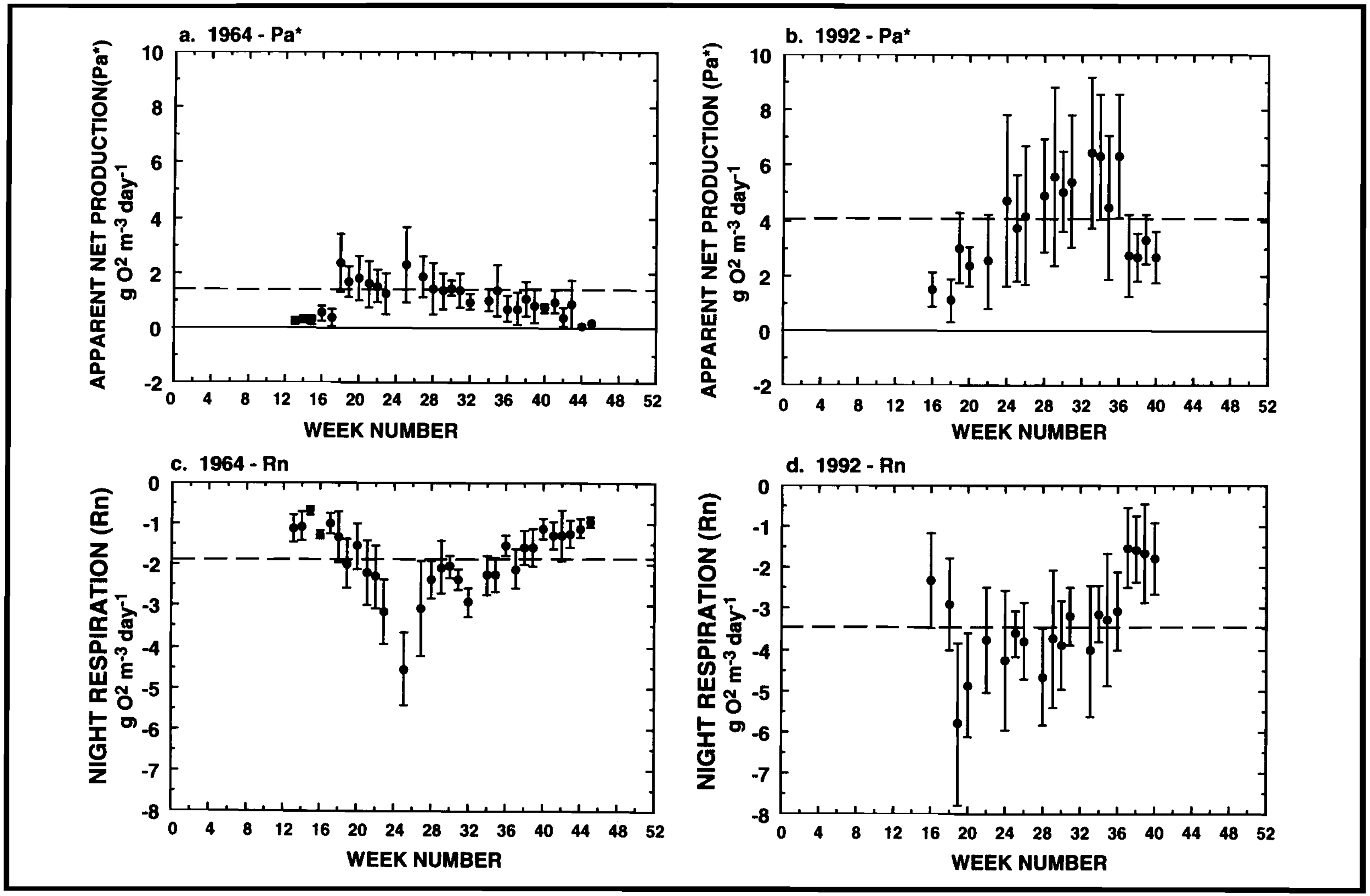


Figure 9-1. A comparison of rates (week averages and standard deviations) of daytime net community primary production (Pa*) and community night respiration (Rn) measured during 1964 and 1992 at the Benedict Bridge (MD Route 231 bridge), Patuxent River. Rates were based on diel measurements of dissolved oxygen and converted to estimates of metabolism using technique of Odum and Hoskins (1958).
The 1964 data were collected by Cory (pers. comm.) and the 1992 data were collected by Sweeney (1995).

9.4.1 Qualitative Description of the 1996 High Frequency Data Set

There was clear seasonal-scale pattern in temperature with values in June starting at 19 - 20 C and steadily increasing. Temperature values were in the range of 25 - 30 C during July and August and then declined from 10th September, 1996 through mid-October to values in the range of 15 - 20 C. Superimposed on this seasonal pattern were clear uni-modal diurnal temperature changes. In general these fluctuations were on the order of 1 - 2 C but larger (3 - 4 C) and smaller (< 1 C) diel changes were also apparent. Daily minimum values were almost always observed near sunrise and maximum values near sun set. It is probable that the magnitude of diel oscillations in temperature are mainly related to the amount of radiation present on a given day. Finally, there is another level of variability evident in the data set that may be related to weather events, particularly changes in river flow conditions. Specifically, seasonal scale changes in temperature were not characterized by uniformly continuous increases (June through mid-September) or decreases (mid- September through mid-October) in values. Rather, there are deviations, generally on temporal scales of 2 to 5 days, wherein temperatures departed from the larger seasonal pattern. It is proposed that non-seasonal temperature declines were due to surges in river flow (generally cooler water) and that non-seasonal temperature increases were due to periods of very clear weather (local heating).

Salinity generally increased through the period of record, starting in June at about 4 to 5 ppt and finishing in October at 7 to 8 ppt. As expected, the diel pattern was bi-modal reflecting the semi-diurnal tides in the Patuxent estuary. Generally, tidal salinity differences were on the order of 1 to 2 ppt but considerably larger excursions were also occasionally evident. For example, on August 24 - 26, 1996 salinity changed from 5 to 10 ppt in one tidal period. Since this excursion was toward higher values it is suspected that an intrusion of high salinity water from the Bay was involved. This salinity record also offers the opportunity to better understand the temporal relationships between river flow measured at the fall line in Bowie, MD (Station No. 01594440) and estuarine response. In the second example, during early June, 1996 there was a period when salinity values were quite stable from day to day, then declined steadily for a four day period and recovered to previous levels after five additional days. It seems probable that the salinity decline was due to a freshwater surge from the drainage basin.

The dissolved oxygen (DO) record is shown in Figures 9-2.1.a. - 9-2.5.b. for the period June through October, 1996. The data set has considerably greater variability than that observed for temperature or salinity which was expected since there are both physical and biological oxygen sources and sinks. However, several distinct patterns were evident. First, there was a generally pronounced uni-modal diel pattern in dissolved oxygen (DO) concentration with highest values in the late afternoon and minimum values around sunrise. This pattern would be expected if biological oxygen production (from algal photosynthesis during daytime periods) and oxygen consumption (from all heterotrophs) were dominant processes in diel oxygen dynamics. This pattern would not be evident if biological processes were very small or if physical advective processes were very large, neither of which seems to be the case. Second the magnitude of these diel dissolved oxygen (DO) changes varied considerably (400 - 500 %) among days as would be expected under variable sunlight conditions. We expect to be able to resolve some of this level of variability using Photosynthetically Active Radiation (PAR) data collected as part of the Chesapeake Bay Observing System (CBOS) at Solomons, MD. Third, the magnitude of diel dissolved oxygen (DO) changes appears to be greater during July, August and early September than during either June or October. Again, this is consistent with routine measurements of phytoplankton photosynthetic rates which are also typically high during the middle of summer. Finally, dissolved oxygen (DO)

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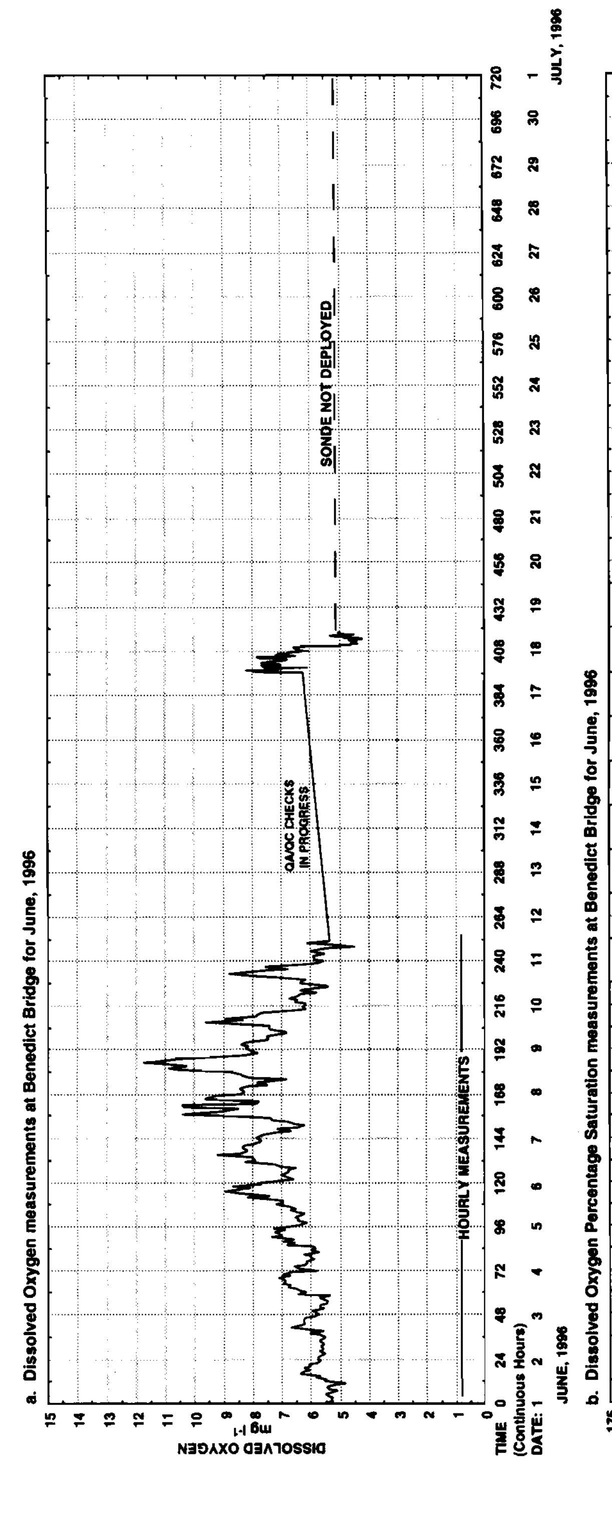
Figure 9-2.1.a. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen (mg l^{-1}) data vs time (hours) for June, 1996 (1st June, 1996 through 1st July, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

9-2.1.b. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen percentage saturation (%) data vs time (hours) for June, 1996 (1st June, 1996 through 1st July, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.



a. Dissolved Oxygen measurements at Benedict Bridge for June, 1996

b. Dissolved Oxygen Percentage Saturation measurements at Benedict Bridge for June, 1996

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Figure 9-2.2.a. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen (mg l^{-1}) data vs time (hours) for July, 1996 (1st July, 1996 through 1st August, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

9-2.2.b. Plot of high frequency (hourly measurements in July; 15 minute measurements during July through October) surface water dissolved oxygen percentage saturation (%) data vs time (hours) for July, 1996 (1st July, 1996 through 1st August, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

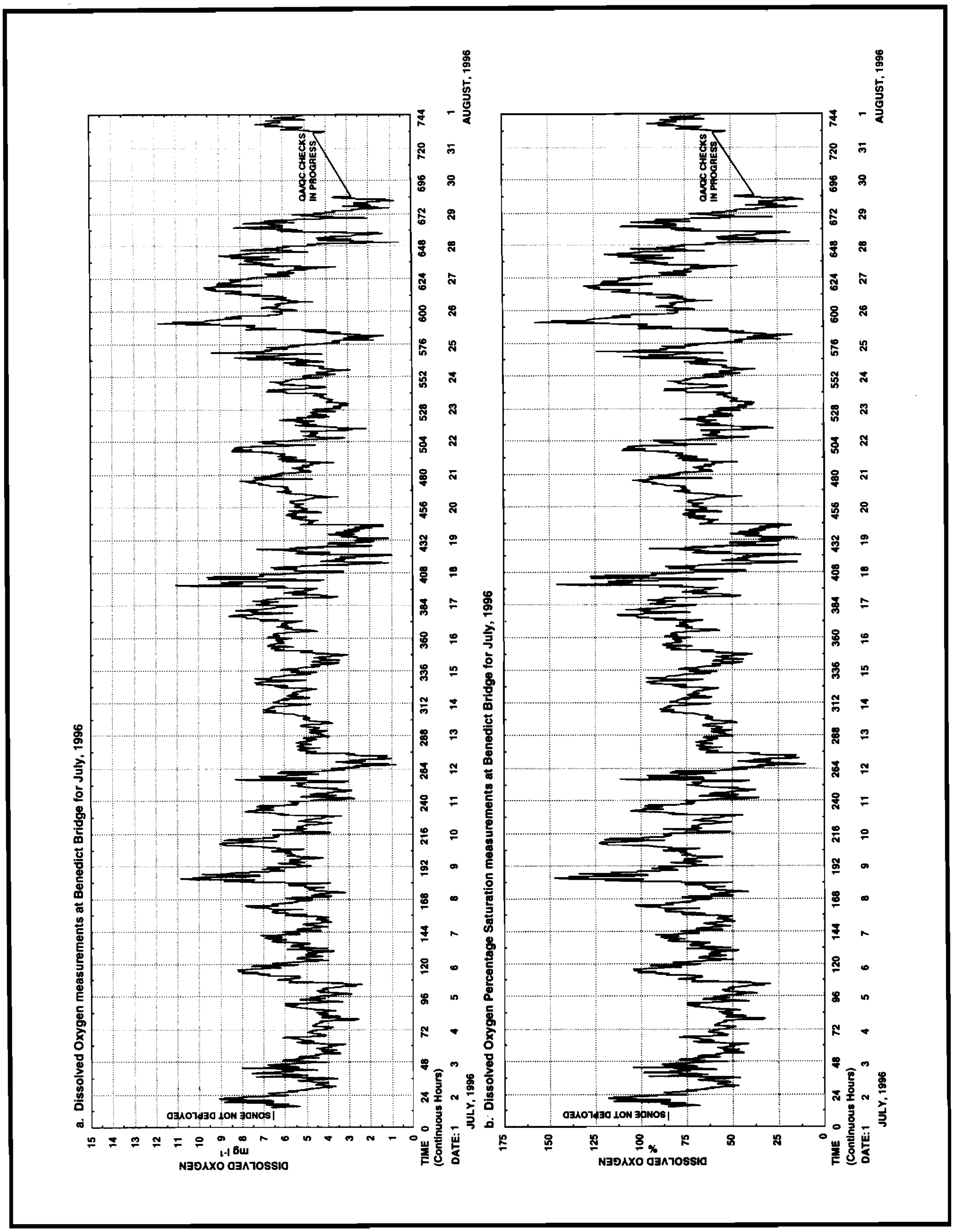
a. Dissolved Oxygen measurements at Benedict Bridge for July, 1996
DISSOLVED OXYGEN
mg l-1
SONDE NOT DEPLOYED
QA/QC CHECKS IN PROGRESS
TIME (Continuous Hours)
0 24 48 72 96 120 144 168 192 216 240 264 288 312 336 360 384 408 432 456 480 504 528 552 576 600 624 648 672 696 720 744
DATE: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 1
JULY, 1996
AUGUST, 1996
b. Dissolved Oxygen Percentage Saturation measurements at Benedict Bridge for July, 1996
DISSOLVED OXYGEN
%
SONDE NOT DEPLOYED
QA/QC CHECKS IN PROGRESS
TIME (Continuous Hours)
DATE: 1
JULY, 1996
AUGUST, 1996

