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**MARYLAND CHESAPEAKE BAY WATER QUALITY
MONITORING PROGRAM**

ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT NO. 15

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Summary page only - NO HARD COPY OF DATA SUBMITTED

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(SAV) HABITAT EVALUATION**

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and October 1997

PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in DNR Contract RAT-6/97-027 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 Science (UMCES).

This report contains a 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, 1997 through December 31, 1997. Work performed during calendar year 1997 includes significant modifications relative to previous years and continues to reflect the changing goals of this monitoring program as long-term data, programs and processes are evaluated.

The data tables in Appendix B, reflect efforts begun in August, 1990 to verify and standardize all EPC files. Station code names and locations used in data tables can be found in Chapter 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 have recently been diversified and now include: (1) characterization of the present state (status) of the Patuxent River relative to sediment-water nutrient and oxygen exchanges; (2) determination of long-term trends in the Patuxent River that develop in sediment-water exchanges in response to pollution control programs; (3) integration of sediment information collected in this program with other elements of the monitoring program; (4) development of a more cost-effective and spatially inclusive approach to measurement of the status and trends associated with sediment-water nutrient and oxygen exchanges; (5) evaluation of the submerged aquatic vegetation (SAV) habitat potential of the Patuxent River including water quality conditions, epiphyte growth potential and SAV propagule availability; (6) high frequency monitoring of dissolved oxygen (DO) conditions and community metabolism rates at one station in the Patuxent River and (7) reconstruction of fall line nutrient loading rates from 1960 through 1977, a period prior to the present monitoring program during which many changes in the Patuxent Basin took place.

River flow from the Patuxent Basin to the estuary in 1997 was intermediate between flows measured in 1995 (very dry year) and 1996 (very wet year) and were slightly above the 20 year average. River flows were elevated during winter-spring and again in the late fall and low during the summer months. This temporal pattern mirrored the long-term average. River flow is well correlated with fall line nutrient loading rates (which are not yet available for 1997); using flow as an index of load suggests that total nitrogen (TN) and total phosphorus (TP) loads in 1997 were also intermediate between the depressed loads of 1995 and the elevated loads of 1996.

Measurements of sediment-water nutrient, oxygen and inorganic carbon exchanges were made four times between mid-June and mid-September during 1997 at four locations in the Patuxent River (St. Leonard Creek [STLC], Broomes Island [BRIS], Marsh Point [MRPT] and Buena Vista [BUVA]). Rates of sediment oxygen consumption (SOC) were close to the long-term average at all four SONE stations; ammonium fluxes were average or enhanced (in July only) at the most up river station (Buena Vista [BUVA]), very substantially reduced at the mid-estuary stations (Marsh Point [MRPT] and Broomes Island [BRIS]) and slightly reduced at the lower river station (St. Leonard Creek [STLC]); nitrite plus nitrate fluxes did not differ markedly from the long-term average; phosphorus fluxes were average at the up river site (Buena Vista [BUVA]), much reduced at the mid-river sites (Marsh Point [MRPT] and Broomes Island [BRIS]) and remained quite low at the lower estuary site (St. Leonard Creek [STLC]). Compared to the elevated fluxes observed during high flow and nutrient load years, fluxes during 1997 were substantially reduced, especially at the mid river stations. These findings are as expected given the lower loads probably experienced during 1997. Inorganic carbon (TCO₂) fluxes (a measure of total sediment metabolic activity) appear to be positively correlated with sediment organic matter content and with nutrient loading rates. A distinctive gradient of increasing TCO₂ fluxes was evident in the Patuxent with highest fluxes proximal to nutrient and organic matter sources in the upper estuary. Fluxes at all stations were lower during 1997 than during 1996 consistent with a less nutrient-rich estuary during the most recent year.

The long-term data set (13 years) collected from 1985 through 1997 at four sediment-oxygen nutrient exchanges (SONE) stations in the Patuxent River was evaluated to determine current status and trends using methodologies developed by the monitoring program. Status of sediment-water

exchanges in the Patuxent River exhibited a large range from very poor to good; except for sediment oxygen consumption (SOC), exchange status generally degraded from the lower river to upper river. Since fluxes are ultimately regulated by the organic matter supply rate to sediments it is not surprising that nutrient fluxes were in the poor status range in the most enriched portion of the estuary. Sediment oxygen consumption (SOC) rates were in the good range in the upper estuary because the water column in this zone of the estuary is well mixed and there is almost always adequate dissolved oxygen in bottom waters to support relatively high SOC rates. There were not many significant trends (either interannual or seasonal) in sediment-water exchanges which is not surprising since there has also been considerable interannual variability in important features influencing exchanges (river flow, nutrient loading rates). However, it appears that SOC, ammonium flux and nitrite flux are all increasing at the most up river station (Buena Vista [BUVA]) and these trends are quite strong. Phosphorus flux also appears to be decreasing at one of the mid river stations (Broomes Island [BRIS]) but the statistical strength of the trend was not as strong.

A method designed to greatly increase spatial coverage of SONE measurements was initiated during 1996 and, because initial results were quite encouraging, the approach (with a few modifications) was continued during 1997. Results of sediment chlorophyll-a mapping in the Patuxent River indicated relatively small, but statistically significant, month to month variability in the mass of deposited chlorophyll-a from March through June, 1997 and then increasing mass through September. During most of the monitoring period chlorophyll mass tended to be highest in deeper areas (possibly because of particulate material focusing) and in the saltier portion of the mesohaline reach. It is in this reach that water column monitoring data indicate that spring and summer algal blooms occur with regularity. Thus, there is an emerging understanding linking production and deposition of labile organic matter in this system. For the second year, a MINI-SONE set of measurements was completed at six stations in the Patuxent River. MINI-SONE measurements are a simplification of SONE measurements (e.g. one sediment core per station) and have been added to the EPC program as an interim means of increasing the spatial extent of sediment process measurements and to assist in the development of predictive statistical models of sediment-water exchanges. MINI-SONE flux measurements made in 1997 were almost uniformly smaller in magnitude than those observed during 1996. This is consistent with current understanding of the influence of loading on sediment-water exchanges (loads were higher in 1996 than in 1997). Sediment chlorophyll-a mass was used as one of several key variables (others include sediment Eh and bottom water oxygen and nutrient concentrations), to develop statistically significant regression models (linear single and multiple variable models) for sediment oxygen consumption (SOC), ammonium, nitrite plus nitrate and phosphorus fluxes. This analysis was performed using 1996 data, repeated using 1997 data and finally using the combined 1996 and 1997 data sets. Results indicate that this approach has great merit.

A new series of monitoring activities were initiated in the Patuxent River during 1997 and these were directed at evaluating water quality and habitat conditions relative to seagrass (submerged aquatic vegetation [SAV]) growth. Included in this effort were: (1) monthly or bi-weekly measurements of water quality and light conditions at 10 littoral zone stations in the Patuxent River ranging from low salinity to mesohaline locations; (2) monthly or bi-weekly measurements of epiphyte growth potential based on deployment of artificial substrates; (3) evaluation of the degree to which water quality and light information collected from off-shore waters represented conditions in littoral areas; (4) monthly or bi-weekly measurements of SAV propagule availability based on collections made with *in-situ*

propagule traps; and (5) evaluation of short-term variability of water quality and light conditions associated with tidal stage. SAV were found at all but two of the sites during spring and very early summer; SAV disappeared from all sites by early July. SAV were not found at the site with the poorest water quality conditions (most up river site) and the site with the best water quality conditions (near Solomons Island). Most stations had some of the SAV criteria in the favorable range for some of the growing season but no station had criteria favorable for growth during all of the growing season. There were very strong seasonal changes in water quality conditions at all stations but differences among stations along this estuarine reach were not as strong as expected, except for the most up river site where water quality conditions were quite poor compared to the other nine sites. There were some notable differences between littoral and channel water quality conditions (especially for light availability and suspended solids) but similarities were more the rule than the exception. It appears that additional evaluation of this issue is needed, using data already collected rather than needing additional data collection. Temporal variability associated with tidal stage was generally small; however, variability on the time scale of days could be large and was seemingly caused by variability in weather conditions, especially wind speed and direction. Finally, epiphytic growth potential measurements yielded a wealth of data, some of which suggested potentially important factors regulating SAV recolonization and growth and some of which were compromised by technical difficulties associated with a new and developing technique. In general, epiphytic growth was relatively low during spring, very high during summer (especially at the upper river sites) and declined during fall. The nature of epiphytic fouling was complex being composed of plant, colonial animal and inorganic materials. It is also clear that epiphytic fouling rate (as measured by *in-situ* incubation of mylar™ strips) was not linearly related to time of incubation but is probably also influenced by the manner in which the strips are suspended in the water column. There seems to be little question, despite some methodological problems, that the potential for epiphytic fouling is high in most of the mesohaline region of the Patuxent River estuary during the summer period.

A time series (15 minute intervals) of temperature, salinity and dissolved oxygen measurements was continued at the lower end of the turbidity maximum zone of the Patuxent River (MD Route 231 Bridge near Benedict, MD) from May through October 1997. High frequency data at this stations are now available for 1964-1969, 1992, 1996 and 1997. The 1997 data set was analyzed for patterns of primary production, community respiration and compliance with surface water dissolved oxygen criteria. Results indicated that production and respiration rates were higher than rates measured during the mid-1960's but lower than rates observed in 1992 and 1996. This procedure adds an additional sensitive monitoring tool for gauging the recovery of the Patuxent River in response to reduced nutrient loading rates. In general dissolved oxygen levels in surface waters at this site were greater than 5 mg l⁻¹; however, concentrations lower than this were occasionally observed during summer months.

Nutrient loading rates (total nitrogen [TN] and total phosphorus [TP]) were developed for the period 1960 through 1977 for the Patuxent River at the fall line (located near Bowie, MD). These rates were estimated from historical rainfall, river flow and nutrient concentration data and from statistical modeling of more contemporary loading rates. During the decade of the 1960's TN and TP annual fall line loads averaged about 1200 kg N day⁻¹ and 275 kg P day⁻¹, respectively; during the decade of the 1970's TN and TP loads averaged about 2500 kg N day⁻¹ and 800 kg P day⁻¹, respectively; during the 1980's TN and TP loads averaged about 4500 kg N day⁻¹ and 300 kg P day⁻¹, respectively; during the first half of the 1990's TN and TP loads were about 2000 kg N day⁻¹ and 200 kg P day⁻¹,

respectively. When combined with below fall line point source loads, TN loads in the late 1970's and early 1980's reached 6000 kg N day⁻¹ in some years. The lowest recent TN loading rates occurred during 1995 and were about 2000 kg N day⁻¹. Current TP loading rates are comparable to those estimated for the 1960's when estuarine water quality and habitat conditions were reported to be quite good. Current TN loads have generally decreased during the past 8-10 years but are still about twice those estimated for the early 1960's.

2. INTRODUCTION

During the past decade much has been learned about the effects of both natural and anthropogenic nutrient inputs (*e.g.*, nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and oxygen conditions in deep waters (Nixon, 1981, 1988; Boynton *et al.*, 1982; Kemp *et al.*, 1983; D'Elia *et al.*, 1983; Garber *et al.*, 1989; 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 and algal blooms are sustained through summer and fall periods by benthic recycling of essential nutrients (3) deposition of organic matter from surface to deep waters links these processes of production and consumption, and (4) submerged aquatic vegetation (SAV) communities are responsive to water quality conditions.

2.1. 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. A portion of this newly produced organic matter sinks to the bottom, decomposes and thereby contributes to the development of anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative and large nutrient storage capacities of estuarine sediments ensure a large return flux of nutrients from sediments to the water column that can sustain continued high rates of phytoplanktonic growth and biomass accumulation. Continued growth and accumulation supports high rates of deposition of organics to deep waters, creating and sustaining hypoxic and anoxic conditions typically associated with eutrophication of estuarine systems. To a considerable extent, it is the magnitude of these processes which determines 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 are expected and 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.

Within the context of this model a monitoring study of sediment processes, water column metabolism and submerged aquatic vegetation (SAV) habitat conditions has been developed. Portions of the program have been active since 1985 (sediment processes [SONE]) while others are more recent, specifically the MINI-SONE program (1995), the high frequency monitoring program (1996) and the SAV habitat evaluation (1997). At present all activities of the EPC are focused on the Patuxent River estuary. The working hypothesis is that if nutrient and organic matter loading to this

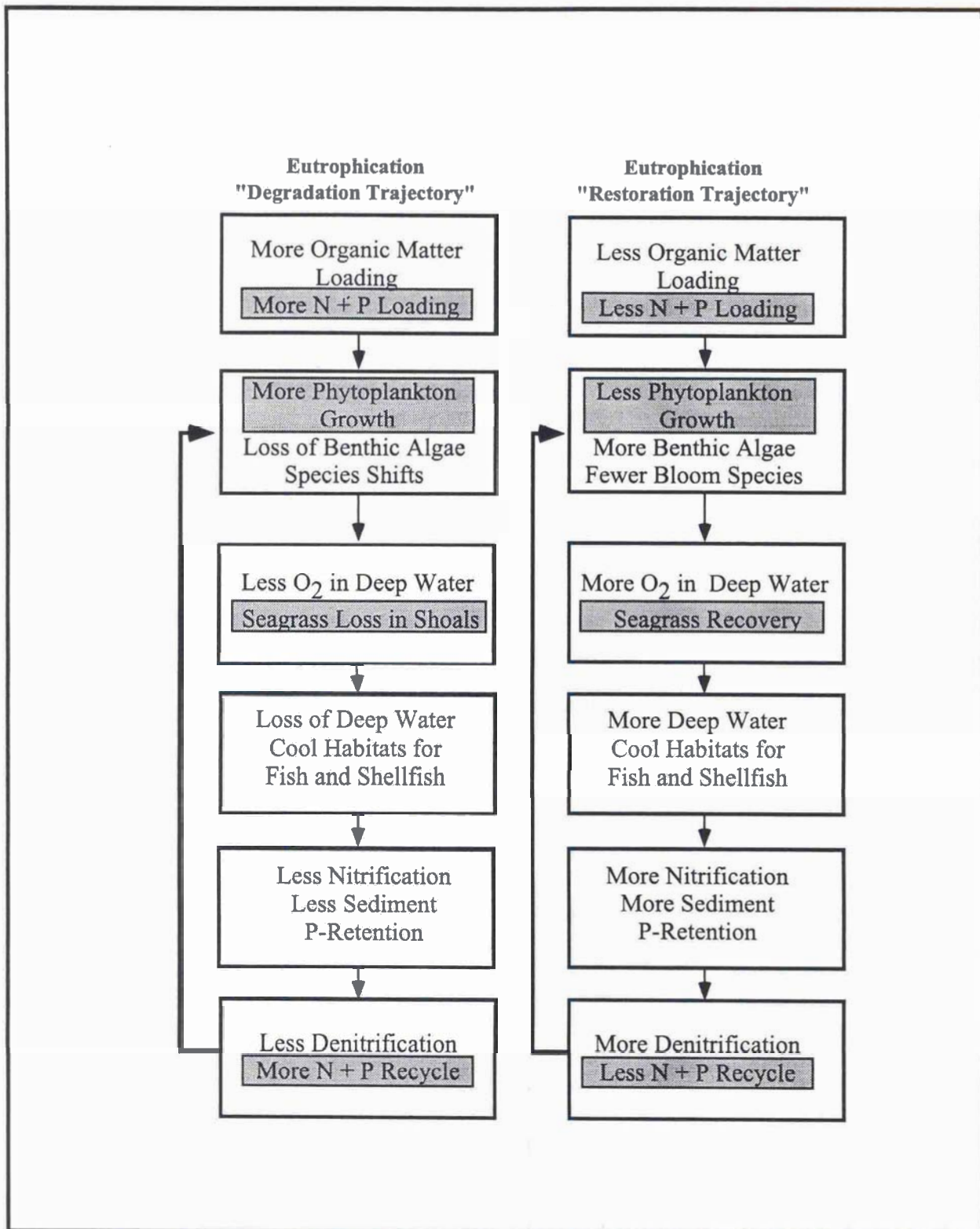


Figure 2-1. A simplified schematic diagram indicating degradation and restoration trajectories of an estuarine ecosystem. Lightly shaded boxes in the diagram indicate components of the EPC program in the Patuxent River. (Adapted from Kemp, *pers. comm.*, HPEL)

targeted estuary decrease then the cycle of deposition to sediments, sediment oxygen demand, release of sediment nutrients and continued high algal production will also decrease and the potential for SAV recolonization will increase.

2.2 Objectives of the Water Quality Monitoring Program

The Ecosystem Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program conducted monitoring of sediment oxygen and nutrient exchanges (SONE), investigated techniques to increase the spatial coverage of SONE measurements based on sediment chlorophyll-a and other bottom water quality distributions, evaluated habitat conditions relative to SAV reintroduction, conducted high frequency (daily) measurements of community metabolism and dissolved oxygen conditions and developed estimates of nutrient loading rates to this estuarine system for a 17 year period prior to the initiation of long-term monitoring programs. The Patuxent River estuary, where EPC efforts are concentrated, is an area of particular interest because substantial reductions in nutrient loading rates have been achieved in this system.

The Ecosystem Processes Component (EPC) has been modified since its inception in 1984 but the overall objectives have remained the same and are consistent with those of other Monitoring Program Components:

- Characterize the present state (status) of the Patuxent estuary (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and oxygen consumption rates and rates of sediment community metabolism.
2. Determine the long-term trends that develop in sediment-water exchanges in response to pollution control programs.
3. Develop a technique for estimating the performance of estuarine sediments which allows greater spatial resolution than is possible with current approaches.
4. Evaluate near-shore water quality conditions relative to submerged aquatic vegetation (SAV) habitat across a range of spatial and temporal scales in the Patuxent River estuary. This includes providing estimates of the relative abundance of SAV propagules in the Patuxent River estuary and an investigation of the potential for light attenuation due to epiphytic fouling of SAV leaves.
5. Continue high frequency measurements of community metabolism and dissolved oxygen characteristics at one site in the Patuxent estuary and relate these rates to nutrient load conditions and dissolved oxygen criteria, respectively.
6. Retrieve historic water quality data (nutrient concentrations) and river flows for the Patuxent River and use these data to estimate fall line total nitrogen

(TN) and total phosphorus (TP) loads on a monthly basis from 1960 through 1977. This period precedes operation of any long-term monitoring programs and includes the period immediately prior to the development of the watershed (early 1960's) through the period when land uses were changing rapidly (mid-1970's).

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

2.3 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 its 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 program 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, 1995, 1996 and 1997). 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 entered another phase of re-evaluation. Since the last evaluation, programs have collected and analyzed additional information, nutrient reduction strategies have been implemented and, in some areas, habitat improvements have been accomplished. The overall goal of the 1997 re-evaluation was the assessment of the progress of the program and the implementation of necessary modifications where needed to the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay.

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3. METHODS USED IN THE ACQUISITION OF DATA

F.M. Rohland and W.R. Boynton

3.1 CONTINUING STUDIES: SONE, MINI-SONE, SURFICIAL SEDIMENT CHLOROPHYLL-a MAPPING AND HIGH FREQUENCY MONITORING ELEMENTS

3.1.1 Location of Stations for Three Program Elements: SONE, MINI-SONE and Surficial Sediment Chlorophyll-a Mapping

3.1.1.1 Sediment Oxygen and Nutrient Exchanges (SONE) Locations

During June, July, August and September, 1997, SONE measurements were taken at four stations in one major tributary river, the Patuxent River. The locations are shown in Figure 3-1, and specific location details are given in Tables 3-1.1, 3-1.2, 3-1.3 and 3-1.4 (also EPC Data Dictionary, Boynton and Rohland, 1990; Figure B-6 and Tables B-5.2 and B-5.3). Six other SONE stations in the lower Choptank River (Horn Point [HNPT]), the Potomac River and mainstem bay region (R-64 and Point No Point [PNPT]) were not sampled during 1997.

3.1.1.2 Location of MINI-SONE Stations

MINI-SONE stations were selected from among the 37 surficial sediment chlorophyll-a mapping stations on the Patuxent River. Locations of the MINI-SONE stations were determined based on a suite of water quality and surficial sediment characteristics found at each of the chlorophyll-a mapping stations during March, April, May, 1997. These parameters included bottom water temperature, salinity, nutrient and oxygen conditions as well as surficial sediment chlorophyll-a concentrations. The MINI-SONE stations were chosen to represent the fullest possible range of sediment flux conditions found on the Patuxent River. Six stations were chosen for MINI-SONE measurements: PX07, PX15, PX21, PX23, PX25 and PX33. Five of these six stations were sampled in 1996 as part of the MINI-SONE program element, the exception was PX33 which was substituted for PX32. It was felt that during 1997 the water quality and surficial sediment parameters at PX33 better represented the range of conditions found on the Patuxent River compared to station PX32. MINI-SONE stations were sampled in June, July, August and September, 1997.

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

In the Patuxent River tributary, 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 3-2). The stations represent both a salinity and depth gradient and were

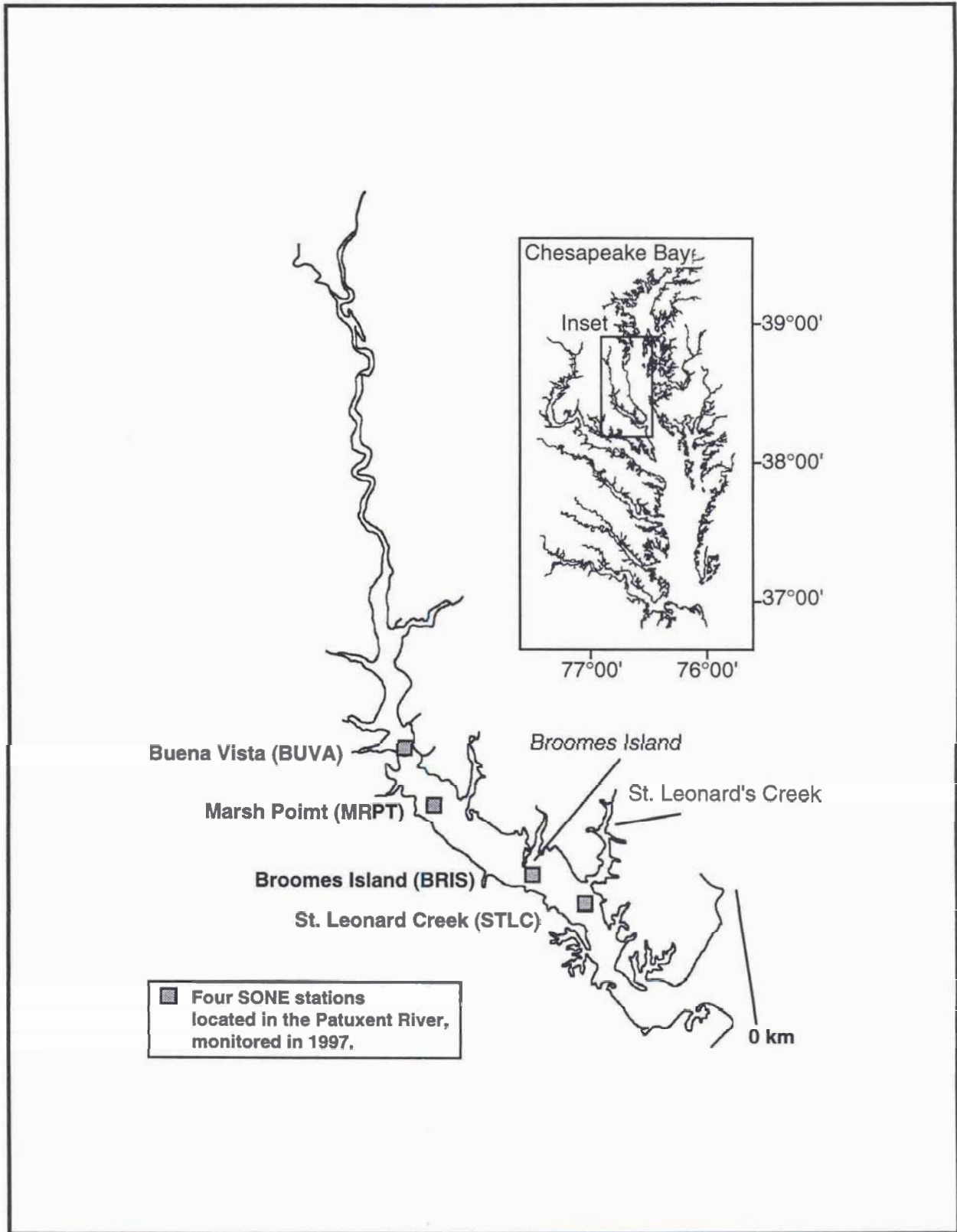


Figure 3-1. Location of four Sediment Oxygen and Nutrient Exchanges (SONE) Monitoring Stations sampled in the Patuxent River, Chesapeake Bay (1984 - 1997).

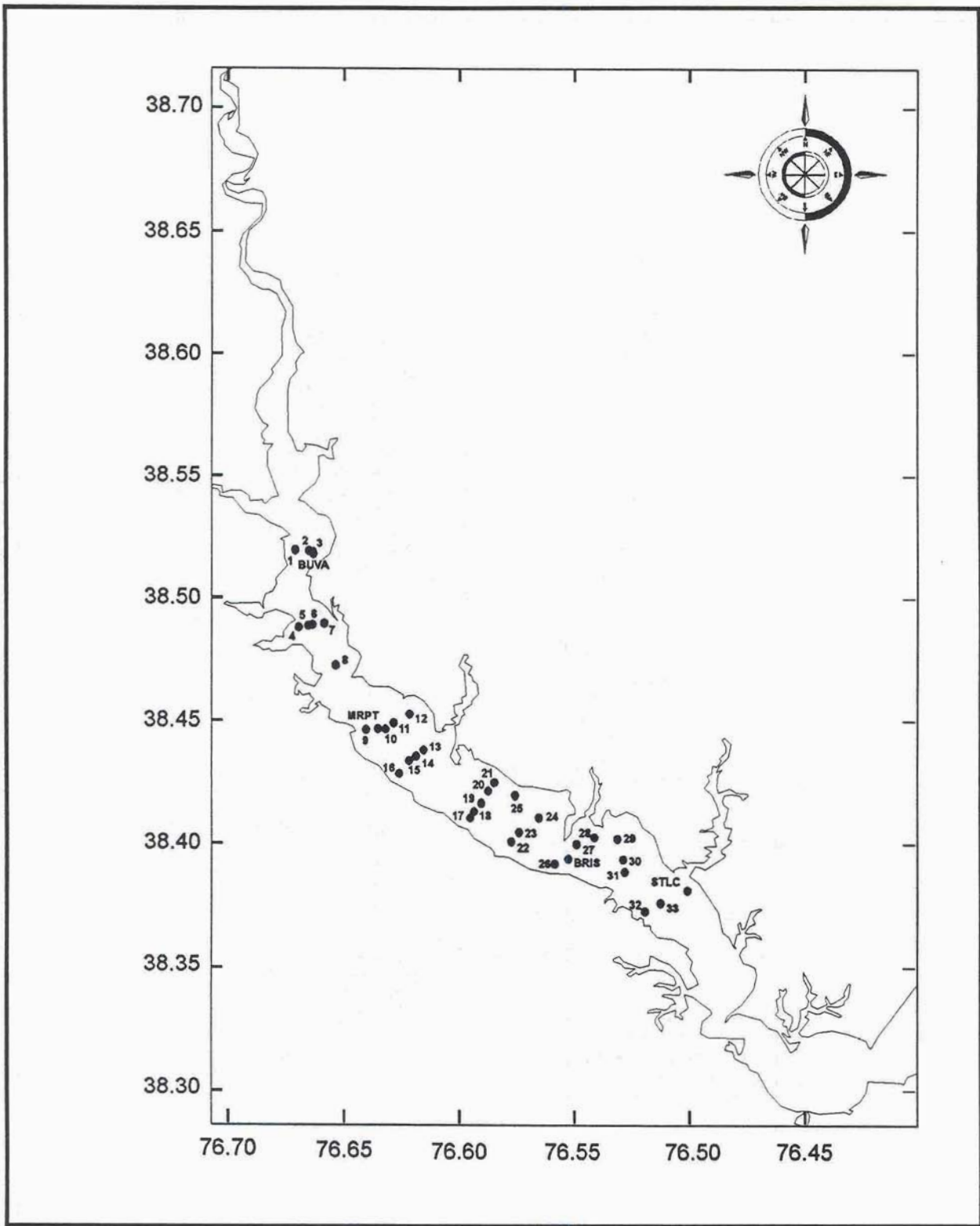


Figure 3-2. Location of thirty-seven (37) stations in the Patuxent River used in the Surficial Sediment Chlorophyll-a Mapping Study.
Latitude and longitude are in degrees and decimal minutes and seconds.

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

REGION	STATION NAME	STATION CODE NAME	DATA TABLE ORDER		
			A	B	C
Patuxent River	Buena Vista	BUVA	2	4	4
	Marsh Point	MRPT		3	3
	Broomes Island	BRIS		2	2
	St Leonard Creek	STLC	1	1	1

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.

C = Four SONE stations in the Patuxent River were sampled in June, July, August and September, 1997. Numerical Ranking indicates the order in which they appear in the SONE 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). After this date, measurements were made five times per year (May, June, July, August and October).

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

STATION CODE	LATITUDE (DGPS)	LONGITUDE (DGPS)	STATION DEPTH (m)	MDE STATION	BAY SEGMENT
Patuxent River					
BUVA	38° 31.050'	76° 39.783'	5.8	XDE9401	RET1
MRPT	38° 26.767'	76° 37.900'	5.2	XDE5339	LE1
BRIS	38° 23.600'	76° 33.067'	15.0	XDE2792	LE1
STLC	38° 22.817'	76° 30.067'	7.0	XDE2792	LE1

Table 3-1.3. SONE Station Code and Description

STATION CODE NAME	DESCRIPTION
Patuxent River	
BUVA	0.75 nautical miles north of Route 231 Bridge at Benedict, MD (R km ¹ = 31.5)
MRPT	14.5 nautical miles upstream of Patuxent River mouth (R km ¹ = 23.4)
BRIS	10 nautical miles upstream of Patuxent River mouth (R km ¹ = 16.1)
STLC	7.5 nautical miles upstream of Patuxent River mouth (R km ¹ = 12.1)

NOTES:

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

Table 3-1.4. Station Salinity

STATION CODE	SALINITY CODE
Patuxent River	
BUVA	O
MRPT	M
BRIS	M
STLC	M

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

Table 3-2. Chlorophyll-a Mapping Station Locations and Salinity

Station	Station Code	Average Depth (m)	Latitude	Longitude	Median Salinity (ppt) (Code)
Teagues Point	PX 01	3.7	38° 31.17'	76° 40.28'	7.0 (M)
	PX 02	6.3	38° 31.15'	76° 39.93'	7.6 (M)
Buena Vista	BUVA	6.0	38° 31.12'	76° 39.82'	7.7 (M)
	PX03	3.2	38° 31.08'	76° 39.81'	7.4 (M)
Billiard Point	PX04	2.9	38° 29.28'	76° 40.19'	8.1 (M)
	PX05	5.1	38° 29.32'	76° 39.94'	8.6 (M)
	PX06	9.5	38° 29.34'	76° 39.83'	9.0 (M)
Buzzard Island	PX07	2.2	38° 29.37'	76° 39.53'	7.3 (M)
Sheridan Point	PX08	8.5	38° 28.36'	76° 39.23'	9.3 (M)
Marsh Point	PX09	3.9	38° 26.79'	76° 38	8.3 (M)
Point	MRPT	6.1	38° 26.81'	76° 38.13'	9.7 (M)
	PX10	11.5	38° 26.80'	76° 37.93'	12.0 (M)
	PX11	6.4	38° 26.95'	76° 37.72'	9.3 (M)
Kitts Point	PX12	3.6	38° 27.17'	76° 37.31'	7.9 (M)
Prision Point	PX13	6.0	38° 26.29'	76° 36.94'	9.3 (M)
	PX14	6.7	38° 26.14'	76° 37.14'	11.1 (M)
	PX15	11.8	38° 26.03'	76° 37.32'	12.1 (M)
	PX16	4.2	38° 25.68'	76° 37.54'	8.0 (M)
Rolin Creek	PX17	6.5	38° 24.64'	76° 35.73'	9.4 (M)
	PX18	7.3	38° 24.79'	76° 35.57'	10.8 (M)
	PX19	13.7	38° 25.00'	76° 35.44'	12.0 (M)
	PX20	5.8	38° 25.29'	76° 35.26'	10.3 (M)
	PX21	3.6	38° 25.50'	76° 35.10'	8.6 (M)
Gattons	PX22	7.3	38° 24.06'	76° 34.66'	10.5 (M)
	PX23	12.5	38° 24.29'	76° 34.46'	12.5 (M)
	PX24	7.0	38° 24.65'	76° 33.94'	10.1 (M)
Grapevine Cove	PX25	3.9	38° 25.19'	76° 34.56'	8.8 (M)

Table 3-2. Chlorophyll-a Mapping Station Locations and Salinity (Continued)

Station	Station Code	Average Depth (m)	Latitude	Longitude	Median Salinity (ppt) (Code)
	PX26	3.3	38° 23.52'	76° 33.52'	8.8 (M)
Broomes Island	BRIS	16.5	38° 23.64'	76° 33.17'	10.2 (M)
Broomes Island	PX27	5.5	38° 24.00'	76° 32.95'	9.5 (M)
Island Neck	PX28	3.5	38° 24.17'	76° 32.49'	9.4 (M)
	PX29	5.5	38° 24.13'	76° 31.89'	10.0 (M)
	PX30	8.5	38° 23.63'	76° 31.74'	10.9 (M)
Sotterly Point	PX31	11.9	38° 23.33'	76° 31.70'	12.3 (M)
Greenwell State Park	PX32	8.8	38° 22.38'	76° 31.17'	11.2 (M)
	PX33	19.8	38° 22.58'	76° 30.76'	10.5 (M)
St. Leonard Creek	STLC	7.5	38° 22.88'	76° 30.06'	9.2 (M)

Table 3-3. MINI-SONE Station Locations (DGPS)

Station Abbreviation	Latitude	Longitude
PX07	38° 29.350'	76° 39.383'
PX15	38° 25.983'	76° 37.167'
PX21	38° 25.500'	76° 37.017'
PX23	38° 24.283'	76° 34.367'
PX25	38° 25.183'	76° 34.483'
PX33	38° 22.519'	76° 30.615'

sampled once a month during March through September, 1997. These months were chosen to document the settling of the spring bloom to the bottom sediments of the Patuxent River as well as summer sediment conditions.

3.1.2. Sampling Frequency

3.1.2.1 Sampling frequency for SONE and MINI-SONE elements

The sampling frequency for the sediment oxygen and nutrient exchanges program which includes both SONE and MINI-SONE elements is based on the seasonal patterns of sediment water exchanges observed in previous studies conducted in the Chesapeake Bay region (Kemp and Boynton, 1980, 1981; Boynton *et al.*, 1982; 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.
2. A period during which macrofaunal biomass is low but water temperature and water column metabolic activity high with hypoxia or 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 fluxes, high releases of ammonium (NH_4^+), phosphate (PO_4^{3-}) and silicate ($\text{Si}(\text{OH})_4$).
3. A period in the fall when anoxia is not present and macrofaunal community abundance is low but re-establishing (October - November). Characteristics of sediment water nutrient and oxygen exchanges typically include the following: increased sediment oxygen consumption (SOC) rates, intermediate release rates of ammonium (NH_4^+), phosphate (PO_4^{3-}) and silicate ($\text{Si}(\text{OH})_4$) 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 and MINI-SONE studies involve four monthly measurements made between June and September, 1997. Sampling dates for these cruises together with alpha-numeric cruise identification codes can be found in Table 3-4.