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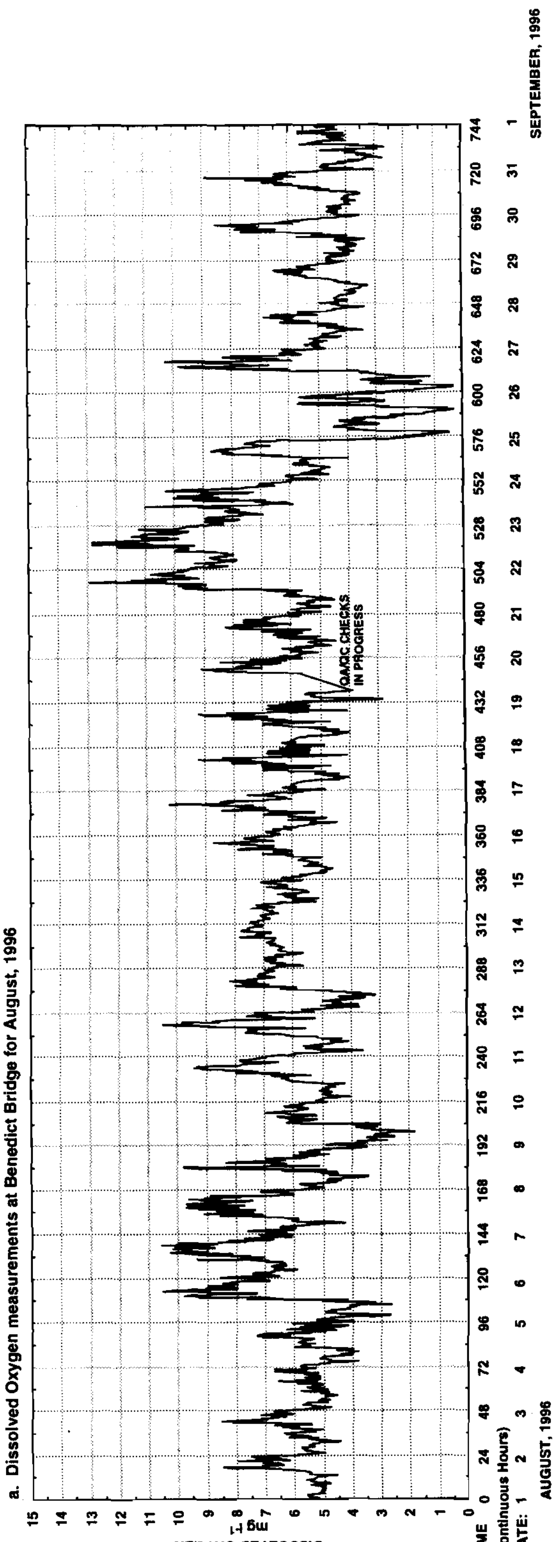
Figure 9-2.3.a. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen (mg l^{-1}) data vs time (hours) for August, 1996 (1st August, 1996 through 1st September, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

It appears that on 25 August and 26 August there is an intrusion of oxygen deficient deep water into the shallow well mixed Benedict area.

9-2.3.b. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen percentage saturation (%) data vs time (hours) for August, 1996 (1st August, 1996 through 1st September, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

It appears that on 25 August and 26 August there is an intrusion of oxygen deficient deep water into the shallow well mixed Benedict area.

a. Dissolved Oxygen measurements at Benedict Bridge for August, 1996



b. Dissolved Oxygen Percentage Saturation measurements at Benedict Bridge for August, 1996

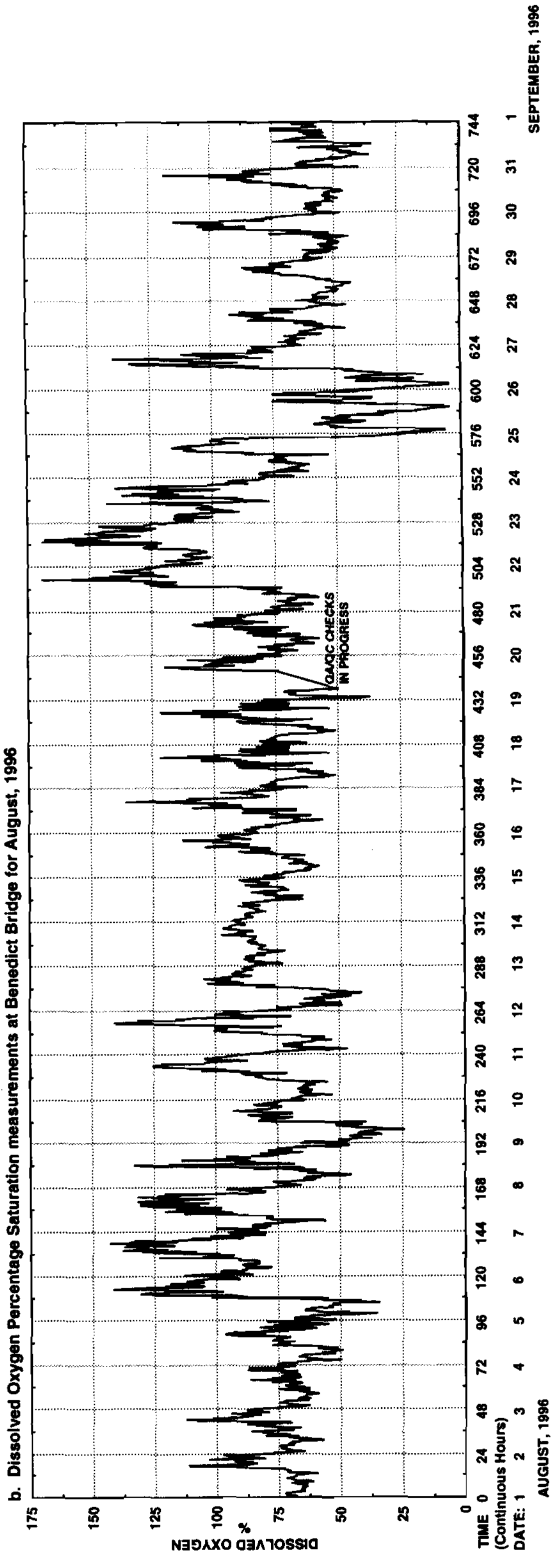


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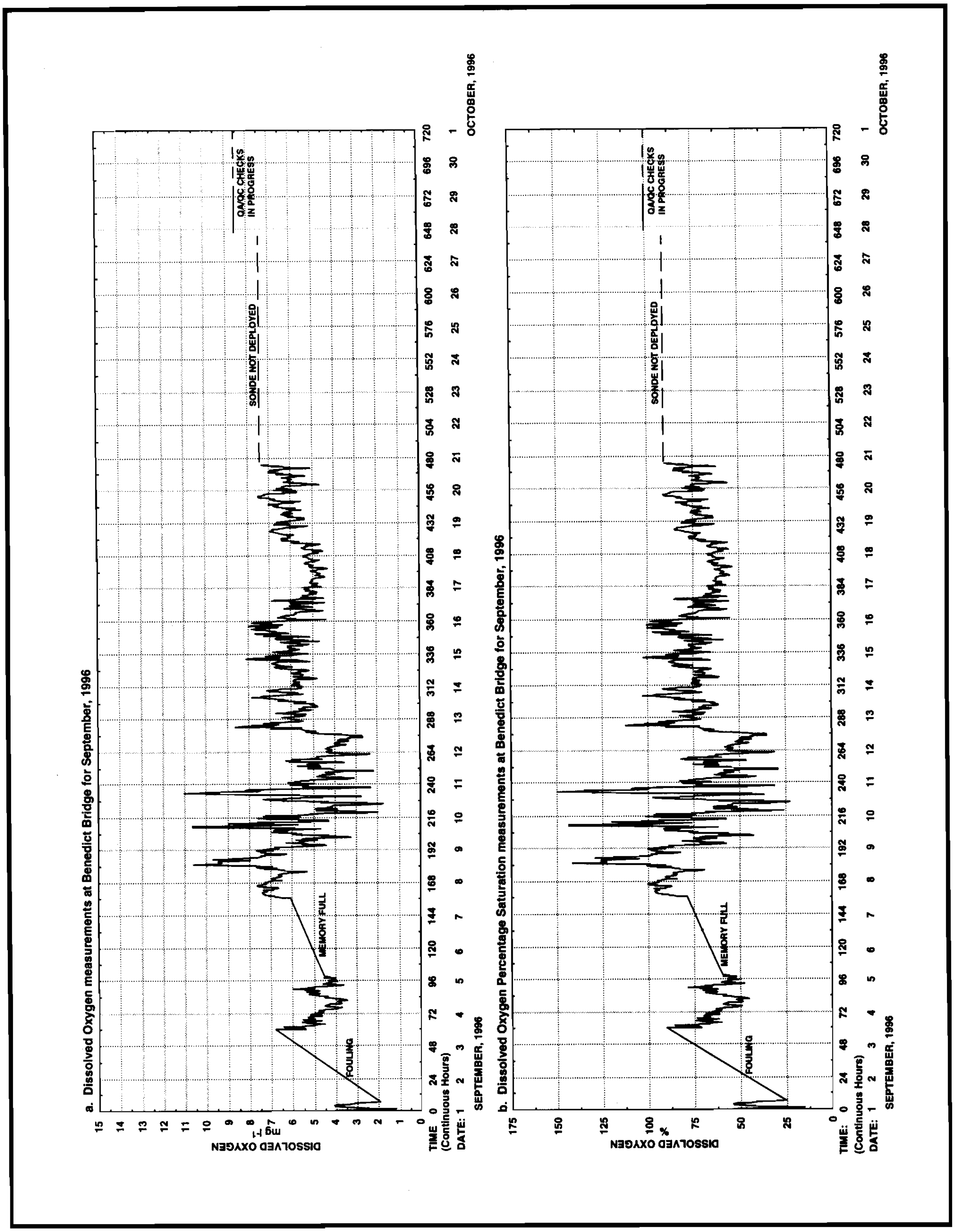
Figure 9-2.4.a. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen (mg l^{-1}C) data vs time (hours) for September, 1996 (1st September, 1996 through 1st October, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

9-2.4.b. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen percentage saturation (mg l-1) data vs time (hours) for September, 1996 (1st September, 1996 through 1st October, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.



a. Dissolved Oxygen measurements at Benedict Bridge for September, 1996

b. Dissolved Oxygen Percentage Saturation measurements at Benedict Bridge for September, 1996

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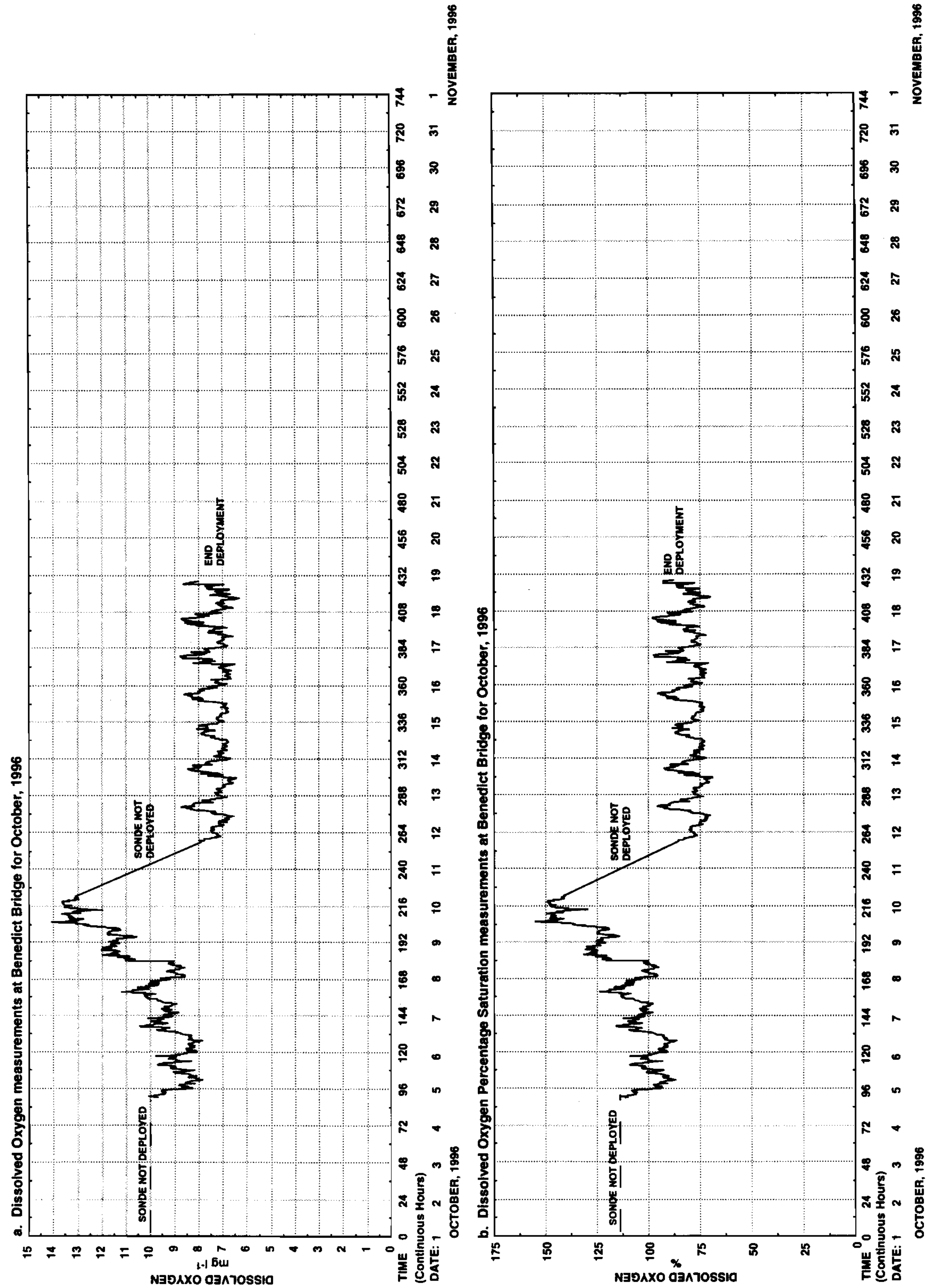
Figure 9-2.5.a. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen (mg l^{-1}) data vs time (hours) for October, 1996 (1st October, 1996 through 1st November, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.

9-2.5.b. Plot of high frequency (hourly measurements in June; 15 minute measurements during July through October) surface water dissolved oxygen percentage saturation (%) data vs time (hours) for October, 1996 (1st October, 1996 through 1st November, 1996) measured at Benedict, MD using a Hydrolab DataSonde-3 suspended 1 meter below the water surface.


a. Dissolved Oxygen measurements at Benedict Bridge for October, 1996
DISSOLVED OXYGEN
mg l-1
SONDE NOT DEPLOYED
SONDE NOT DEPLOYED
END DEPLOYMENT
TIME
(Continuous Hours)
DATE:
OCTOBER, 1996
NOVEMBER, 1996
b. Dissolved Oxygen Percentage Saturation measurements at Benedict Bridge for October, 1996
DISSOLVED OXYGEN
%
SONDE NOT DEPLOYED
SONDE NOT DEPLOYED
END DEPLOYMENT
TIME
(Continuous Hours)
DATE:
OCTOBER, 1996
NOVEMBER, 1996

concentrations at 1 meter depth generally ranged between 4 and 9 mg l^{-1} (Figures 9-2.1.b. - 9-2.5.b.), there were significant amounts of time when values were lower, even in surface waters. For example, during June, 1996 there were only two dissolved oxygen (DO) measurements below 5 mg l^{-1} while on the order of 50 observations were at or below 2 mg l^{-1} during July and August. There were a few instances when dissolved oxygen (DO) was below mg l^{-1}. During September the frequency of low dissolved oxygen (DO) observations decreased and during October there were no observations below 5 mg l^{-1}.

9.5 Compliance with Dissolved Oxygen Habitat Criteria

Living resource habitat criteria have been established for dissolved oxygen to provide a systematic way of assessing the degree to which dissolved oxygen conditions in Chesapeake Bay are sufficient to support growth and survival of important living resources. The requirements reflect a recognition that detrimental levels of oxygen stress can result from prolonged or repeated exposure to sub-lethal concentrations and acute mortality following exposure to lethal concentrations (Table 9-1.). Because of the nature of the criteria, high frequency (at least hourly) dissolved oxygen measurements are required to accurately assess compliance with these requirements. Since high frequency monitoring is not a regular component of the Chesapeake Bay Water Quality Monitoring Program, these data and the data resulting from the Chesapeake Bay Observing System are among the small number of data sets available for properly assessing compliance.

The high frequency data collected at Benedict Bridge were analyzed to assess compliance with criteria a) through c) (Table 9-1). Of the 3,267 hours of dissolved oxygen data collected during June through October 1996, dissolved oxygen in surface waters at Benedict Bridge was less than 1 mg l^{-1} for a total of 5.75 hours during 7 separate incidents. A case by case investigation of the incidents suggests that two may have resulted from instrument error. The remaining 5 cases, however, involve consistently low dissolved oxygen concentrations in the hours prior to sunrise. Overall, the 3.5 hours during which concentrations did not comply with requirement "a" (Table 9-1.) do not seem to be important; however, the fact that concentrations as low as these occurred in surface waters indicates an excessively high level of metabolic activity.

On 39 occasions during the period of record dissolved oxygen declined to less than 3 mg l^{-1} after an interval of less than 48 hours since the previous excursion below 3 mg l^{-1}. These events occurred with regularity from early July through middle September, 1996 (Figure 9-3.) and violate the second component of part "b" of the dissolved oxygen habitat criteria (Table 9-2.). Thus, chronic oxygen stress was a consistent feature of habitats in the vicinity of Benedict Bridge during summer 1996. However, there were no occasions when dissolved oxygen concentrations remained below 3 mg l^{-1} for a period of 12 hours or more.

Finally, it was found that dissolved oxygen in surface waters at the Benedict Bridge was always in compliance with part (c) of the habitat criteria, which requires a monthly mean concentration greater than 5 mg l^{-1}. The monthly mean dissolved oxygen concentrations for each month from June through October were 6.79, 5.46, 5.96, 5.56, and 8.57, respectively. Since daytime biweekly sampling would generally yield a mean concentration in the vicinity of these means, and would not reveal pre-dawn minimums associated with diel fluctuations, it is clear that high frequency sampling is required to adequately characterize dissolved oxygen conditions in surface waters.

Table 9-1. The living resource habitat requirements for dissolved oxygen.

a. The dissolved oxygen concentration should be at least 1.0 mg l^{-1} at all times throughout Chesapeake Bay and its tributaries, including subpycnocline waters.
b. Dissolved oxygen concentrations between 1.0 and 3.0 mg l^{-1} should not occur for longer than 12 hours and the interval between excursions of dissolved oxygen between 1.0 and 3.0 mg l^{-1} should be at least 48 hours throughout Chesapeake Bay and its tidal tributaries, including subpycnocline waters.
c. Monthly mean dissolved oxygen concentrations should be at least 5.0 mg l^{-1} throughout the above-pycnocline waters of Chesapeake Bay and its tidal tributaries.
d. Dissolved oxygen concentrations should be at least 5.0 mg l^{-1} at all times throughout the above pycnocline waters of anadramous fish spawning reaches, spawning rivers and nursery areas of Chesapeake Bay and its tidal tributaries as defined in Habitat Requirements for Chesapeake Bay Living Resources, 1991 revised edition.
e. In addition, where dissolved oxygen conditions presently exceed the requirements, these conditions should be maintained.

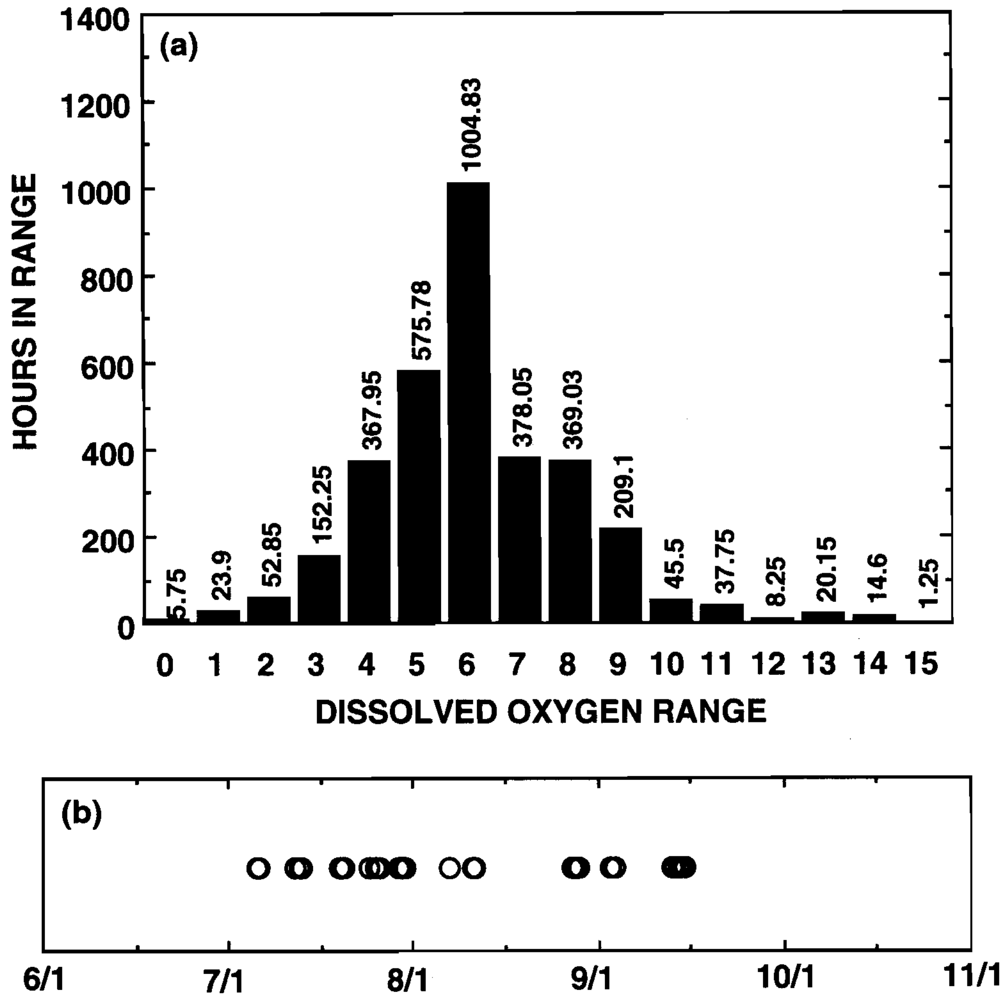


Figure 9-3. The distribution of dissolved oxygen observations integrated over time (a) and the temporal distribution of excursions below 3 mg l^{-1} with less than 48 hours between excursions. For example, (a) shows that dissolved oxygen concentrations were between 0 and 1 mg l^{-1} for 5.75 hours during the record.
b. Panel showing violations of part (b) of the dissolved oxygen habitat criteria.

9.6 Open Water Metabolism Measurements in the Patuxent River

9.6.1 Background and Definitions

Measurements of both the gross and net metabolism of an ecosystem are useful descriptors of ecosystem function for a number of reasons. Gross production and respiration are an indication of the overall activity of a system. High metabolism is usually associated with enriched systems, and many of the undesirable effects associated with eutrophication can be associated with high gross metabolism. Gross production minus gross respiration yields the net metabolism, which is often near zero. However, over the long term, even small departures from net metabolism may be important from the perspective of understanding ecosystem function (Kemp *et al.* 1997). Importantly, like sediment fluxes, ecosystem metabolism measurements are rates and are particularly useful for understanding ecosystem behavior.

We used a high frequency time series of water temperature, salinity and dissolved oxygen on the Patuxent River at Benedict Bridge (MD 231) to generate daily estimates of surface water (top 1 m) metabolism for late spring through early fall 1996. We used an open water technique which relies on the daily excursions in dissolved oxygen caused by the diel cycle of incident irradiance (sunlight). While assumptions are required as with all other techniques, the open water technique is especially useful for characterizing ecosystems because it integrates across ecosystem components, time and space. Open water techniques are also particularly well-suited to metabolically active systems such as Patuxent River.

In a typical day, oxygen is produced in excess of consumption during the day and consumed at night with no primary production due to darkness. This results in a diel pattern in which oxygen reaches a daily maximum in late afternoon and declines overnight to a minimum shortly after dawn. This diel pattern is affected by air-sea exchange of dissolved oxygen which results in an air-to-sea transfer of oxygen when the dissolved oxygen concentration is less than the solubility (undersaturated) and the opposite when the concentration exceeds the solubility. The exchange of oxygen is proportional to the degree of over- or under-saturation. Our metabolism estimates are based on this conceptual model.

The parameters that we estimated are defined as follows:

Rn	The amount of oxygen consumed (g O_2 m^{-3}) between sunset and sunrise on the following morning.
Rn/hr	The rate of oxygen consumption (g O_2 m^{-3} hr^{-1}) between sunset and sunrise on the following morning.
Pa	The net production of oxygen (g O_2 m^{-3}) between sunrise and sunset.
Pg	The gross production of oxygen (g O_2 m^{-3}) between sunrise and sunset assuming daytime respiration rate is equivalent to the Rn/hr during the subsequent night.
SRm	The "metabolic sunrise" defined for each day as the time at which dissolved oxygen reaches its minimum.
SSm	The "metabolic sunset" defined for each day as the time at which dissolved oxygen reaches its maximum.

Pa* The net production of oxygen (g O_2 m^{-3} day^{-1}) observed during the period of net autotrophy. This occurs daily between the times of the minimum (SRm) and maximum (SSm) dissolved oxygen concentration.