Table 3-4. SONE Cruise Identifier

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 1	AUG 1984	27 AUG	30 AUG	Aquarius
SONE 2	OCT 1984	15 OCT	18 OCT	Aquarius
SONE 3	MAY 1985	6 MAY	9 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	3 MAY	8 MAY	Aquarius
SONE 8	JUN 1986	23 JUN	26 JUN	Aquarius
SONE 9	AUG 1986	18 AUG	22 AUG	Aquarius
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	9 NOV	16 NOV	Aquarius
SONE 15	APR 1988	17 APR	22 APR	Aquarius
SONE 16	JUN 1988	1 JUN	7 JUN	Aquarius
SONE 17	AUG 1988	15 AUG	21 AUG	Aquarius
SONE 18	NOV 1988	1 NOV	9 NOV	Aquarius
SONE 19	APR 1989	4 APR	10 APR	Aquarius
SONE 20	JUN 1989	12 JUN	16 JUN	Aquarius
SONE 21	JUL 1989	12 JUL	14 JUL	Aquarius
SONE 22	AUG 1989	14 AUG	16 AUG	Aquarius
SONE 23	OCT 1989	16 OCT	18 OCT	Aquarius
SONE 24	MAY 1990	1 MAY 8 MAY	3 MAY 8 MAY	Orion Aquarius
SONE 25	JUN 1990	11 JUN	14 JUN	Aquarius
SONE 26	JUL 1990	16 JUL	19 JUL	Aquarius

Table 3-4. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 27	AUG 1990	27 AUG	30 AUG	Aquarius
SONE 28	OCT 1990	15 OCT	18 OCT	Aquarius
SONE 29	MAY 1991	6 MAY	9 MAY	Aquarius
SONE 30	JUN 1991	10 JUN	13 JUN	Aquarius
SONE 31	JUL 1991	22 JUL	25 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	8 SEP	10 SEP	Aquarius
SONE 40	OCT 1992	5 OCT	8 OCT	Aquarius
SONE 41	MAY 1993	17 MAY	20 MAY	Aquarius
SONE 42	JUNE 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

Table 3-4. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 50	AUG 1994	8 AUG	11 AUG	Orion
SONE 51	SEP 1994	12 SEP	14 SEP	Orion
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	8 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 23JUL	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	11 AUG	22 AUG	Orion
SONE 61	SEP 1996	9 SEP 12 SEP 16 SEP	9 SEP 13 SEP 16 SEP	Orion
MINI-SONE 4	SEP 1996	13 SEP	13 SEP	Orion
SONE 62	JUN 1997	17 JUN	18 JUN	Aquarius
MINI-SONE 5	JUN 1997	18 JUN	19 JUN	Aquarius
SONE 63	JUL 1997	18 JUL 21 JUL	18 JUL 21 JUL	Orion
MINI-SONE 6	JUL 1997	21 JUL	21 JUL	Orion
SONE 64	AUG 1997	15 AUG 18 AUG	15 AUG 18 AUG	Orion
MINI-SONE 7	AUG 1997	18 AUG	19 AUG	Orion

Table 3-4. SONE Cruise Identifier (Continued)

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 65	SEP 1997	9 SEP	10 SEP	Orion
MINI-SONE 8	SEP 1997	9 SEP	10 SEP	Orion

NOTES:

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

3.1.2.2 Sampling Frequency for Surficial Sediment Chlorophyll-a Mapping

The surficial sediment chlorophyll-a mapping stations were sampled once a month during March, April, May, June, July, August and September, 1997. These months were chosen as optimum times to document the spatial distribution and magnitude of labile organic material deposited to sediments during and following spring and summer algal bloom.

3.1.3 Field Methods

3.1.3.1 Field Methods for SONE and MINI-SONE Elements

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.

3.1.3.1.1 Water Column Profiles

At each of the SONE and MINI-SONE stations, vertical water column profiles of temperature, salinity and dissolved oxygen are measured at 2 meter intervals from the surface to the bottom. The turbidity of surface waters is measured using a Secchi disc.

3.1.3.1.2 Water Column Nutrients

Near-bottom (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: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) and dissolved inorganic phosphorus corrected for salinity (DIP or PO_4^{3-}).

3.1.3.1.3 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 of sediment depth. At each MINI-SONE station, Eh is measured every centimeter to 2 cm depth, then every other cm thereafter. 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 beginning in October, 1993, two measurements (2 - 3 mm and to 1 cm) were recorded. Particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), are sampled to a depth of 2 - 3 mm (surface scrape).

3.1.3.1.4 Sediment Cores

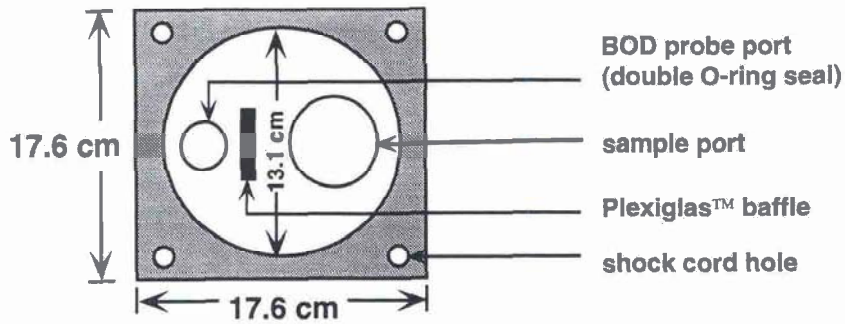
Both the SONE and MINI-SONE program elements rely on the same field and laboratory techniques to estimate sediment-water oxygen and nutrient fluxes. However, stations sampled using MINI-SONE protocols use a slightly abbreviated set of measurements compared to the standard SONE techniques. Stations being sampled with the standard SONE techniques use three replicated cores and a blank to estimate sediment-water flux, whereas MINI-SONE stations only use a single sediment core with no blank. Other minor differences between the SONE and MINI-SONE measurements are noted below where applicable. In each case, intact sediment cores constitute a benthic microcosm where changes in oxygen, nutrient and other compound concentrations are determined. An overview of the measurement technique follows and the details of the techniques are provided in Boynton and Rohland (1990).

Sediment cores are collected at each station using a modified Bouma box corer. These cores are then transferred to a Plexiglass cylinder (15 cm diameter x 30 cm length) and inspected for disturbances such as large macrofauna or cracks in the sediment surface. If the sample is satisfactory, the core is fitted with an O-ring sealed top containing various sampling ports, and a gasket sealed bottom (Figure 3-3). The core is then placed in a darkened, temperature controlled holding tank where overlying water in the core is slowly replaced by fresh bottom water to ensure that water quality conditions in the core closely approximate *in situ* conditions. For the standard SONE stations, water is also exchanged in the blank core.

During the period in which the flux measurements are taken, the cores are placed in a darkened temperature controlled bath to maintain ambient temperature conditions. The overlying water in a core is gently circulated with no induction of sediment resuspension via stirring devices attached to the oxygen probes. Oxygen concentrations are recorded and overlying water samples (35 ml) are extracted from each core every 60 minutes during the incubation period. Standard SONE stations are incubated for 4 hours and a total of 5 measurements are taken, while MINI-SONE stations are incubated for 3 hours with a total of 4 measurements taken. As a water sample is extracted from a core, an equal amount of ambient bottom water is added to replace the lost volume. Water samples are filtered and immediately frozen for later analysis for ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) and dissolved inorganic phosphorous (DIP or PO_4^{3-}). 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.

In addition to the samples collected for nutrient analysis, water (75 ml), is also extracted for analysis of TCO_2 . The bottom water is transferred via a syringe to a small BOD bottle and then fixed with mercuric chloride (HgCl_2) to stop metabolism. The addition of mercuric chloride (HgCl_2) is appropriate for either oxic or anoxic conditions. A total of 4 samples are collected from each core at both the SONE or MINI-SONE stations. TCO_2 fluxes are computed in the same way as nutrient and dissolved oxygen fluxes.

Enlarged View of Top Plate



Cross Section of Incubation Chamber

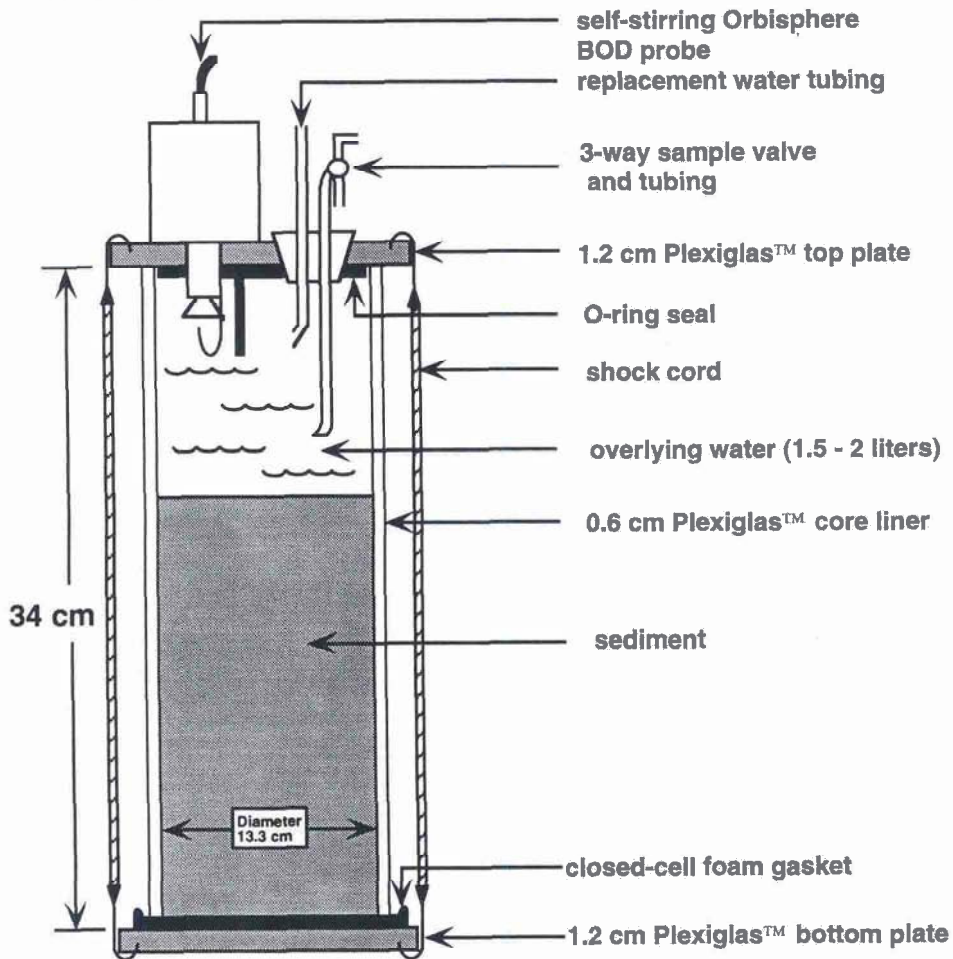


Figure 3-3. Schematic Diagram of the Incubation Chamber

3.1.3.2. Chlorophyll-a Measurements at Patuxent River Surficial Sediment Chlorophyll-a Mapping Stations

At each of 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. Bottom water quality parameters: temperature, conductivity, salinity and dissolved oxygen are recorded. In addition, secchi disk measurements are taken.

3.1.4 Chemical Analyses used in SONE, MINI-SONE and Surficial Sediment Chlorophyll-a Mapping Elements

Detailed reference material pertaining to all chemical analyses used can 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 ($\text{NO}_2^- + \text{NO}_3^-$), 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. The colorimetric methods of Johnson *et al.* (1987) are used to analyze the water samples for dissolved inorganic carbon (TCO_2). A detailed description of the TCO_2 method is given in Boynton *et al.*, (1996).

3.1.5 High Frequency Monitoring at Patuxent mid-River location near Benedict, MD

High frequency field measurements at a single location (38 degrees 30.8 minutes North latitude, 76 degrees 40.2 minutes West longitude; center span of MD Route 231 Bridge) in the mesohaline portion of the Patuxent River were continuous for 5 months during 1997, from 20 May through 21 October. Submersible CTD instruments recorded dissolved oxygen (DO), temperature and salinity every 15 minutes at a depth of one meter below the water surface. In addition to high frequency measurement by sensors, water samples were collected each week and analyzed for dissolved oxygen using the standard modification of the classical Winkler titration procedure (American Public Health Association, Inc., 1966; Strickland and Parsons, 1972) and for chlorophyll-a using Strickland and Parsons (1972) and Shoaf and Lium (1976) methods. Dissolved oxygen (DO) analyzes were used to supplement sensor air saturation calibration and to compute *in-situ* phytoplankton community production and respiration rates by the light-dark bottle method (Gaarder and Gran, 1927). Data from high frequency meteorological instruments, including photosynthetically active radiation (PAR), air temperature, wind velocity and rainfall measured at Solomons, MD were also collected.

3.1.5.1. Field Data Collection Methods

Submersible CTD instruments were attached to a surface float array configured to position probe sensors one meter below the water surface. The floating array was secured to a taut-line mooring anchored from the center span bulwarks of the bridge, which suspended the probe a constant depth below the surface. Maintaining a constant water height above the probe in this way precluded the vertical stratification components of dissolved oxygen (DO), temperature, salinity and light attenuation effects.

CTD instruments were rotated each week to ensure optimum sensor operation and to upload data. The Yellow Springs Instruments (YSI) Model 6920 and Hydrolab DataSonde-3 were programmed to collect the following parameters every 15 minutes: date, time, temperature, specific conductance, salinity, dissolved oxygen saturation, dissolved oxygen concentration and battery voltage. Prior to each week-long deployment, instruments were disassembled, cleaned, fitted with fresh batteries, sensor electrolyte and DO membrane. Following manufacturers specifications, sensors were calibrated before each deployment for conductivity using a 0.1 molar potassium chloride solution; new DO membranes were allowed to 'relax' overnight before the sensor was calibrated for air saturation.

During weekly field visits, the replacement CTD was positioned next to the CTD to be retrieved, while a horizontally-positioned 2.5 liter Niskin bottle at probe depth was triggered to collect a water sample. This provided overlapping readings from each CTD and also a discrete water sample that corresponded precisely to both beginning and end-points for respective data records. From the Niskin bottle, one 300-ml BOD bottle was filled and preserved immediately for later completion of the Winkler titration analysis. A second opaque 'dark' BOD bottle was filled and stored in a constant temperature water bath for 12 to 18 hours prior to preservation. A third bottle was filled and kept in the dark on ice for later chlorophyll-a analysis.

When CTD's were retrieved, any visible evidence of biofouling was noted. Biofouling on DO sensor membranes has been found to cause lower readings than from clean sensors or water samples analyzed by Winkler titration. Beginning and end-point Winkler determinations can also be used to confirm pre-deployment and post-deployment air saturation calibration.

Refrigerated water samples for chlorophyll-a analysis were filtered using 47 mm Whatman glass microfiber (GF/F) 0.1 micron pads, frozen and sent to the Nutrient Analytical Services Laboratory (NASL) for pigment extraction and spectrophotometer measurements. Raw data was uploaded following CTD retrieval each week. Winkler titration of preserved water samples was completed each week and results were combined with high frequency data to produce graphs of all data.

3.1.5.2 Preliminary Assessment of Field Data

Throughout the deployment phase of the project, great care was taken to provide several means to verify sensor data using classical *in-situ* sampling techniques to calibrate instruments. A procedure was adopted to provide overlapping data during weekly field visits from both the sensor to be retrieved and the replacement sensor, in addition to a discrete water sample that corresponded

precisely to both beginning and end-points for respective sensor data. When the sensor that had been in the water for a week was retrieved, the DO sensor membrane was closely examined and a scaled value was recorded to indicate the degree of biofouling observed. Initial comparisons of *in-situ* Winkler determinations to sensor end-point measurements indicated there were lower readings from fouled sensors than from clean sensors. Pre-deployment and post-deployment sensor calibrations in air and *in-situ* dissolved oxygen determinations by Winkler methods were retained for later calibration validation and correction if needed.

After sensors were retrieved each week, raw data was downloaded and graphics were created for examination of time series to ensure that data appeared within acceptable limits determined by weekly calibration throughout the deployment phase of the project. By “splicing” plots of time series records from successive weeks together, the coincidence of overlapping temperature, salinity and dissolved oxygen measurements at end and beginning points provided a means to qualitatively assess data, in addition to the pre-deployment and post-deployment sensor calibrations and the *in-situ* dissolved oxygen determinations by Winkler methods (Figure 4-1).

3.2. NEW STUDIES: PATUXENT RIVER SUBMERGED AQUATIC VEGETATION (SAV) HABITAT EVALUATION

As part of the 1997 EPC component of the Chesapeake Bay Monitoring Program, the Patuxent River Estuary was targeted for evaluation of habitat criteria vital to submerged aquatic vegetation (SAV). This evaluation is composed of several discrete, but complementary study elements examining both near-shore and selected off-shore locations. These studies include:

1. water column monitoring of light attenuation, dissolved and particulate nutrient concentrations, algal biomass and physical characteristics.
2. evaluation of light attenuation due to epiphytic fouling,
3. evaluation of SAV propagule availability,
4. high frequency tidal cycle evaluation of water quality, and
5. SAV bed mapping.

Collectively these studies provide insight into near-shore SAV habitat conditions.

3.2.1 Station Locations

Ten near-shore stations were selected in the mesohaline portion of the Patuxent River Estuary and tributaries to reflect a variety of nutrient, salinity and wave exposure regimes. Consideration was also given to locate stations in, or adjacent to, existing SAV beds as well as areas where SAV is not currently present. In addition, two transects each consisting of three water quality stations were established between a near-shore station and the main river channel. These transect stations were intended to coincide with mid-channel sampling locations of the Maryland DNR Water Quality Monitoring Stations (Magnien *et al.*, 1993). Both near-shore and transect station locations are shown in Figure 3-3. and listed in Table 3-5.

3.2.2 Sampling Frequency

Sampling was conducted at least monthly from April through October 1997. The contract indicates that where possible biweekly sampling is preferred however at times only monthly sampling was feasible due to the demands of a crowded summer schedule. A total of 12 SAV sampling cruises were completed.

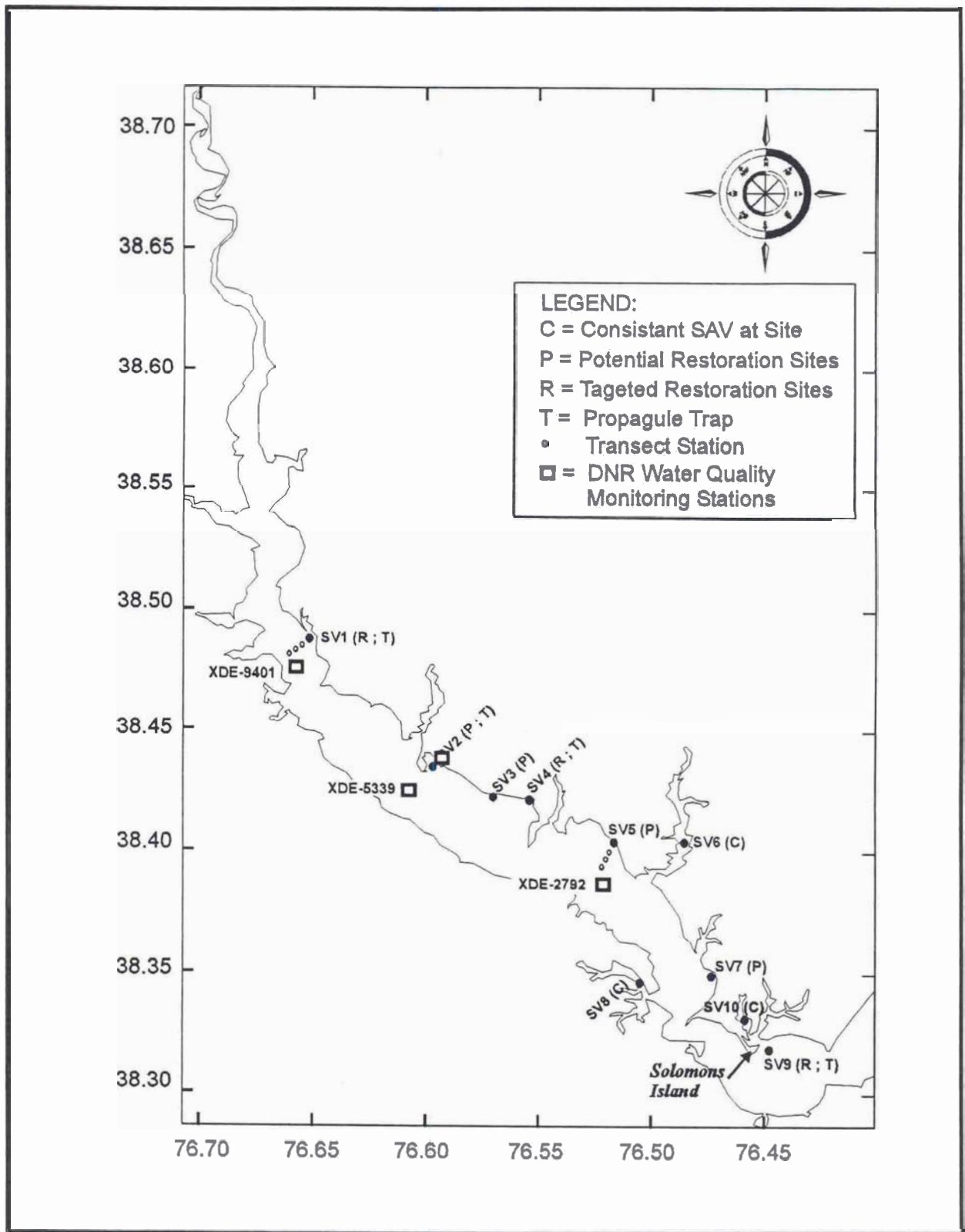


Figure 3-4. Map of transects and location of Submerged Aquatic Vegetation (SAV) stations on the Patuxent River.
Latitude and longitude are in degrees and decimal minutes and seconds.

Table 3-5. Submerged Aquatic Vegetation (SAV) Station Abbreviations and Locations: Latitude and Longitude (DGPS).

Geographic Location of Station	Station Abbreviation	Latitude	Longitude
Buzzard Island Station 1	SV1A	39° 19.268'	76° 27.129'
Buzzard Island Station 2*	SV1B	38° 29.090'	76° 39.233'
Buzzard Island Station 3*	SV1C	38° 29.026'	76° 39.384'
Buzzard Island Station 4*	SV1D	38° 29.016'	76° 39.441'
Jack Bay	SV02	38° 28.086'	76° 35.934'
Parkers Wharf	SV03	38° 25.328'	76° 34.329'
Broomes Island	SV04	38° 25.200'	76° 33.101'
Jefferson Patterson Park Station 1	SV5A	38° 24.534'	76° 31.299'
Jefferson Patterson Park Station 2*	SV5B	38° 24.280'	76° 31.525'
Jefferson Patterson Park Station 3*	SV5C	38° 23.753'	76° 31.736'
Jefferson Patterson Park Station 4*	SV5D	38° 23.431'	76° 32.092'
St Leonard Creek	SV06	38° 23.709'	76° 29.105'
Hungerford Creek	SV07	38° 20.982'	76° 28.307'
Cuckold Creek	SV08	38° 20.856'	76° 30.208'
Point Sandy	SV09	38° 19.016'	76° 27.119'
Chesapeake Biological Laboratory Pier Calvert Marine Museum	SV10	38° 19.846'	76° 27.684'

* Indicates a transect station.

3.2.3 Field Methods

3.2.3.1 Water Quality Monitoring

At each of the near-shore and transect stations, water quality parameters were measured at 0.5 meters below the water surface. This water depth roughly corresponds to mid-water column depth at each of the near-shore stations where total water depth was approximately 1 meter mean low water. Water column physical parameters and water column nutrients were measured at this depth.

3.2.3.1.1 Physical Parameters

Temperature, salinity, conductivity, and dissolved oxygen measurements were collected with a Hydrolab Surveyor II or a Yellow Springs International (YSI) 600R multi-parameter water quality monitor. Water column turbidity was estimated with a secchi disk, while water column light flux in the photosynthetically active frequency range (PAR) was measured with a *Li-Cor* LI-192SA underwater quantum sensor. Light flux measurements were collected at three discrete water depths in order to calculate water column light attenuation (K_d). Weather and sea-state conditions such as air temperature, percent cloud cover, wind speed and direction, total water depth, and wave height were also recorded.

3.2.3.1.2 Water Column Nutrients

Whole water samples were collected with a hand pump, and a portion immediately filtered with a 25 mm, 0.7 μm (GF/F) glass fiber filter. Both the filtered portion and the remaining whole water samples were placed in coolers for transport back to the laboratory for further processing. The filtered portion was analyzed by the Nutrient Analytical Services Laboratory (NASL) for ammonium (NH_4^+), nitrate (NO_2^-), nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$), phosphate (PO_4^{3-}), total dissolved nitrogen (TDN) and total dissolved phosphorus (TDP). Whole water portions were filtered in the laboratory using 25 mm (particulate carbon [PC] and particulate nitrogen [PN] only) and 47 mm 0.7 μm (GF/F) glass fiber filters and were analyzed by NASL for the following particulate nutrients: particulate carbon (PC), particulate nitrogen (PN) and particulate phosphorus (PP), total suspended solids (TSS), and total and active chlorophyll-a concentrations where total chlorophyll-a includes chlorophyll-a plus breakdown products.

3.2.3.1.3 Chemical Analysis Methodology

Methods of analysis for water column nutrients appear in section 3.4.

3.2.3.2 Epiphyte Growth Study

In order to assess the light attenuation potential of epiphytic growth on the leaves of submerged aquatic vegetation (SAV), artificial substrata in the form of thin strips of Mylar™ polyester plastic were deployed at each of the ten near-shore stations for periods of two to four weeks. During each cruise throughout the sampling season, replicate strips exposed to natural fouling were retrieved and new strips deployed. The use of transparent Mylar™ provided a means to estimate light attenuation due to epiphytic growth and sediment accumulation, as well as to quantify the organic and inorganic components of the fouling.

3.2.3.2.1 Description of Epiphyte Collector Arrays

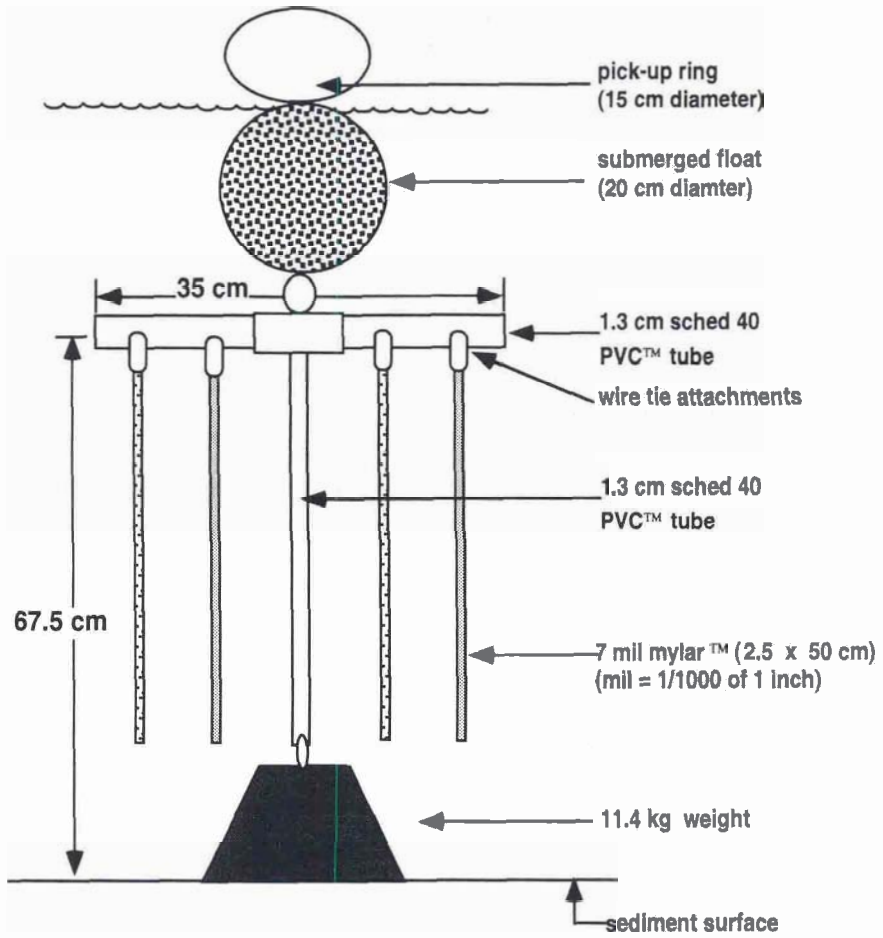
Each collector array (Figure 3-5.) consists of a horizontal PVC frame in the form of an "H" connected to a concrete anchor by a vertical PVC shaft. A steel cable running through the center of the vertical shaft is connected to a subsurface float that holds the array upright and allows it to rotate freely in the current. The horizontal "H" frame was positioned approximately two feet above the sediment surface such that the Mylar™ strips would extend to near the sediment surface. Each collector array holds up to ten strips per deployment. Mylar™ strips (2.5 cm wide x 51 cm long and 0.7 mil thick) were suspended vertically from the sub-surface frame (Figure 3-4) such that the uppermost end of each strip was fixed to the array and the lower end was free to move in the current. However, small (¼ oz) weights attached to the lower end of each strip helped maintain a vertical position under strong current conditions. Although this deployment configuration does not truly simulate the accumulation of epiphytes on actual SAV leaves, it does provide for comparisons of epiphytic fouling rates among sites with varying water quality conditions.

3.2.3.2.2 Sampling the Epiphyte Collector Arrays

To retrieve the epiphyte collector strips the entire collector array was removed from the water and placed on the deck of the boat. On each sampling date, typically 3 replicate strips (exposed for the minimum time interval of 2-4 weeks) were removed for light attenuation measurements, and placed in individual PVC transport tubes. These tubes were then filled with station water and placed on ice in a cooler for transport back to the laboratory. Several strips were allowed to remain deployed for up to 4 weeks to provide a longer exposure interval. Therefore, on some sampling dates, two sets of strips, each having a different period of exposure, were removed for light attenuation measurements.

On each sampling date, an additional strip was haphazardly chosen for chlorophyll concentration analysis. This strip was cut into small sections and placed directly into a 60 ml centrifuge tube. The tube was then placed in a cooler for transport back to the laboratory. The samples were immediately frozen upon arrival at the laboratory and transferred to NASL for analysis.

An additional strip was removed for analysis of total volatile solids (TVS). This strip was also placed in an individual PVC transport tube filled with distilled water instead of station water. Distilled water was necessary to avoid possible contamination from particles suspended in station water.



Top View of Collector

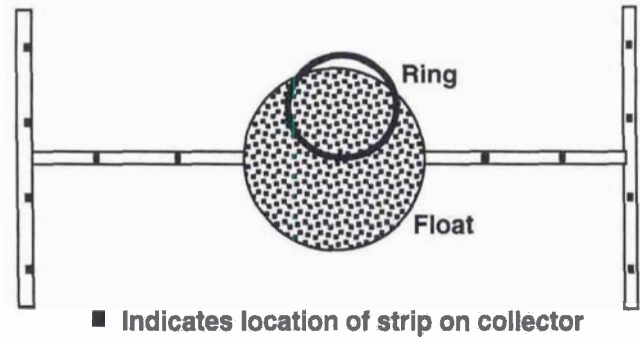


Figure 3-5. Diagram of Epiphyte Collector Array.

3.2.3.2.3 Measuring Epiphyte Light Attenuation

Measurements of light attenuation due to epiphytic growth and fouling on the Mylar™ strips were accomplished with the use of the "LAMA" or Light Attenuation Measurement Apparatus (Figure 3-6). The LAMA basically consists of a fixed light source, a *Li-Cor* Li-192SA underwater quantum sensor, and a strip support track. This configuration is similar to that used by Burt *et al.*, 1995. All light flux measurements were made in filtered seawater. The Li-192SA quantum photo sensor measures photosynthetically active radiation (PAR).

When each fouled strip is removed from the transport tube, it is gently placed on the support track and held in place with small pins. It is then placed in the water bath between the light sensor and the light source to filter light as it passes through the epiphytic growth. Light flux measurements were taken within three pre-marked regions of each strip (top, middle, and bottom) to investigate possible depth effects. Since light flux reaching the sensor is somewhat arbitrary, flux through a blank (clean) strip is measured after every few strips and used as a correction factor. The difference between the light flux recorded through the blank and that recorded through the fouled strips is the light attenuation. The LAMA has been configured such that light flux reaching the sensor through a blank strip is in the range of 90-105 $\mu\text{mol}^{-1} \text{m}^{-2} \text{sec}^{-1}$.

3.2.3.2.4 Processing Inorganic Epiphyte Material

Mylar™ strips collected for TSS/TVS analysis are first scraped of all material, and the strip is rinsed with distilled water. The scraped material is retained and the strip discarded. Water from the transport tube is added to the scraped material and both are diluted to a fixed volume (400 - 500 ml). The solution is mixed as thoroughly as possible on a stir plate until homogenized. A small aliquot (10 to 50 ml) is then extracted with a glass pipette and filtered through a 47 mm 0.7 μm (GF/F) glass fiber filter. Beginning in June 1997 an additional aliquot was filtered onto another glass fiber filter as a duplicate. In most instances, the amount of fouling material was quite large and could not be filtered in its entirety. Once filtered, the pads were immediately frozen and delivered to NASL for analysis.

3.2.3.3 SAV Propagule Flux Study

At four of the near-shore sampling stations, replicate propagule traps were deployed to ascertain the presence or absence of a flux of SAV propagules to areas where SAV currently does not exist. The traps were located at SV1A (Buzzard Island), SV02 (Jack Bay), SV04 (Broomes Island), and SV09 (Solomons Island; Figure 3-3). These traps were sampled along with the water quality monitoring and the epiphyte growth study. At all the stations except Broomes Island, the traps were arranged in a transect line perpendicular to the shoreline. Due to space limitation at Broomes Island the traps at were placed at four points around a piling. Samples were collected in April (once), May (twice), June (twice) and July (once).

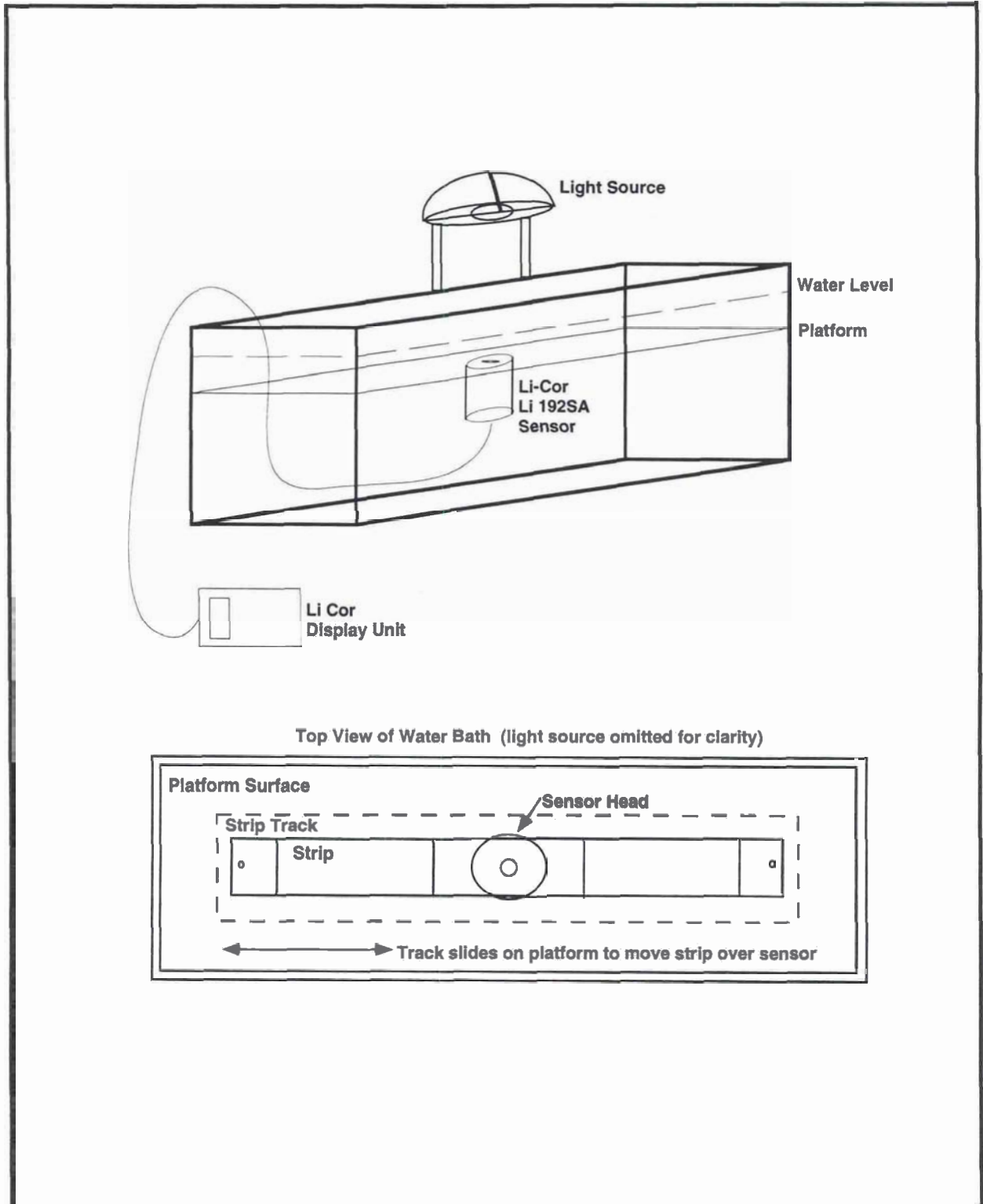


Figure 3-6. Light Attenuation Measurement Apparatus (LAMA) used in the laboratory to measure photosynthetically active radiation (PAR), passing through Mylar™ strips which have been exposed to estuarine waters for 2 to 4 week periods.