Pg* The gross production of oxygen (g O_2 m^{-3} day^{-1}) during the period of net autotrophy assuming that the concurrent respiration rate is equal to Rn/hr during the subsequent night.

9.6.2 Estimation Algorithms

All of the metabolic parameters can be calculated quickly once several operations are performed on the entire time series. These operations are as follows:

(1) Obtain the times of sunset and sunrise (available from the US Naval Observatory, http://riemann.usno.navy.mil/AA/) for each day and estimate from the prior and subsequent values for dissolved oxygen concentration (DO) and percent oxygen saturation (POSAT) and a value at precisely those times. Create a DAYPART label identifying all the original observations as either "Day" or "Night."

(2) For each observation in the data set, calculate the change in DO since the preceding observation (DDO), the mean POSAT over the same time interval, and the duration of the time interval in hours (Dt).

(3) Calculate an estimate of the air-sea oxygen exchange (ASEXCH) during the interval assuming a constant exchange coefficient of 0.5 g O_2 m^{-2} hr^{-1} at 100% saturation deficit. This equation is

$$ASEXCH = 0.5 * \Delta t * (100 - POSAT) / 100$$

The resulting units are g O_2 m^{-2}.

(3) For each observation in the time series, calculate the corrected net oxygen production (CNOP) by subtracting ASEXCH from DDO. Since this calculation pertains only to the near-surface water, ASEXCH is multiplied by 1 m to obtain identical units.

(4) Identify the minimum and maximum DO observations for each day. Create a METPART label identifying daytime observations preceding the minimum as "Pre-dawn," daytime observations following the maximum "Pre-dusk," the remaining daytime observations "Day" and all night-time observations "Night."

(5) Create a date variable (METDAY) identifying a "metabolic day" which includes one daytime period and the following night rather than the usual 24 period. (Note that this "day" may encompass slightly more or less than 24 hours.)

Once the above operations were completed, the metabolic parameter values were calculated for each metabolic day (sunrise to sunrise) by summing the values described above if the METPART label has a particular value or values. These conditions are summarized in Table 9.2. The parameters Rn/hr, Pg and Pg* were calculated from those in

Table 9-2. using the formulas in Table 9-3. Once all of these parameters were calculated, any daily observations for which insufficient data was available were eliminated.

Table 9-2. A key to the calculation of the metabolic parameters.
The "yield to sum", when summed for all values in a day with the appropriate "METPART Label" yields the "Parameter" in the "Units" specified.

Parameter	Variable to Sum	METPART Label	Units
Day	Dt	Day	Hours
Night	Dt	Night	Hours
Pre-Dawn	Dt	Pre-Dawn	Hours
Pre-Dusk	Dt	Pre-Dusk	Hours
Rn	CNOP	Night	g O_2 m^{-3} day^{-1}
Pa	CNOP	Pre-Dawn, Day or Pre-Dusk	g O_2 m^{-3} day^{-1}
Pa*	CNOP	Day	g O_2 m^{-3} day^{-1}

Table 9-3. The formulas for calculating R/n, Pg and Pg* from parameters described in Table 9-2. and resulting units.

Parameter	Method of Calculation	Units
Rn/hr	Rn/Night	g O_2 m^{-3} hr^{-1}
Pg	Pa+(Rn/Night)*(Pre-Dawn+Day+Pre-Dusk)	g O_2 m^{-3} day^{-1}
Pg*	Pa*+(Rn/Night)*(Pre-Dawn+Day+Pre-Dusk)	g O_2 m^{-3} day^{-1}

9.6.3 Preliminary Results and Discussion of Metabolism Calculations

9.6.3.1 Validity of Observations

Summary statistics for the principle metabolic parameters and the duration of the components of the metabolic day are shown in Table 9-4. Estimates were obtained for 90 days out of the 141 day study period, the remaining days having been eliminated due to missing or incomplete data. Most of the values fell within expected ranges. The exceptions include three negative values for Rn, six negative values for Pg and one negative value for Pg*. Since these values defy interpretation except as the sum of a valid value and random error, they are included in analyses only where excluding them would bias the result (*i.e.* when calculating summary statistics such as the mean). In each case, hypothetical explanations for the invalid observations can be proposed in terms of violations of the model assumptions. The negative values for Rn can be attributed to advection of water masses, an underestimate of air-sea oxygen exchange, or both. Because Pa* is positive by definition, the single negative estimate for Pg* resulted from a negative estimate for Rn on that day. The six negative estimates for Pg could have resulted from either one of the same problems mentioned for Rn, or a violation of the assumption that daytime respiration equals respiration during the following night.

9.6.3.2. The Pre-Dawn and Pre-Dusk Periods

The pre-dawn period is the time between the moment of sunrise and the time at which positive net production of dissolved oxygen begins. This delay can most likely be attributed to insufficient irradiance immediately following sunrise. In approximately 10% of the observations, this period was less than 0.5 hours, while in an additional 10% of observations this period was greater than 6.5 hours in duration. In general, a modest interval of 1 to 4 hours was observed between sunrise and the onset of positive net production. Many relationships have been examined, including the relationship of the length of the predawn period to PAR. Though the common conceptual model of metabolism and primary production would suggest that a strong relationship was present, this is not the case. There are clearly a number of interacting factors. At a minimum an additional years' data will be required to better explain these data.

The pre-dusk period is the duration of time between the end of positive net production and sunset. This interval could result from a number of factors, including a decrease in primary production due to decreasing irradiance in late afternoon or incipient nutrient limitation. Like the pre-dawn period, the duration of the pre-dusk period usually lasted from 1 to 4 hours.

The persistent presence of these periods indicates that the net production calculated over this period (Pa) under-represents the autotrophic activity during the day. The parameter Pa* records the maximum amount of positive production during the day. All subsequent references to net daytime production will refer to Pa*.

9.6.3.3. Respiration

Nighttime respiration was as large as 7.5 g O_2 m^{-3} day^{-1}. More than 90% of observations were larger than 1 g O_2 m^{-3} day^{-1}, while the median respiration was 2.9 g O_2 m^{-3} day^{-1}. The broad pattern in the respiration estimates is an increase from early June through late August, followed by a decrease through fall (Figure 9-4.). This pattern reflects that of water temperature (Figure 9-4.d.). An exponential equation of the form fit to the data assuming

Table 9-4. Summary statistics for the preliminary estimates of metabolic parameters for Patuxent River at Benedict Bridge during June through October, 1996.
The units of Pa, Pa^*, Pg and Pg^* are g O_2 m^{-3} day^{-1}. The units of Pre-Dawn, Day, and Pre-Dusk are hours. The parameters are defined in section 9-6. The values of Rn have been multiplied by -1 such that a consumption of oxygen is shown as positive respiration.

Parameter	Mean	Median	Minimum	Maximum
Pa	0.34	0.23	-4.29	6.29
Pa*	3.45	2.93	0.39	9.46
Pg	4.27	3.66	-2.07	12.78
Pg*	7.35	6.96	-0.18	16.02
Rn	2.85	2.87	-4.36	7.53
Pre-Dawn	3.1	2.7	0	10.2
Day	7.8	8.0	0.5	13.3
Pre-Dusk	2.7	2.6	0.1	8.4

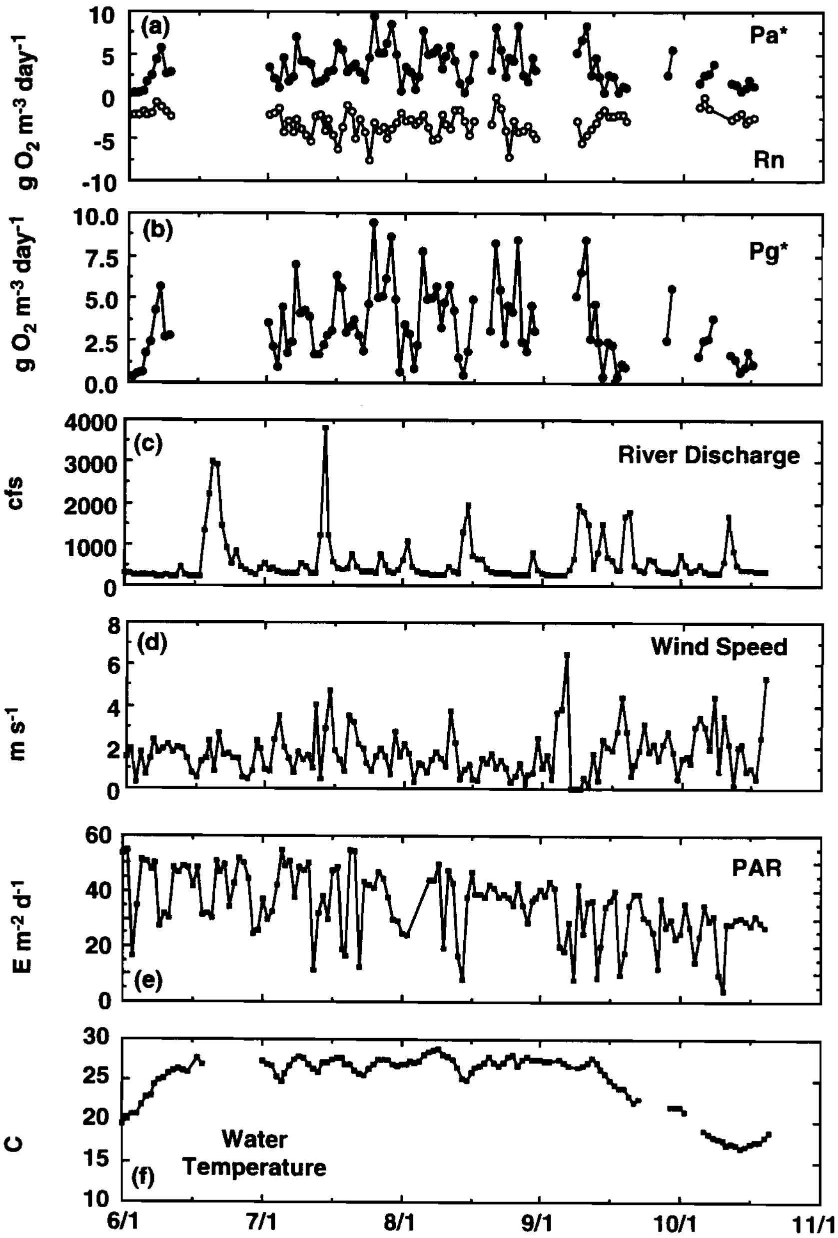


Figure 9-4.a. The time series of daytime apparent production (Pa*) and nighttime respiration (Rn) in the Patuxent River at Benedict Bridge during summer 1996; b. the time series of gross production (Pg*); c. daily mean river discharge measured by the USGS at Bowie; d. vector average wind speed at Chesapeake Biological Laboratory; e. daily integrated photosynthetically active radiation (PAR) at Chesapeake Biological Laboratory and f. daily mean surface water temperature at Benedict Bridge.

log-normal errors is shown in Figure 9-5.a. While there is obviously a large amount of unexplained variability, the temperature dependence is significant ($p < 0.05$). The estimated Q_{10} is 2.43 with 95% confidence interval (1.56,3.78). This is very close to the Q_{10} reported for middle Chesapeake Bay surface waters (2.36) by Smith and Kemp (1995). The respiration estimates, however, are much greater than those reported by Smith and Kemp (1995). At 25 C, the mean nighttime respiration predicted for Benedict Bridge is 2.54 g O_2 m^{-3}. Converted to an hourly rate (divide by 10.4 hours) this is 0.24 g O_2 m^{-3} hr^{-1}, or almost 5 times the plankton respiration rate predicted for 25 C by the relationship reported by Smith and Kemp (1995) for middle Chesapeake Bay surface waters. These estimates are among the highest recorded in estuaries (Hopkinson, 1985). There are a number of possible explanations for this. The most obvious is that the Benedict Bridge area of Patuxent River is extremely metabolically active. Another explanation is that these open water metabolism measurements include components of the ecosystem other than the plankton (*e.g.* benthos) and may reflect more than the respiration due to 1 m^3 of water due to downward diffusion of oxygen. As a general indication of this, the summer oxygen consumption for the lower water column and benthos in the lower Patuxent reported by Hagy (1996) is in the same range as these respiration estimates. A third explanation is that estimates of respiration made using oxygen bottles have been repeatedly shown to underestimate metabolism (Kemp and Boynton, 1980). It is likely that each of these explanations is correct to some extent.

9.6.3.4. Net Daytime Production (Pa^*)

The period of net autotrophic production ("Day" in Table 9-4.) ranged in duration from 30 minutes to nearly the entire daytime period. Pa^* varied between 0.39 and 9.46 g O_2 m^{-3} day^{-1} and averaged 3.45 g O_2 m^{-3} day^{-1} (Table 9-4.). Net daytime production was highly variable from day to day (Figure 9-4.) and was highest during July and August. Like respiration, daytime net production was positively related to water temperature (Figure 9-5.b.). However, an analysis of model residuals shows that the model relating the log of net production to water temperature fails to predict either the highest occurrences of net production or the lowest. However, no additional variability could be explained by including daily integrated photosynthetically active radiation (PAR), daily mean river flow, wind speed, or any of several parameters expressing either river flow or log river flow levels lagged by several days. On 9 occasions during the record, net production was especially high (Figure 9-4.) due to an unknown factor, combination of factors or sequence of events that can generate high net production, but only for very short periods of time.

The net production estimates compared reasonably well with estimates from oxygen bottle studies in the middle Chesapeake Bay (Smith and Kemp, 1995) if the photic depth was assumed to be several meters for the purpose of converting areal units to per volume units.