3.2.3.3.1 Description of Propagule Traps

The propagule traps are modified versions of those used by Rybicki and Carter (1995) and consist of several vertical prongs of vinyl coated construction mesh attached to a weighted PVC frame (Figure 3-7). The base of each propagule trap is a (2' x 2') square frame of PVC pipe filled with steel rebar. Attached to the PVC is a flat sheet of 1 inch square, vinyl coated construction mesh. Ten vertical projections (10" x 5") of the same construction mesh are attached to the base. These vertical projections serve to catch SAV fragments or propagules moving through the water column. To locate and retrieve the traps, a four-point rope harness is attached to the corners of each PVC frame. A sub-surface float and a surface float are used to keep the lines from tangling and help in the retrieval process.

3.2.3.3.2 Sampling Techniques and Data Collected

Propagule traps were carefully removed from the water and brought aboard the boat for a thorough examination. Any SAV propagules found were placed in labeled ziplock bags and transported to the laboratory for identification and measurement. Before returning the traps to the water any excess detrital material was removed.

Once in the laboratory, each fragment or propagule was identified to species if possible and a variety of measurements were made. These included: overall length, number of nodes, number of seeds, number of bifurcations, and the sample weight (blotted dry). When the number of propagules exceeded the capability to process them efficiently, a sub-sample of 20 fragments was taken and the remaining fragments were weighed.

3.2.3.4 SAV Bed Mapping

At SAV station SV07 (Hungerford Creek), an existing SAV bed of *Potamogeton pectinatus* was mapped in order to estimate bed density and track bed progress over time. To accomplish this, a series of 9 regularly spaced transects, 15 meters apart were established perpendicular to the shoreline. Along these transects, approximately 20, ¼ meter square quadrats were laid down on a regular interval of 3 meters from the shoreline to ~ 2 meters in water depth. The density of SAV within each quadrat was recorded. If more than one species were present, the contribution of each species was recorded. SAV density categories were defined as follows: 0%, 1-25%, 26-50%, 51-75%, 76-99%, and 100% SAV coverage. Evaluation of SAV cover within each quadrat was based upon subjective estimates of cover. Although a certain amount of error is introduced with this type of evaluation, it was felt that this method provided more information than a presence/absence evaluation. Quadrats were only assigned to the 100% SAV cover category when no bottom was observed.

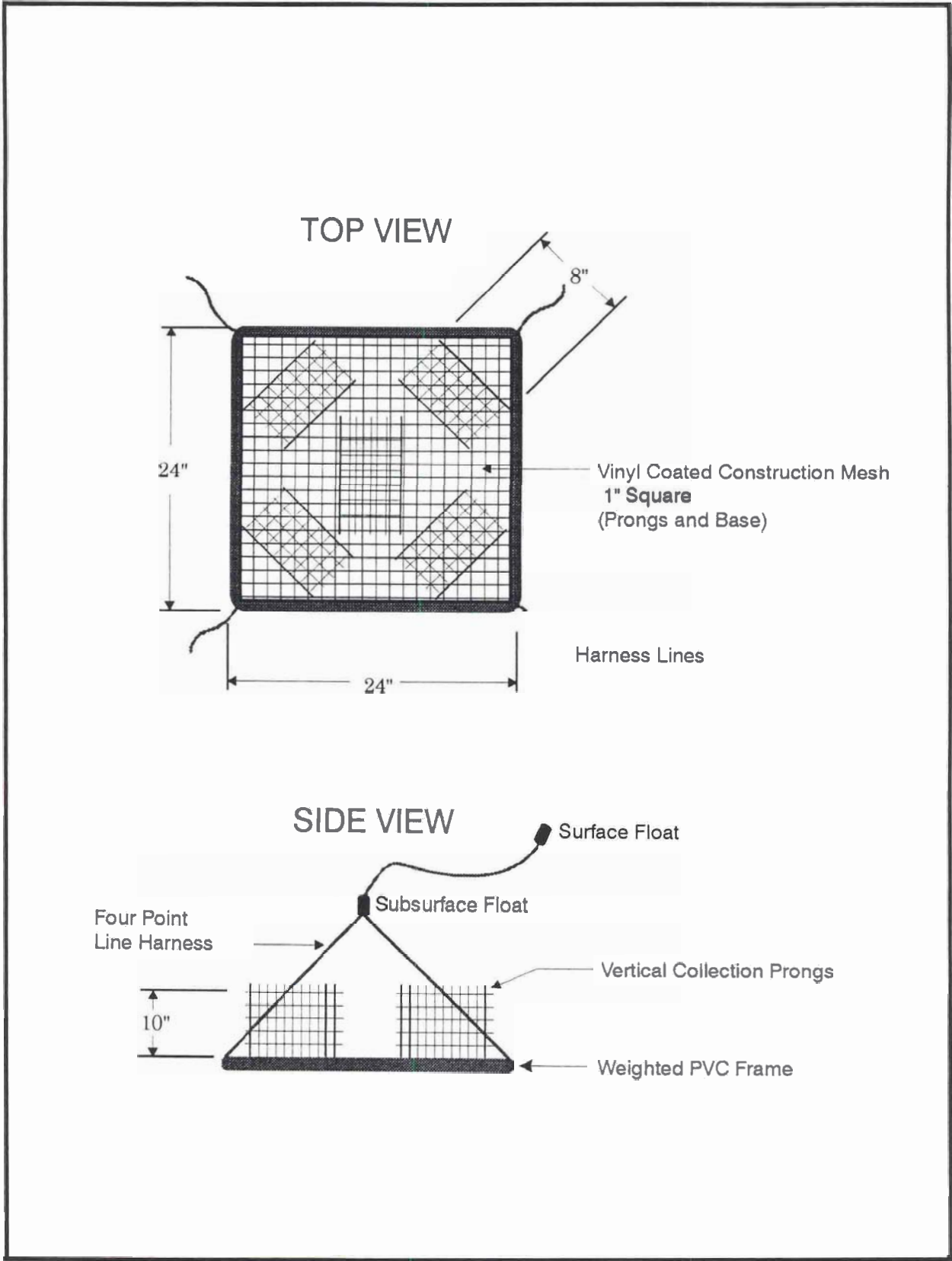


Figure 3-7. Diagram of the Submerged Aquatic Vegetation (SAV) Propagule Trap.

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

F.M. Rohland

Data collected between 1984 and 1997 for the Sediment Oxygen and Nutrient Exchanges (SONE) Program has been organized into five major data sets and one small data set. Data from each of the additional studies (MINI-SONE, sediment chlorophyll-a mapping, SAV elements and high frequency 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 program 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. Hard copy data listings for 1996 and 1997 will be appended to Volume V as a part of the final deliverables submitted with this report..

Additionally Appendix B (Part II) of this report contains SONE data tables listings of variables measured during 1997. 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 (TCO₂) values are incorporated in the sediment-water flux data table (Tables B-6.1; SONE 62).

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 4-1) 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 EPC 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 meta-data file to fulfill the requirements of the EPA Chesapeake Bay Liaison Office (EPA/CBLO).

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
DA	Damaged epiphyte array
DS	Damaged epiphyte strip
EE	Foil pouch very wet when received from field, therefore poor replication between pads, mean reported
FF	Poor replication between pads; mean reported
HD	Particulate and chlorophyll-a samples only taken at -1.0 cm of the Eh profile
HH	Sample not taken
JJ	Amount filtered not recorded (Calculation could not be done)
LA	Lost epiphyte array
LL	Mislabeled
LS	Lost epiphyte strip
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
NR	No replicate analyzed for epiphyte strip chlorophyll-a concentration
PA	Propagule trap added during cruise on June 5th, 1997
PF	Propagule trap not found in field
PG	Propagules weighed as a group, individual weights not recorded
PP	Assumed sample volume (pouch volume differs from data sheet volume; pouch volume used)
PU	Propagule trap found, but turned upside down

Table 4-1. Analysis Problem Codes (Continued)

ANALYSIS PROBLEM CODE	DESCRIPTION
QQ	Although value exceeds a theoretically equivalent or greater value (e.g., PO4F>TDP), the excess is within precision of analytical techniques and therefore not statistically significant
RR	No sample received
SD	All sampling at station discontinued for one or more sampling periods
SS	Sample contaminated in field
SW	Shallow water, light flux measured at two points only
TF	Dissolved oxygen probe failure
TL	Instrument failure in research laboratory
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 Surficial 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, May, June, July, August and September, 1997. 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 during the MINI-SONE study conducted in June, July, August and September, 1997. 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 five 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.

WATER COLUMN NUTRIENTS (Filename: **H2ONUTxx**, Table D-2, added in 1997) report bottom water dissolved nutrient concentrations.

SEDIMENT PROFILES (Filename: **MNSPRFxx**, Table D-3) include redox potential and sediment measurements of total and active chlorophyll-a concentrations.

CORE DATA (Filename: **MNCDATxx**, Table D-4) lists dissolved oxygen and nutrient measurements in MINI-SONE sediment-water flux chambers.

SEDIMENT-WATER FLUX (Filename: **MNFLUXxx**, Table D-5) is a summary table providing oxygen and nutrient flux data.

4.4 Benedict Bridge High Frequency Monitoring data set

This report does not contain data listings for variables measured in during 1997 (20 May, 1997 through 21 October, 1997) at the Benedict Bridge during the High Frequency Monitoring Program. However a summary of the variables and sampling is included as Appendix E (Table E-1). QA/QC checks have identified missing data which have been documented in the data files using the appropriate code.

4.5 Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation data sets

Appendix F of this report contains data listings for variables measured during the SAV Evaluation conducted from April through October, 1997. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor indicating the month (mm) and the year (yy) of the SAV samples were collected.

WATER QUALITY MEASUREMENTS (Filename: **WCNDmmyy**, Table F-1) contains temperature, salinity and dissolved oxygen data measured at 0.5 meters below the water surface.

WATER COLUMN LIGHT ATTENUATION MEASUREMENTS (Filename: **WCLTmmyy**, Table F-2) reports photosynthetically active radiation (PAR) measurements to at least three depths and the subsequent calculated K_d values for each station.

WATER COLUMN NUTRIENT MEASUREMENTS (Filename: **WCNTmmyy**, Table F-3) contains dissolved nutrients, particulate nutrients and chlorophyll-a (active and total) concentrations in the surface waters at each station.

EPIPHYTE LIGHT ATTENUATION MEASUREMENTS (Filename: Raw data file - **ELTRmmyy**, Table F-4; Mean data file - **ELTMmmyy**, Table F-5) includes 3 light transmission measurements, top, mid and bottom and data relating to strip type. Similar measurements were also taken with a clean strip that is used as a "blank" value to determine relative light attenuation.

EPIPHYTE NUTRIENT MEASUREMENTS (Filename: Raw data file - **ENTRmmyy**, Table F-6; Mean data file - **ENTMmmyy**, Table F-7) contains epiphyte chlorophyll-a concentrations (total and active), total epiphyte dry weight and percent inorganic fraction measurements.

PROPAGULE COUNT DATA (Filename: **Raw data file - PCTRmmyy**, Table F-8; Mean data file - **PCTMmmyy**, Table F-9) lists count, identification and measurement data for propagules. **Propagule summary table** provides final count and average values for each propagule variable measured.

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

4.6.1 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 5-1) 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.

4.6.2 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.

4.6.3 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.

4.6.4. 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. The fourth international inter-comparison report was published in 1991 (Kirkwood, Aminot and Pertilä, 1991).

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 $[\text{NH}_4^+]$, nitrite $[\text{NO}_2^-]$, nitrite plus nitrate $[\text{NO}_2^- + \text{NO}_3^-]$ and dissolved inorganic phosphorus [DIP or PO_4^{3-}] 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).

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

Results from the weekly Winkler titration of preserved water samples were combined with high frequency data to produce graphs of all data. The graphs (Figure 4-1.) allowed visual inspection of all data together, beginning with the initial deployment date, as a means to rapidly assess and resolve any equipment or procedural problems. Synoptic meteorological data was also used to distinguish apparent data anomalies due to natural events from those caused by equipment malfunctions. This weekly data inspection served as preliminary data QA/QC throughout the field deployments.

Patuxent River - Benedict Bridge

May 20 - June 30, 1997

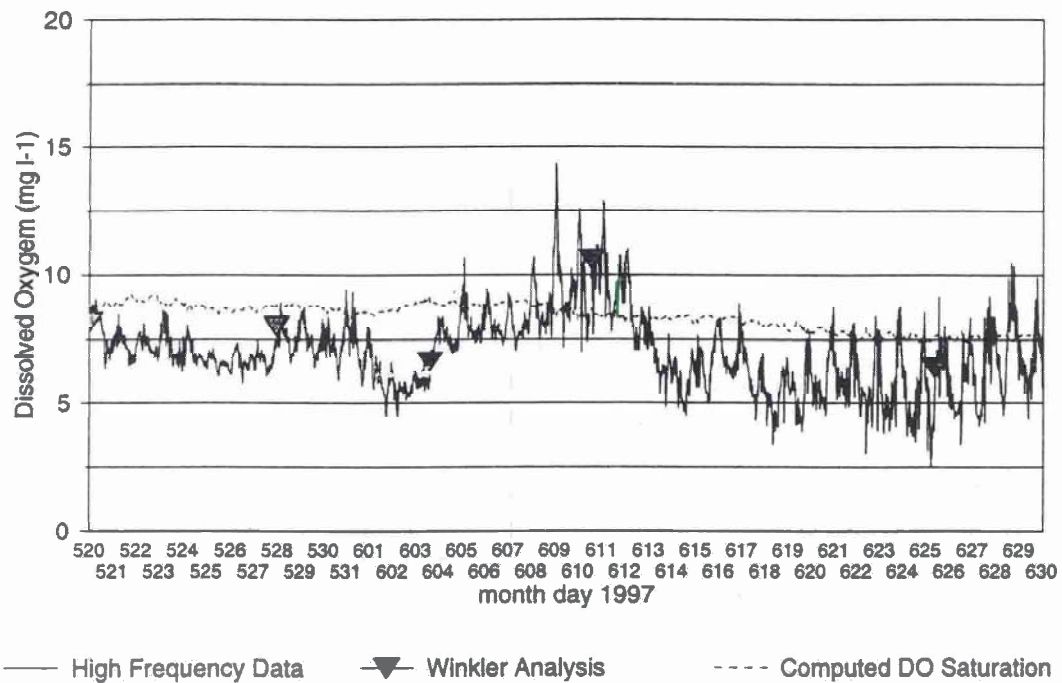


Figure 4-1. A portion of the high frequency monitoring data set for dissolved oxygen (DO) collected at Benedict Bridge from May 20 through June 30, 1997.

Solid triangles indicate DO concentrations determined from Winkler titrations. The dashed line indicates the computed DO concentrations at 100% saturation (given observed temperature and salinity conditions). Plots such as this are visually examined for outliers and other indications of probe malfunction as a routine part of QA/QC procedures.

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5. SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) PROGRAM: 1997 PATUXENT RIVER STUDY

W.R. Boynton, F.M. Rohland and J.M. Frank

One of the continuing objectives of the Ecosystem Processes Component (EPC) Program has been 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 and 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 in some instances where current (*i.e.* 1997) data are not yet available.

5.1 Patuxent River Flow Characteristics in 1997

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 Patuxent River Flows

Annual average river flows from the Patuxent River during the period 1978 through 1997 are shown in Figure 5-1. a. The twenty year average (1978 - 1997) is indicated by a horizontal line on this figure (James *et al.*, 1990; James, *pers. comm.*, 1994, 1995, 1996 and 1997). The twenty year average for the Patuxent River was 381 cfs. Flows in the Patuxent River were above the twenty year average in 1978 (450 cfs) and 1979 (749 cfs), below this average from 1980 to 1982 (165 cfs to 353 cfs), higher than this average during 1983 (506 cfs) and 1984 (438 cfs), generally lower than the twentieth year average from 1985 through 1988 (217 cfs to 306 cfs) and above this average in 1989 (475 cfs) and 1990 (374 cfs). In 1991 (272 cfs) and 1992 (269 cfs) annual average flows were lower than the twentieth year average. Flows were well above average in 1993 (446 cfs) and in 1994 (453 cfs) and below average in 1995 (280 cfs). Freshwater inputs (and probably diffuse source nutrient inputs) were far above average during 1996 (704 cfs) and were the highest annual flows recorded with the exception of 1979. Data for 1997 indicate that this was an average year with an annual average value of 412 cfs. River flows from the Patuxent River have either been near or below the twenty year average value during the Ecosystem Processes Component monitoring period (1985 through 1997)

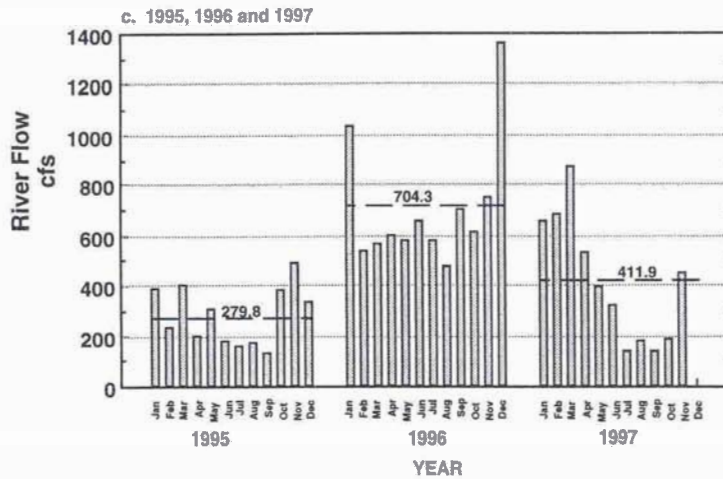
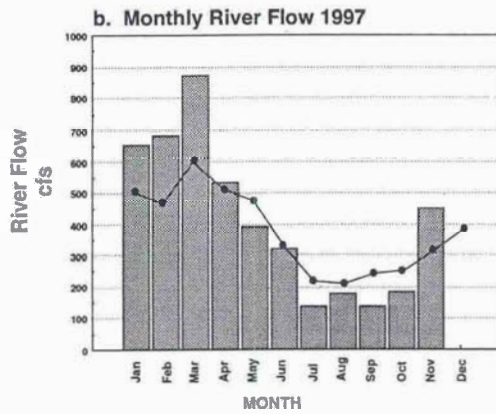
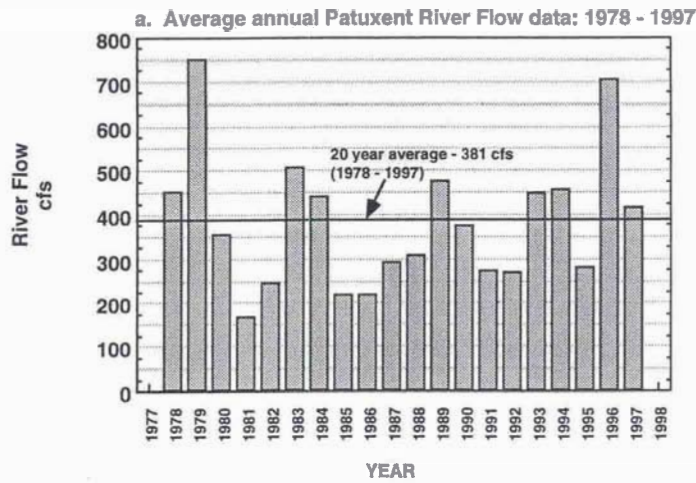


Figure 5-1.a. Bar graphs of average annual river flow from the Patuxent River for the period 1978 through 1997.

b. Bar graphs of average 1997 monthly river flows from the Patuxent River. The dot and line plot represents the long-term average flow for the period 1978 through 1997.

c. A comparison of yearly river flows from the Patuxent River for 1995, 1996 and 1997, the three years used to determine status. Flows were measured at Bowie, MD (01594440). Flow data was taken from: James *et al.*, 1990; J. Manning, *pers. comm.*, 1992 and 1993; R. James, *pers. comm.*, 1994, 1995, 1996 and 1997.

Only eleven months of preliminary data were available for 1997.

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, including, 1997.

5.1.2 Average Monthly Patuxent 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 from the Patuxent river are shown as a series of bar graphs (Figure 5-1.b). In this figure the vertical bars represent average monthly flows for 1997 while the bold dots represent average monthly flows calculated over a longer time period (1978 - 1997).

Peak or seasonally high flows during 1997 were recorded between January and April, with the highest value 871 cfs recorded in March, 1997. Flows decreased during the summer months but flows increased sharply in November (451 cfs; Figure 5-1.b).

The pattern of river flow for the three years used in the calculation of the current status of the tributary clearly indicated that 1995 was a dry year with an average flow rate of 279.9 cfs, that 1996 was an extremely wet year with an average flow rate of 704.3 cfs (extremely large flows were recorded in January, 1996, 1,035 cfs, and December, 1996, 1357 cfs; Figure 5-1.c). Flows in 1997 were average (411.9 cfs) and the flow values were intermediate between those recorded in the preceding two years (Figure 5-1.c).

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.

5.2 Physical and Chemical Characteristics of Bottom Waters and Sediments: Sediment-water Fluxes and *in-situ* Environmental Conditions in the Patuxent River in 1997

5.2.1 Overview and Approach

In this section the observed magnitude of sediment-water exchanges in the Patuxent River 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 analyzes were reported and in more recent reports a series of regression analyzes 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 in the Patuxent River in 1997

5.2.2.1 Temperature

Bottom water temperature conditions in the Patuxent River during 1997 ranged from 18.7 C at Broomes Island (BRIS) in June to 30.0 C at Buena Vista (BUVA) in July (Tables B1-62 - B1-65).

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 1997 than in 1995.

5.2.2.2 Salinity

Bottom water salinity conditions in the Patuxent River during 1997 ranged from 4.1 ppt in June at Broomes Island (BRIS) to 14.9 ppt in August at Broomes Island ([BRIS]; (Tables B1-62. - B1-65.).

Salinity in the Patuxent River was noticeably lower at all four stations in 1997 than in previous years characterized by low river inputs (such as 1995).

5.2.2.3 Dissolved Oxygen

Bottom water dissolved oxygen conditions in the Patuxent River during 1997 ranged from 0.08 mg l⁻¹ in July at Marsh Point (MRPT) to 6.74 mg l⁻¹ in June at Buena Vista ([BUVA]; Tables B1-62. - B1-65.).

The pattern of low summer dissolved oxygen concentrations in deep waters was not as severe in the Patuxent River as in recent wet years (1996) and during the late 1980's. This may be a reflection of the progress made in reducing nutrient loading rates (see Chapter 11 of this Report). For example, July and August bottom water dissolved oxygen values were low at two of the three Patuxent River sites prone to summer hypoxia (St. Leonard Creek [STLC], Broomes Island [BRIS] and Marsh Point [MRPT]) but the hypoxia was not generally as severe as at mainstem Chesapeake Bay or Potomac locations. By September oxygen conditions had recovered to reasonable levels.

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 1997 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 1 cm the sediment column) total sediment chlorophyll-a mass for the Patuxent River during 1997 ranged from 82.3 mg m⁻² in July at St. Leonard Creek (STLC) to 269.4 mg m⁻² in September at Marsh Point ([MRPT]; Tables B3-62 - B3-65).

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 the four SONE stations in the Patuxent River during 1997 ranged from 336 mV in July at Buena Vista (BUVA) to 391 in September at Broomes Island ([BRIS]; Tables B3-62 - B3-65). The 1997 values were quite similar to those observed in previous years in the Patuxent River.

5.2.2.6 Bottom Water Nutrient Concentrations

Ammonium (NH₄⁺) concentrations at the four Patuxent River SONE stations in June, 1997 ranged from 0.5 μM N (Marsh Point [MRPT]) to 12.1 μM N (Broomes Island [BRIS]; Table B-2.62). Values in July, 1997 ranged from 2.7 μM N (Buena Vista [BUVA]) to 19.7 μM N (Marsh Point [MRPT]; Table B-2.63). Values in August, 1997 ranged from 0.4 μM N at St. Leonard Creek (STLC) to 12.6 μM N at Buena Vista (BUVA), while values for September, 1997 ranged from 2.1 μM N (St Leonard Creek [STLC]) to 3.2 μM N (Buena Vista [BUVA]; Table B-2.65)

Nitrite (NO₂⁻) concentrations at the four Patuxent River SONE stations in June, 1997 ranged from 0.19 μM N (Buena Vista [BUVA]) to 0.93 μM N (Broomes Island [BRIS]; Table B-2.62). Values in July, 1996 ranged from 0.20 μM N (Buena Vista [BUVA]) to 0.39 μM N (Marsh Point [MRPT]; Table B-2.2). In August, 1997 values ranged from 1.32 μM N (Buena Vista [BUVA]) to 9.21 μM N (St. Leonard Creek [STLC]; Table B-2.3) while values for September, 1997 ranged from 3.26 μM N (St. Leonard Creek [STLC]) to 8.64 μM N (Marsh Point [MRPT]; Table B-2.4).

Concentrations of nitrite plus nitrate (NO₂⁻ + NO₃⁻) at the four Patuxent River SONE stations in the Patuxent River in 1997 ranged from 0.86 μM N (St. Leonard Creek [STLC]) to 13.0 μM N (Broomes Island [BRIS]; Table B-2.1). Values in July, 1997 ranged from 0.92 μM N (St. Leonard Creek [STLC]) to 1.22 μM N (Buena Vista [BUVA]; Table B-2.2). Values in August, 1997 ranged from 2.45 μM N (Buena Vista [BUVA]) to 9.56 μM N (St. Leonard Creek [STLC]; Table B-2.3) while values for September, 1997 ranged from 3.91 μM N (St. Leonard Creek [STLC]) to 9.77 μM N (Marsh Point [MRPT]; Table B-2.4).

Dissolved inorganic phosphorus (DIP) concentrations at four SONE stations in the Patuxent River in June, 1997 ranged from 0.05 $\mu\text{M P}$ (St. Leonard Creek [STLC]) to 0.29 $\mu\text{M P}$ (Buena Vista [BUVA]; Table B-2.1). Values in July, 1997 ranged from 0.10 $\mu\text{M P}$ (St. Leonard Creek [STLC]) to 0.73 $\mu\text{M P}$ (Buena Vista [BUVA]; Table B-2.2). Values in August, 1997 ranged from 0.24 $\mu\text{M P}$ (St. Leonard Creek [STLC]) to 1.75 $\mu\text{M P}$ (Buena Vista [BUVA]; Table B-2.3) while values for September, 1997 ranged from 0.61 $\mu\text{M P}$ (St. Leonard Creek [STLC]) to 1.59 $\mu\text{M P}$ (Buena Vista [BUVA]; Table B-2.4). Values for all dissolved nutrients recorded in 1997 were intermediate between those observed during 1995 (dry year) and 1996 (wet 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) at the four SONE stations in the Patuxent River ranged from 2.71 percent dry weight in July, 1997 at St. Leonard Creek (STLC) and in September, 1997 at Buena Vista (BUVA) to 3.28 percent dry weight in August, 1997 at Broomes Island ([BRIS]; Tables B3-62 and B3-65). 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 in the bay regions.
2. Particulate nitrogen (PN) at the four SONE stations in the Patuxent River ranged from 0.32 percent dry weight in September, 1997 at Buena Vista (BUVA) to 0.45 percent dry weight at Marsh Point (MRPT) in September, 1997 (Tables B3-62 and B3-65). 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 in the bay region.
3. Particulate phosphorus (PP) at the four SONE stations in the Patuxent River ranged from 0.049 percent dry weight in June, 1997 at St. Leonard Creek (STLC) to 0.133 percent dry weight in August and September, 1997 at Marsh Point ([MRPT]; Tables B3-62 and B3-65). 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 in the bay region.

5.3 Characteristics of Sediment-Water Oxygen and Nutrient Fluxes: 1997 Patuxent River Study

Monthly average sediment-water fluxes are summarized using box and whisker plots (Figures 5-1.1 through 5-1.4) for four variables: sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$), and phosphate (PO_4^-). Data from the Patuxent River were collected at four stations, two of which, Buena Vista (BUVA) and St Leonard Creek (STLC) were sampled over a period of thirteen calendar years, 1985 through 1997, while the two remaining stations, Marsh Point (MRPT) and Broomes Island (BRIS), were sampled over a shorter period of nine years (1989 through 1997). These four stations 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 1997 (SONE 62 [June 1997] through SONE 65 [September 1997]; mean flux value of three replicates) are shown as bold dots superimposed on the box (Figures 5-1.1 through 5-1.4). The Y axis represents the complete range of flux values derived from the complete flux data set for that parameter. The order of the four stations in these figures reflects their spatial position in the Patuxent River from the turbidity maximum zone (Buena Vista [BUVA]) to the middle regions of the estuary (Marsh Point [MRPT] and Broomes Island [BRIS]) to the estuary (St. Leonard Creek [STLC]).

It is important to note that positive flux values indicate fluxes from sediment to water while negative flux values indicate fluxes from water to sediment.

5.3.1 Sediment Oxygen Consumption (SOC)

Mean monthly sediment oxygen consumption (SOC) for 1997, ranged from $-1.06 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Marsh Point (MRPT) to $-2.87 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Buena Vista (BUVA) in June, 1997; from $-0.14 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Marsh Point (MRPT) to $-2.4 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Buena Vista (BUVA) in July 1997; from $-0.28 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Broomes Island (BRIS) to $-1.11 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Buena Vista (BUVA) in August, 1997 and from $-0.67 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Marsh Point (MRPT) to $-1.14 \text{ g O}_2 \text{ m}^{-2} \text{ day}^{-1}$ at Buena Vista (BUVA) in September, 1997 (Figure 5-1.1; Tables B6-62 - B6-65). *Note that: larger negative sediment oxygen consumption (SOC) flux values indicate larger rates of oxygen loss to sediments.*

The 1997 observations exhibited the same pattern as previous years showing markedly decreased rates of sediment oxygen consumption (SOC) early in the sampling period (June), while summer

values were lower (July through September). The smallest fluxes were recorded in July and/or August as is typical where bottom waters had depressed dissolved oxygen (DO) concentrations; spring rates of sediment oxygen consumption (SOC) were modest to high at all other stations in the Patuxent as were bottom water dissolved oxygen (DO) levels. In general sediment oxygen consumption (SOC) tends to be higher in low flow years when bottom water dissolved oxygen concentrations remain higher. Bottom water dissolved oxygen (DO) concentrations reached low levels ($<1 \text{ mg l}^{-1}$) during July and August, 1997 and this, in turn, depressed sediment oxygen consumption (SOC) rates.

5.3.2 Ammonium (NH_4^+) Fluxes

Average monthly ammonium (NH_4^+) fluxes in the Patuxent River during 1997, ranged from $49.8 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Marsh Point (MRPT) to 268.3 at Buena Vista (BUVA) in June, 1997; from $205.3 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at St. Leonard Creek (STLC) to $662.1 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Buena Vista (BUVA) in July, 1997; from $165.7 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Broomes Island (BRIS) to $358.5 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Buena Vista (BUVA) in August, 1997 and from $99.0 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at St. Leonard Creek (STLC) to $350.5 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Buena Vista (BUVA) in September, 1997 (Figure 5-1.2; Tables B6-62 - B6-65).

The values recorded in 1997 followed temporal trends exhibited in previous years; fluxes tended to peak in July (early summer) and decline during the latter portion of the summer. One large ammonium value ($662.1 \mu\text{MN m}^{-2} \text{ hr}^{-1}$) was recorded in July at Buena Vista (BUVA). The magnitude of fluxes tended to be below the long-term mean at all Patuxent stations except Buena Vista (BUVA) and fluxes were especially reduced at both Broomes Island (BRIS) and Marsh Point (MRPT). Flux reduction at these station is especially interesting because these stations typically have large summer releases of ammonium and are typically hypoxic, a condition that tends to enhance ammonium fluxes. Overall, reduced fluxes suggests a reduction in the organic matter supply rate to sediments which is probably a reflection of decreasing nutrient loading rates. 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.

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

Average monthly nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) fluxes for 1997 ranged from $-51.49 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Broomes Island (BRIS) to $120.28 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at St. Leonard Creek (STLC) in June, 1997; from $-12.47 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Marsh Point (MRPT) to $22.1 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at St. Leonard Creek (STLC) in July, 1997; from $-56.93 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Broomes Island (BRIS) to $-8.00 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Buena Vista (BUVA) in August, 1997 and from $-31.45 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at Marsh Point (MRPT) to $24.65 \mu\text{MN m}^{-2} \text{ hr}^{-1}$ at St. Leonard Creek (STLC) in September, 1997 (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.*

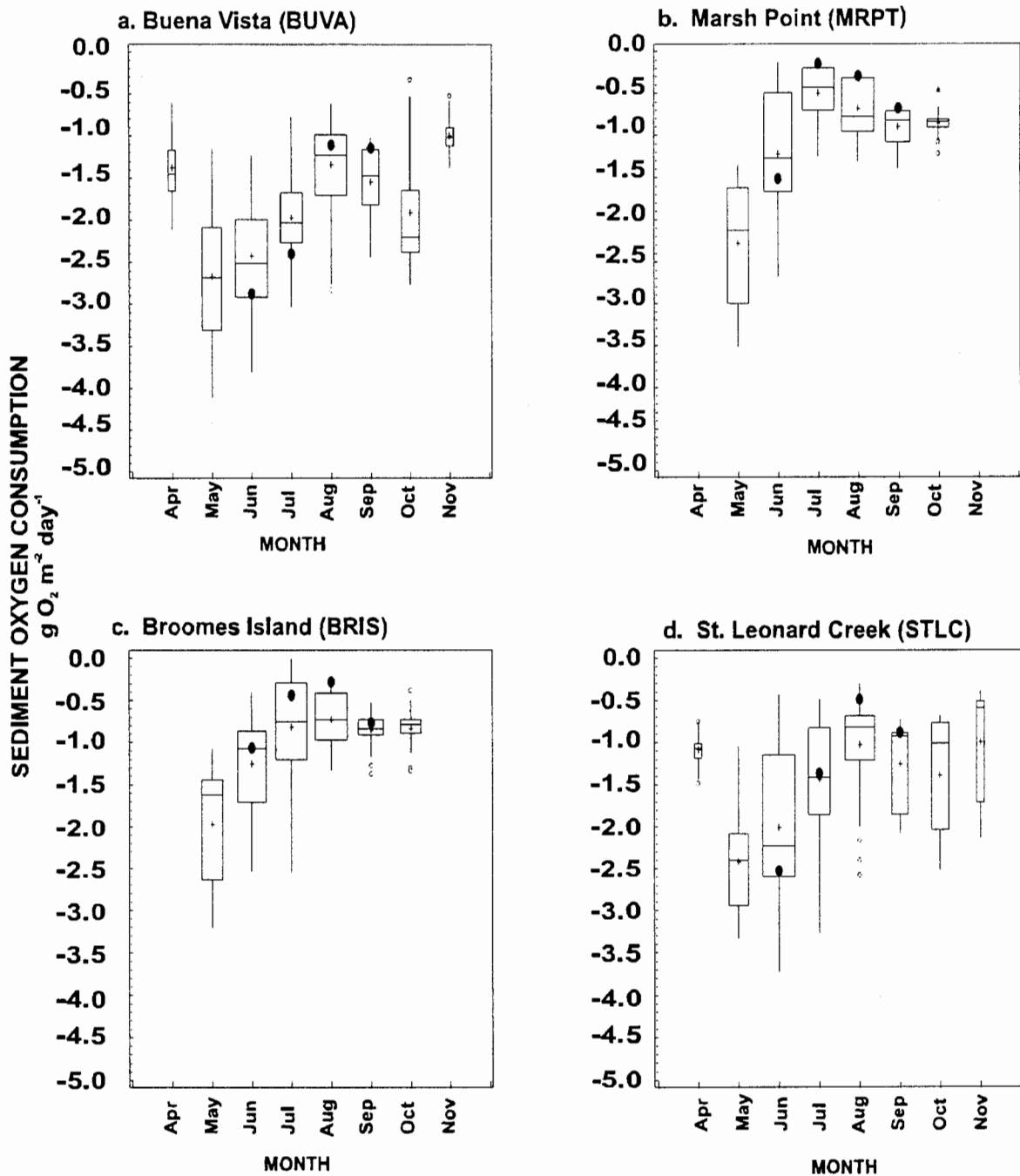


Figure 5-2.1. Box and whisker plots for sediment oxygen consumption (SOC) rates for April to November at four SONE stations located in the Patuxent River.

a. Buena Vista (BUVA); b. Marsh Point (MRPT); c. Broomes Island (BRIS) and d. St Leonard Creek.