9.6.3.5. Gross Production (Pg^*)

Gross production (Pg^*) averaged 7.35 g O_2 m^{-3} day^{-1} and reached a maximum of 16.02 g O_2 m^{-3} day^{-1} (Table 9-4.). Due to uncertainty in the component parameter estimates and other sources of error, the minimum observed value was less than zero. Since this estimate is invalid, the true parameter value must be very small, perhaps near zero. Gross production is related to water temperature (Figure 9-5.), as would be expected; however, significant additional variability can be explained by adding PAR into a multiple regression with the log of gross production as the dependent variable ($r^2 = 0.60$; Figure 9-6.). Interestingly, the significant relationship between gross production and PAR appears to result from the sum of separate but weak effects of PAR distributed over net production and respiration. This suggests the high PAR enhances overall metabolic activity, but that production and respiration are often coupled on short time scales. In fact, Figure 9-4. shows that net production was never sustained at its highest levels for more than one day, while gross production remained at its peak levels for two or more consecutive days on 5 separate occasions. An explanation for this is that high net production requires a decoupling of gross production and respiration, which is not likely to persist. In contrast, high gross production requires simply a high level of metabolic activity, which can clearly be sustained in Patuxent River for longer periods of time.

As with net production, the model for gross production never predicts levels of gross production as high as those observed in the data and overestimates gross production at intermediate levels (Figure 9-6.). This indicates the need for additional explanatory variables or perhaps a change in the functional form of the relationship with water temperature or PAR.

9.6.3.6. Relationship of Metabolism Estimates to Historical Values

These estimates of metabolic parameters can best be compared to those of Sweeney (1995) because the same open water method was used in both studies and the parameter definitions are identical (Figure 9-7.). Each parameter was substantially greater in 1992 than in 1964, which Sweeney attributed to increasing nutrient loading. In 1996, each parameter was lower than in 1992 but higher than in 1964. A number of factors could explain this observation; however, there is no reason to believe that nutrient loading declined (the loading estimates are not yet available). A likely explanation for the decrease in metabolism relative to 1992 is that high river flow in 1996 lowered the standing stock of planktonic organisms. It is also possible that turbidity decreased the *in situ* irradiance, decreasing the overall metabolic activity. An additional observation of interest is that the relative magnitude of daytime apparent production (Pa^*) and night time respiration (Rn) changed between 1964 and 1992 or 1996. In fact, Pa^*/Rn changed from less than 1 to greater than one. This probably reflects an increase in the ratio of inorganic nutrient loading to organic matter loading. The causes and significance of this change are a matter for further investigation.

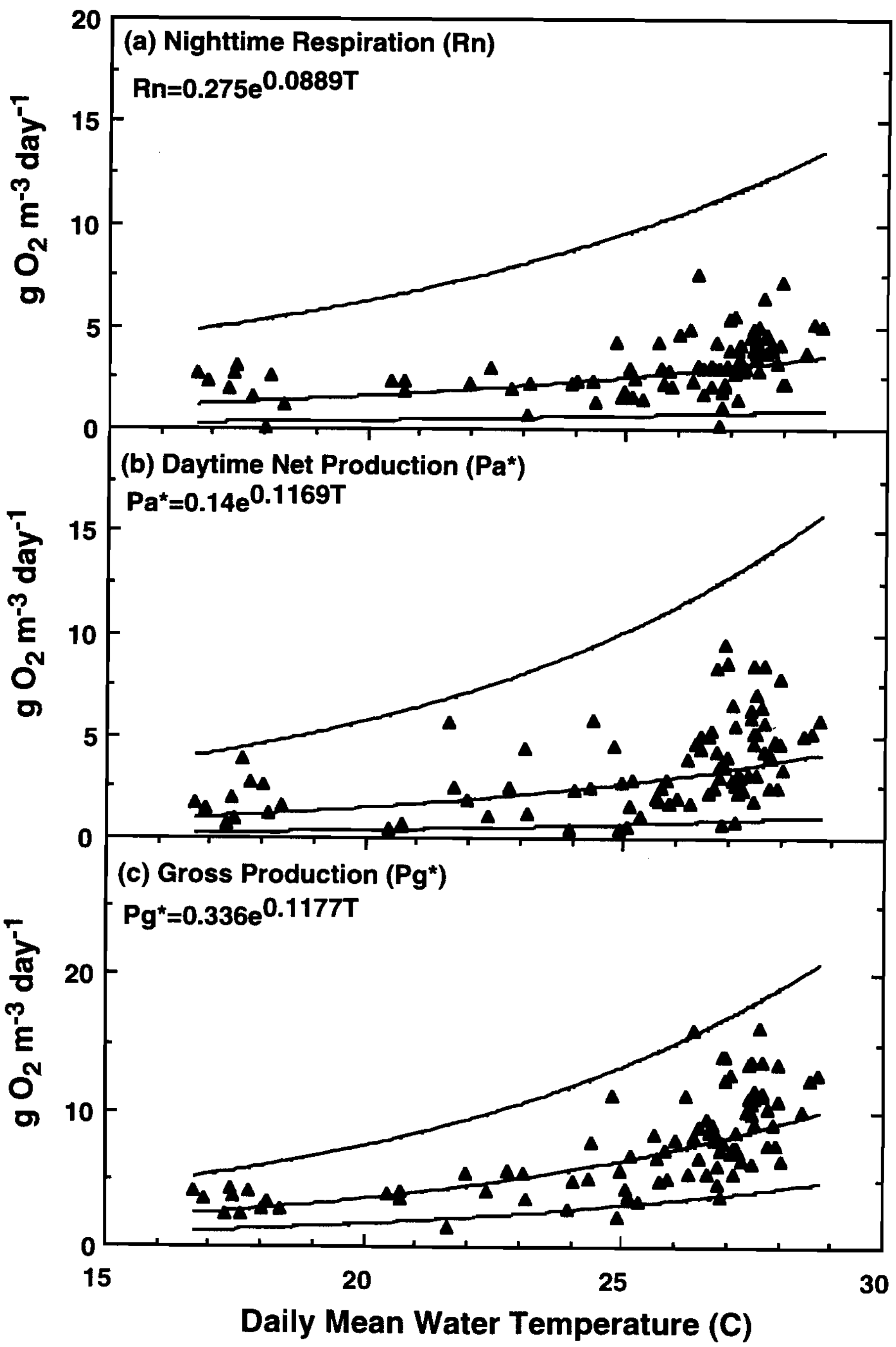


Figure 9-5. The relationship between daily mean water temperature and Rn (a), Pa* (b) and Pg* (c) at Benedict Bridge.
An Arrhenius function has been fitted to the data assuming lognormal multiplicative errors. The three lines in each graph are the predicted values and the upper and lower bounds of the 95% prediction interval.

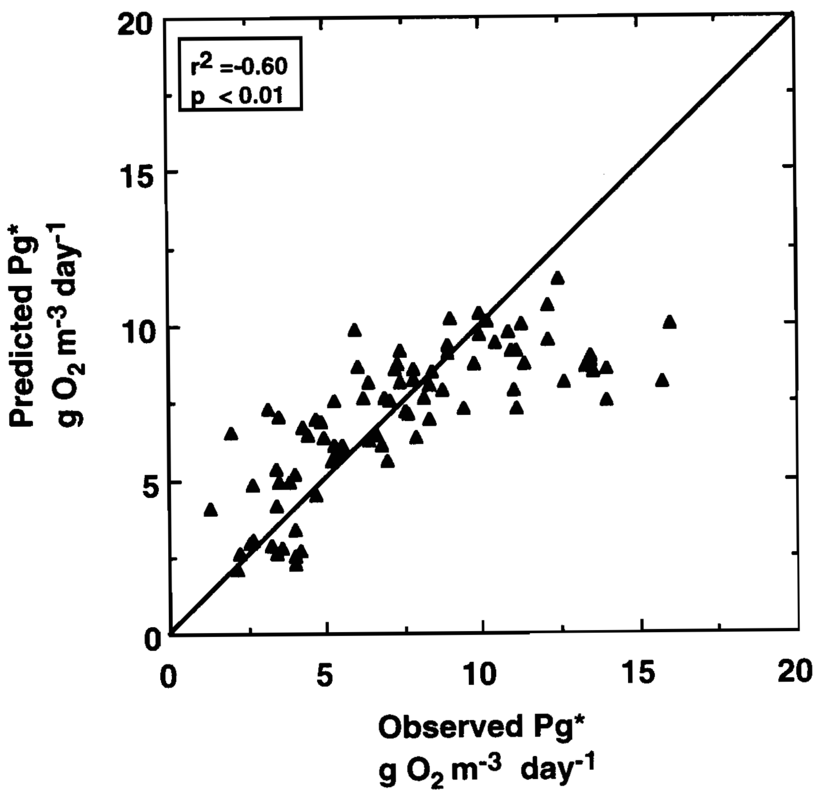


Figure 9-6. Observed gross prediction versus gross production predicted by a multiple regression of the log of the gross production on water temperature and photosynthetically active radiation (PAR).

The line is a 1:1 reference line.

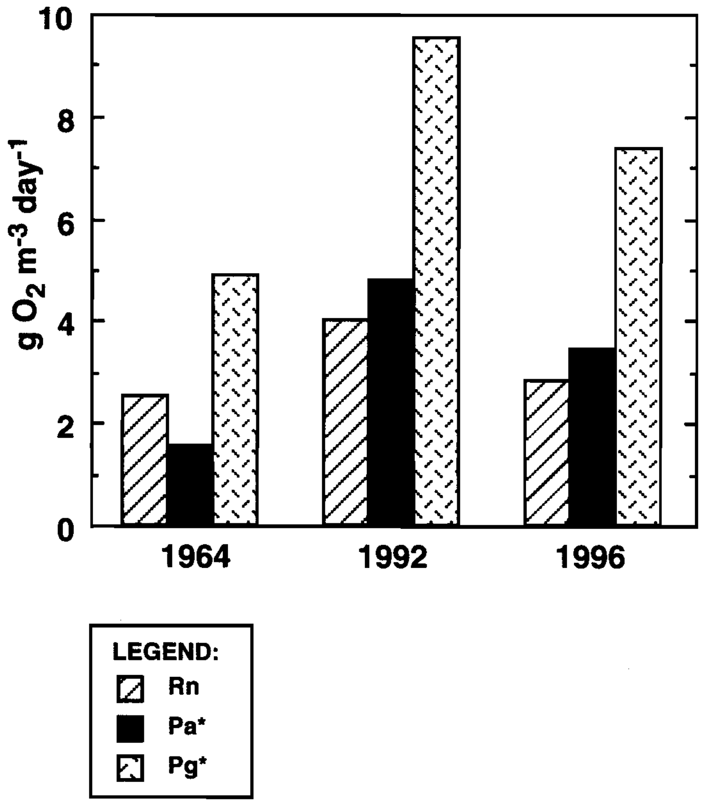


Figure 9-7. Summer average nighttime respiration (Rn), daytime net production (Pa*) and gross production (Pg*) estimates for Benedict Bridge from Sweeney (1995) for 1964 and 1992 and from 1996.

The definition of Pg for this study is equivalent to Pg in Sweeney (1995).*

10. RECONSTRUCTING PATUXENT RIVER FLOW AND NUTRIENT LOADS

10.1 Background and Approach

One of the primary goals of the Chesapeake Bay Program is to reduce nutrient loads to the Bay and tributary rivers. This is an ambitious task but despite myriad problems progress has been made and in some areas the progress has been very considerable (e.g. Patuxent River estuary). Because nutrient load reduction is difficult, it is of particular utility to have some estimates of loading rates during times when estuarine water quality and habitat conditions were more pristine and to use those rates as one of several guides in deciding how much future nutrient load reduction is appropriate.

Several nutrient load estimates have been produced for the Patuxent River and there has been a continuing evaluation of loads conducted on a routine basis since 1984 (USGS Fall line Monitoring Program). The data collected since 1984 were used in conjunction with previously collected water quality data to hind cast fall line loads back to 1978. Thus, from 1978 through 1996 there are very good estimates of load available. Domotor *et al.* (1989) also gathered available information concerning sewage treatment plant discharges both above and below the fall line beginning in 1960. Point source TN loads were found to be very small in the early 1960's ($\sim$200 kg day^{-1}) but increased to about 2500 kg day^{-1} by the mid-1980's. Point source TP loads exhibited a similar sharp rise (50 kg day^{-1} in 1963 to 500 kg day^{-1} in 1980) but thereafter decreased very sharply due to management actions. However, Domotor *et al.*(1989) did not attempt a reconstruction of diffuse source loads at the fall line for years prior to 1978. Jaworski *et al.* (1992) estimated annual TN and TP loads for 1963 and 1969-1971 and these amounted to about 2500-3000 kg N day^{-1} and 500-700 kg P day^{-1}, respectively. More recently, Boynton *et al.* (1995) constructed TN and TP budgets for the Patuxent River which also included an estimate of pristine condition loads (early 1600's) which were found to be about 5 and 20 times lower for TN and TP loads, respectively, than loads measured for the mid-1980's. Unlike so many other estuarine systems, there are data available to make at least reasonable approximations of loads in the Patuxent for earlier time periods and these estimates all indicate that loads increased markedly until recent years when management actions have reversed this trend.

The specific goal of this section of the report is to present results of efforts to reconstruct monthly TN and TP load estimates at the Patuxent fall line (Bowie, MD) for the period 1960-1977. The basic approach was to (1) use rainfall data to reconstruct river flow at the fall line and (2) use both nutrient concentration data collected at the fall line during the 1960's and 1970's (of which little was available) and concentrations which were backcasted from more recent measurements. The monthly concentration and flow data were combined to yield load estimates. This time period (1960's and early 1970's) was selected because there are data available from the estuary which indicate that seagrasses were abundant, low dissolved oxygen conditions in deep waters rare or nonexistent and patterns of community production and respiration similar to those observed in non-eutrophic systems. Thus, nutrient loads reconstructed for this period will provide a first estimate of the general magnitude of loads associated with an estuary which was in good condition.

10.2 Reconstructing River Flow

River flow data were not collected regularly at the USGS Bowie, MD gauge on the Patuxent River prior to 1977, so it was necessary to estimate flow rates for the period 1960 through 1977 using data from the Laurel, MD gauge, which is 21 miles upstream from Bowie. Concurrent daily flow data for the period 1977 through 1995 were used to derive an empirical function which could be applied to the earlier data from the Laurel gauge. While daily flow data were used for modeling, the data were later combined into monthly means, the time scale of interest.