The complete flux data set 1985 through 1997 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1997. September values for all stations only include six years data, 1991 through 1997. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1997. 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.

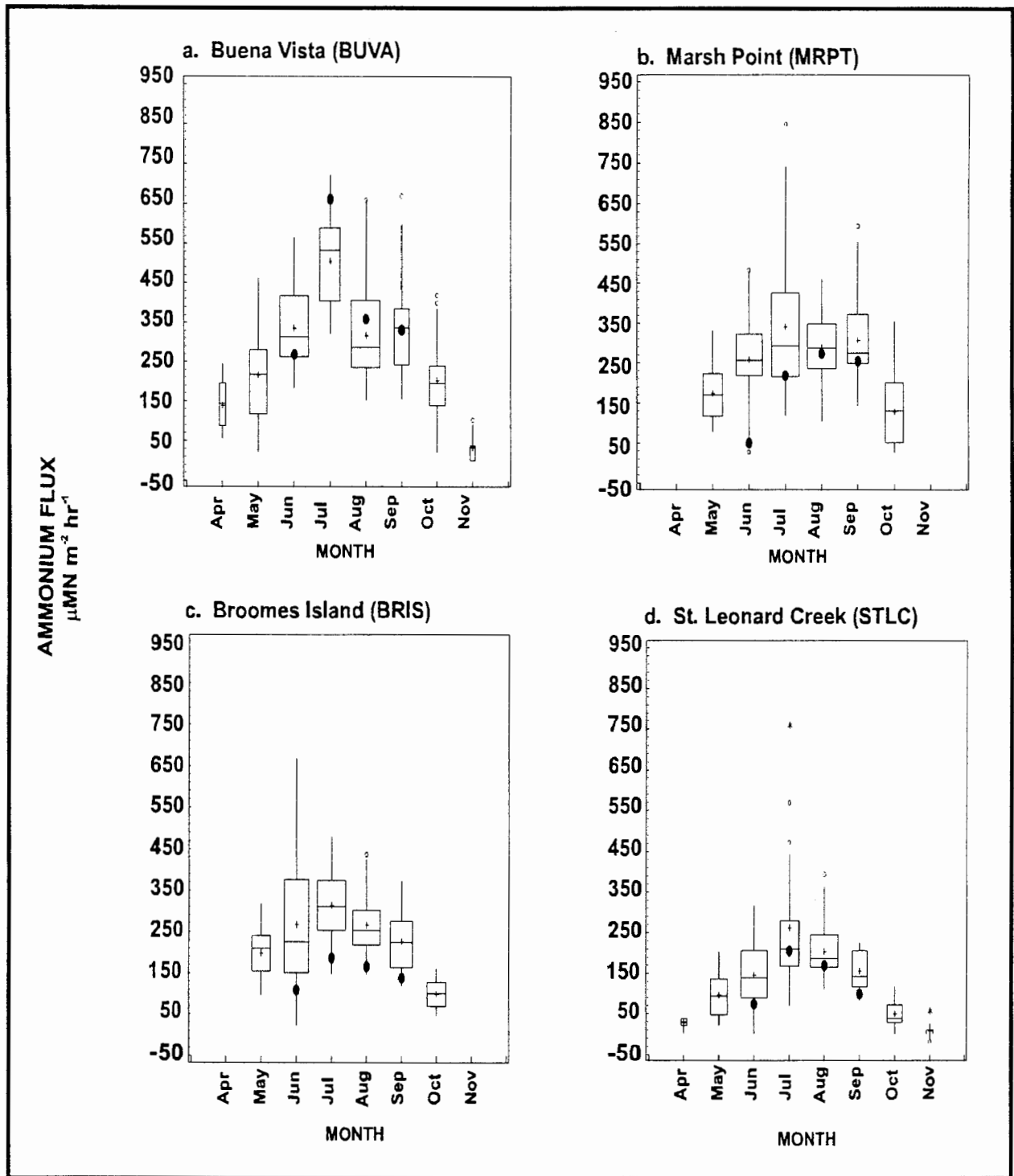


Figure 5-2.2. Box and whisker plots for ammonium (NH_4^+) flux rates for April to November at four SONE stations located in the Patuxent River.

a. Buena Vista (BUVA); b. Marsh Point (MRPT); c. Broomes Island (BRIS) and d. St. Leonard Creek (STLC).

The complete flux data set 1985 through 1997 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1997. September values for all stations only include six years data, 1991 through 1997. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1997. 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.

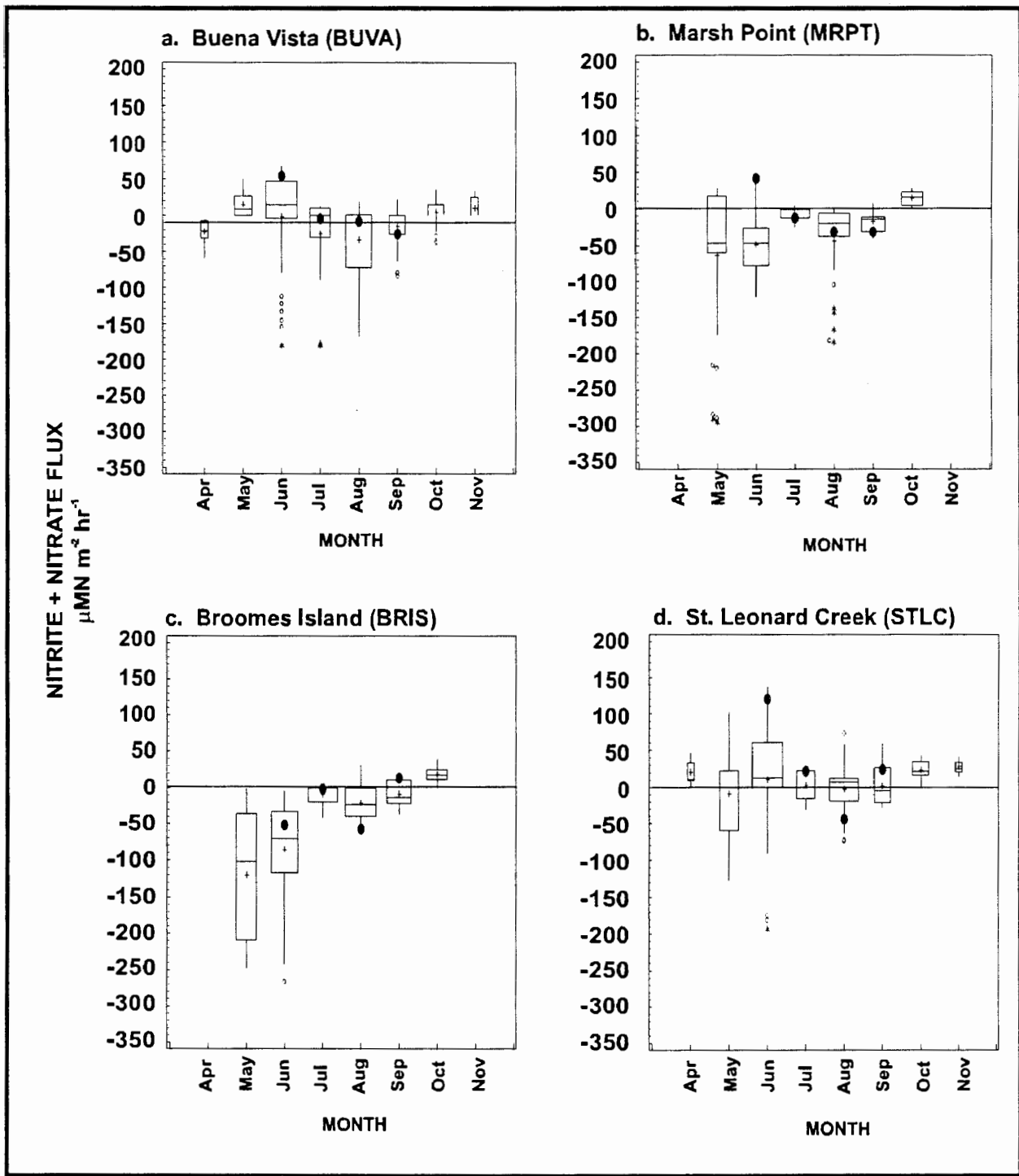


Figure 5-2.3. Box and whisker plots for nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) flux rates for April to November at four SONE stations located in the Patuxent River.

a. Buena Vista (BUVA) b. Marsh Point (MRPT); c. Broomes Island (BRIS) and d. St Leonard Creek (STLC).

The complete flux data set 1985 through 1997 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1997. September values for all stations only include six years data, 1991 through 1997. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1997. 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.

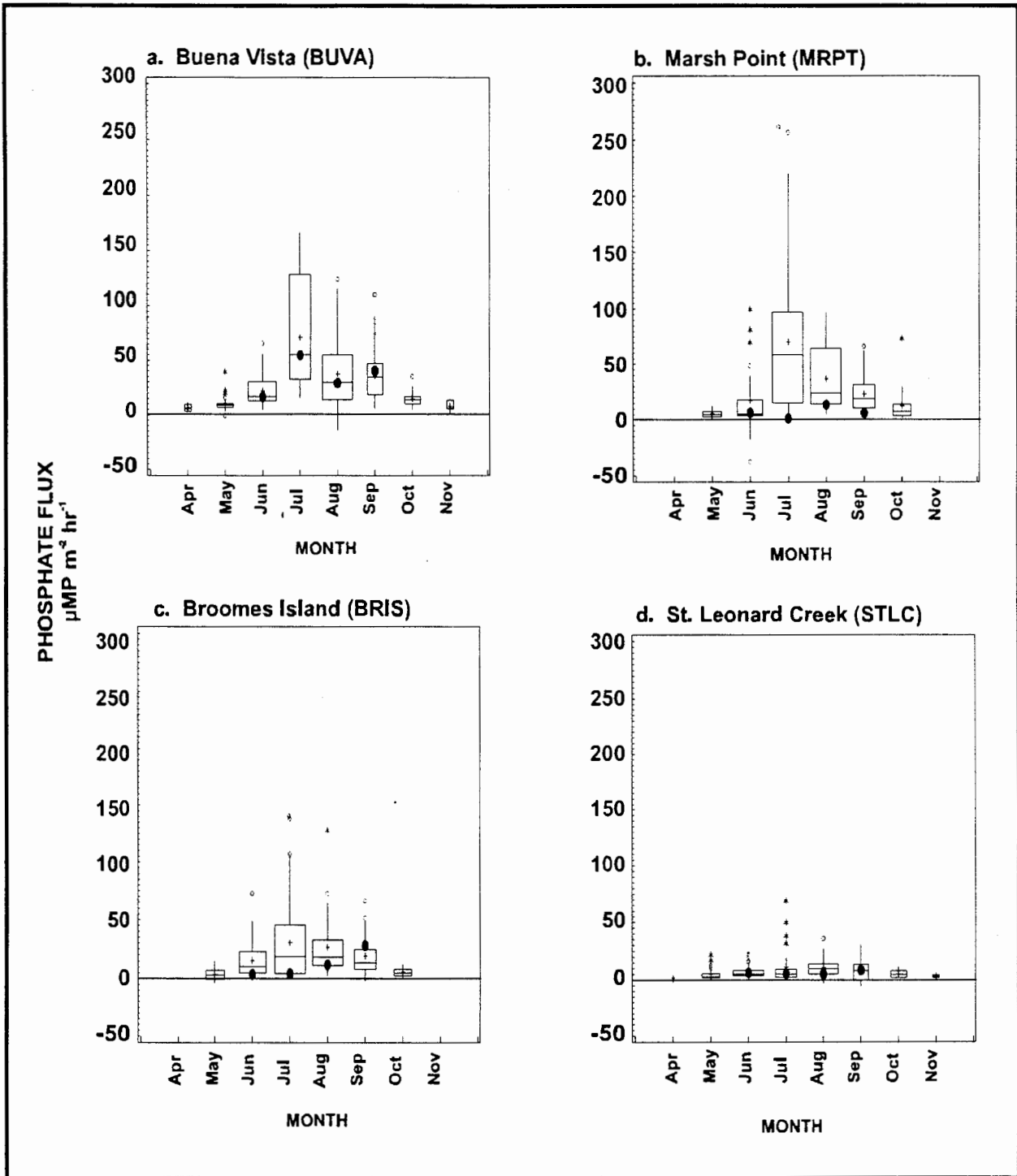


Figure 5-2.4. Box and whisker plots for phosphorus (PO_4^{3-} or DIP) flux rates for April to November at four SONE stations located in the Patuxent River. a. Buena Vista (BUVA); b. Marsh Point (MRPT); c. Broomes Island (BRIS) and d. St Leonard Creek (STLC).

The complete flux data set 1985 through 1997 was used to plot the graph. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on data from 1989 through 1997. September values for all stations only include six years data, 1991 through 1997. The bold solid dots indicate average monthly fluxes from one set of triplicate flux values recorded in 1997. 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.

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 three stations in June, 1997 (St. Leonard Creek [STLC], Marsh Point [MRPT] and the most up-river station in the Patuxent, Buena Vista [BUVA]). 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 1997, 10 of 16 triplicated nitrite plus nitrate flux measurements were more positive than the long-term average, again indicating improving sediment quality conditions.

In contrast, during 1996 the overwhelming pattern was nitrite plus nitrate flux ($\text{NO}_2^- + \text{NO}_3^-$) from water to sediments which was to be expected during a wet year when water column nitrate concentrations were high. During 1995, a 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. 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.

5.3.4 Dissolved Inorganic Phosphorus (PO_4^{3-} or DIP) Fluxes

Average monthly dissolved inorganic phosphorus (DIP) fluxes in the Patuxent River during 1997 ranged from $3.84 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Broomes Island (BRIS) to $16.49 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Buena Vista (BUVA) in June 1997; from $1.55 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Marsh Point (MRPT) to $54.71 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Buena Vista (BUVA) in July, 1997; from $5.29 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at St. Leonard Creek (STLC) to $29.22 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at St. Leonard Creek (STLC) in August, 1997 and from $6.22 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Marsh Point (MRPT) to $40.25 \mu\text{MP m}^{-2} \text{hr}^{-1}$ at Buena Vista (BUVA) in September, 1997 (Figure 5-1.4; Tables B6-58 - B6-61).

The spatial pattern of phosphorus fluxes in the Patuxent River in 1997 are consistent with those reported for both ammonium (NH_4^+) and nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$); fluxes were generally higher at upriver sites in closer proximity to nutrient sources.

In some contrast to the 1996 observations, dissolved inorganic phosphorus (PO_4^{3-}) fluxes in 1997 were the most outstanding finding of the EPC-SONE program. 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. During 1997 fluxes at Patuxent River stations were noticeably reduced; rates at Broomes Island (BRIS) were half those of the long term mean and fluxes were much more reduced at Marsh Point (MRPT). 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 1997 (and 1995, a low flow year) is what would be expected if this were the case.

5.4. Monitoring Sediment Metabolism under Anoxic and Oxic Conditions in the Patuxent River: Dissolved inorganic carbon (TCO₂) Flux Approach

One of the goals of the Ecosystem Processes Component of the Chesapeake Bay Monitoring Program is to assess temporal and spatial variability 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, in 1996, 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 was incredibly labor intensive, requiring extensive handling on the research vessel, month-long incubations of sediment cores under temperature controlled laboratory conditions and tedious analytical analyzes.

Until recently this approach was the only way to obtain reasonable measurements of total sediment metabolism in the context of a monitoring program. However, new analytical technology has now made it possible to routinely measure total carbon dioxide (TCO₂) concentrations with great precision. The importance of this rests on the fact that carbon dioxide (CO₂) 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 (CO₂) concentration in seawater against the huge background concentrations which are present.

Measurements of dissolved inorganic carbon (TCO₂) flux were made using the routine intact sediment core approach of the sediment oxygen and nutrient exchanges (SONE) program at four Patuxent River SONE stations during 1996 and 1997. Average monthly dissolved inorganic carbon (TCO₂) fluxes in 1997 ranged from 1672 μmol CO₂ m⁻² hr⁻¹ at Broomes Island (BRIS) to 4205 μmol CO₂ m⁻² hr⁻¹ at Buena Vista (BUVA) in June 1997; from 1670 μmol CO₂ m⁻² hr⁻¹ at Broomes Island (BRIS) to 3958 μmol CO₂ m⁻² hr⁻¹ at Buena Vista (BUVA) in July, 1997; from 1677 μmol CO₂ m⁻² hr⁻¹ at Broomes Island (BRIS) to 4147 μmol CO₂ m⁻² hr⁻¹ at Buena Vista (BUVA) in August, 1996 and from

1071 $\mu\text{M CO}_2 \text{ m}^{-2} \text{ hr}^{-1}$ at Broomes Island (BRIS) to 3923 $\mu\text{M CO}_2 \text{ m}^{-2} \text{ hr}^{-1}$ at Buena Vista (BUVA) in September, 1997 (Figure 5-2; Tables B6-62 - B6-64).

Monthly average rates at stations in the Patuxent River exhibited some strong trends during both 1996 and 1997 (Figure 5-3). First, rates were lower at the 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 up-river stations exhibited a strong seasonal signal with highest fluxes in June and July and lower values in August and September during 1996, a very high flow and high production year. This pattern indicates that total sediment metabolism is most closely linked to organic matter supply during the present year rather than predominantly to organic matter which has accumulated in the sediment column over many years. This observation is important because it suggests relatively rapid (year or two) rather than slow (decade) time scales for depletion of labile organic water stocks. There was little or no seasonal pattern observed during 1997, a year of lower river flow.

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 particulate organic carbon (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 $\text{g C m}^{-2} \text{ day}^{-1}$ to 1.2 $\text{g C m}^{-2} \text{ day}^{-1}$. 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 (See Chapter 10 for measurements of primary production rates). 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 5-4). For example, rates in the inner portion of the Patapsco River averaged almost 10 $\text{mmol m}^{-2} \text{ hr}^{-1}$ during summer of 1994 (equivalent to about 3 $\text{g C m}^{-2} \text{ day}^{-1}$). Lower rates were observed in the outer portions of the harbor and Back River as expected probably because loading rates are 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.

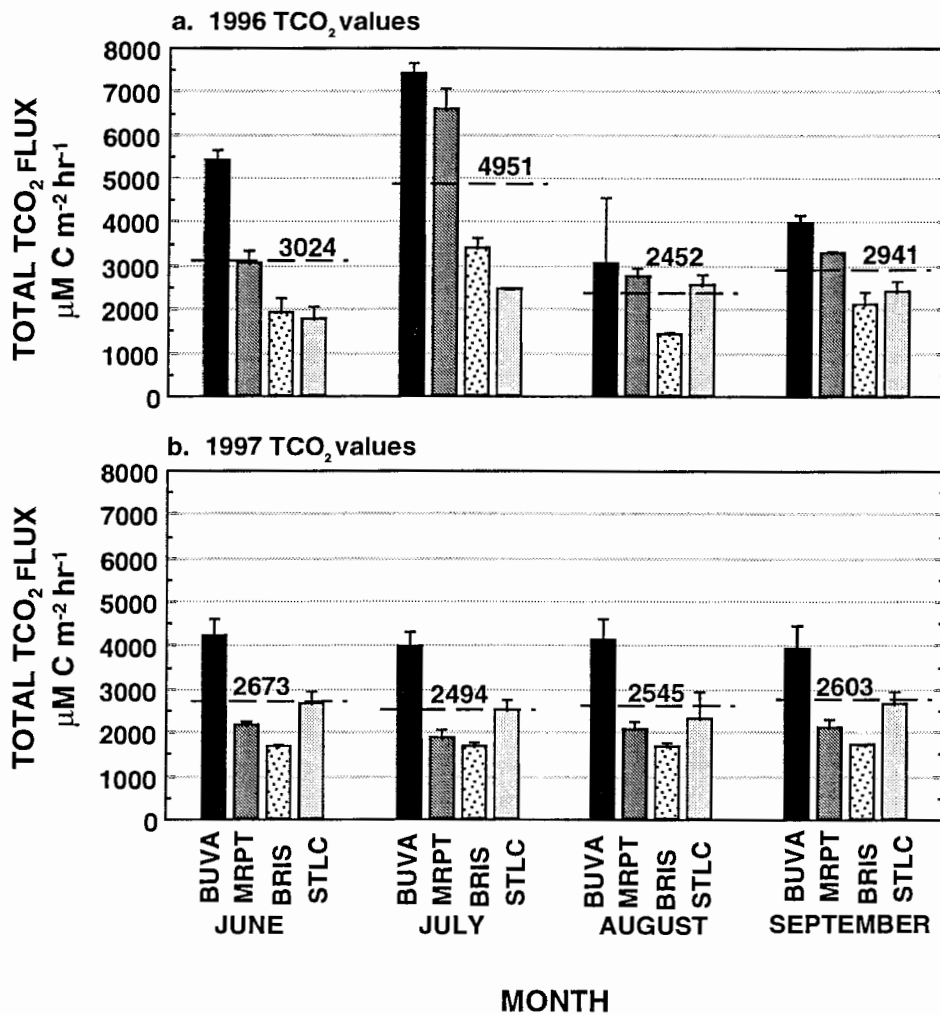


Figure 5-3. Mean monthly dissolved inorganic carbon (TCO₂) fluxes measured in 1997 for the months June through September at four SONE stations located in the Patuxent River. Mean values for each month are indicated as broken lines on the graphic.

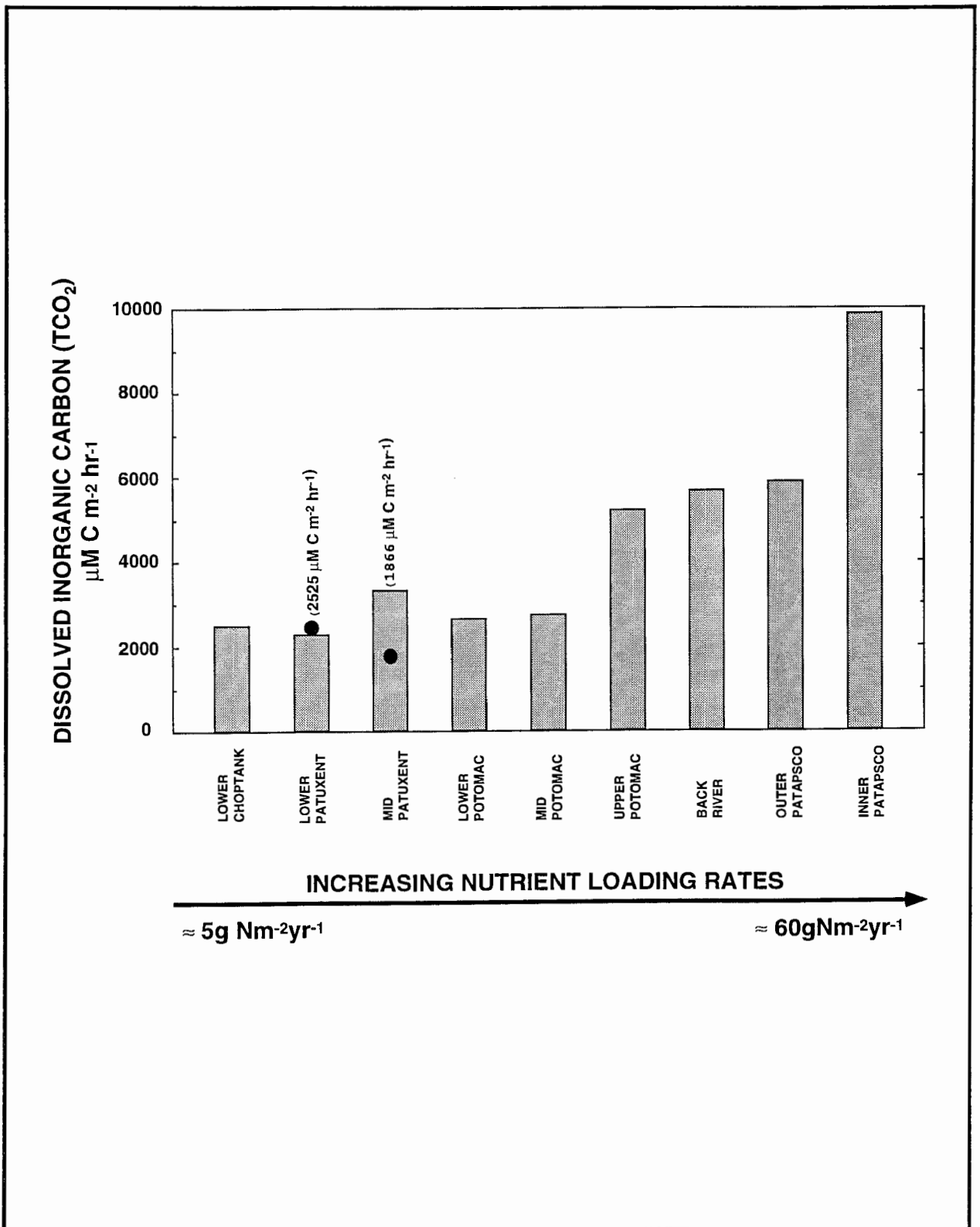


Figure 5-4. A bar graph showing a general relationship between dissolved inorganic carbon (TCO₂) flux and total nitrogen (TN) loading rates based on 1995 data. The values given at either extreme of the x-axis are from Boynton et al. (1995). The remaining bars are arranged based on qualitative assessments of load. Refer to Boynton et al. (1995) for information regarding station locations.

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6. SEDIMENT-WATER FLUX STATUS AND TRENDS: 1997 PATUXENT RIVER STUDY

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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 thirteen complete years (1985 - 1997) 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 analyzes 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.

More recently (1996) a standardized protocol was developed by the Monitoring Program to examine data for status and trend characteristics. This protocol is described and used in the following sections to characterize the current status of sediment-water exchange processes at four Patuxent River SONE stations and to evaluate the Patuxent River SONE data set for interannual trends.

6.1 Sediment-Water Quality Status in the Patuxent River

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. The SONE 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.

6.1.1 Development of the Status Bars

6.1.1.1 Development of the Benchmark

The SONE flux data set collected Bay-wide for the years 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. Two stations (St Leonard Creek [STLC] and Buena Vista [BUVA]) had complete data sets comprising thirteen years (1985 - 1997) of data while the other two stations which were added to the SONE program in 1989, Broomes Island (BRIS) and Marsh Point (MRPT) had data sets comprising 9 years (1989 - 1997). This thirteen year period includes the widest observed 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. Thus every flux measurement made at all four 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 three of the four stations monitored classified as mesohaline while the fourth 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 five 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.

6.1.1.2 Determination of Current Status for the Patuxent River

A median value for the years 1995, 1996 and 1997 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 reducing 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 1996 was a very wet year; in contrast, 1995 was a dry year and 1997 was intermediate in flow between these two years.

6.1.2 Evaluation of the Current Status for the Patuxent River

i. Sediment Oxygen Consumption (SOC)

The current status (median of 1995, 1996 and 1997 data) of sediment oxygen consumption (SOC) fluxes at the four SONE stations in the Patuxent River is indicated in Figure 6-1.b.i. 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 four SONE stations in the Patuxent river, two had SOC rates in the fair range, and two were in the good range. The pattern of SOC fluxes in the Patuxent River 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. Status for the previous period (1994, 1995 and 1996) is provided in Figure 6-1.a.ii and indicates only small changes between evaluation periods.

ii. Ammonium (NH_4^+)

The current status (median of 1995, 1996 and 1997 data) of ammonium fluxes at the four SONE stations in the Patuxent River 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 four SONE stations in the Patuxent River two had ammonium fluxes 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). One of the three years considered was an exceptionally high flow year and ammonium fluxes at two down river sites were in the fair category (St. Leonard Creek [STLC] and Broomes Island [BRIS]). These sites behaved as expected moving towards the good category when river flows returned to normal levels in 1997. The other two sites had values in the poor range. Status for the previous period (1994, 1995 and 1996) is provided in Figure 6-1.a.ii and indicates only small changes between evaluation periods.

iii. Nitrite (NO_2^-)

The current status (median of 1994, 1995 and 1996 data) of nitrite fluxes at the eight SONE stations in the Patuxent River is indicated in Figure 6-1.b.iii. In the case of nitrite fluxes it appears appropriate to judge high values (positive values) as good because of the well established linkage

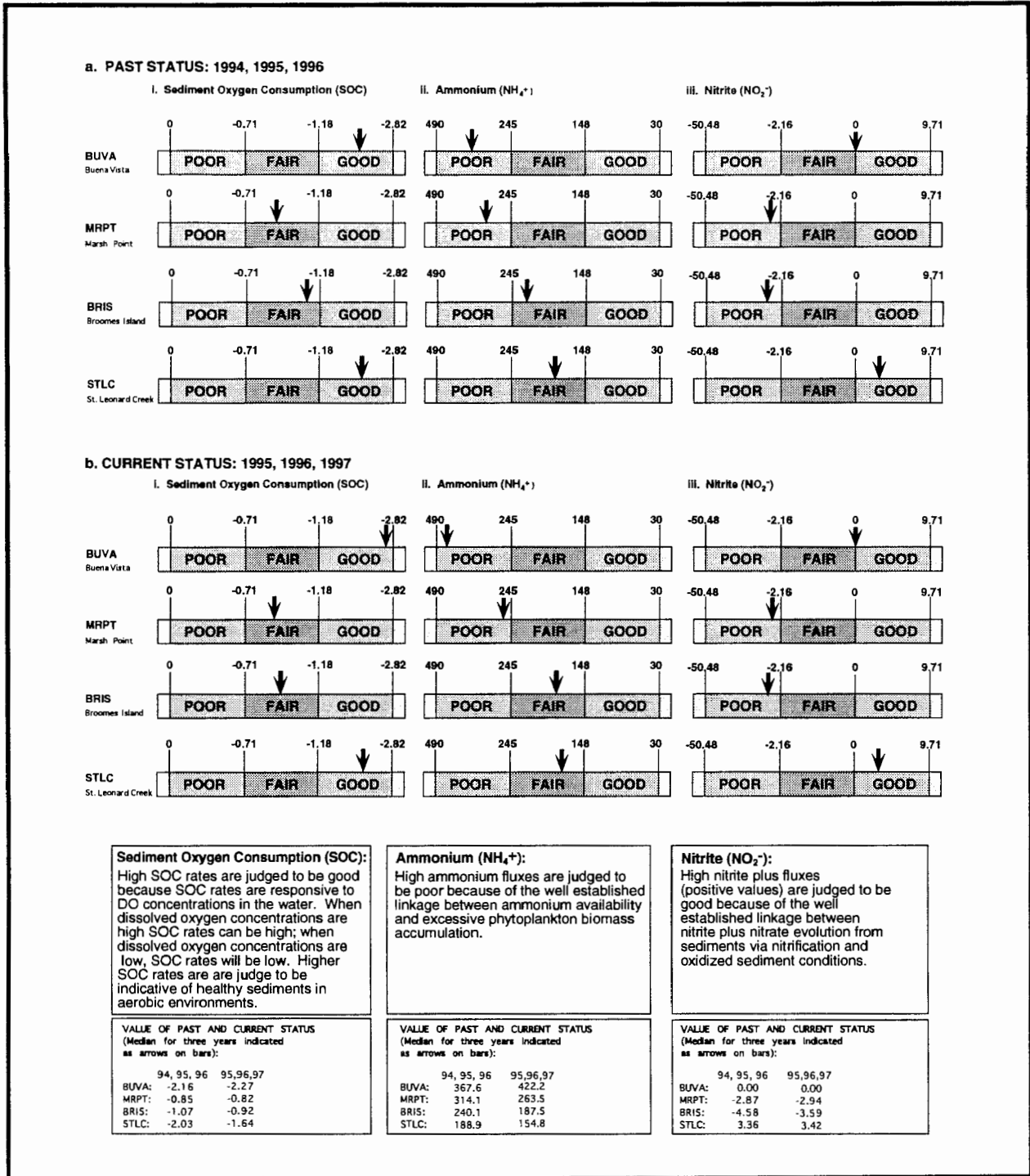


Figure 6-1. A summary of the status of sediment oxygen and nutrient exchanges for four SONE stations in the Patuxent River for five flux variables:

a. Sediment Oxygen Consumption (SOC), b. Ammonium (NH₄⁺), c. Nitrite (NO₂⁻).

All flux data for each variable collected at each station between 1985 and 1997 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 1995, 1996 and 1997. The general criteria for judging the flux status as good, fair or poor is indicated below the figure.

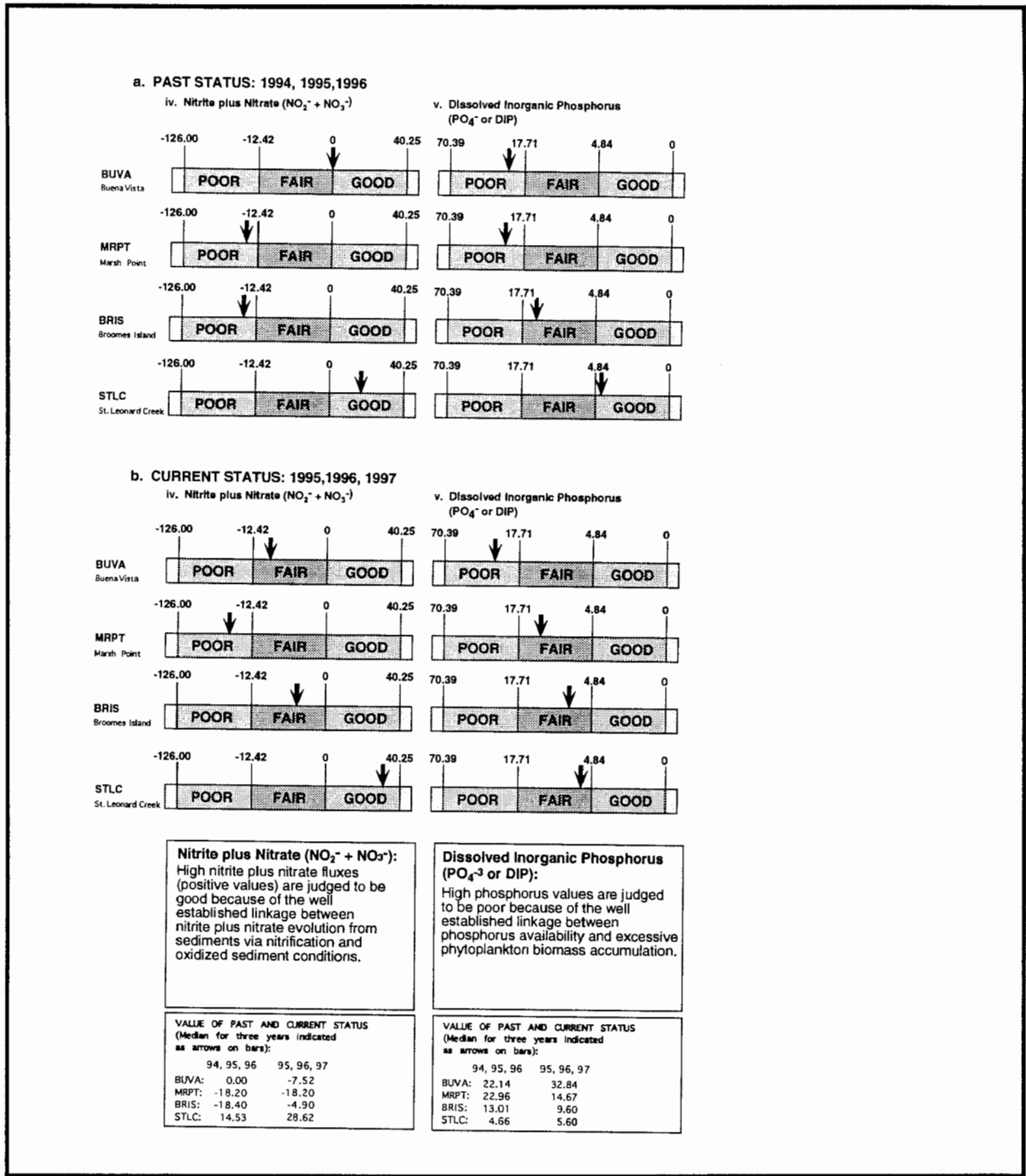


Figure 6-1. A summary of the status of sediment oxygen and nutrient exchanges for four SONE stations in the Patuxent River for five flux variables:

d. Nitrite plus Nitrate ($\text{NO}_2^- + \text{NO}_3^-$) e. Dissolved Inorganic Phosphorus (PO_4^{3-} or DIP).