The flow at Laurel is strongly regulated by a dam, while the flow at Bowie includes a larger unregulated component. This causes the Laurel flow to not reflect short time-scale flow variations, which is not a problem for the present purposes, but also causes the flow to reflect seasonal reservoir level management to a greater extent than the Bowie flow rate. To correct for the latter problem, the month of the year was introduced into the model as a discrete variable. Thus, the estimated flow at Bowie, Q_B on a day which occurred during the i^{th} month of the year is , where a is the slope of the response to the flow rate at Laurel, Q_L is the flow rate at Laurel and C_i is the effect due to the month i. This is a linear regression where the intercept is different for each month. The model predicts 54% of the daily variability, reflecting the lack of ability of the highly regulated flow at Laurel to predict daily fluctuations; however, the model predicted 90% of the variability in the monthly mean flows. Since these were the flow rates of interest, the model is sufficient. Estimated monthly flows are provided in Table 10.1.

10.3 Estimating Nutrient Concentrations at the Patuxent Fall line (Bowie, MD)

Estimating nutrient concentrations at the fall line is by far the most uncertain component of this analysis. The fundamental reason for this uncertainty is the fact that reliable measurements of concentrations of the appropriate variables are very scarce for the time periods of interest. Water quality reports concerning the Patuxent River were reviewed for the period 1960 - 1977 to obtain information; a number of individuals were interviewed (J. A. Mihursky, Chesapeake Biological Laboratory; James Allison, MD Dept Nat Res, Retired; Sherman Garrison, MD Dept Nat Res) to find if we had overlooked some data from this time period; the EPA-Chesapeake Bay Program historical data set was inspected (Marcia Olsen, *pers. comm.*); the water treatment plant staff at Bowie were consulted for water quality records. The end result of considerable effort was that we were not able to obtain concentration measurements for appropriate variables (TN, TP, NH_4^+, NO_2^- + NO_3^-, DIP) prior to 1967 and the data record between 1967 and 1977 was, at best, poor.

While using actual measurements of concentration at the fall line, coupled with flow measurements, would be the preferred method for estimating load, we were forced to adopt an alternative approach for estimating concentrations for the 1960-1977 period. Our approach involved the following: (1) monthly fall line load estimates from 1977 - 1991 were divided by concurrent monthly flows at the fall line yielding concentration values; (2) these concentration values (TN, TP, NH_4^+, NO_2^- + NO_3^-, DIP) were then added to a data set of concentration measurements for the period prior to 1978 (an incomplete data set with a great many missing values and no values prior to 1967) and the full concentration data set examined as a function of time (i.e. concentration plotted against the month of measurement); (3) all variables exhibited decreasing concentrations in recent years (post 1989) and several (TN and NO23) decreasing trends back in time preceding maximum concentrations in the late 1980's; (4) TN and NO23 concentrations were replotted as a function of time for each month (i.e. January data for the period 1967-1988 versus year of measurement) and linear regression models fitted to the data; (5) these models were then used to predict concentrations (for each month of the year) for each year between 1960 and 1977 (an example is provided in Figure 10-1.); (6) for those months in which the regression model was not significant, the concentration from the year closest to 1960 was used for that month in all subsequent years up to 1977 (Figure 10-1.).

10.4 Nutrient Load Characteristics: 1985-1995

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 10-2. for the period 1985 - 1995. 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 1995. 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.

10.5 Reconstructed Nutrient Loads: 1960-1977

Average monthly river flow rates were multiplied by estimated monthly concentration and monthly load estimates derived for TN and TP for the period 1960 - 1977 (Figure 10-3. and Table 10.1). Loads ranged between 146 kg N day^{-1} and 10,301 kg N day^{-1} for TN and from 41 kg P day^{-1} to 1411 kg P day^{-1} for TP. In general, loads were lower than those observed during the 1970's and mid-1980's. The effect of storms such as Tropical Storm Agnes in June, 1972 are clearly indicated. In part, the lower loads of the 1960's resulted because there were fewer sewage treatment plants in operation during this period but also because river flows were uniformly low during this period indicating lower diffuse source loading. During the decade of the 1960's TN and TP annual fall line loads averaged about 1300 kg N day^{-1} and 275 kg P day^{-1}, respectively; during the decade of the 1970's TN and TP annual fall line loads averaged about 3000 kg N day^{-1} and 450 kg P day^{-1}, respectively; during the decade of the 1980's TN and TP annual fall line loads averaged about 4500 kg N day^{-1} and 400 kg P day^{-1}, respectively, and during the first half of the 1990's, TN and TP annual fall line loads averaged about 3300 kg N day^{-1} and 190 kg P day^{-1}, respectively (Figure 10-4.).

10.6 Unresolved Problems and Future Activities

There is a certain amount of uncertainty associated with both components (flow and concentration) used in making these estimates. Since the monthly correlation between rainfall and flow is so high (>0.90) it is doubtful that improvements in this component will greatly change the results. The same is not true for the concentration estimates. However, several things can be done to possibly improve these estimates. First, there may still be some data available for the 1960's which we have not yet uncovered; we intend to continue searching until we are satisfied that all possible sources have been examined. Second, for several months we did not find a concentration versus time relationship and in these cases we used the concentration nearest to 1960 that was available. In all instances these concentrations were considerably higher than those used for adjacent months which were based on regression models. Our intuition suggests that the former concentrations are overestimates, especially in years close to 1960. To improve these concentration estimates we plan to investigate the possibility of using seasonally averaged data (e.g. winter month concentrations versus time) for computing loads.

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977.
Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	Predicted River Flow at Bowie, MD (cfs)	Estimated Total Nitrogen Concentration (mg N l^{-1})	Estimated Total Nitrogen Load (Kg N day^{-1})	Estimated Total Phosphorus Concentration (mg N l^{-1})	Estimated Total Phosphorus Load (Kg N day^{-1})
1960	1	284	2.0	1388	0.30	208.2
1960	2	477	0.8	935	0.50	583.5
1960	3	484	0.8	899	0.80	947.6
1960	4	494	3.0	3623	0.41	495.1
1960	5	428	0.4	429	0.06	62.8
1960	6	237	2.6	1506	0.25	144.9
1960	7	154	1.1	432	0.40	150.9
1960	8	135	2.0	652	0.35	116.0
1960	9	136	0.7	218	0.25	83.0
1960	10	163	0.4	146	0.90	359.0
1960	11	230	2.9	1634	0.48	270.5
1960	12	262	1.8	1122	0.30	192.4
1960	**Average**	**290**	**1.5**	**1082**	**0.42**	**301.1**
1961	1	283	2.0	1385	0.30	207.8
1961	2	654	0.9	1446	0.50	799.6
1961	3	593	0.9	1258	0.80	1160.2
1961	4	641	3.0	4703	0.41	642.8
1961	5	494	0.5	652	0.06	72.5
1961	6	313	2.6	1991	0.25	191.4
1961	7	225	1.3	710	0.40	219.9
1961	8	135	2.1	692	0.35	115.2
1961	9	135	0.8	277	0.25	82.3
1961	10	162	0.6	219	0.90	357.0
1961	11	241	2.9	1707	0.48	282.6
1961	12	263	1.8	1124	0.30	192.8
1961	**Average**	**345**	**1.6**	**1347**	**0.42**	**360.3**
1962	1	285	2.0	1395	0.30	209.3
1962	2	308	1.0	758	0.50	376.3
1962	3	559	1.0	1334	0.80	1093.4
1962	4	479	3.0	3512	0.41	480.0
1962	5	350	0.7	574	0.06	51.4
1962	6	231	2.6	1470	0.25	141.3
1962	7	155	1.4	545	0.40	151.8
1962	8	137	2.2	751	0.35	117.7
1962	9	132	1.0	332	0.25	80.9
1962	10	162	0.7	293	0.90	356.3
1962	11	228	2.9	1621	0.48	268.3
1962	12	262	1.8	1122	0.30	192.3
1962	**Average**	**274**	**1.7**	**1142**	**0.42**	**293.3**

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977. (Continued). Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	River Flow at Bowie, MD (cfs)	Total Nitrogen Concentration (mg N l^{-1})	Total Nitrogen Load (Kg N day^{-1})	Total Phosphorus Concentration (mg N l^{-1})	Total Phosphorus Load (Kg N day^{-1})
1963	1	284	2.0	1388	0.30	208.2
1963	2	309	1.1	839	0.50	377.5
1963	3	305	1.1	808	0.80	596.1
1963	4	272	3.0	1997	0.41	273.0
1963	5	287	0.8	563	0.06	42.2
1963	6	226	2.6	1438	0.25	138.3
1963	7	158	1.6	610	0.40	154.4
1963	8	135	2.4	783	0.35	115.8
1963	9	133	1.2	393	0.25	81.3
1963	10	161	0.9	364	0.90	353.7
1963	11	227	2.9	1610	0.48	266.5
1963	12	263	1.8	1127	0.30	193.3
1963	**Average**	**230**	**1.8**	**993**	**0.42**	**233.3**
1964	1	359	2.0	1757	0.30	263.5
1964	2	436	1.2	1295	0.50	533.3
1964	3	494	1.2	1441	0.80	967.0
1964	4	436	3.0	3198	0.41	437.0
1964	5	348	0.9	793	0.06	51.1
1964	6	221	2.6	1407	0.25	135.2
1964	7	155	1.7	655	0.40	151.8
1964	8	135	2.5	826	0.35	115.6
1964	9	132	1.4	448	0.25	80.6
1964	10	159	1.1	433	0.90	350.4
1964	11	223	2.9	1580	0.48	261.6
1964	12	260	1.8	1114	0.30	190.9
1964		**280**	**1.9**	**1245**	**0.42**	**294.8**
1965	1	285	2.0	1393	0.30	208.9
1965	2	312	1.3	1005	0.50	381.5
1965	3	381	1.3	1212	0.80	745.4
1965	4	379	3.0	2781	0.41	380.1
1965	5	287	1.1	746	0.06	42.2
1965	6	222	2.6	1415	0.25	136.0
1965	7	155	1.9	707	0.40	151.3
1965	8	136	2.6	877	0.35	116.6
1965	9	135	1.6	520	0.25	82.7
1965	10	178	1.3	566	0.90	392.4
1965	11	228	2.9	1616	0.48	267.4
1965	12	257	1.8	1099	0.30	188.4
1965	**Average**	**246**	**1.9**	**1161**	**0.42**	**257.7**

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977. (Continued). Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	River Flow at Bowie, MD (cfs)	Total Nitrogen Concentration (mg N l^{-1})	Total Nitrogen Load (Kg N day^{-1})	Total Phosphorus Concentration (mg N l^{-1})	Total Phosphorus Load (Kg N day^{-1})
1966	1	278	2.0	1358	0.30	203.8
1966	2	302	1.4	1051	0.50	369.8
1966	3	297	1.4	1023	0.80	581.2
1966	4	263	3.0	1932	0.41	264.0
1966	5	282	1.2	822	0.06	41.4
1966	6	218	2.7	1415	0.25	133.5
1966	7	149	2.0	732	0.40	145.3
1966	8	125	2.8	848	0.35	107.3
1966	9	122	1.8	526	0.25	74.9
1966	10	156	1.5	567	0.90	343.8
1966	11	223	2.9	1579	0.48	261.3
1966	12	257	2.8	1760	0.30	188.6
1966	**Average**	**223**	**2.1**	**1135**	**0.42**	**226.2**
1967	1	278	2.0	1360	0.30	204.1
1967	2	303	1.5	1130	0.50	370.7
1967	3	575	1.5	2134	0.80	1125.6
1967	4	301	3.0	2212	0.41	302.4
1967	5	371	1.3	1200	0.06	54.5
1967	6	216	2.7	1400	0.25	132.1
1967	7	148	2.2	782	0.40	144.8
1967	8	281	2.9	1996	0.35	240.9
1967	9	178	1.9	843	0.25	108.6
1967	10	156	1.7	637	0.90	343.1
1967	11	222	2.9	1578	0.48	261.2
1967	12	322	1.8	1378	0.30	236.3
1967	**Average**	**279**	**2.1**	**1388**	**0.42**	**293.7**
1968	1	559	2.0	2734	0.30	410.0
1968	2	328	1.6	1306	0.50	401.3
1968	3	424	1.6	1687	0.80	830.6
1968	4	316	3.0	2318	0.41	316.8
1968	5	328	1.5	1165	0.06	48.2
1968	6	305	2.6	1939	0.25	186.4
1968	7	187	2.3	1054	0.40	182.9
1968	8	143	3.0	1061	0.35	122.5
1968	9	141	2.1	733	0.25	86.4
1968	10	168	1.9	765	0.90	370.8
1968	11	233	2.9	1650	0.48	273.1
1968	12	266	1.8	1140	0.30	195.5
1968	**Average**	**283**	**2.2**	**1463**	**0.42**	**285.4**