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 1995, 1996 and 1997. The general criteria for judging the flux status as good, fair or poor is indicated below the figure.

between nitrite evolution from sediments and oxidized sediment conditions. Among the SONE stations, two had nitrite fluxes in the poor range and the other two were in the good range although one was a borderline case between fair and good. 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. Status for the previous period (1994, 1995 and 1996) is provided in Figure 6-1.a.ii and indicates only small changes between evaluation periods.

vi. Nitrite plus Nitrate ($\text{NO}_2^- + \text{NO}_3^-$)

The current status (median of 1995, 1996 and 1997 data) of nitrite plus nitrate fluxes at the four SONE stations in the Patuxent River is indicated in Figure 6-1.b.iv. 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 four SONE stations in the Patuxent River, one was in the good range, St. Leonard Creek (STLC), two stations were in the fair range (Broomes Island [BRIS] and Buena Vista [BUVA]) and one in the poor range (Marsh Point [MRPT]). There was considerable improvement in status at two sites (Broomes Island [BRIS] and Buena Vista [BUVA]), probably because of improved dissolved oxygen conditions.

v. Dissolved Inorganic Phosphorus (PO_4^{3-} or DIP)

The current status (median of 1995, 1996 and 1997 data) of dissolved inorganic phosphorus fluxes at the four SONE stations in the Patuxent River is indicated in Figure 6-1.b.v. 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 four SONE stations in the Patuxent River, three had phosphorus fluxes in the fair range while the station farthest upstream, Buena Vista (BUVA), was in the poor range. It should be noted here that high river flow years have a particularly strong influence on phosphorus fluxes (fluxes increase). One of the three years considered, 1996, was an exceptionally high flow year and phosphorus fluxes at several sites were enhanced enough to place them deep within the fair or poor categories in the previous evaluation (Figure 6-2.a.v). As expected two of these sites moved towards or into the fair category when river flows return to more normal levels during 1997.

6.2 Sediment Oxygen and Nutrient Exchanges (SONE) Trends: 1997 Patuxent River Study

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 NOT corrected for river flow, as is the case for testing other variables for trends within the monitoring program.

6.2.1 Current Testing (Seasonal Kendall Test) for Seasonal Trends: 1985 - 1997 data from the Patuxent River

Trend analysis is one method which can be used 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).

6.2.2. Sediment Oxygen Nutrient and Exchanges (SONE) Flux Data Set for the Patuxent River

Flux data were collected over a period of thirteen years (1985 - 1997) during seven months (April through November) at 4 stations in the Patuxent River (Buena Vista [BUVA], Broomes Island [BRIS], Marsh Point [MRPT] and St. Leonard Creek [STLC]). 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 were completed. A plot of the complete data set for each flux variable was prepared, an example for ammonium (NH_4^+) values at Buena Vista (BUVA) is included (Figure 6-2). Extreme outliers were examined 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 are 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.

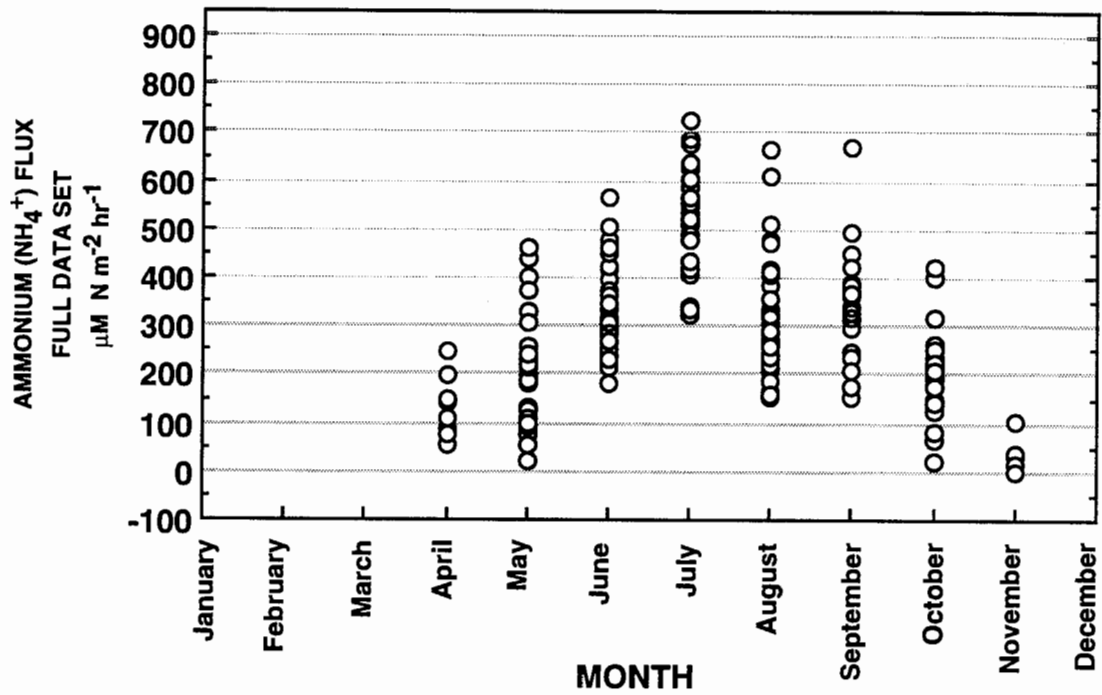


Figure 6-2. Plot of full flux data set (1985 - 1997) for ammonium (NH₄⁺) at Buena Vista (BUVA) for Quality Assurance and Quality Control (QA/QC) checking.

6.2.3 Results of Kendall Tests for Detection of Inter-Annual Trends for the Patuxent River

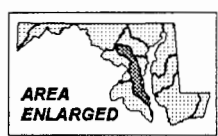
Three graphics (Figures 6-3.a - 6-3.c) summarize results of the four flux variables measured at four sites (Buena Vista [BUVA], Broomes Island [BRIS], Marsh Point [MRPT] and St. Leonard Creek [STLC]) in the Patuxent River estuary.

An overview of the significance of trends is summarized in Table 6-1. Annual values and seasonal combination values for observed data are presented in Table 6-2. The figures include results for a total of four sediment-water flux variables, sediment oxygen consumption (SOC), inorganic phosphorus, nitrite and nitrite plus nitrate.

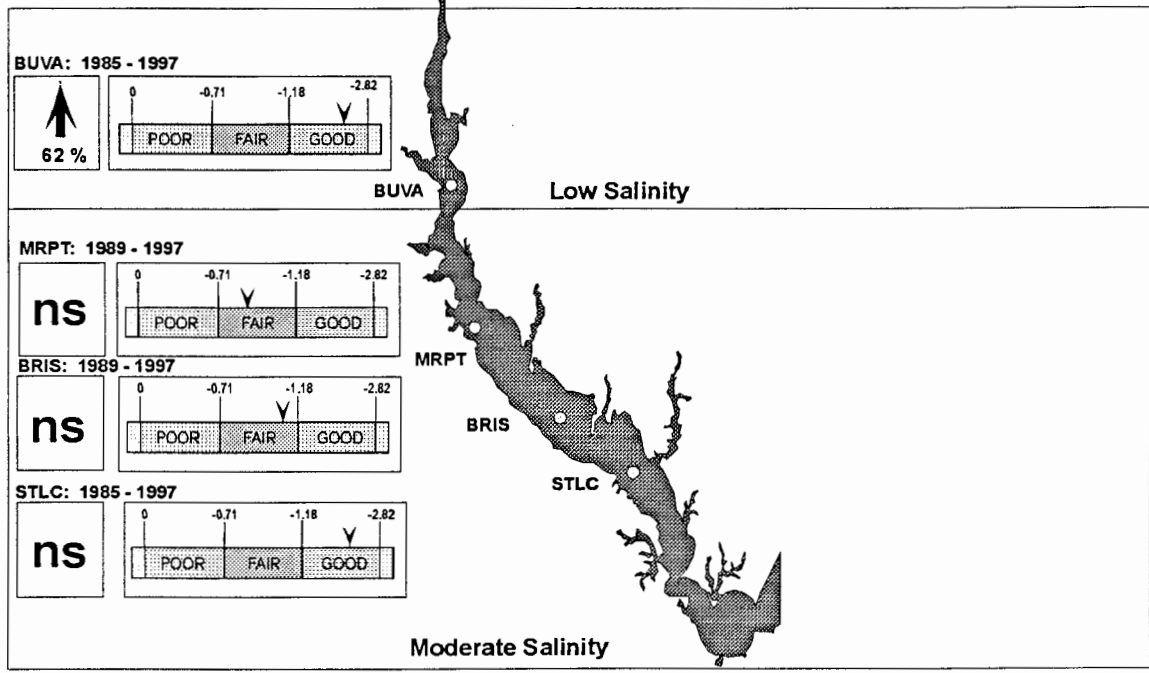
Testing for trends at the annual time scale resulted in few statistically significant results ($p < 0.01$). In the Patuxent River estuary sediment oxygen consumption (SOC) fluxes indicated a significant decreasing trend at the upper estuary station at Buena Vista (BUVA). It is important to note that decreasing values (increasingly negative) of sediment oxygen consumption (SOC) indicate that dissolved oxygen flux from water to sediments has increased during the study period and in this context is considered to be an improving trend in sediment quality. A significant increasing trend was indicated for both ammonium (NH_4^+) and nitrite (NO_2^-) in the Patuxent River estuary for this same station, Buena Vista (BUVA) and, in the case of these nutrients, is considered to be a degrading trend.

There were no significant annual trends for dissolved inorganic phosphorus or nitrite plus nitrate fluxes in the Patuxent River estuary. During the last 13 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 are difficult to detect unless they are very large and persist for a few consecutive years.

Sediment Oxygen Consumption



TREND STATUS



KEY

○ = SONE station

STATUS = average condition during 1995 to 1997.

TREND = Significance of Seasonal Kendall Test Statistic (Observed data $p < 0.01$) with direction of slope indicated.

Figure 6-3.a. Map showing status and trends at four stations in the Lower Patuxent River for (observed data) sediment oxygen consumption (SOC) fluxes. Observed data indicates that no river flow adjustments were applied to the raw data.

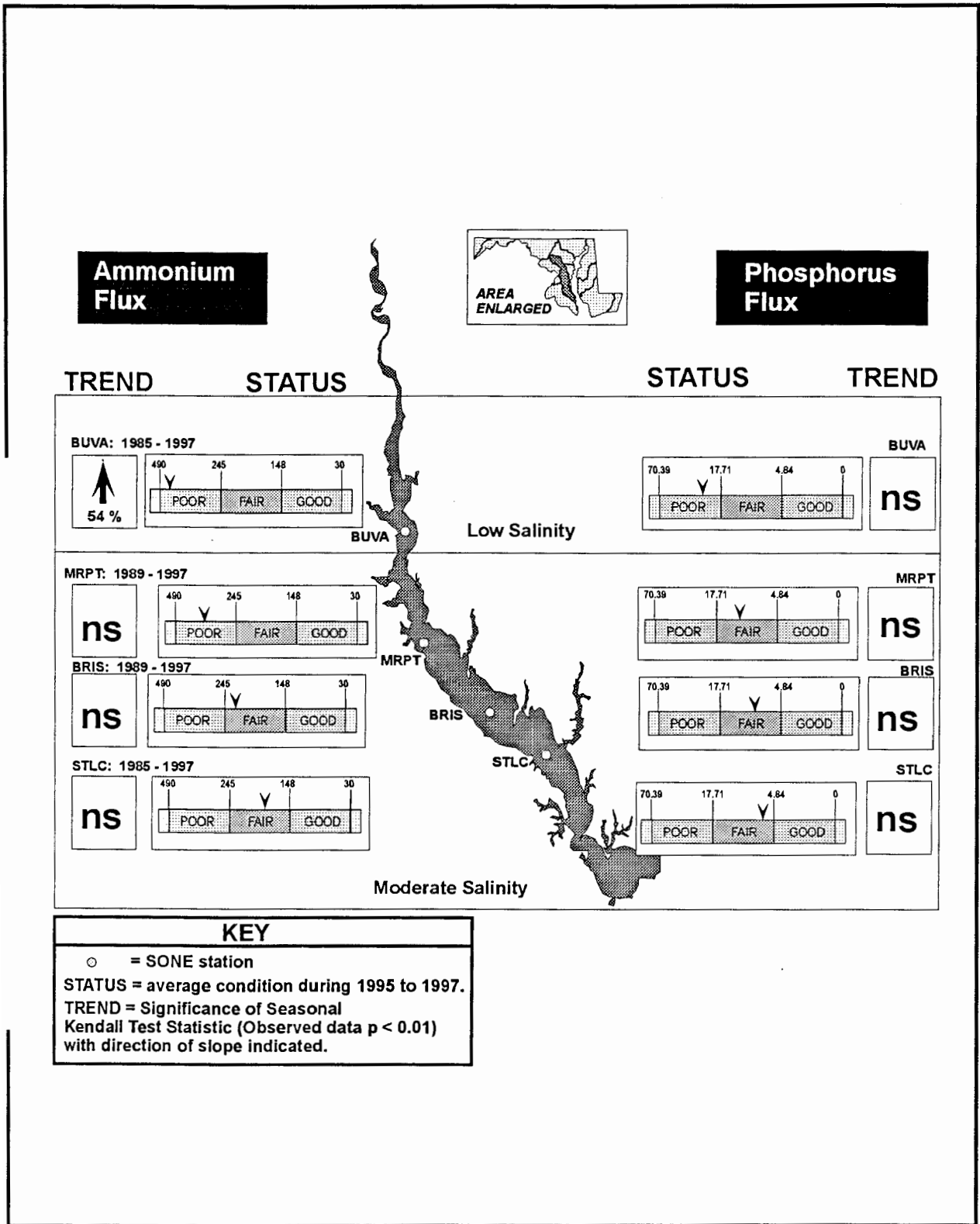


Figure 6-3.b. Map showing status and trends at four stations in the Lower Patuxent River for two flux variables (observed data), ammonium (NH_4^+) and phosphorus fluxes (PO_4^{3-}). Observed data indicates that no river flow adjustments were applied to the raw data.

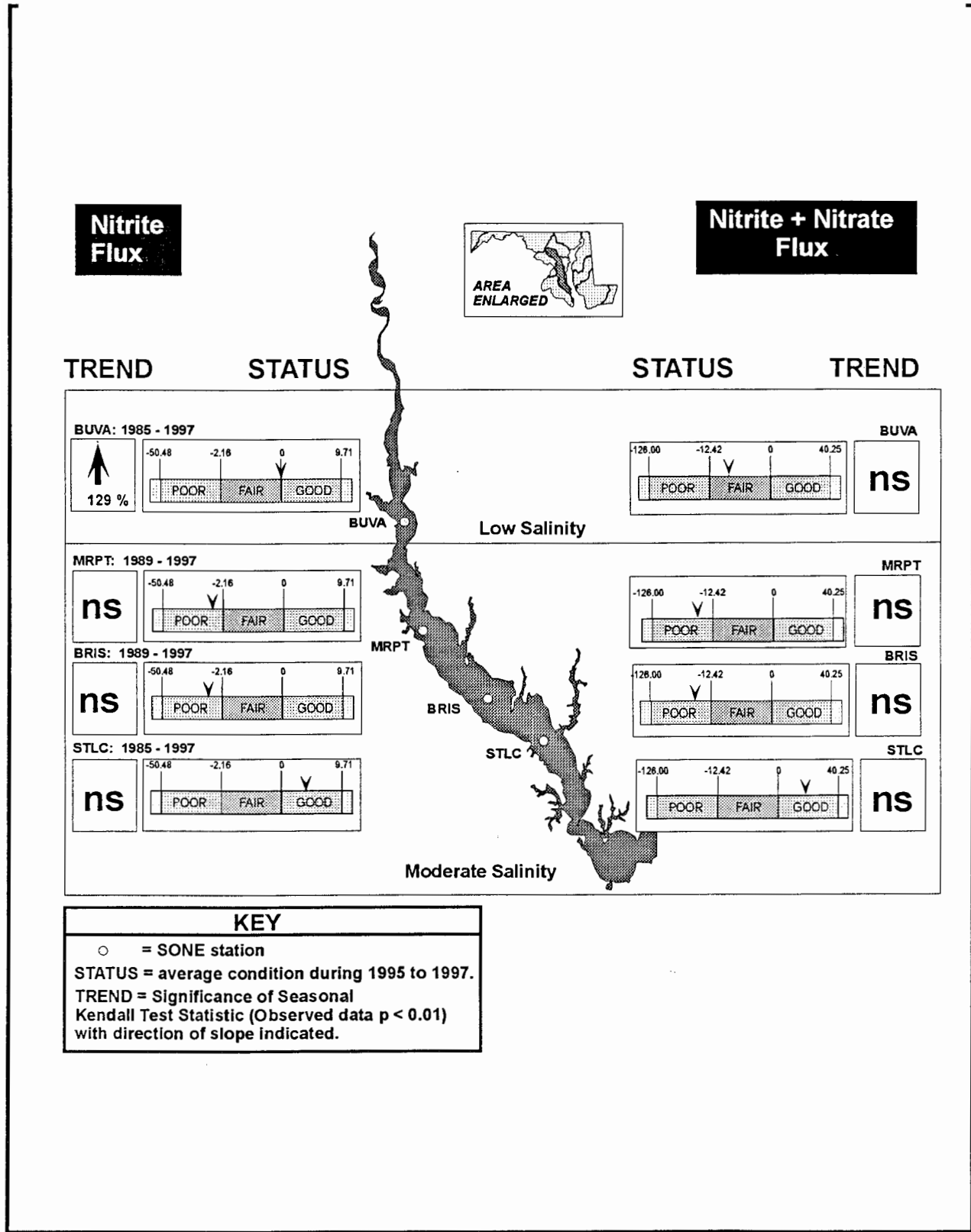


Figure 6-3.c. Map showing status and trends at four stations in the Lower Patuxent River for two flux variables (observed data), nitrite (NO_2^-) and nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$). Observed data indicates that no river flow adjustments were applied to the raw data.

Table 6-1. A condensed summary of significant trends (observed data) detected for sediment-water exchange data using seasonal Kendall Test statistic.

Observed data indicates that no river flow adjustments were applied to the raw data.

Significance: ** $p = 0.01$; *** $p = 0.001$

NOTE: Upward pointing arrows indicate that the trend was judged as improving;

Downward pointing arrows (none indicated) would have indicated degrading trends.

Station	Month									Season Combination			
	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Annual	Jun-Sep	Jun-Aug	Jul-Aug	
a. Sediment Oxygen Consumption (SOC; $g O^2 m^{-2} day^{-1} yr^{-1}$)													
BUVA										** ↑	** ↑	** ↑	** ↑
b. Ammonium (NH_4^+; $\mu M N m^{-2} hr^{-1}$)													
BUVA										** ↑	** ↑	** ↑	** ↑
BRIS					** ↑								
c. Nitrite (NO_2^-; $\mu M N m^{-2} hr^{-1}$)													
BUVA										** ↑			
STLC				** ↑									
d. Nitrite plus nitrate ($NO_2^- + NO_3^-$; $\mu M N m^{-2} hr^{-1}$)													
No significant trends													
e. Dissolved Phosphorus (PO_4^{3-}; $\mu M P m^{-2} hr^{-1}$)													
No significant trends													

Table 6-2. Table of Seasonal Kendall Test Statistics (observed data) at four SONE stations for four seasonal and an annual variable.

Observed data indicates that no river flow adjustments were applied to the raw data.

Significance: ** $p = 0.01$; *** $p = 0.001$

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

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
Buena Vista (BUVA): 1985 - 1997				
Sign	-88	-67	-70	-50
p value	0.002**	0.01**	0.01**	0.01**
Slope	-0.084	-0.073	-0.084	-0.090
Marsh Point (MRPT): 1989 - 1997				
Sign	0	8	-1	-9
p value	1.00	0.68	1.00	0.55
Slope	0.000	0.008	-0.000	-0.026
Broomes Island (BRIS): 1989 - 1997				
Sign	-34	-27	-26	-26
p value	0.08	0.13	0.11	0.07
Slope	-0.054	-0.054	-0.084	-0.107
St Leonards Creek (STLC): 1985 - 1997				
Sign	-30	-19	-12	-24
p value	0.28	0.47	0.65	0.19
Slope	-0.043	-0.030	-0.109	-0.062

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

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
Buena Vista (BUVA): 1985 - 1997				
Sign	70	65	70	60
p value	0.01**	0.01**	0.006**	0.002**
Slope	9.749	10.656	11.763	16.093
Marsh Point (MRPT): 1989 - 1997				
Sign	21	3	10	12
p value	0.29	0.91	0.57	0.42
Slope	9.447	3.217	8.570	10.816
Broomes Island (BRIS): 1989 - 1997				
Sign	-29	-25	-22	-14
p value	0.13	0.16	0.18	0.34
Slope	-8.367	-8.683	-8.525	-7.168
St Leonards Creek (STLC): 1985 - 1997				
Sign	-11	-6	-3	6
p value	0.72	0.85	0.94	0.79
Slope	-0.704	-0.560	-0.438	1.203

Table 6-2. Table of Seasonal Kendall Test Statistics (observed data) at four SONE stations for four seasonal and an annual variable (Continued).

Observed data indicates that no river flow adjustments were applied to the raw data.

Significance: ** $p = 0.01$; *** $p = 0.001$

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

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
Buena Vista (BUVA): 1985 - 1997				
Sign	54	39	34	16
p value	0.01**	0.04*	0.06	0.31
Slope	0.968	0.748	0.572	0.539
Marsh Point (MRPT): 1989 - 1997				
Sign	6	-8	-1	0
p value	0.79	0.68	1.00	1.00
Slope	0.098	-0.150	-0.050	-0.035
Broomes Island (BRIS): 1989 - 1997				
Sign	2	1	-10	-18
p value	0.96	1.00	0.57	0.21
Slope	0.000	0.111	-0.495	-1.114
St Leonards Creek (STLC): 1985 - 1997				
Sign	32	30	19	27
p value	0.11	0.11	0.28	0.06
Slope	1.048	1.093	0.837	1.400

d. Nitrite plus Nitrate ($\text{NO}_2^- + \text{NO}_3^-$; $\mu\text{M N m}^{-2} \text{ hr}^{-1} \text{ yr}^{-1}$)

STATION	Annual	Jun - Sep	Jun - Aug	Jul - Aug
PATUXENT RIVER:				
Buena Vista (BUVA): 1985 - 1997				
Sign	-25	-3	-6	-10
p value	0.37	0.94	0.83	0.61
Slope	-0.928	-0.236	-0.305	-1.053
Marsh Point (MRPT): 1989 - 1997				
Sign	7	11	12	4
p value	0.75	0.56	0.49	0.83
Slope	0.352	0.714	0.857	0.344
Broomes Island (BRIS): 1989 - 1997				
Sign	12	14	1	-5
p value	0.55	0.45	1.00	0.77
Slope	1.425	1.855	0.000	-0.163
STATION St Leonards Creek (STLC): 1985 - 1997				
Sign	4	-1	-16	-2
p value	0.91	1.00	0.54	0.96
Slope	0.309	-0.094	-0.690	-0.138

Table 6-2. Table of Seasonal Kendall Test Statistics (observed data) at four SONE stations for four seasonal and an annual variable (Continued).

Observed data indicates that no river flow adjustments were applied to the raw data.

Significance: ** $p = 0.01$; *** $p = 0.001$

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:				
Buena Vista (BUVA): 1985 - 1997				
Sign	16	21	14	28
p value	0.58	0.42	0.59	0.16
Slope	0.255	0.622	0.602	1.889
Marsh Point (MRPT): 1989 - 1997				
Sign	1	-7	6	-10
p value	1.00	0.73	0.75	0.51
Slope	0.047	-1.195	0.495	-1.919
Broomes Island (BRIS): 1989 - 1997				
Sign	-23	-25	-32	-24
p value	0.24	0.16	0.05	0.09
Slope	-0.410	-0.878	-1.398	-1.435
STATION St Leonards Creek (STLC): 1985 - 1997				
Sign	1	-5	2	-12
p value	1.00	0.88	0.97	0.56
Slope	0.001	-0.094	0.007	-0.230

6.2.4 Results of Seasonal Kendall Tests for Detection of Monthly Trends for the Patuxent River

The results from the monthly Seasonal Kendall tests are presented as a table using observed rather than flow corrected data (Table 6-3). 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 6-3. The n value indicates the number of observations used in the analysis.

i. Sediment Oxygen Consumption (SOC)

No significant trends were found in Table 6-3.a.

ii. Ammonium (NH_4^+)

Significant trends were indicated for ammonium (NH_4^+) fluxes at $p < 0.05$ in July and August at Buena Vista (BUVA; degrading trend) and August at Broomes Island (BRIS; improving trend; Table 6-3.b).

iii. Nitrite (NO_2^-)

A positive (improving) significant trend was indicated for nitrite (NO_2^-) fluxes in the Patuxent River at St. Leonard Creek (STLC) in July (Table 6-3.c).

iv. Nitrite plus Nitrate ($\text{NO}_2^- + \text{NO}_3^-$)

A positive (improving) significant trend ($p < 0.05$) for nitrite plus nitrate flux was observed for September at St. Leonard Creek ([STLC]; Table 6-3.d). This positive trend is considered to be good since nitrite plus nitrate fluxes from sediments to water is an indication of nitrification activity which requires dissolved oxygen (DO) in bottom waters.

v. Dissolved Inorganic Phosphorus (PO_4^{3-} or DIP)

One significant trend was found for phosphorus (PO_4^{3-}) in the Patuxent River at Broomes Island (BRIS) for August (Table 6-3.e). This trend was one of decreasing flux which is considered good because decreasing phosphorus fluxes from sediments to overlying waters decreases nutrient availability.

Table 6-3. Table of Monthly Seasonal Kendall Test Statistics (observed data) at four SONE stations for five SONE variables.

Observed data indicates that no river flow adjustments were applied to the raw data.

“.” or blank cells in the table indicate that no data was collected or the data was insufficient to perform the analysis.

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:								
Buena Vista (BUVA): 1985 - 1997								
Sign	1	-12	-20	-18	-32	3	-9	-1
p value	.	0.18	0.25	0.08	0.06	0.77	0.24	.
n	3	8	13	9	13	7	7	3
Marsh Point (MRPT): 1989 - 1997								
Sign		-5	8	-7	-2	9	-3	
p value		0.47	0.40	0.61	0.92	0.24	0.72	
n		6	8	9	9	7	6	
Broomes Island (BRIS): 1989 - 1997								
Sign		5	0	-10	-16	-1	-12	
p value		0.47	1.00	0.36	0.12	1.00	0.06	
n		6	8	9	9	7	6	
St Leonards Creek (STLC): 1985 - 1997								
Sign	3	-8	12	-16	-8	-7	-3	-3
p value	.	0.40	0.50	0.12	0.63	0.38	0.77	.
n	3	8	13	9	12	7	7	3

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

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
Buena Vista (BUVA): 1985 - 1997								
Sign	-3	8	10	20	40	-5	1	-1
p value	.	0.40	0.58	0.04*	0.02*	0.56	1.00	.
n	3	8	13	9	13	7	7	3
Marsh Point (MRPT): 1989 - 1997								
Sign		9	-2	2	10	-7	9	
p value		0.14	0.90	0.92	0.36	0.38	0.14	
n		6	8	9	9	7	6	
Broomes Island (BRIS): 1989 - 1997								
Sign		-5	-8	10	-24	-3	1	
p value		0.47	0.40	0.36	0.01***	0.77	1.00	
n		6	8	9	9	7	6	
St Leonards Creek (STLC): 1985 - 1997								
Sign	1	-10	-9	-4	10	-3	3	1
p value	.	0.28	0.62	0.76	0.58	0.77	0.77	.
n	3	8	13	9	13	7	7	3

Table 6-3. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at four SONE stations for five SONE variables (Continued)

Observed data indicates that no river flow adjustments were applied to the raw data.

“.” or blank cells in the table indicate that no data was collected or the data was insufficient to perform the analysis.

Significance: * $p = 0.05$; ** $p = 0.01$; *** $p = 0.001$

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

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
Buena Vista (BUVA): 1985 - 1997								
Sign	0	11	18	11	5	5	4	0
p value	.	0.06	0.08	0.36	0.73	0.56	0.48	.
n	1	6	9	9	10	7	5	1
Marsh Point (MRPT): 1989 - 1997								
Sign		3	-1	0	0	-7	11	
p value		0.72	1.00	1.00	1.00	0.38	0.06	
n		6	8	9	9	7	6	
Broomes Island (BRIS): 1989 - 1997								
Sign		-5	8	-12	-6	11	6	
p value		0.47	0.40	0.26	0.61	0.14	0.47	
n		6	8	9	9	7	6	
St Leonards Creek (STLC): 1985 - 1997								
Sign	0	1	-8	24	3	11	1	0
p value	.	1.00	0.48	0.002**	0.86	0.14	1.00	.
n	1	6	9	8	10	7	6	1

d. Nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$; $\mu\text{M N m}^{-2} \text{hr}^{-1} \text{yr}^{-1}$)

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER:								
Buena Vista (BUVA): 1985 - 1997								
Sign	-3	-11	4	0	-10	3	-8	0
p value	.	0.27	0.85	1.0	0.54	0.77	0.38	.
n	3	8	13	9	12	7	7	3
Marsh Point (MRPT): 1989 - 1997								
Sign		-7	8	2	2	-1	3	
p value		0.27	0.40	0.92	0.92	1.00	0.72	
n		6	8	9	9	7	6	
Broomes Island (BRIS): 1989 - 1997								
Sign		-3	6	-5	0	13	1	
p value		0.72	0.55	0.76	1.00	0.07	1.00	
n		6	8	9	9	7	6	
St Leonards Creek (STLC): 1985 - 1997								
Sign	-1	2	-14	14	-16	15	5	1
p value	.	0.90	0.43	0.11	0.36	0.03*	0.56	.
n	3	8	13	8	13	7	7	3

Table 6-3. Table of Monthly Seasonal Kendall Test Statistics (Observed data) at four SONE stations for five SONE variables (Continued).

Observed data indicates that no river flow adjustments were applied to the raw data.

“.” or blank cells in the table indicate that no data was collected or the data was insufficient to perform the analysis.

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:								
Buena Vista (BUVA): 1985 - 1997								
Sign	-3	4	-14	-2	30	7	-7	1
p value	.	0.72	0.37	0.92	0.08	0.38	0.38	.
n	3	8	12	9	13	7	7	3
Marsh Point (MRPT): 1989 - 1997								
Sign		1	16	-2	-8	-13	7	
p value		1.00	0.06	0.92	0.48	0.07	0.27	
n		6	8	9	9	7	6	
Broomes Island (BRIS): 1989 - 1997								
Sign		3	-8	-4	-20	7	-1	
p value		0.72	0.40	0.76	0.04*	0.38	1.00	
n		6	8	9	9	7	6	
St Leonards Creek (STLC): 1985 - 1997								
Sign	-2	10	14	0	-12	-7	-3	1
p value	.	0.28	0.43	1.00	0.50	0.38	0.77	.
n	3	8	13	9	13	7	7	3

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7. SEDIMENT CHLOROPHYLL-a MAPPING ON THE PATUXENT RIVER

R.M. Stankelis, W.R. Boynton and J.M. Frank

It has been shown (e.g. Boynton *et al.*, 1992a; Garber *et al.*, 1989) that there are strong relationships between sediment-water oxygen and nutrient fluxes and the amount of labile organic material deposited to the sediment surface. The use of surficial sediment chlorophyll-a as an index of this labile organic material has proven useful for predicting certain sediment-water exchanges (Cowan and Boynton, 1996; Cowan *et al.*, 1996; Boynton *et al.*, 1997). The goal of the surficial sediment chlorophyll-a mapping study was two-fold. First, it is possible to construct interpolated contour maps of sediment chlorophyll-a using high resolution spatial data for the Patuxent River and thereby identify specific areas of interest. Second, this high-resolution data can be coupled with predictive flux models to construct flux contour maps and estimate integrated sediment-water exchanges across the estuary as a whole. If such maps and predictive flux models can be produced and coupled, this would represent a significant improvement in the spatial coverage of the SONE program.

Thirty seven (37) stations on the Patuxent River located between Benedict MD., and Point Patience (Figure 3-2) were sampled monthly from March through September in 1997 and March through May 1996. These stations were chosen to represent a range of depth and salinity regimes throughout the mesohaline portion of the river. Contour maps of surficial sediment chlorophyll-a were created for each month using *Surfer*TM contouring software. Actual data were interpolated to a uniform grid of 0.002 degrees latitude and longitude using a kriging method. Contours of sediment chlorophyll-a were then created from this uniform grid. Representative chlorophyll-a contour maps for 1997 are shown in Figure 7-1.1 through Figure 7-1.7.

7.1 Distribution of Sediment Chlorophyll-a in Space and Time

An analysis of covariance (ANCOVA) was used to evaluate monthly and yearly trends in sediment chlorophyll-a concentrations in the Patuxent River. Since data were collected from March through May in 1996 and March through September in 1997, separate models were used to evaluate yearly and monthly differences in sediment chlorophyll-a. For both models, water column depth served as a covariate, while month and year served as fixed effects.

To evaluate inter-annual variation, data collected from March through May 1996 and 1997 were used in the analysis. The results of the analysis show that depth was a significant ($P < 0.001$) covariate explaining much of the variation in the data. Total sediment chlorophyll-a was found to be significantly higher in 1996 (114.4 mg m^{-2}) compared to 1997 (95.3 mg m^{-2}). On a monthly basis, mean total chlorophyll-a in May (121.0 mg m^{-2}) was significantly higher than either March (98.3 mg m^{-2}) or April (95.3 mg cm^{-2}). These results are consistent with those found using 1996 data alone.

An evaluation of 1997 monthly (March through September) sediment chlorophyll-a values indicate significant differences among months. The lowest mean total chlorophyll-a (83.2 mg m^{-2}) was found in March, while the highest mean total chlorophyll-a (169.4 mg m^{-2}) was found in September. Figure

7-2 illustrates the mean total sediment chlorophyll-a for each month. Bonnferoni *post-hoc* tests indicate that September chlorophyll-a concentrations were significantly higher ($P < 0.05$) than any other month sampled.

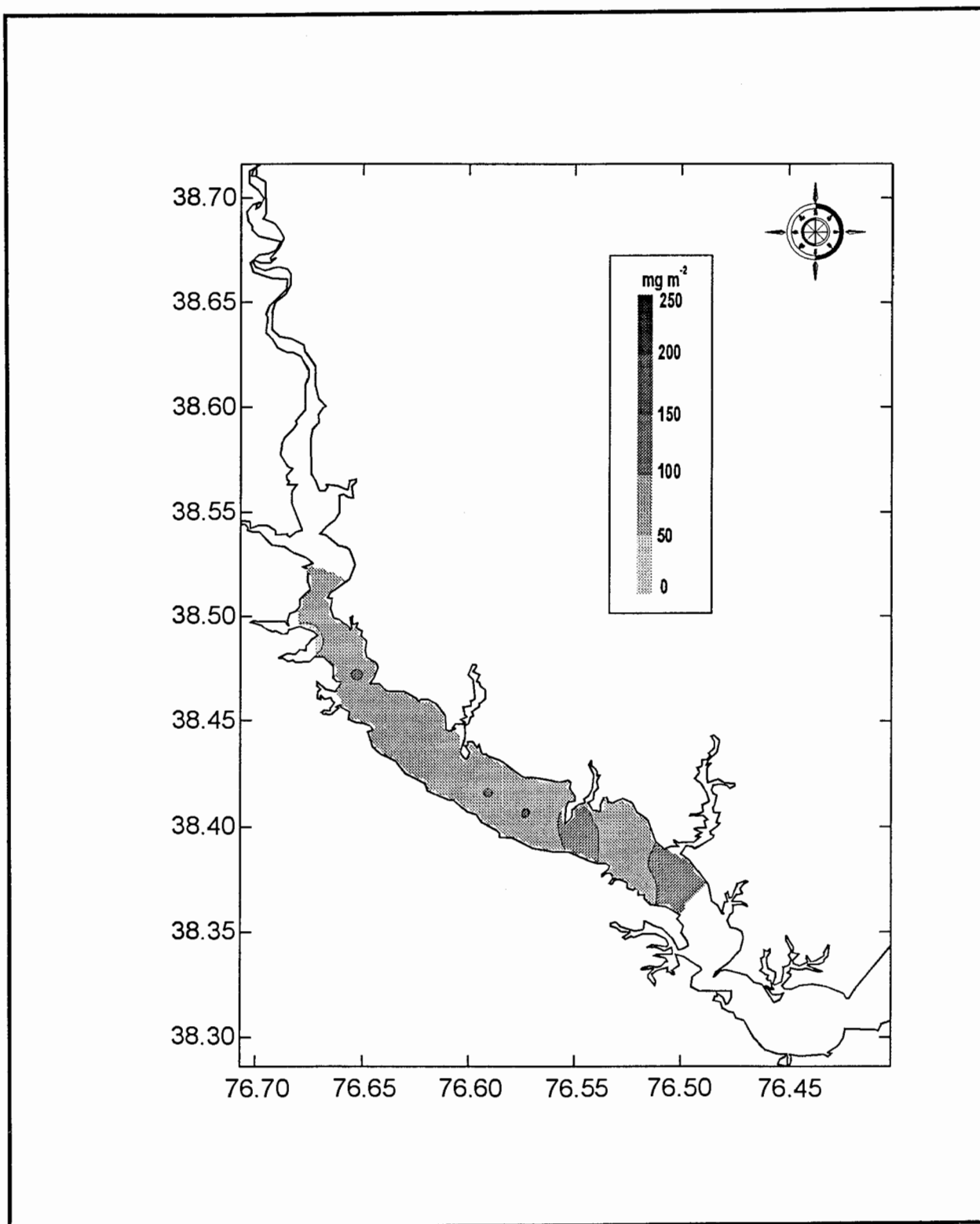


Figure 7-1.1. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during March, 1997 (sediment chlorophyll-a mapping cruise #4, Table C-2.4). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.
Latitude and longitude are in degrees and decimal minutes and seconds.

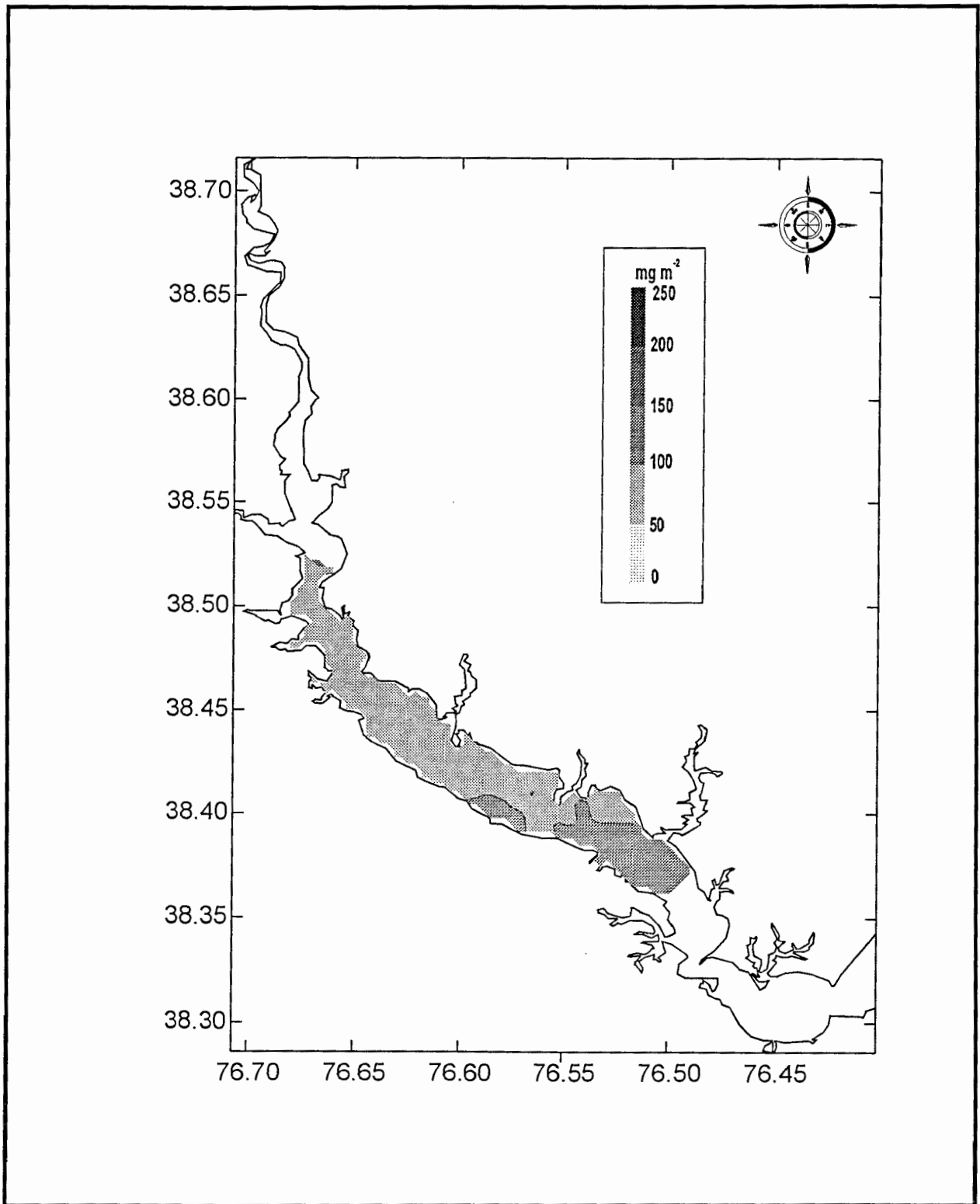


Figure 7-1.2. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during April, 1997 (sediment chlorophyll-a mapping cruise #5, Table C-2.5). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.
Latitude and longitude are in degrees and decimal minutes and seconds.

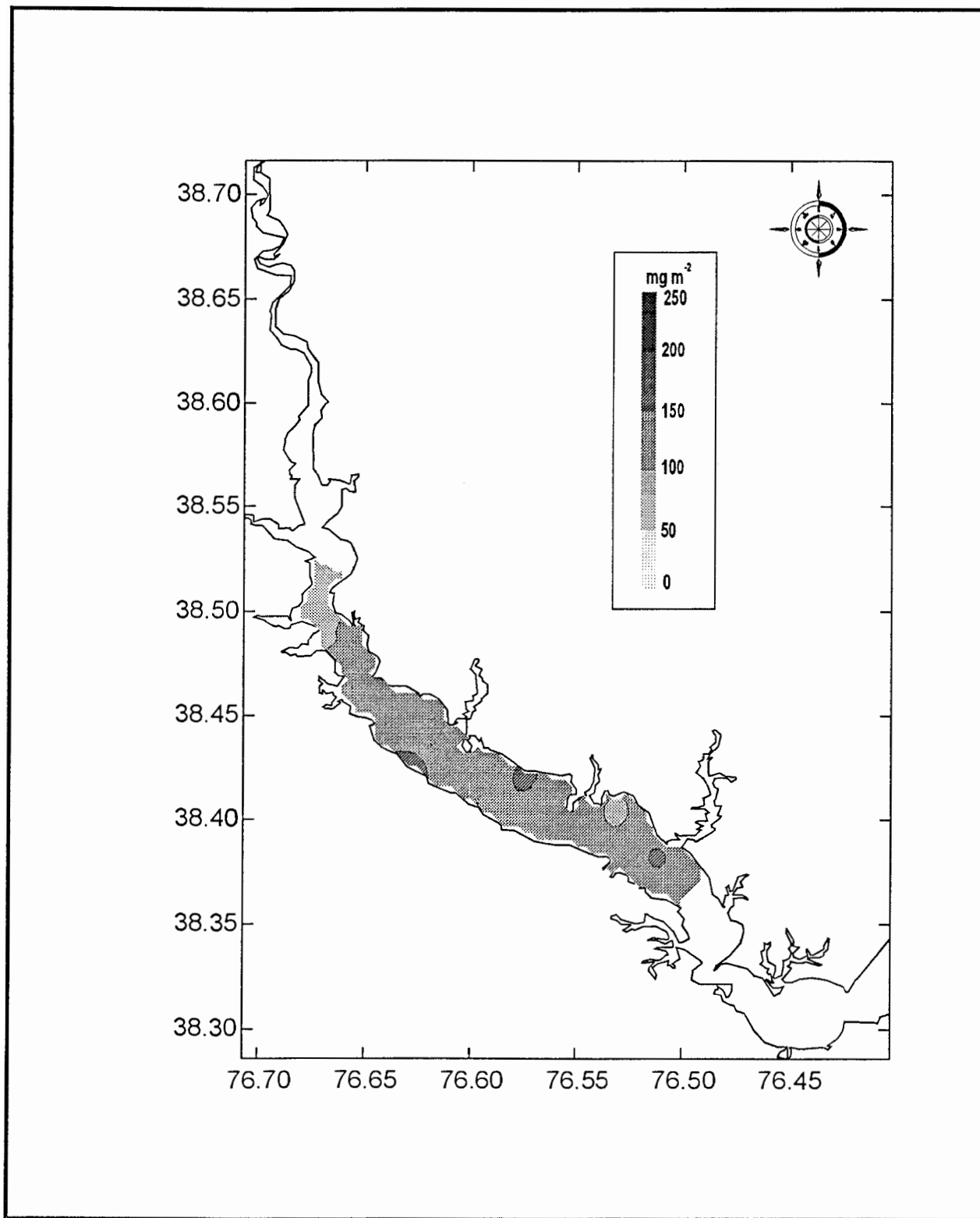


Figure 7-1.3. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during May, 1997 (sediment chlorophyll-a mapping cruise #6, Table C-2.6). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

Latitude and longitude are in degrees and decimal minutes and seconds.

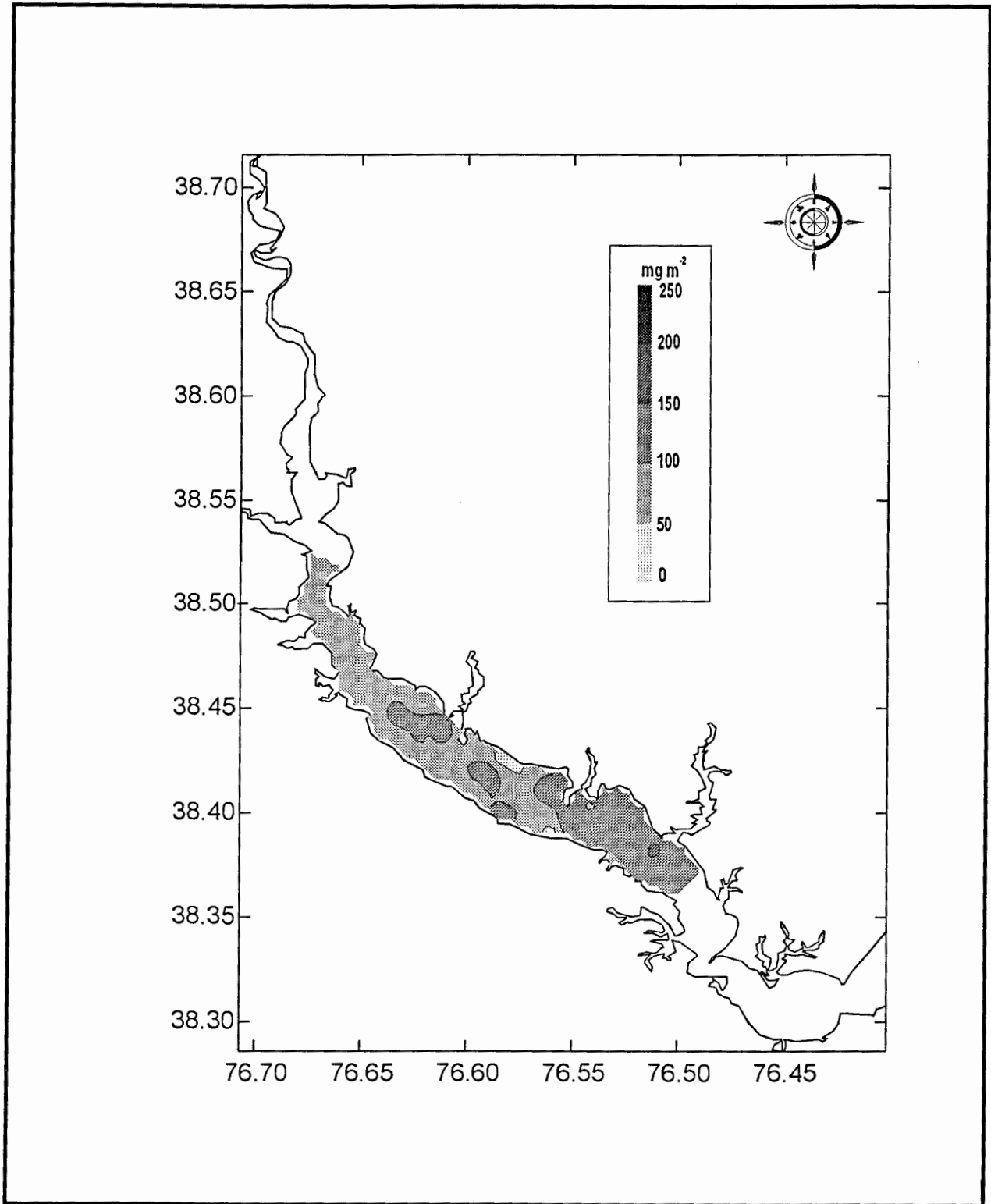


Figure 7-1.4. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during June, 1997 (sediment chlorophyll-a mapping cruise #7, Table C-2.7). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

Latitude and longitude are in degrees and decimal minutes and seconds.

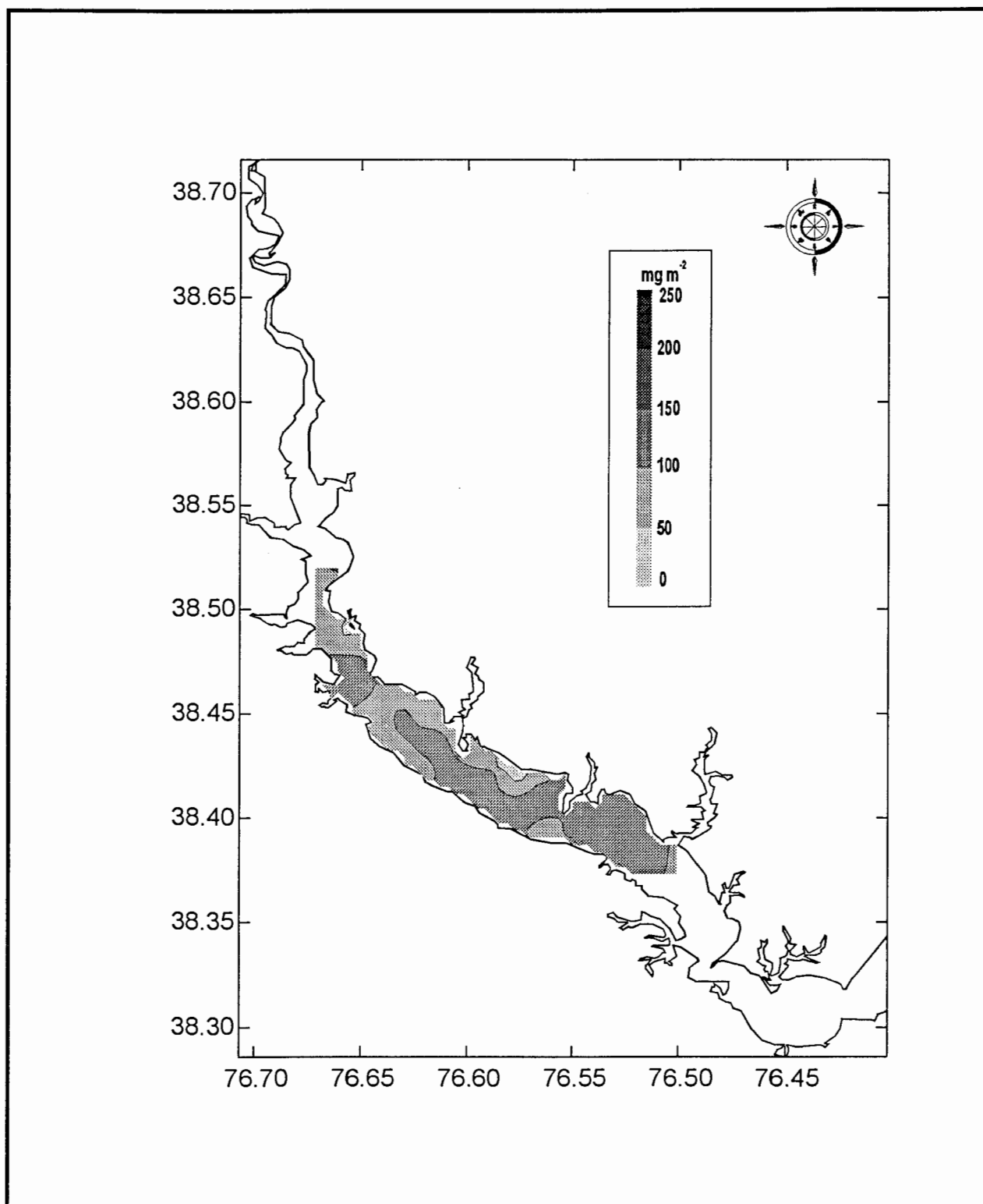


Figure 7-1.5. Total Sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during July, 1997 (sediment chlorophyll-a mapping cruise #8, Table C-2.8). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.
Latitude and longitude are in degrees and decimal minutes and seconds.

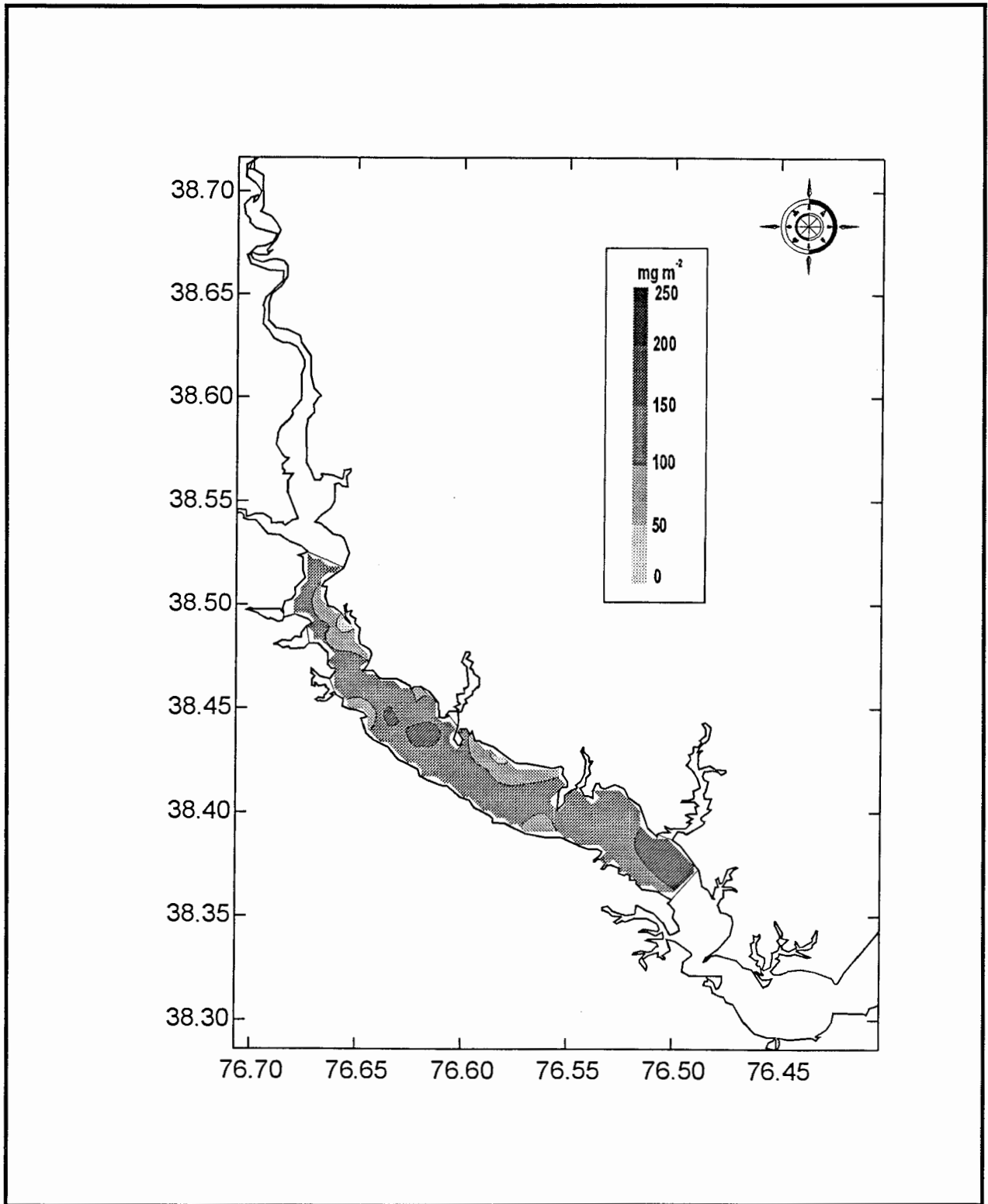


Figure 7-1.6. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during August, 1997 (sediment chlorophyll-a mapping cruise #9, Table C-2.9). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples. *Latitude and longitude are in degrees and decimal minutes and seconds.*

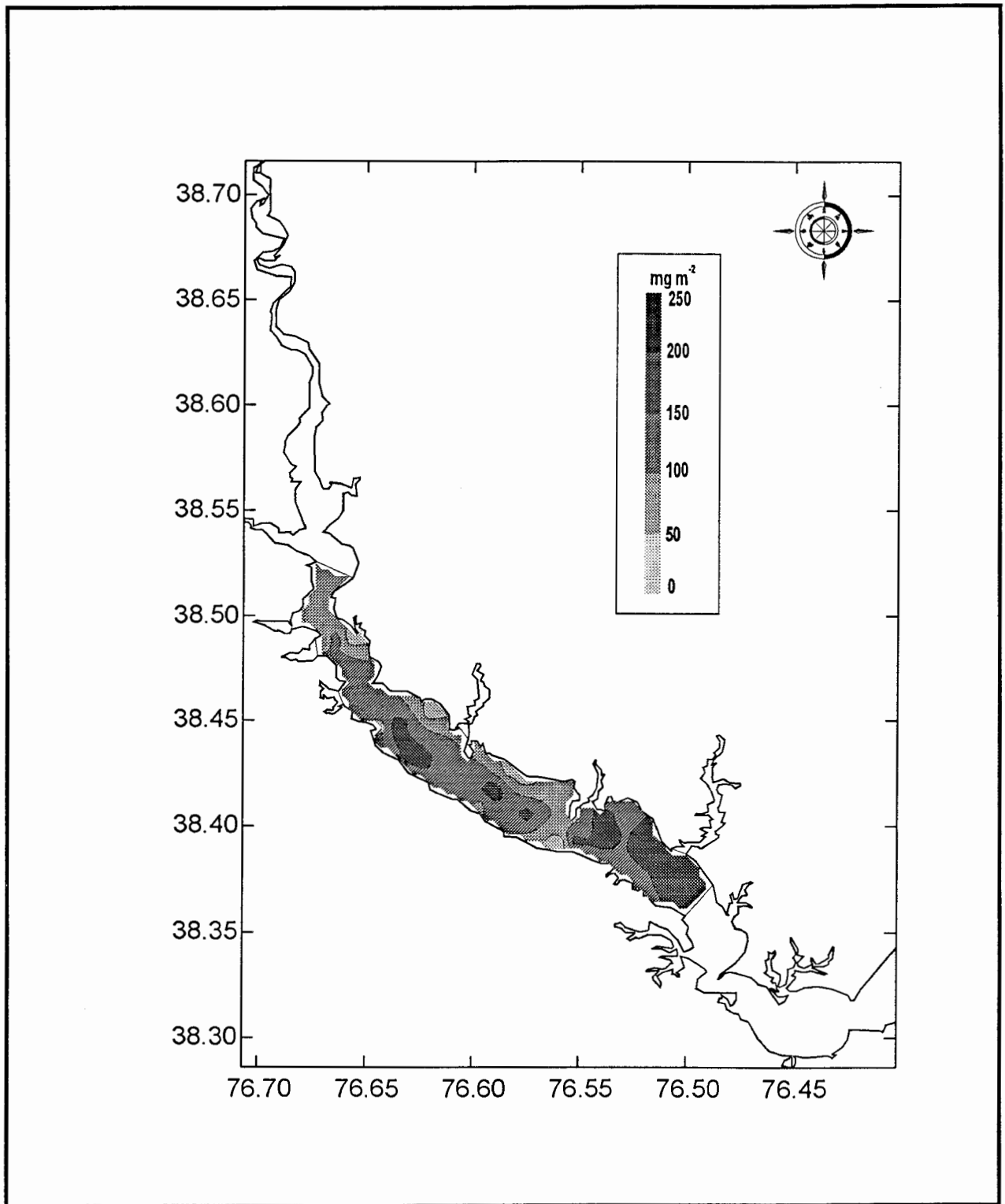


Figure 7-1.7. Total sediment chlorophyll-a concentrations contoured within the study area based on samples collected at thirty-seven (37) stations in the Patuxent River during September, 1997 (sediment chlorophyll-a mapping cruise #10, Table C-2.10). Sediment chlorophyll-a concentrations were based on 1 cm deep sediment samples.

Latitude and longitude are in degrees and decimal minutes and seconds.

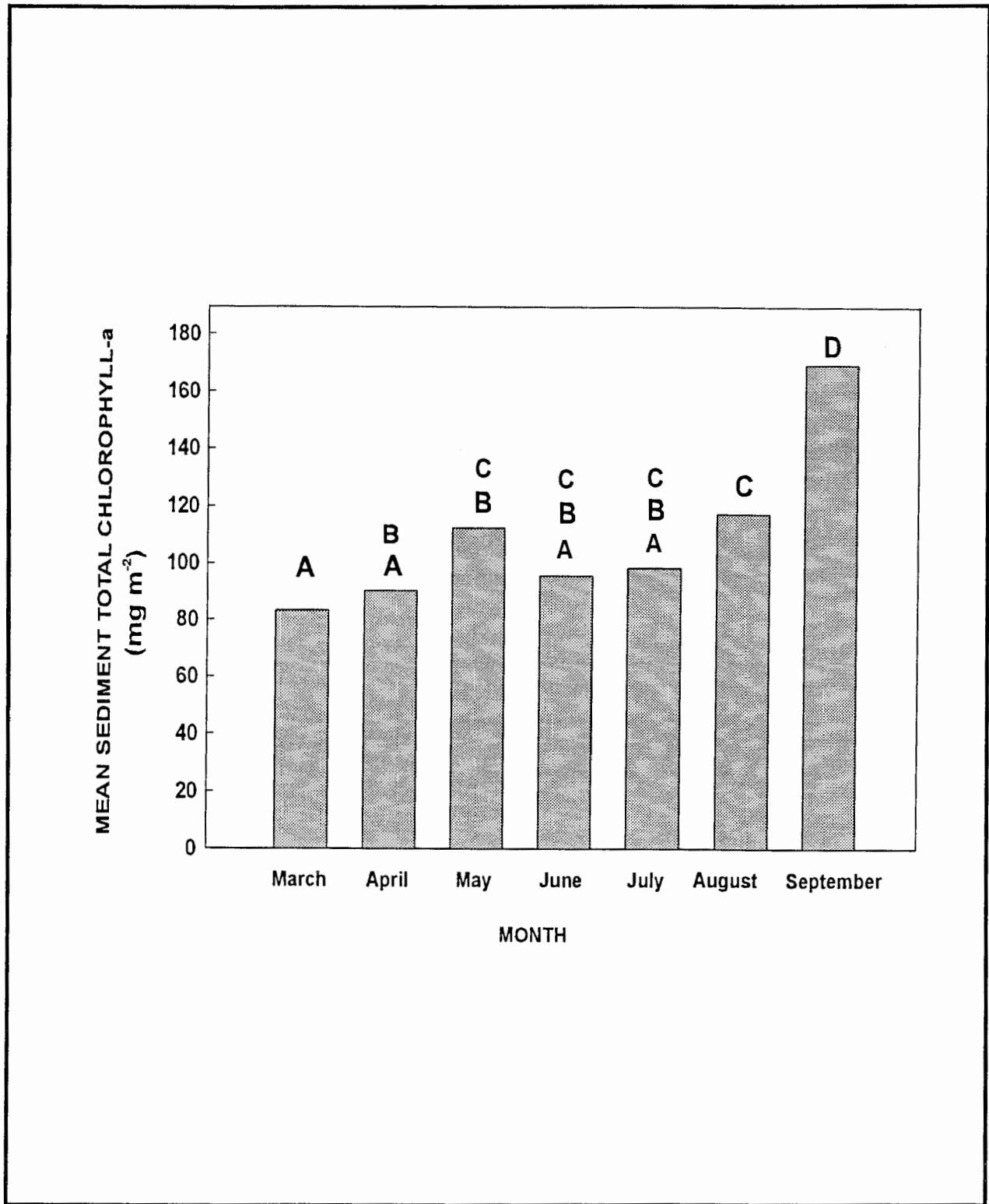


Figure 7-2. Mean total sediment chlorophyll-a concentrations (collected to 1 cm depth) in the Patuxent River from March through September, 1997. A comparison of monthly mean sediment total chlorophyll-a concentrations were conducted with Bonfferoni *post-hoc* tests. Months with the same letter designations are not significantly different from one another.

7.2 Discussion

In both 1996 and 1997 sediment total chlorophyll-a values were higher in May compared to either March or April and probably represents the deposition of the spring phytoplankton bloom to the sediments. This accumulation of labile organic matter appears to slow during June and July as temperatures increase. The decomposition rate of settling material likely increases, leaving smaller standing stocks of chlorophyll-a on the sediment surface. However, this modest peak in sediment chlorophyll-a observed in May and subsequent decline is much smaller than that observed in other portions of the Chesapeake Bay (Cowan and Boynton, 1996). The general seasonal pattern of sediment chlorophyll-a is similar to that observed in other portions of the Chesapeake Bay; however, the differences in magnitude between months are different. For example, in the Chesapeake Bay mainstem, sediment chlorophyll-a values reach a peak in late spring while in the Patuxent River (1997) the peak was not observed until September. By August, sediment total chlorophyll-a concentrations began to increase again indicating that deposition rates exceeded decomposition rates. In fact, the mean August chlorophyll-a concentration ($117.3 \mu\text{g chl cm}^{-2}$) was higher than May (112.5 mg m^{-2}). By September, sediment chlorophyll-a concentrations reached the highest values measured all year despite relatively warm temperatures. Therefore, it appears that high standing stocks of chlorophyll-a can be maintained under relatively high temperatures as long as depositional rates are high enough to compensate for decomposition.

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8. MINI-SONE MEASUREMENTS ON THE PATUXENT RIVER

R.M. Stankelis, W.R. Boynton and J.M. Frank

Sediment-water oxygen and nutrient exchanges coupled with depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and benthic habitat conditions (*e.g.* Boynton *et al.*, 1982a; Koop *et al.*, 1990; Kemp and Boynton, 1992). The magnitude and direction of these exchanges (fluxes) either into, or out of sediments, are often powerful indicators of the general health of benthic habitats. For example, fluxes of nitrite or nitrate are indicative of existing or recently existing oxic bottom waters. Large fluxes of phosphorus (PO_4^{3-}) indicate hypoxic bottom water and anoxic sediments. However, measurement of sediment-water exchanges can be difficult, expensive, and time consuming. Because these fluxes can vary both temporally and spatially within an estuary, it is often difficult to assess the overall condition of an estuary when few measurements are made. The initiation of MINI-SONE measurements in the Patuxent River addresses this limitation in two ways. First, because MINI-SONE measurements use abbreviated techniques (see Section 3.1) to estimate sediment-water exchanges compared to the standard SONE techniques, greater spatial resolution can be achieved with similar effort. Second, these measurements can be used to calibrate statistical models that will further expand the spatial resolution of sediment-water flux estimates. Thus, this approach significantly reduces the costs of monitoring sediment-water exchanges and provides an improved monitoring tool with greater spatial coverage.

8.1 Comparison of MINI-SONE Data: 1996 and 1997

Since MINI-SONE stations were specifically chosen to represent a range of salinity and depth regimes along the Patuxent river, it was not surprising to find significant differences in fluxes among the stations (Figure 8-1). For example, on a seasonal basis, the highest mean ammonium flux in 1997 was $404.9 \mu\text{Mol m}^{-2} \text{hr}^{-1}$ found at Buena Vista, while the lowest was $31.2 \mu\text{Mol m}^{-2} \text{hr}^{-1}$ at station PX21. Sediment oxygen consumption (SOC) in 1997 was highest at Buena Vista ($-1.88 \text{ g O}_2 \text{ m}^{-2} \text{hr}^{-1}$) and lowest at station PX23 ($-0.53 \text{ g O}_2 \text{ m}^{-2} \text{hr}^{-1}$). Despite inter-annual differences in these sediment-water fluxes, the relative ranking among stations was generally preserved for ammonium and SOC fluxes (Figure 8-1.a and 8-1.b). In other words, stations with high flux remained high in both years and stations with lower flux remained low during both years.

For combined nitrite and nitrate ($\text{NO}_2^- + \text{NO}_3^-$) flux there were marked differences among stations as well (Figure 8-1.c). Station PX25 had the highest mean positive flux (out of the sediment) at $64.1 \mu\text{Mol m}^{-2} \text{hr}^{-1}$, while station PX15 had the lowest mean negative flux (into the sediment) of $-49.75 \mu\text{Mol m}^{-2} \text{hr}^{-1}$. Again, despite inter-annual differences in magnitude, the relative direction of these fluxes (into or out of the sediment) remained the same at eight out of ten stations. In general the shallow stations ($< 6.0 \text{ m}$) tended to have positive $\text{NO}_2^- + \text{NO}_3^-$ fluxes while the deeper stations (with the exception of STLC) had negative $\text{NO}_2^- + \text{NO}_3^-$ fluxes.