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977. (Continued). Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	River Flow at Bowie, MD (cfs)	Total Nitrogen Concentration (mg N l^{-1})	Total Nitrogen Load (Kg N day^{-1})	Total Phosphorus Concentration (mg N l^{-1})	Total Phosphorus Load (Kg N day^{-1})
1969	1	288	2.0	1411	0.30	211.6
1969	2	313	1.7	1324	0.50	382.7
1969	3	308	1.7	1305	0.80	602.3
1969	4	276	3.0	2028	0.41	277.2
1969	5	292	1.6	1131	0.06	42.9
1969	6	228	2.6	1447	0.25	139.2
1969	7	156	2.4	936	0.40	152.9
1969	8	140	3.2	1082	0.35	119.6
1969	9	133	2.3	747	0.25	81.1
1969	10	163	2.0	817	0.90	359.8
1969	11	232	2.9	1648	0.48	272.7
1969	12	266	1.8	1138	0.30	195.1
1969	**Average**	**233**	**2.3**	**1251**	**0.42**	**236.4**
1970	1	284	2.0	1390	0.30	208.5
1970	2	367	1.8	1645	0.50	448.6
1970	3	371	1.8	1672	0.80	726.2
1970	4	620	3.0	4551	0.41	622.0
1970	5	485	1.7	2033	0.06	71.2
1970	6	287	2.6	1828	0.25	175.7
1970	7	333	2.6	2116	0.40	326.3
1970	8	155	3.3	1250	0.35	132.7
1970	9	149	2.5	908	0.25	91.3
1970	10	177	2.2	963	0.90	388.7
1970	11	230	2.9	1632	0.48	270.1
1970	12	262	1.8	1122	0.30	192.3
1970	**Average**	**310**	**2.4**	**1759**	**0.42**	**304.5**
1971	1	285	2.0	1394	0.30	209.1
1971	2	919	1.9	4353	0.50	1123.8
1971	3	523	2.0	2497	0.80	1024.2
1971	4	353	3.0	2588	0.41	353.6
1971	5	478	1.8	2154	0.06	70.1
1971	6	306	2.6	1944	0.25	186.9
1971	7	231	2.7	1548	0.40	226.1
1971	8	506	3.4	4247	0.35	433.1
1971	9	815	2.7	5326	0.25	498.4
1971	10	436	2.4	2580	0.90	961.0
1971	11	545	2.9	3864	0.48	639.5
1971	12	495	1.8	2118	0.30	363.1
1971	**Average**	**491**	**2.4**	**2884**	**0.42**	**507.4**

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977. (Continued). Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	River Flow at Bowie, MD (cfs)	Total Nitrogen Concentration (mg N l^{-1})	Total Nitrogen Load (Kg N day^{-1})	Total Phosphorus Concentration (mg N l^{-1})	Total Phosphorus Load (Kg N day^{-1})
1972	1	498	2.0	2435	0.30	365.3
1972	2	846	2.0	4224	0.50	1035.3
1972	3	721	2.1	3629	0.80	1410.6
1972	4	781	3.0	5730	0.41	783.1
1972	5	661	2.0	3189	0.06	97.0
1972	6	1619	2.6	10301	0.25	990.5
1972	7	570	2.9	4022	0.40	557.9
1972	8	207	3.6	1805	0.35	177.2
1972	9	148	2.9	1030	0.25	90.2
1972	10	174	2.6	1105	0.90	382.1
1972	11	424	2.9	3007	0.48	497.6
1972	12	738	1.8	3158	0.30	541.4
1972	**Average**	**615**	**2.5**	**3636**	**0.42**	**577.3**
1973	1	527	2.0	2580	0.30	387.1
1973	2	744	2.1	3903	0.50	910.7
1973	3	564	2.2	2992	0.80	1104.6
1973	4	899	3.0	6595	0.41	901.4
1973	5	657	2.1	3380	0.06	96.4
1973	6	385	2.6	2450	0.25	235.6
1973	7	300	3.0	2220	0.40	293.1
1973	8	150	3.7	1355	0.35	128.2
1973	9	157	3.0	1168	0.25	96.1
1973	10	179	2.8	1221	0.90	394.0
1973	11	239	2.9	1697	0.48	280.9
1973	12	510	1.8	2184	0.30	374.4
1973	**Average**	**443**	**2.6**	**2645**	**0.42**	**433.5**
1974	1	537	2.0	2626	0.30	394.0
1974	2	404	2.2	2221	0.50	494.4
1974	3	411	2.3	2290	0.80	805.3
1974	4	588	3.0	4316	0.41	589.8
1974	5	347	2.2	1894	0.06	50.9
1974	6	292	2.6	1859	0.25	178.7
1974	7	169	3.2	1314	0.40	165.6
1974	8	144	3.8	1349	0.35	123.2
1974	9	191	3.2	1502	0.25	116.6
1974	10	174	3.0	1270	0.90	384.1
1974	11	235	2.9	1670	0.48	276.4
1974	12	273	1.8	1169	0.30	200.4
1974	**Average**	**314**	**2.7**	**1957**	**0.42**	**314.9**

Table 10-1. Historical estimates of monthly river flow, TN and TP concentrations and TN and TP loads at the fall line (Bowie, MD) of the Patuxent River for the period 1960 - 1977. (Continued). Details concerning estimation techniques are provided in the text. The loads reported here include above fall line point source loads reflected in TN and TP concentrations (i.e. point source loads were not independently estimated). Point source loads below the fall line were quite small (< 400 kg N day^{-1} and > 75 kg P day^{-1}) prior to 1978.

YEAR	MONTH	River Flow at Bowie, MD (cfs)	Total Nitrogen Concentration (mg N l^{-1})	Total Nitrogen Load (Kg N day^{-1})	Total Phosphorus Concentration (mg N l^{-1})	Total Phosphorus Load (Kg N day^{-1})
1975	1	406	2.0	1985	0.30	297.8
1975	2	484	2.3	2780	0.50	591.5
1975	3	643	2.4	3747	0.80	1257.9
1975	4	480	3.0	3522	0.41	481.3
1975	5	551	2.4	3186	0.06	80.9
1975	6	278	2.6	1765	0.25	169.8
1975	7	348	3.3	2823	0.40	340.3
1975	8	143	4.0	1388	0.35	122.6
1975	9	976	3.4	8128	0.25	597.0
1975	10	404	3.2	3128	0.90	890.3
1975	11	415	2.9	2945	0.48	487.5
1975	12	410	1.8	1753	0.30	300.6
1975	**Average**	**461**	**2.8**	**3096**	**0.42**	**468.1**
1976	1	855	2.0	4182	0.30	627.3
1976	2	569	2.5	3417	0.50	696.5
1976	3	450	2.5	2742	0.80	880.3
1976	4	460	3.0	3376	0.41	461.4
1976	5	390	2.5	2382	0.06	57.3
1976	6	297	2.6	1888	0.25	181.5
1976	7	179	3.5	1516	0.40	175.1
1976	8	174	4.1	1743	0.35	148.9
1976	9	147	3.6	1293	0.25	90.1
1976	10	176	3.3	1445	0.90	388.5
1976	11	256	2.9	1819	0.48	301.0
1976	12	314	1.8	1345	0.30	230.5
1976	**Average**	**356**	**2.8**	**2262**	**0.42**	**353.2**
1977	1	312	2.0	1527	0.30	229.0
1977	2	324	2.6	2029	0.50	396.9
1977	3	354	2.6	2254	0.80	693.7
1977	4	467	3.0	3424	0.41	468.0
1977	5	315	2.6	2022	0.06	46.2
1977	6	250	2.6	1589	0.25	152.7
1977	7	178	3.6	1575	0.40	174.6
1977	8	160	4.2	1651	0.35	136.6
1977	9	143	3.8	1319	0.25	87.5
1977	10	172	3.5	1485	0.90	378.1
1977	11	237	2.9	1680	0.48	278.0
1977	12	366	1.8	1566	0.30	268.4
1977	**Average**	**273**	**2.9**	**1843**	**0.42**	**275.8**

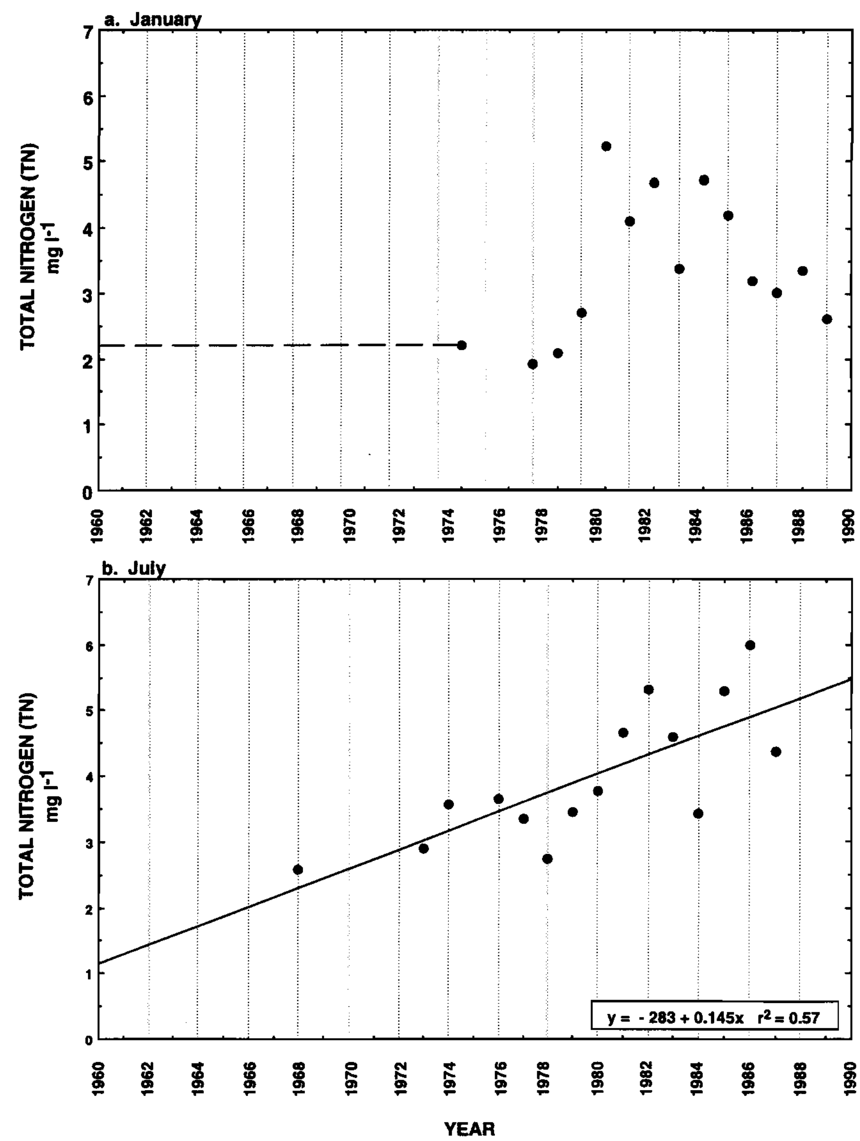


Figure 10-1. Two scatter plots of total nitrogen (TN) at the Patuxent River fall line versus year for the period 1960 - 1990.
a. January: The horizontal line indicates the concentration used for each month of January between 1960 and 1977.
b. July: The regression line indicates the concentration used for each month of July between 1960 and 1977.

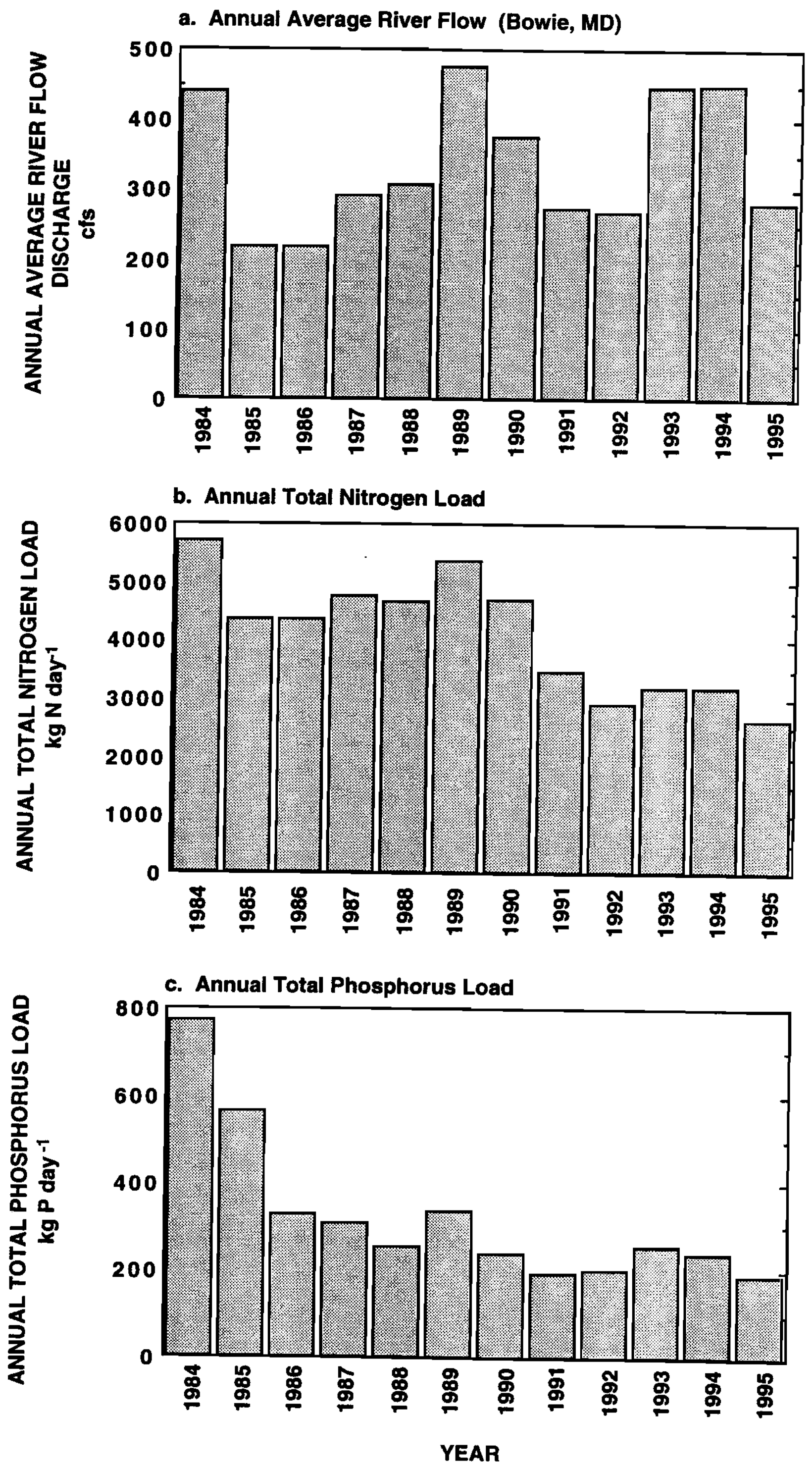


Figure 10-2. Bar graphs showing annual average river flow (measured at Bowie, MD) total nitrogen (TN) and total phosphorus (TP) loads (kg day^{-1} as N or P) for the Patuxent River estuary.
Total nitrogen (TN) and total phosphorus (TP) loads were calculated as the sum of the fall line loads plus below fall line point source loads.

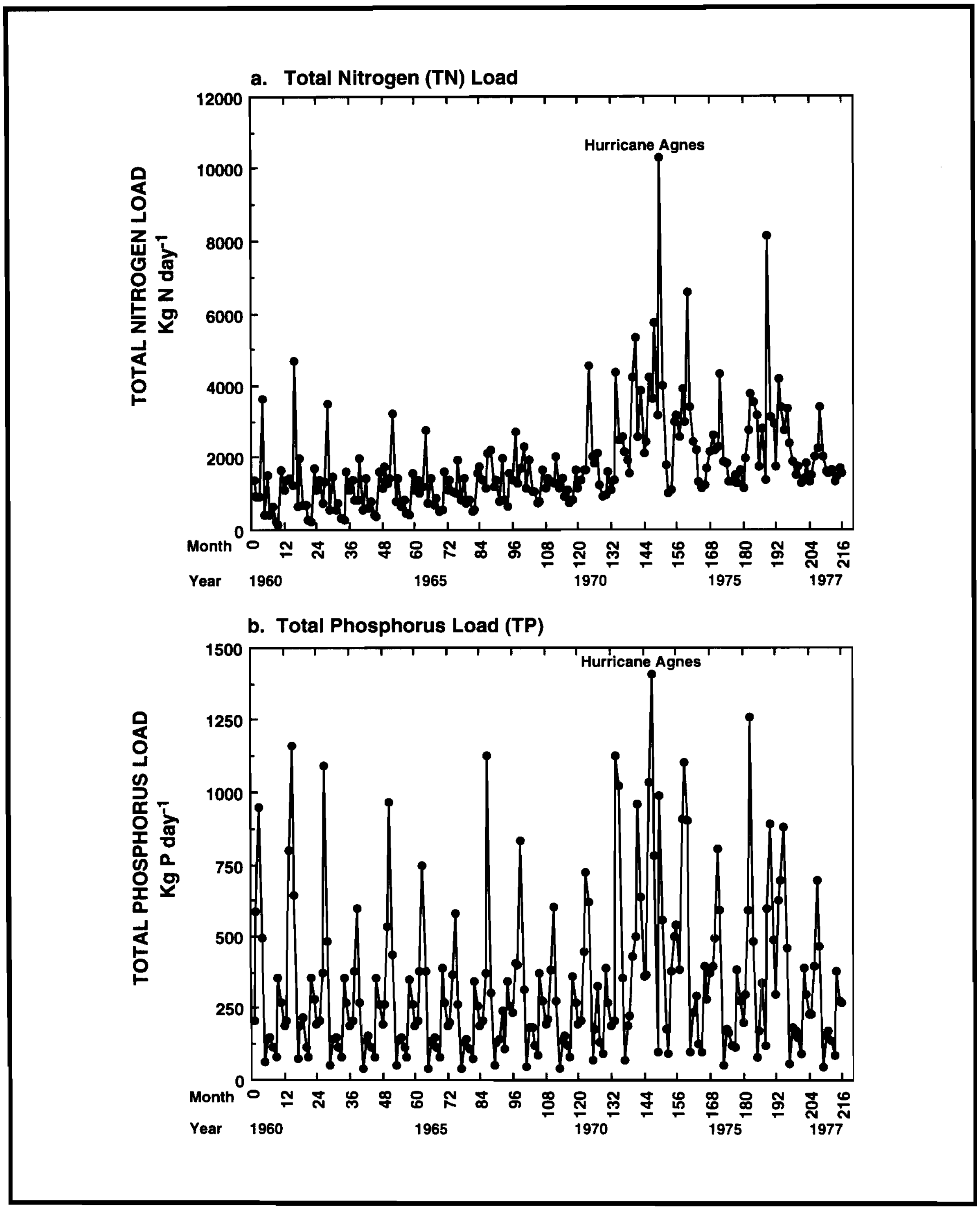


Figure 10-3. Line graphs of monthly average total nitrogen (TN) and total phosphorus (TP) loading at the fall line of the Patuxent River.
a. Total nitrogen load;
b. Total phosphorus load
Numbers along the x-axis represent months beginning with January, 1960 and ending with December, 1977. See text for details concerning calculation of loading rates.

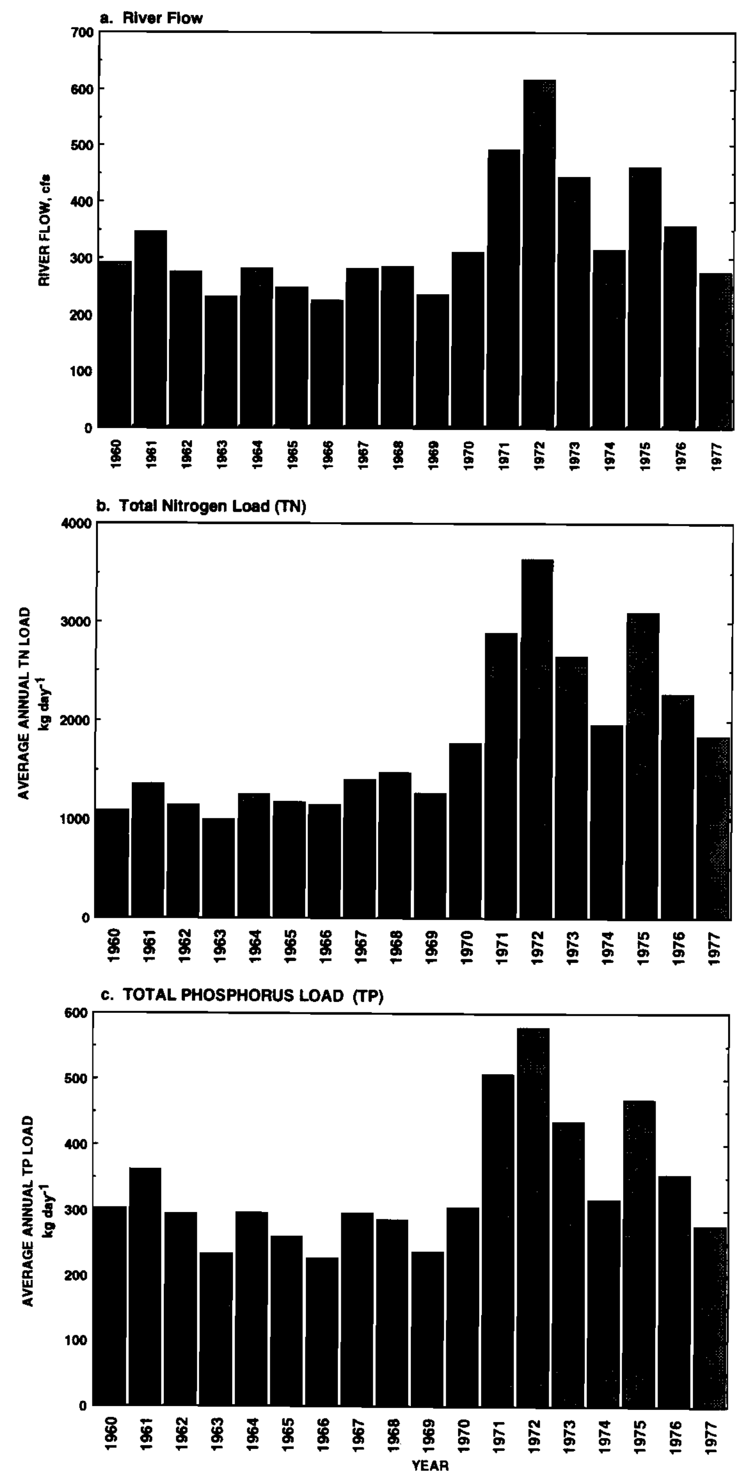


Figure 10-4. A series of bar graphs indicating:
a. Annual average river flow;
b. Average annual total nitrogen (TN) and
c. Average total phosphorus (TP) loads to the Patuxent River estuary.
See text for details concerning how these rates were estimated.

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, 1991, 1992, 1993b, 1994, 1995b and 1996) 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 associated with flood events. Both TN and TP loads during 1995 were, or were close to, the lowest on record since 1984. This inspection of loads will be extended to include 1996 data when they become available. Given the persistently very high flows during 1996, diffuse source loads were also probably elevated, at least compared to those observed during 1995

- Dissolved oxygen conditions at SONE locations in the Patuxent River were not as high as those observed during 1995 which was a low flow (and nutrient load year) year. At both the Broomes Island (BRIS) and St. Leonard Creek (STLC) locations, summer dissolved oxygen conditions were depressed early in summer but rebounded during late summer. Dissolved oxygen concentrations at the deeper stations in the mainstem bay and Potomac were very low probably reflecting the influences of high river flow.

- Ammonium (NH_4^+) fluxes at the two down river locations (STLC and BRIS) in the Patuxent River were comparable to those recorded in earlier years despite the influences of high river flows. This may be a response to nutrient load reductions. Ammonium fluxes at the upper Patuxent River stations were high, very probably in response to wet conditions. Ammonium fluxes were not large at the deeper stations. It is probable that because of high river flow some portion of the organic matter that would normally deposit at these sites was transported to more southerly portions of the bay.

- With no exceptions, fluxes of nitrate plus nitrite (NO_2^- + NO_3^-) were considerably more negative (*i.e.* directed to sediments from the water column). Positive nitrate flux (or smaller fluxes directed into sediments) is a definite sign of sediment nitrification activity which is a microbial process converting ammonium to nitrate and requires that oxygen be present. Positive nitrate fluxes are a sign of improved sediment quality. The fact that this did not occur during a year of higher than normal nutrient loading rates is another indication that bay sediments are responsive to nutrient loading rates and DO conditions. Even relatively low DO conditions in deep waters can improve water quality by decreasing sediment-water nutrient exchange rates;

these conditions were marginally achieved at several SONE stations (STLC and BRIS) in the lower Patuxent River during 1996.

- 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 which resulted during this very low flow year. The opposite condition was evident in 1996 at stations in the upper Patuxent River and several deeper sites where DO conditions were poor. 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. It should be noted that phosphorus fluxes at stations in the lower Patuxent remained relatively low despite the wet year and this may well be a reflection of the effects of TP load reductions.

- 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.

- An analysis of sediment oxygen and nutrient exchanges (SONE) data for status and trends was completed for all SONE stations. Indications of current status (average of fluxes during 1994, 1995 and 1996) were as expected; status was poor or fair in areas exposed to high rates of loading, status was poor or fair in areas with low DO levels during summer months and status was poor or fair at locations proximal to nutrient sources. At other locations status was fair to good for most flux variables. The high load years of 1994 and 1996 probably moved several status bars towards poorer conditions than would have been the case if recent river flows had been lower. There were few statistically significant trends evident at SONE stations. We conclude that nutrient load reductions have not yet been in place long enough and reductions have not been large enough to allow detection of trends in these variables.

- Results of sediment chlorophyll mapping in the Patuxent River indicated substantial month to month variability in the mass of deposited chlorophyll and in the spatial distribution of this material. During late winter chlorophyll mass was occasionally highest in shoal areas (possibly because of in-situ benthic diatom production) but was highest in deep waters during summer. Using sediment chlorophyll mass as a key variable, statistically significant regression (linear single and multiple variable models) models were developed for SOC, ammonium, phosphorus and nitrite plus nitrate fluxes. This analysis will be repeated during 1997 to confirm these relationships but the indication at this point is that these fluxes can be reasonably predicted based on a limited suite of readily measured variables.

- The Benedict Bridge high frequency sampling effort generated a nearly continuous record of salinity, water temperature and dissolved oxygen from June 1, 1996 through October 18, 1996. The high frequency sampling is important because extreme values often observed for only short periods of time may have a large ecological impact due to the non-linear nature of many biological responses. These extreme values are not likely to be observed with conventional periodic sampling and if measured may be perceived as erroneous without the context of high frequency observations. An algorithm was developed to estimate metabolic parameters such as net production and respiration using the high frequency dissolved oxygen observations. Net daytime production was in the range of 0 to 9 g O_2 m^{-3} day^{-1}, while nighttime respiration was in the range of 0 to 7.5 g O_2 m^{-3} day^{-1}. These observations indicated a generally lower level of metabolic activity than was observed in 1992, but greater than in 1964.

- Annual average Patuxent River TN and TP 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 decrease through 1995. 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.

- Average monthly load estimates derived for the period 1960 - 1977 ranged between 146 kg N day^{-1} and 10,301 kg N day^{-1} for TN and from 41 kg P day^{-1} to 1411 kg P day^{-1} for TP. In general, loads were lower than those observed during the 1970's and mid-1980's. The effect of storms such as Tropical Storm Agnes in June, 1972 are clearly indicated. In part, the lower loads of the 1960's resulted because there were fewer sewage treatment plants in operation during this period but also because river flows were uniformly low during this period indicating lower diffuse source loading. During the decade of the 1960's TN and TP annual fall line loads averaged about 1300 kg N day^{-1} and 275 kg P day^{-1}, respectively; during the decade of the 1970's TN and TP annual fall line loads averaged about 3000 kg N day^{-1} and 450 kg P day^{-1}, respectively; during the decade of the 1980's TN and TP annual fall line loads averaged about 4500 kg N day^{-1} and 400 kg P day^{-1}, respectively, and during the first half of the 1990's, TN and TP annual fall line loads averaged about 3300 kg N day^{-1} and 190 kg P day^{-1}, respectively (Figure 10-4.).

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