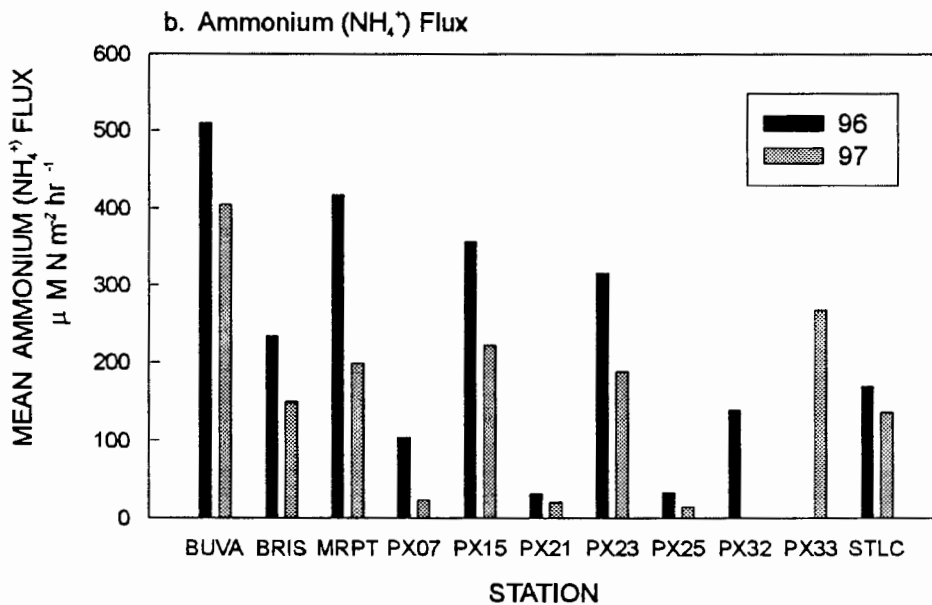
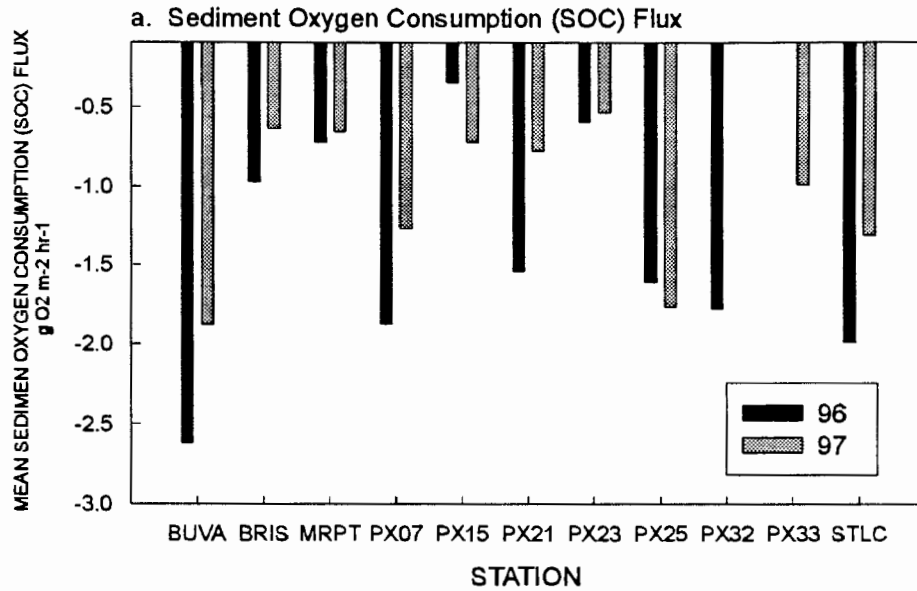


Figure 8-1. Comparison of Patuxent River MINI-SONE mean flux values calculated using monthly measurements for June through September, 1996 and 1997 for four variables:
a. Sediment Oxygen Consumption (SOC) fluxes and
b. Ammonium (NH₄⁺) fluxes.

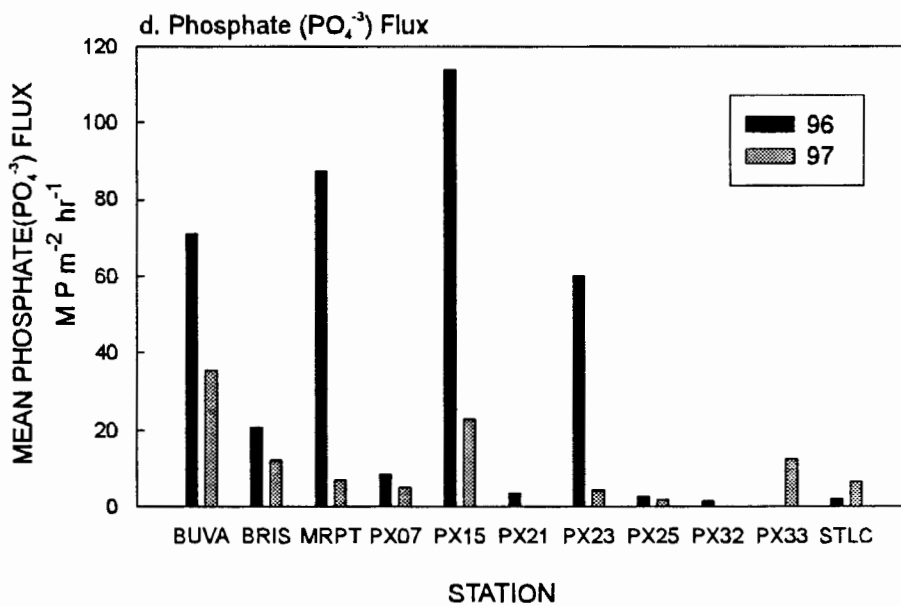
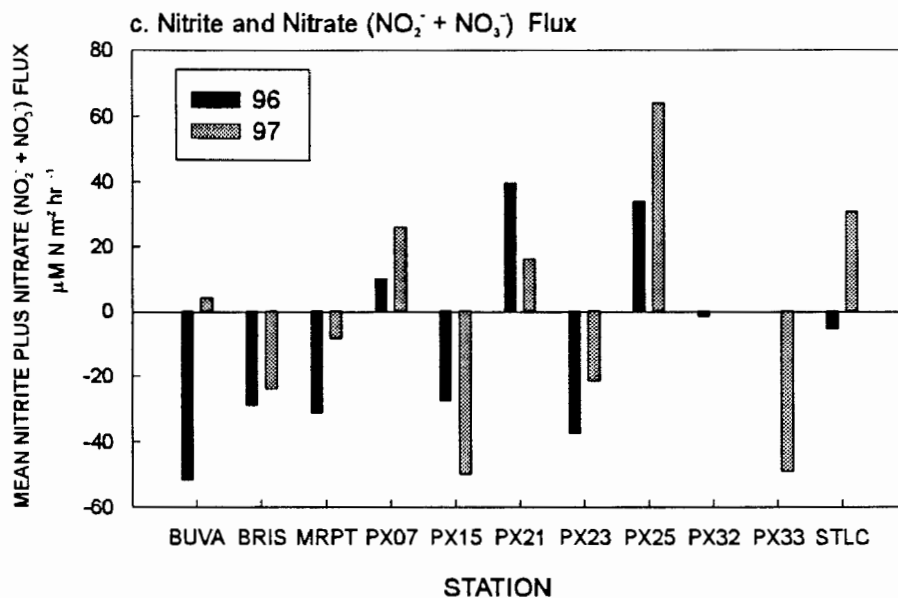


Figure 8-1. Comparison of Patuxent River MINI-SONE mean flux values calculated using monthly measurements for June through September, 1996 and 1997 for four variables:
 c. Nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) fluxes and
 d. Phosphate (PO_4^{3-}) fluxes.

In 1997 phosphate fluxes (PO_4^{3-}) at most MINI-SONE stations were very much reduced compared to 1996. The highest phosphate flux recorded in 1996 was $113.8 \mu\text{Mol P m}^{-2} \text{hr}^{-1}$ at station PX15, while in 1997 the highest flux recorded was only $35.7 \mu\text{Mol P m}^{-2} \text{hr}^{-1}$ found at Buena Vista. In fact in 1997 six out of ten stations had phosphate fluxes less than $10 \mu\text{Mol P m}^{-2} \text{hr}^{-1}$. Although river flow was higher in 1996 compared to 1997 the large reductions in phosphate flux at some stations were probably not due to significant reductions of phosphorus loading, but rather a depletion of phosphorus stores in the river sediments.

8.2 Statistical Analysis of MINI-SONE and Sediment Chlorophyll-a Data

8.2.1 Data Sources

The statistical models presented here were constructed using sediment-water flux, water quality and surficial sediment data collected from six MINI-SONE and four regular SONE stations on the Patuxent River in 1996 and 1997 (Figures 3-1 and 3-2). Sediment-water flux and water quality data were collected monthly from June through September of 1996 and 1997, while surficial sediment chlorophyll-a was collected from March through September of both years. The techniques used to measure sediment-water flux and sediment chlorophyll-a are outlined in Sections 3.1.3.1.4 and 3.1.3.2 of this report, respectively.

8.2.2 Background

It is well known that the regeneration and transformations of nutrients in estuarine sediments is linked chemically and biologically to a suite of bottom water and sediment parameters. Previous studies have shown that factors such as temperature, salinity and bottom water dissolved oxygen concentrations correlate well with certain sediment-water fluxes (*e.g.* Boynton *et al.*, 1980; Cowan and Boynton, 1996; Cowan *et al.*, 1996). Factors such as bottom water dissolved nutrient concentrations also influence diffusion gradients and sediment-water exchanges (*e.g.* Boynton and Kemp, 1985; Sundby *et al.*, 1992). In addition, several studies have shown that the supply of organic material to the sediment surface can have a strong influence on the magnitude of certain fluxes (*e.g.* Kelly and Nixon, 1984; Nixon, 1981; Cowan and Boynton, 1996). In fact some studies have shown that surficial sediment chlorophyll-a concentrations can be well correlated with ammonium flux and indeed explain much of the variation associated with this measurement (*e.g.* Boynton *et al.*, 1995; Cowan and Boynton, 1996). The surficial sediment chlorophyll-a concentration is an indicator of labile organic material available for recycling or other biogeochemical processes.

In 1996, a series of predictive linear regression models were constructed from SONE and MINI-SONE data collected as part of the Chesapeake Bay Water Quality Monitoring Program EPC component (Boynton *et al.*, 1997). The goal of these models was to predict sediment-water oxygen and nutrient fluxes by using a few easily measured water quality or sediment parameters. In that initial analysis, a series of simple and multiple linear regression models were examined for each flux parameter using a combination of water quality and sediment parameters. In order to find the combinations of independent predictor variables (regressors) with high predictive power, a stepwise regression procedure (SAS P.C. statistical software version 6.10) was used to sort through various

combinations of variables to construct the most parsimonious model. However, the final (preferred) models were based on *a priori* assumptions of nutrient dynamics and the need to develop useful tools not just statistical artifacts. The preferred models often were not the most statistically significant possible, but represented the most useful combination of variables found that represent actual sediment water dynamics.

With the addition of 1997 data, it was possible to examine these models for the effects of inter-annual variability and to test their general applicability. Data from 1997 alone was analyzed in a manner similar to the original 1996 data to determine the most parsimonious model. Finally, data collected in both years was merged, and models were created with this expanded data set. As in the original analysis, flux relationships were examined both on a seasonal mean basis (one datum point for each station), and on an individual station basis (one datum point for each cruise) (Boynton *et al.*, 1997).

Model results are summarized in Tables 8-1 and 8-2 to highlight differences between the analyses of individual years and the combined data sets. Results for specific parameters are also shown as scatter plots of actual sediment-water flux plotted against predicted flux values (Figures 8-2 to Figure 8-5). Regression equations and 95% confidence intervals for predictions are shown for each parameter.

8.2.3 Results and Conclusions

Although the model fitting process was the same for 1996 and 1997 data, the parameters included in each of the best-fit models differed between years. For example, the preferred model for 1996 mean seasonal ammonium flux included total sediment chlorophyll-a lagged one month (TCHL1M) and sediment Eh (SEDEHM1). While for 1997, sediment active chlorophyll-a (ACHL) was the only important regressor in the preferred model. In fact, every model differed by one or more parameters between 1996 and 1997 (Figure 8-1). These differences were likely due to inter-annual differences in environmental conditions such as temperature, nutrient loading rates and depositional processes. For example, during the flux sampling period of June through September 1997, the mean bottom water salinity across the estuary was 2.75 ppt higher than in 1996. Also, the estuary average total surficial sediment chlorophyll-a (TCHL) was found to be significantly higher in 1996 (114.4 mg chl m⁻²) compared to 1997 (95.3 mg chl m⁻²).

When the 1996 and 1997 data sets were merged, the models were remarkably similar to each other in content and predictive power. In three out of four models, sediment total chlorophyll-a lagged one month (TCHL1M) was an important predictor of flux. This was not surprising since previous studies have indicated that the deposition of labile organic matter to the sediment surface is an important driver determining the magnitude of several sediment-water fluxes (Cowan *et al.*, 1996 and Boynton *et al.*, 1997). When the appropriate time lag between organic matter deposition and flux measurement is taken into account, surficial sediment chlorophyll-a can be extremely well correlated with ammonium flux ($r^2 = 0.97$; Cowan *et al.*, 1996 and Boynton *et al.*, 1997). However, the high correlation reported by Cowan *et al.* (1996), was based upon stations that span a significant gradient of temperature, salinity and possibly organic matter supply. In contrast, the MINI-SONE stations sampled on the Patuxent River span a much smaller environmental gradient, so it is not surprising that this parameter explains less environmental variation. In the final preferred model, 46% of the

Table 8-1. Summary of Sediment-water Predictive Flux Models:

a. Individual Stations.

Buena Vista (BUVA) was excluded from the analysis for ammonium (NH_4^+) because of the extra high biomass and irrigation rates at this station. All other analyses included Buena Vista (BUVA) data.

Variables are defined as follows:

TCHL1M = total sediment chlorophyll-a (lagged 1 month) 1 cm depth,

SEDEHM1 = sediment Eh @ -1cm,

DO = bottom water dissolved oxygen,

SAL = bottom water salinity (ppt),

TEMP = bottom water temperature (C),

TCHL = total sediment chlorophyll-a.

FLUX	1996 DATA		1997 DATA		1996 - 1997 DATA COMBINED	
	(Preferred Model) Input Variables	r ²	(Preferred Model) Input Variables	r ²	(Preferred Model) Input Variables	r ²
Ammonium (NH_4^+)	TCHL1M SEDEHM1	0.48	DO TCHL	0.75	DO TCHL1M SEDEHM1	0.54
Phosphate (PO_4^{-3})	Bottom water PO_4^{-3} SEDEHM1	0.49	Bottom water PO_4^{-3} TCHL1M	0.25	Bottom water PO_4^{-3} SEDEHM1 Salinity TCHL1M	0.52
Nitrite +Nitrate ($\text{NO}_2^- + \text{NO}_3^-$)	Bottom water $\text{NO}_2^- + \text{NO}_3^-$ TCHL1M	0.79	DO Bottom water $\text{NO}_2^- + \text{NO}_3^-$ TCHL1M	0.59	DO Bottom water $\text{NO}_2^- + \text{NO}_3^-$ TEMP	0.54
Sediment Oxygen Consumption (SOC)	DO TCHL1M TEMP	0.36	DO Salinity TCHL1M	0.47	DO TCHL1M Salinity TEMP SEDEHM1	0.74

Table 8-2. Summary of Sediment-water Predictive Flux Models:

b. Summer Mean Values (values calculated from monthly measurements June through September except where noted).

Buena Vista (BUVA) was excluded from the analysis for ammonium (NH_4^+) because of the extra high biomass and irrigation rates at this station. All other analyses included Buena Vista (BUVA) data.

Variables are defined as follows:

- TCHL1M = total sediment chlorophyll-a (averaged from May through August) 1 cm depth,
- ACHL = active sediment chlorophyll-a (averaged from June through September) 1 cm depth,
- SEDEHM1 = sediment Eh @ -1cm,
- DO = bottom water dissolved oxygen,
- SAL = bottom water salinity (ppt),
- TEMP = bottom water temperature (C),
- TCHL = total sediment chlorophyll-a (averaged from June through September) 1 cm depth.

FLUX	1996 DATA		1997 DATA		1996- 1997 DATA COMBINED	
	(Preferred Model) Input Variables	r ²	(Preferred Model) Input Variables	r ²	(Preferred Model) Input Variables	r ²
Ammonium (NH_4^+)	TCHL1M SEDEHM1	0.86	ACHL	0.89	TCHL1M SEDEHM1	0.84
Phosphate (PO_4^{-3})	Bottom water PO_4^{-3} SEDEHM1	0.87	Bottom water PO_4^{-3} TCHL	0.57	Bottom water PO_4^{-3} SEDEHM1 DO	0.87
Nitrite + Nitrate ($\text{NO}_2^- + \text{NO}_3^-$)	Bottom water $\text{NO}_2^- + \text{NO}_3^-$ TCHL1M TEMP	0.88	Bottom water NH_4^+ Bottom water $\text{NO}_2^- + \text{NO}_3^-$ SEDEHM1	0.96	TCHL1M Bottom water PO_4^{-3} Bottom water $\text{NO}_2^- + \text{NO}_3^-$	0.75
Sediment Oxygen Consumption (SOC)	DO TCHL1M TEMP	0.65	TEMP TCHL1M	0.78	TCHL1M TEMP SEDEHM1	0.89

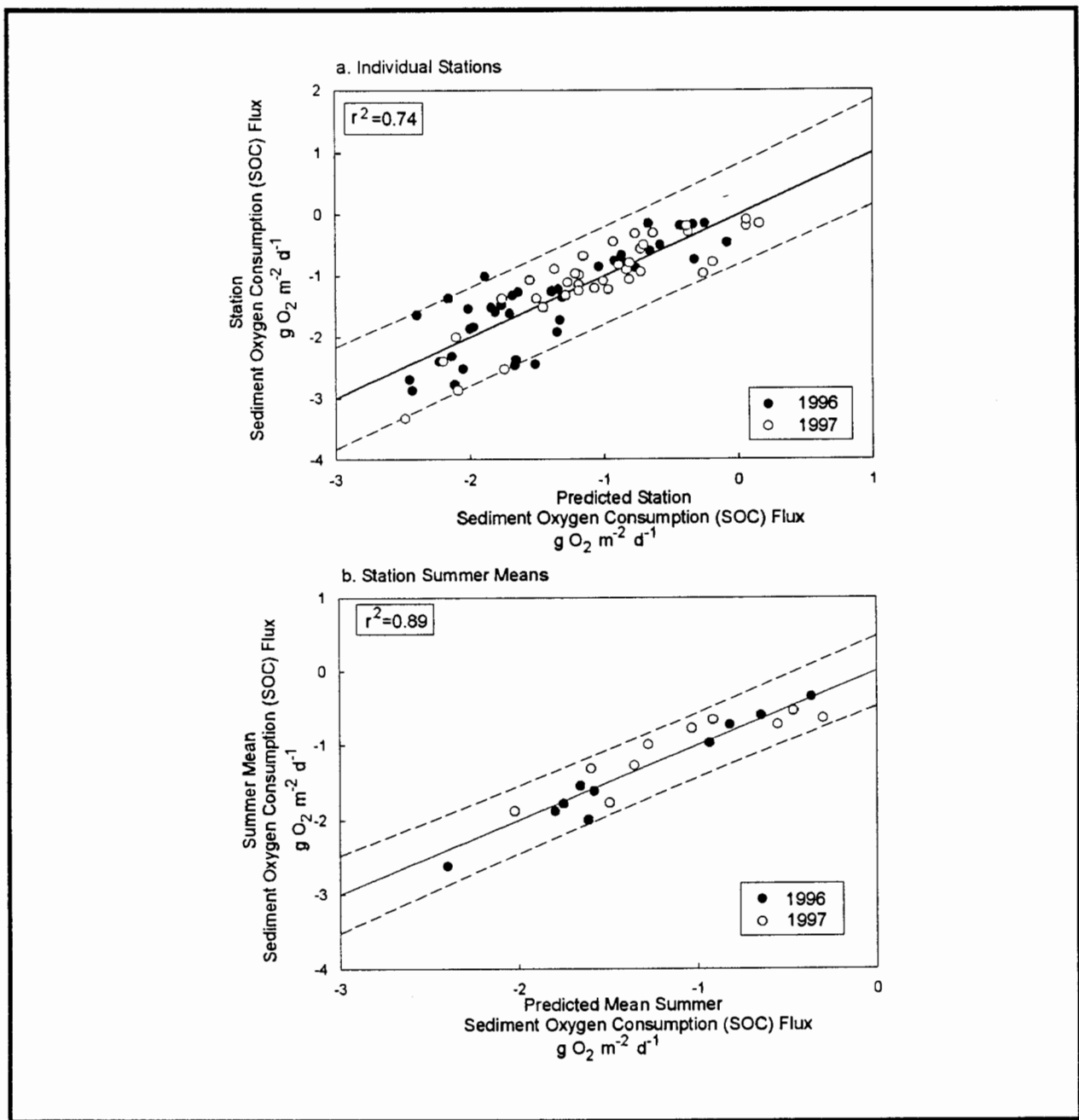


Figure 8-2. Patuxent River 1996 and 1997 summer sediment oxygen consumption (SOC) at MINI-SONE stations vs. predicted flux from best-fit multi-variate linear relationships for:

- a. Individual station values, and**
- b. Four month summer means.**

For individual station values the predicted flux relationship is:

$$\text{FLUX} = -0.11(\text{DO}) - 0.09(\text{TEMP}) + 0.13(\text{SAL}) - 0.004(\text{SEDEHM1}) - 0.005(\text{TCHL1M}) + 1.72.$$

For summer mean values the predicted flux relationship is:

$$\text{FLUX} = -0.58(\text{TEMP}) - 0.006(\text{SEDEHM1}) - 0.01(\text{TCHL1M}) + 16.34$$

where TCHL1M = total sediment chlorophyll-a (averaged from May through August) 1 cm depth,

DO = bottom water dissolved oxygen, SEDEHM1 = sediment Eh @ -1cm,

SAL = bottom water salinity (ppt), TEMP = bottom water temperature (C).

Dashed lines indicate 95% confidence intervals for individual observations.

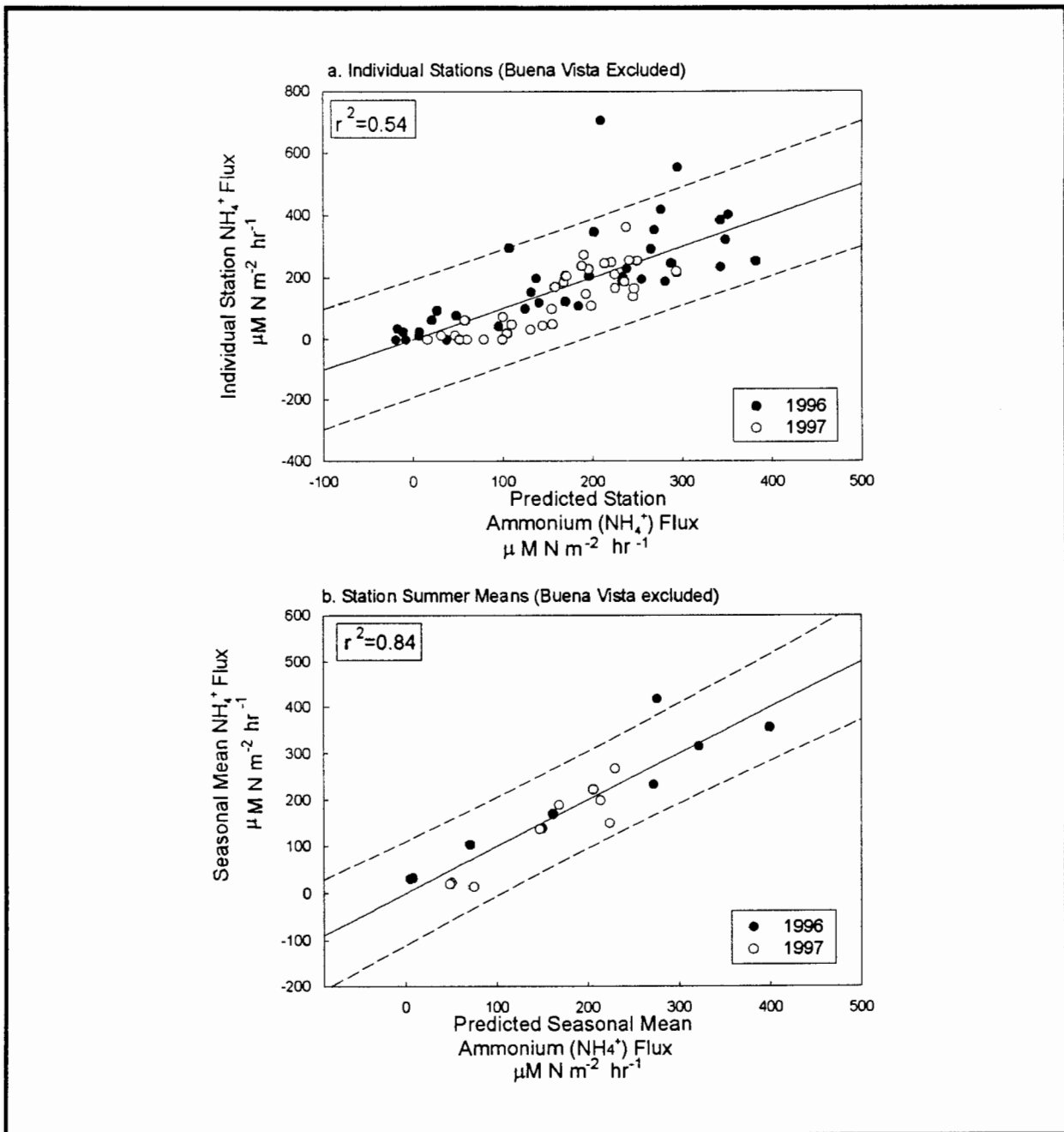


Figure 8-3. Patuxent River 1996 and 1997 summer ammonium (NH_4^+) flux at MINI-SONE stations vs. predicted flux from best-fit multi-variate linear relationships for:

a. Individual station values, and

b. Four month summer means.

For individual station values the predicted flux relationship is:

$$\text{FLUX} = -0.94(\text{TCHL1M}) - 0.33(\text{SEDEHM1}) - 17.42(\text{DO}) + 216.09$$

For summer mean values the predicted flux relationship is:

$$\text{FLUX} = 1.62(\text{TCHL1M}) - 0.62(\text{SEDEHM1}) + 165.98$$

where TCHL1M = total sediment chlorophyll-a (averaged from May through August) 1 cm depth,

DO = bottom water dissolved oxygen, SEDEHM1 = sediment Eh @ -1cm,

Dashed lines indicate 95% confidence intervals for individual observations.

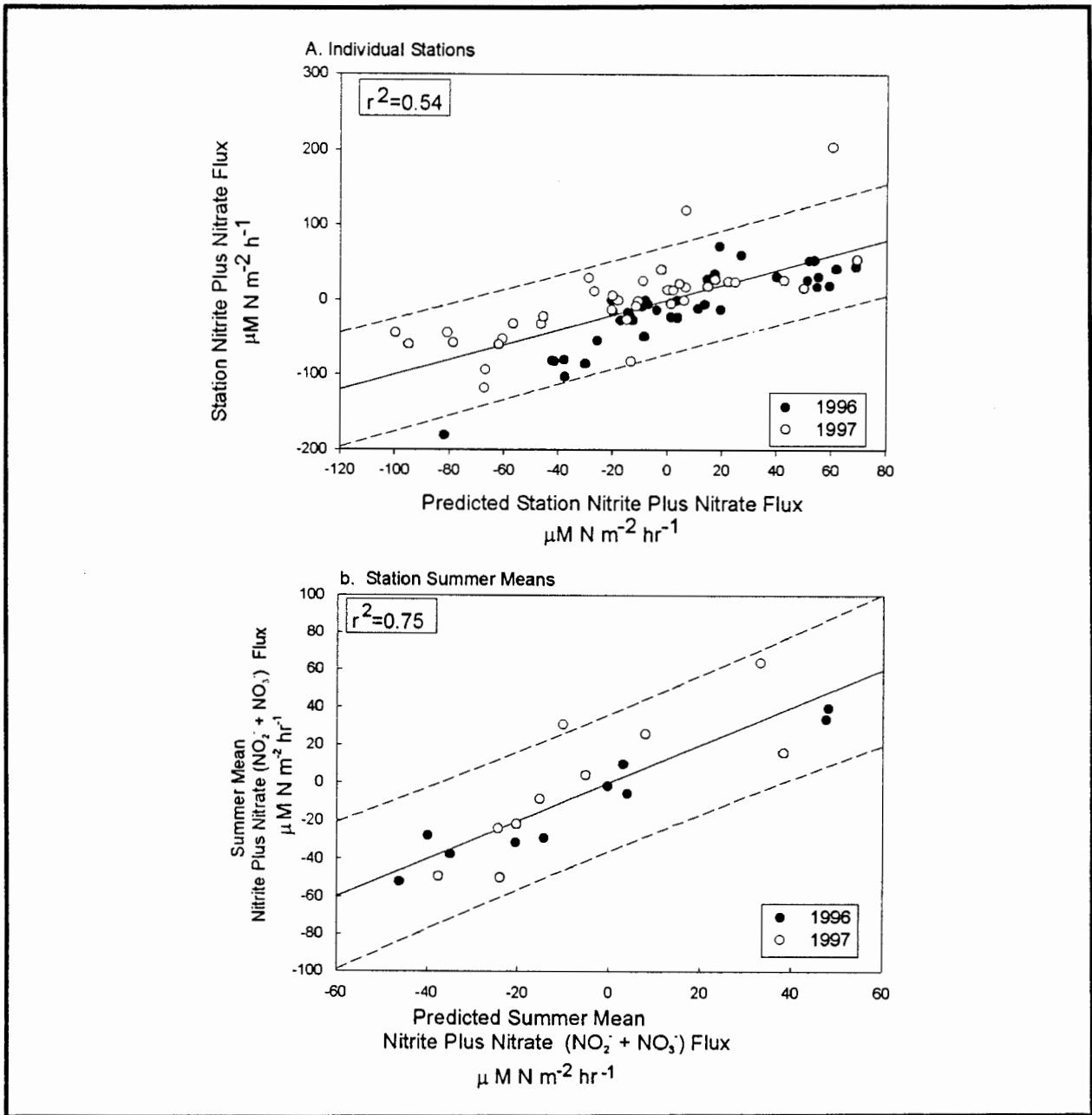


Figure 8-4. Patuxent River 1996 and 1997 summer nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) flux at MINI-SONE stations vs. predicted flux from best-fit multi-variate linear relationships for:

- a. Individual station values, and**
- b. Four month summer means.**

For individual station values the predicted flux relationship is:

$$\text{FLUX} = 10.84(\text{DO}) - 7.86(\text{BWNO23}) - 5.69(\text{TEMP}) + 133.01$$

For summer mean values the predicted flux relationship is:

$$\text{FLUX} = -0.31(\text{TCHL1M}) - 6.60(\text{BWNO23}) - 26.06(\text{BWPO4}) + 75.83$$

where TCHL1M = total sediment chlorophyll-a (averaged from May through August) 1 cm depth,

BWNO23 = bottom water nitrate plus nitrite, BWPO4 = bottom water phosphate,

DO = bottom water dissolved oxygen, SAL = bottom water salinity (ppt),

TEMP = bottom water temperature (C).

Dashed lines indicate 95% confidence intervals for individual observations.

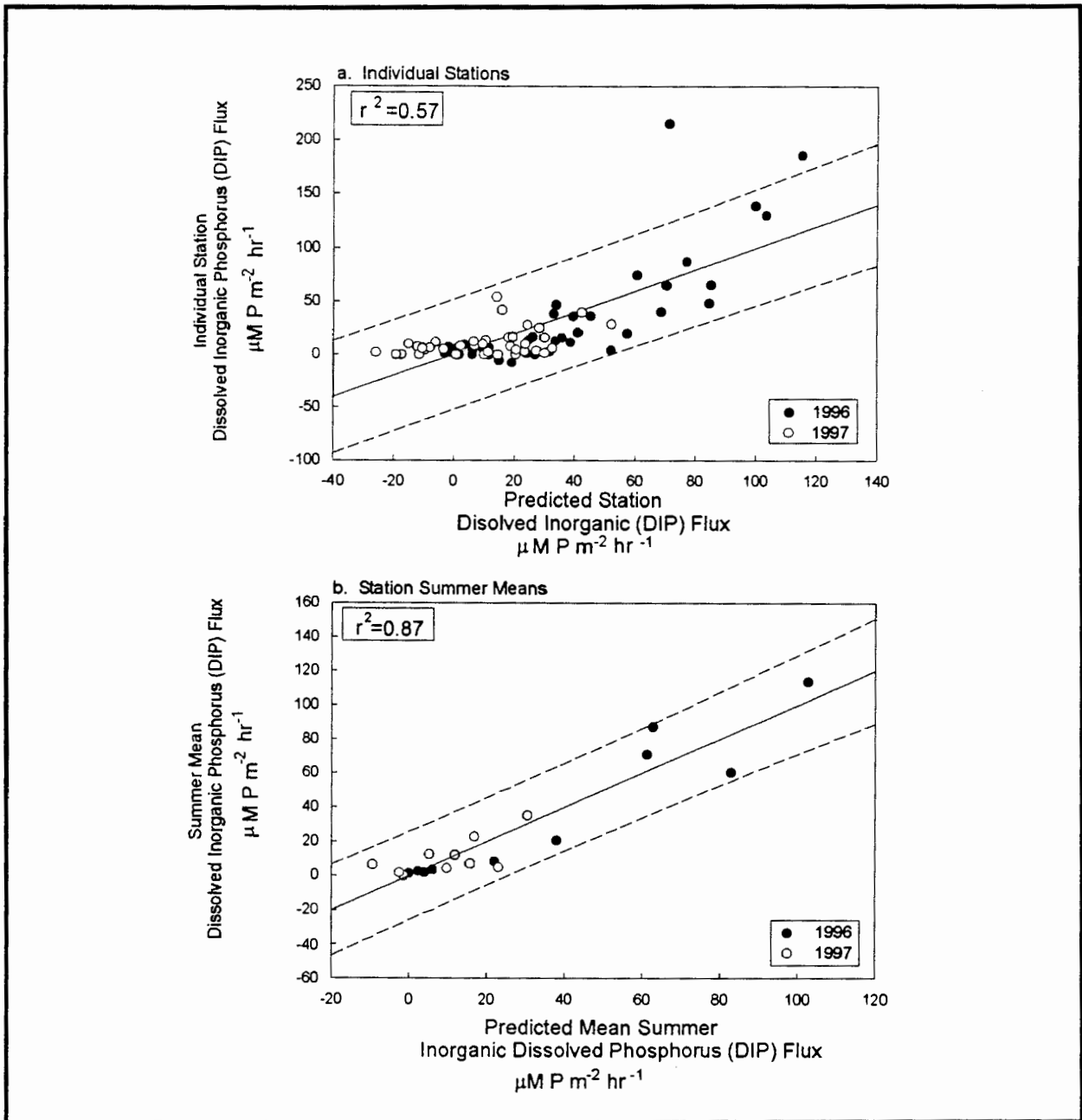


Figure 8-5. Patuxent River 1996 and 1997 summer dissolved inorganic phosphorus (DIP) flux at MINI-SONE stations vs. predicted flux from best-fit multi-variate linear relationships for:

- a. Individual station values, and
- b. Four month summer means.

For individual station values the predicted flux relationship is:

$$\text{FLUX} = -3.60(\text{SAL}) - 0.104(\text{TCHL1M}) + 29.39(\text{BWPO4}) - 0.09(\text{SEDEHM1}) + 52.58$$

For summer mean values the predicted flux relationship is:

$$\text{FLUX} = 3.32(\text{DO}) + 34.47(\text{BWPO4}) - 0.25(\text{SEDEHM1}) + 57.24$$

where TCHL1M = total sediment chlorophyll-a (averaged from May through August) 1 cm depth,

BWPO4 = bottom water PO_4^{-3}

DO = bottom water dissolved oxygen, SEDEHM1 = sediment Eh @ -1cm,

SAL = bottom water salinity (ppt), TEMP = bottom water temperature (C).

Dashed lines indicate 95% confidence intervals for individual observations.

variation in seasonal ammonium flux was explained by sediment total chlorophyll-a when it was lagged by one month (TCHL1M). When sediment redox potential (Eh) measured at one centimeter below the surface (SEDEHM1) was included in the ammonium flux model, 86% percent of the variation in flux was explained (Table 8-2 and Figure 8-2). In fact, sediment redox potential Eh (SEDEHM1) was also important in three of the four models.

In addition to sediment chlorophyll-a and sediment redox potential, dissolved nutrient concentrations directly above the sediment surface were also important regressors in some of the flux models. The greatest percentage of variation in seasonal mean phosphate flux was explained by bottom water concentrations of PO_4^{-3} in 1996, 1997 and in the combined data set. This result is also logical since diffusional processes can play an important role in sediment-water exchanges (Boynton and Kemp, 1985). However, when sediment redox potential and bottom water dissolved oxygen are added as predictor variables 87% of the variation in phosphate flux is explained (Table 8-2, Figure 8-3).

Despite significant differences in environmental conditions between 1996 and 1997, all the models for seasonal mean fluxes were able to explain more than 75% and up to 89% of the variation observed in sediment-water fluxes. Based upon limited exploratory data analysis (Boynton *et al.*, 1997), we believe these models will be applicable to other estuaries outside the Patuxent River. However by including an additional year of Patuxent River data enough variation should be included in the models so that they can indeed be used as predictive tools to estimate sediment-water exchanges based upon a few simple measurements. While there are limitations to this approach, it offers several advantages over traditional flux measurements. First, if measurements can be made with high spatial resolution, a flux contour map can be generated to not only identify potential target areas, but also to obtain an integrated estimate of the estuary as a whole. Second, these types of estimates are not possible with traditional low-resolution sediment-water flux estimates. Finally, this type of technique should be more cost effective than traditional techniques.

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9. PATUXENT RIVER SUBMERGED AQUATIC VEGETATION (SAV) HABITAT EVALUATION

R.M. Stankelis, J.M. Frank, W.R. Boynton and F.M. Rohland

The decline of temperate submerged aquatic vegetation in Chesapeake Bay and its tributaries has been well documented (*e.g.* Stevenson and Confer, 1978; Orth and Moore, 1983). While it is generally believed that SAV decline was the result of increased eutrophication and decreased water quality (*e.g.* Orth and Moore, 1983; Kemp *et al.*, 1983), the determination of minimum habitat requirements for SAV growth and survival in many areas has proven to be challenging (Batuik *et al.*, 1992). Often the conditions necessary for SAV growth and survival are the product of complex interactions among the separate elements of an SAV habitat. While reductions in nutrient loading in recent years have been reflected in improvements in water quality (Boynton *et al.*, 1995), many Chesapeake Bay tributaries historically populated with SAV beds including much of the Patuxent River have not shown significant recovery. This lack of SAV recovery has led to several hypotheses that were investigated in this study. These null hypotheses can briefly be stated as follows:

- * Water quality conditions measured in the mid-channel do not approximate conditions in near shore habitats
- * Near-shore habitats do not receive an adequate supply of SAV propagules to revegetate barren SAV habitat
- * Epiphytic growth on SAV leaves does not attenuate a significant amount of incident light

With these null hypotheses in mind, this study was composed of five discrete but complimentary study elements. Of these five elements, three were concerned with the fundamental issue of assessing water quality conditions in the near-shore habitat where SAV are likely to exist. The first study element was designed to assess the spatial and temporal variability in the near-shore habitat by measuring a suite of water quality water parameters across nutrient, salinity and wave exposure regimes throughout the SAV growing season. The second element (Channel-Shore comparison) was designed to verify the applicability of water quality data typically measured in river channels (often far from the actual shoreline) to the SAV habitat. The third element of the water quality assessment was a tidal cycle study in which high frequency water quality data were collected to evaluate short-term variability. The fourth study element was designed to investigate the contribution of SAV epiphytes to light attenuation at these near-shore locations. Lastly, because SAV beds on the Patuxent River have declined so dramatically, it was postulated that SAV bed growth was limited by propagule availability; therefore, a propagule availability study was undertaken.

9.1 Near Shore Water Quality Evaluation

In order to evaluate near-shore SAV habitat conditions along the mesohaline portion of the Patuxent River, a suite of water quality measurements were collected approximately bi-weekly from April 10, 1997 to October 8, 1997 at each of 10 near-shore sampling stations (Figure 3-4). In addition to

water quality physical parameters such as temperature, salinity and dissolved oxygen, a suite of dissolved and particulate nutrient measurements were also made. In this report, only those parameters thought to be most important to SAV survival are presented (Batuik *et al.*, 1992; Dennison *et al.*, 1993). These include dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), total chlorophyll-a, total suspended solids (TSS), and light attenuation (Kd). The remaining parameters are included in the data section of this report.

9.1.1 Dissolved Oxygen

Dissolved oxygen concentrations at all ten stations ranged from 4.61 mg l⁻¹ at station SV1A to 13.42 mg l⁻¹ at station SV06 (Table 9-1). The lowest values were recorded in the late summer and the highest in the spring. Station means ranged from 7.15 mg l⁻¹, at station SV1A, to 9.06 mg l⁻¹ at station SV10. A correlation between station location and mean dissolved oxygen concentration is indicated by values increasing down river.

9.1.2 Salinity

Salinity values at all ten stations ranged from 3.70 ppt at station SV1A to 15.48 ppt at station SV09 over the course of the entire sampling season (Table 9.1). The lowest values were recorded in the spring and increased steadily over the course of the entire study. Mean salinity values were 8.94 ppt, at station SV1A, and 11.96 ppt at station SV10. As expected, there was a correlation between station location and mean salinity values as indicated by values increasing down river.

9.1.3 Temperature

Temperatures recorded at all ten stations ranged from 8.52 to 29.52° C over the course of the entire sampling season (Table 9-1). The lowest values were recorded in the spring and increasing steadily over the course of the entire study as would be expected. Mean station temperatures ranged from 18.62° C at station SV1A to 22.48° C at station SV10. Station SV1A remained cooler than the other nine stations throughout the study; however, no correlation was found between mean station temperature and station location.

9.1.4 Dissolved Inorganic Phosphorus

Although dissolved inorganic phosphorus (DIP) concentrations varied temporally, concentrations remained relatively low throughout the sampling season (Figure 9-1). With the exception of station SV1A, DIP concentrations remained below 0.32 μM P established as the upper limit for acceptable SAV habitat requirements (Batuik *et al.*, 1992) for most of the season. Dissolved inorganic phosphorus concentrations measured across all stations over the entire sampling season ranged from an absolute minimum of 0.08 μM at station SV5A to a maximum of 1.44 μM at station (SV1A; Table 9-2.). Dissolved inorganic phosphorus concentrations at all stations were lowest in April through early June, but increased moderately through the rest of the season. The five upriver stations (SV1

Table 9-1. Mean water quality data, including maximum and minimum values, recorded between April and October 1997, at each of the ten near shore stations of the Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation.

STATION	TEMP. (C)	MIN-MAX (C)	SALINITY (ppt)	MIN - MAX (ppt)	DISSOLVED OXYGEN (mg l ⁻¹)	MIN - MAX (mg l ⁻¹)
SV1A	18.62	8.52 - 26.71	8.94	3.70 - 13.07	7.15	4.61 - 12.00
SV02	20.53	8.98 - 27.27	10.14	6.30 - 13.90	7.48	5.25 - 12.11
SV03	20.59	8.72 - 27.23	10.15	6.40 - 13.93	7.83	6.21 - 11.60
SV04	21.15	9.29 - 27.82	10.20	6.60 - 13.92	7.89	5.89 - 11.50
SV5A	21.30	10.42 - 27.91	10.49	7.30 - 14.16	8.04	6.19 - 11.44
SV06	22.65	12.39 - 29.25	10.28	7.00 - 14.20	9.41	7.10 - 13.42
SV07	22.15	11.33 - 28.38	11.20	7.50 - 14.87	9.11	7.52 - 11.22
SV08	22.59	12.30 - 28.98	10.77	7.60 - 14.47	9.07	7.20 - 11.02
SV09	20.83	11.05 - 27.10	11.96	8.40 - 15.48	9.27	7.65 - 11.52
SV10	22.48	11.30 - 29.50	11.68	8.30 - 15.38	9.06	7.51 - 12.58

Table 9-2. Maximum and minimum values, recorded between April and October 1997, at each of the ten near shore stations of the Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation for:

- a. Mean dissolved inorganic nitrogen; b. Dissolved inorganic phosphorus (DIP);
- c. Total chlorophyll-a; d. Total suspended solids and e. [Kd] light attenuation coefficient data.

a. Mean Dissolved Inorganic Nitrogen

STATION	DISSOLVED INORGANIC NITROGEN (μM)	MIN-MAX (μM)
SV1A	9.65	0.9 - 57.2
SV02	8.37	0.6 - 40.9
SV03	9.78	0.8 - 45.2
SV04	9.99	0.4 - 50.2
SV5A	12.48	0.5 - 53.6
SV06	9.24	0.7 - 38.2
SV07	12.38	0.8 - 46.6
SV08	9.96	0.5 - 42.0
SV09	14.41	0.6 - 50.7
SV10	11.10	0.6 - 44.9

b. Dissolved Inorganic Phosphorus (DIP)

STATION	DISSOLVED INORGANIC PHOSPHORUS (μM)	MIN-MAX (μM)
SV1A	0.68	0.22 - 1.44
SV02	0.31	0.13- 0.69
SV03	0.29	0.09- 0.89
SV04	0.26	0.10 - 0.79
SV5A	0.23	0.08 - 0.58
SV06	0.17	0.09 - 0.28
SV07	0.18	0.09 - 0.32
SV08	0.16	0.10- 0.32
SV09	0.16	0.09- 0.39
SV10	0.14	0.09- 0.21

Table 9-2. Maximum and minimum values, recorded between April and October 1997, at each of the ten near shore stations of the Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation for:

- a. Mean dissolved inorganic nitrogen; b. Dissolved inorganic phosphorus (DIP);
 c. Total chlorophyll-a; d. Total suspended solids and e. [Kd] light attenuation coefficient data
 (Continued).

c. Total Chlorophyll-a

STATION	TOTAL CHLOROPHYLL-a ($\mu\text{g l}^{-1}$)	MIN-MAX ($\mu\text{g l}^{-1}$)
SV1A	18.62	7.86 - 37.70
SV02	17.35	9.02- 33.80
SV03	16.51	7.64- 39.50
SV04	15.38	7.06 - 40.40
SV5A	12.18	4.69 - 20.70
SV06	10.97	5.38 - 17.92
SV07	12.34	3.33 - 24.06
SV08	16.97	6.48- 45.10
SV09	15.84	8.19- 28.50
SV10	15.82	8.51- 26.00

d. Total Suspended Solids

STATION	TOTAL SUSPENDED SOLIDS ($\mu\text{g l}^{-1}$)	MIN-MAX ($\mu\text{g l}^{-1}$)
SV1A	29.20	8.2 - 27.0
SV02	21.90	7.8 - 43.8
SV03	26.70	7.3- 26.8
SV04	21.30	8.2- 26.4
SV5A	20.90	6.7- 22.8
SV06	15.70	6.4- 53.6
SV07	17.80	6.6- 37.6
SV08	16.10	7.4- 44.8
SV09	16.20	9.3 - 33.3
SV10	14.80	13.4- 55.0

Table 9-2. Maximum and minimum values, recorded between April and October 1997, at each of the ten near shore stations of the Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation for:

a. Mean dissolved inorganic nitrogen; b. Dissolved inorganic phosphorus (DIP);
 c. Total chlorophyll-a; d. Total suspended solids and e. [Kd] light attenuation coefficient data (Continued).

e. [Kd] Light Attenuation Coefficient

STATION	[Kd] LIGHT ATTENUATION COEFFICIENT (m ⁻¹)	MIN-MAX (m ⁻¹)
SV1A	2.72	1.18 - 5.80
SV02	1.93	0.18 - 3.29
SV03	1.65	1.09 - 2.38
SV04	1.72	0.47 - 3.91
SV5A	1.63	0.68 - 2.98
SV06	1.60	0.09 - 2.62
SV07	1.19	0.61 - 2.11
SV08	1.31	0.82 - 1.89
SV09	0.89	0.55 - 1.10
SV10	1.08	0.70 - 1.75

A-SV5A) experienced a much greater seasonal increase in DIP concentrations compared to the more down river stations (Figure 9-1).

In addition to a significant temporal trend, there was a significant spatial trend in DIP concentration as well. Mean station DIP concentrations decreased from up-river to down-river locations (Figure 9-6.), with the highest mean concentration at station SV1A. Mean DIP concentrations per station ranged from a minimum of $0.14 \mu\text{M}$, at SV10, to a maximum of $0.68 \mu\text{M}$, at SV1A. With station SV1A omitted, a significant correlation was found between river location and DIP concentration ($P < 0.001$, $r^2 = 0.91$).

9.1.5 Dissolved Inorganic Nitrogen

Dissolved inorganic nitrogen (DIN) concentrations among all ten stations ranged from a minimum of $0.40 \mu\text{M}$ at station SV04 to a maximum of $57.2 \mu\text{M}$ at station SV1A over the entire sampling season (Table 9.2). At most stations, dissolved inorganic nitrogen (DIN) values, were relatively high through early May, but fell well below the maximum SAV concentration habitat limit of $10.7 \mu\text{M}$ for DIN (Batuik *et al.*, 1992) for the remainder of the season (Figure 9-2). In fact, DIN concentrations at most stations remained less than $0.50 \mu\text{M}$ throughout most of the SAV growing season. This initial draw-down of dissolved nutrients is characteristic of a spring phytoplankton bloom. Unlike DIP there was no significant relationship between mean station DIN concentration and river location (Figure 9-6).

9.1.6 Water Column Total Chlorophyll-a

Total chlorophyll-a concentrations at all ten stations over the entire sampling season ranged from a minimum of $3.33 \mu\text{g l}^{-1}$ at station SV07 to a maximum of $45.10 \mu\text{g l}^{-1}$ at station SV08 (Figure 9-3, Table 9-1). Total chlorophyll-a values at most stations remained above $15.0 \mu\text{g l}^{-1}$ (established as the upper limit of the mesohaline SAV habitat requirement; Batuik *et al.*, 1992) throughout most of the growing season. However for a brief period during May and early June, concentrations fell below the habitat requirement limit (Figure 9-3.). No correlation was evident between total chlorophyll-a station mean concentrations and location (see Figure 9.6) when all stations are considered. However, there was a decrease in water column chlorophyll-a along the main axis of the River from stations SV1A (Buzzard Island) through SV07 (Hungerford Creek).

9.1.7 Total Suspended Solids

Concentrations of total suspended solids (TSS) at all ten stations over the entire sampling season ranged from a minimum of 6.4 mg l^{-1} at station SV06 to a maximum of 55.0 mg l^{-1} at station SV10 (Figure 9-4, Table 9-1). For most of the season TSS concentrations, with the exception of SV10, were above 15.0 mg l^{-1} (the value established as the upper limit of the TSS concentration; Batuik *et al.* 1992). Concentrations of total suspended solids (TSS) decreased from March through early June, but then increased through August when concentrations began to taper off again (Figure 9-4). In addition to the temporal trends observed, a significant spatial trend ($P < 0.001$, $r^2 = 0.80$) was found

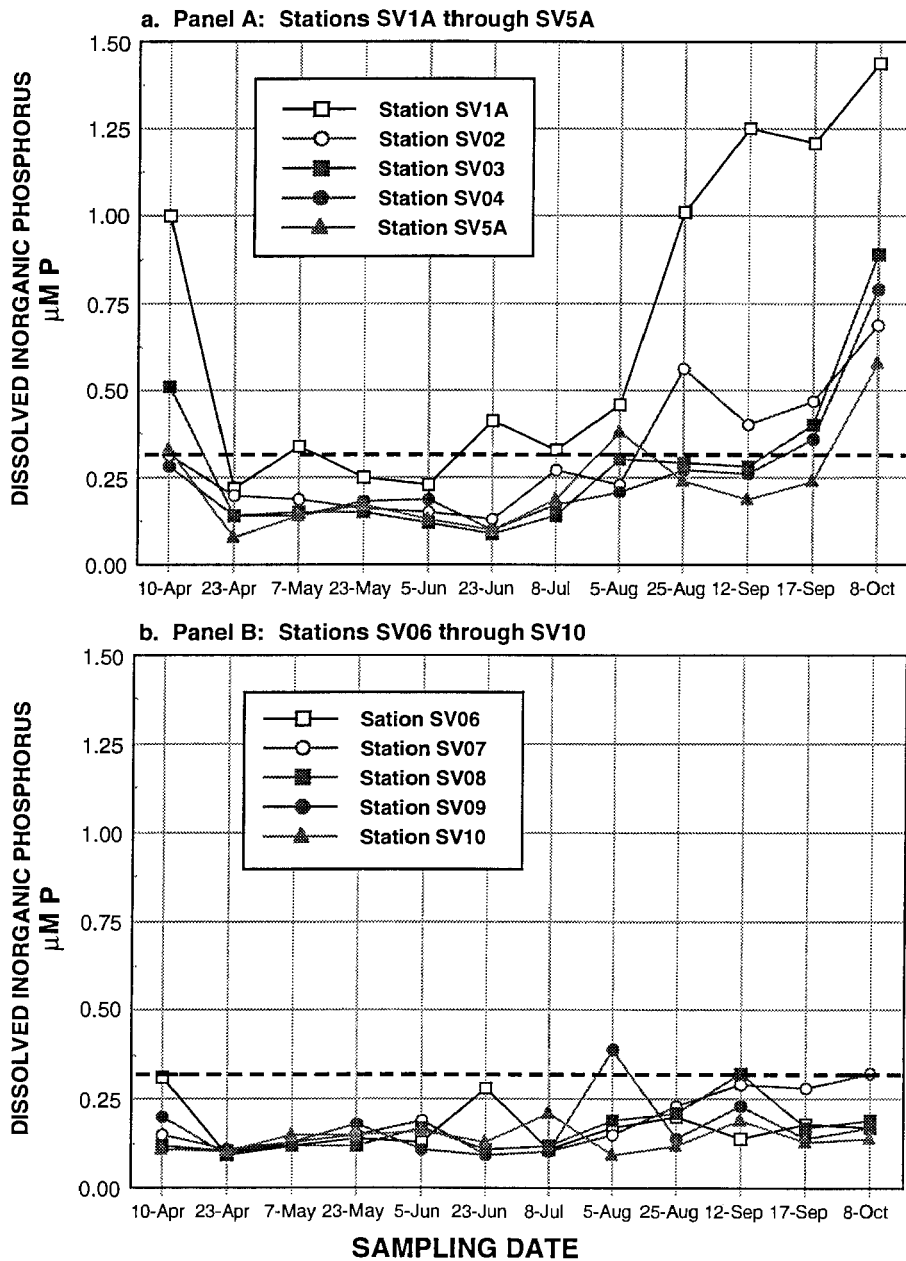


Figure 9-1. Line graphs depicting water column dissolved inorganic phosphorus values for each sampling event between April and October, 1997 at each of the near shore stations of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of SAV habitat requirement concentration for dissolved inorganic phosphorus (DIP) as stated in Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration Targets: A Technical Synthesis (Batuik et al., 1992).

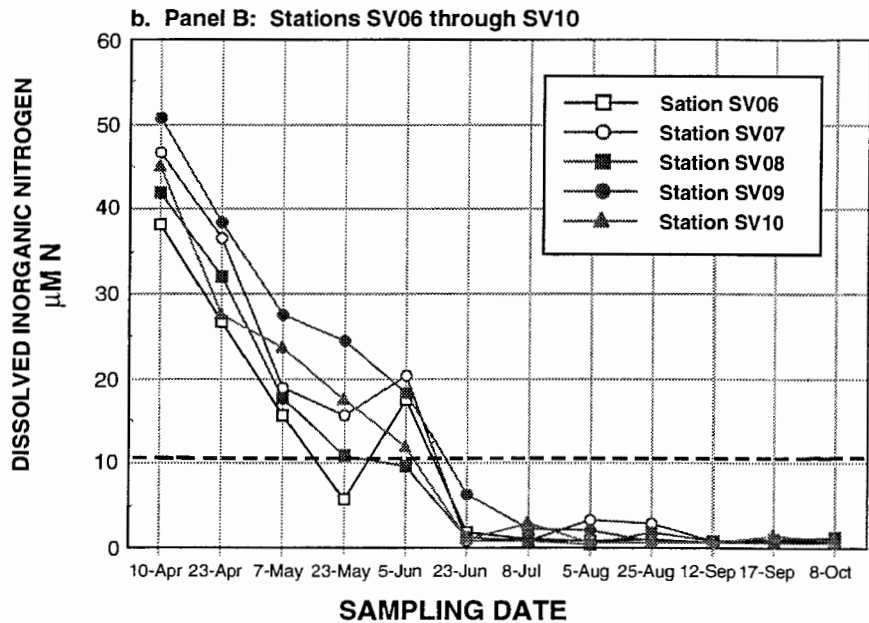
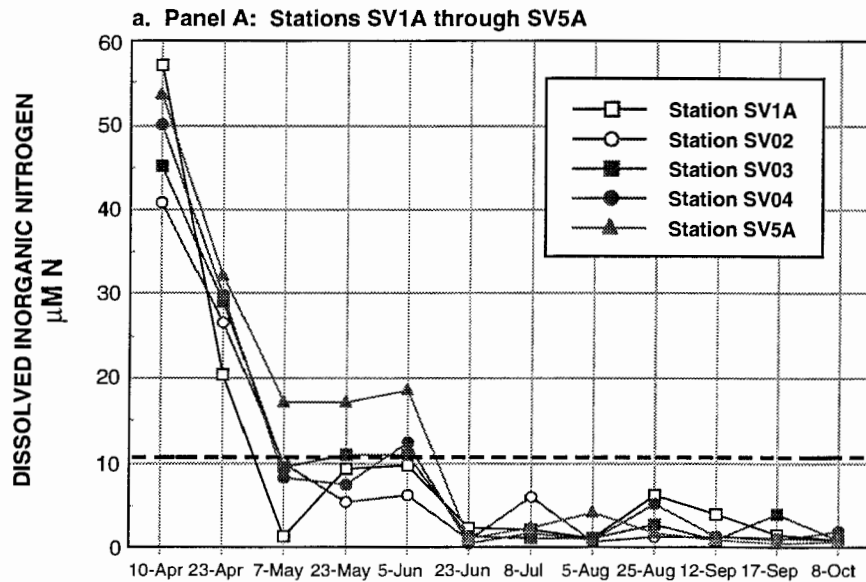


Figure 9-2. Line graphs depicting water column dissolved inorganic nitrogen values for each sampling event between April and October, 1997 at each of the near shore stations of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of SAV habitat requirement concentration for dissolved inorganic phosphorus (DIP) as stated in *Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration Targets: A Technical Synthesis* (Batuik et al., 1992).

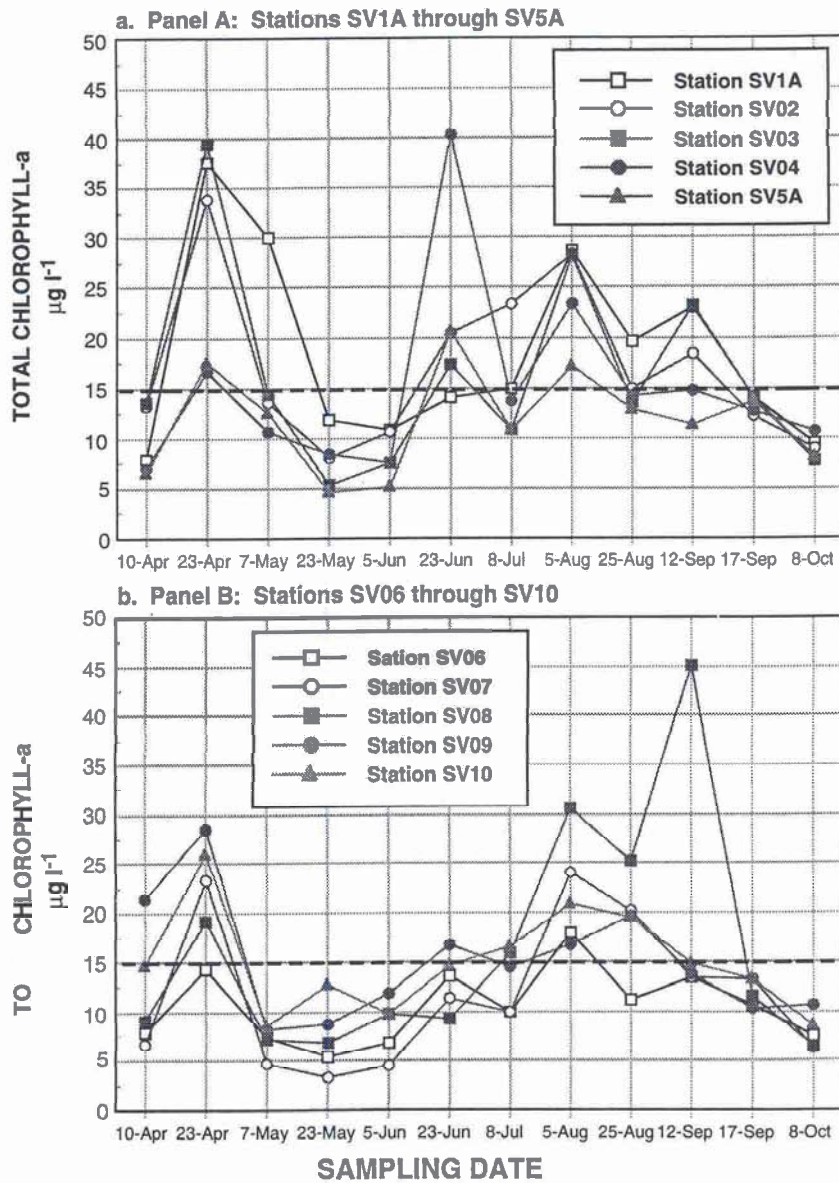


Figure 9-3. Line graphs depicting water column total chlorophyll-a values for each sampling event between April and October, 1997 at each of the near shore stations of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of SAV habitat requirement concentration for dissolved inorganic phosphorus (DIP) as stated in Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration Targets: A Technical Synthesis (Batuik et al., 1992).

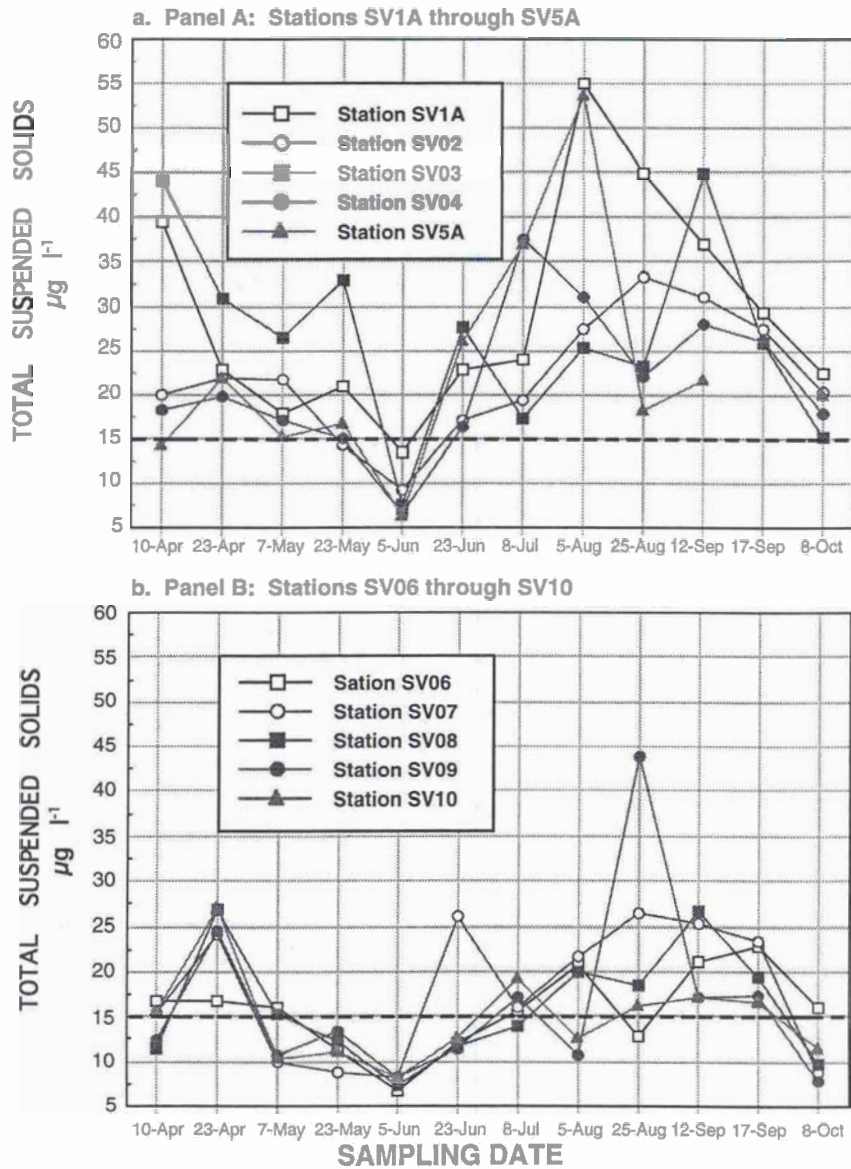


Figure 9-4. Line graphs depicting water column total suspended solid values for each sampling event between April and October, 1997 at each of the near shore stations of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of SAV habitat requirement concentration for dissolved inorganic phosphorus (DIP) as stated in Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration Targets: A Technical Synthesis (Batuik et al., 1992).

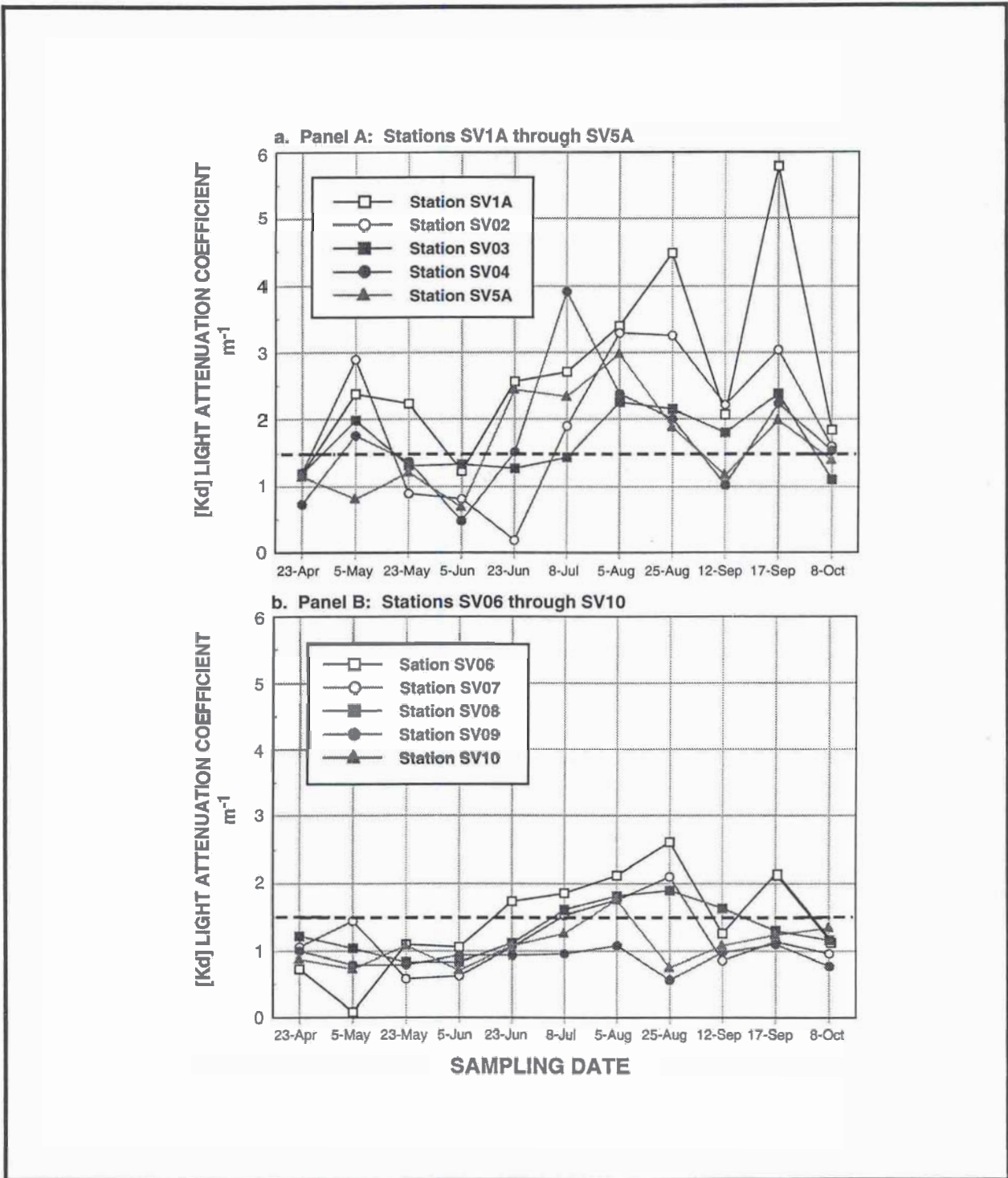


Figure 9-5. Line graphs depicting water column light attenuation coefficient [Kd] values for each sampling event between April and October, 1997 at each of the near shore stations of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of SAV habitat requirement concentration for dissolved inorganic phosphorus (DIP) as stated in Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration Targets: A Technical Synthesis (Batuik et al., 1992).

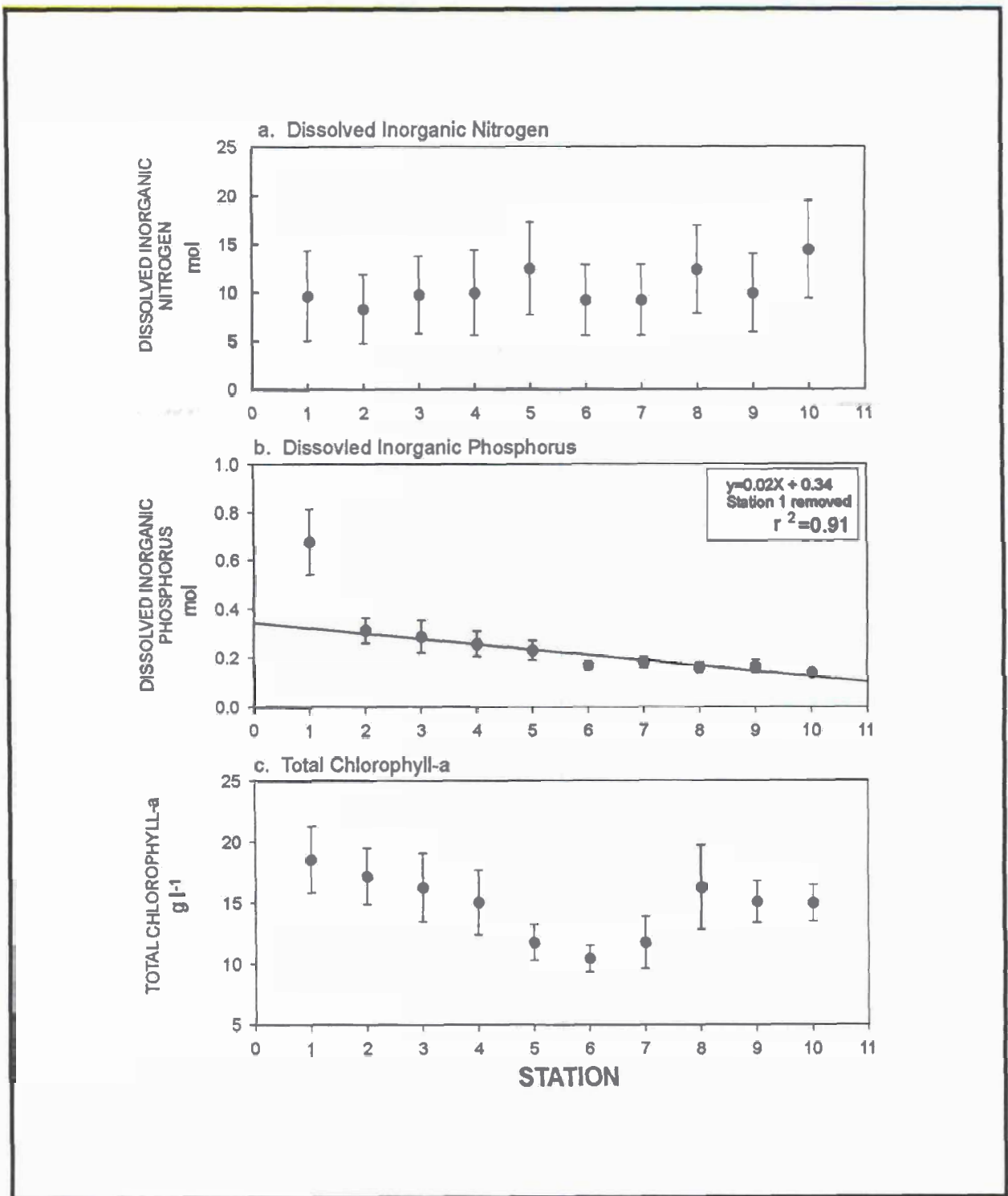


Figure 9-6. Seasonal mean values (± 1 SE) at 10 Submerged Aquatic Vegetation (SAV) stations on the Patuxent River during March through October, 1997 for three water column parameters: a. Dissolved Inorganic Nitrogen (DIN); b. Dissolved Inorganic Phosphorus (DIP); c. Total Chlorophyll-a
 Station 1 was excluded from the regression calculation for DIP.

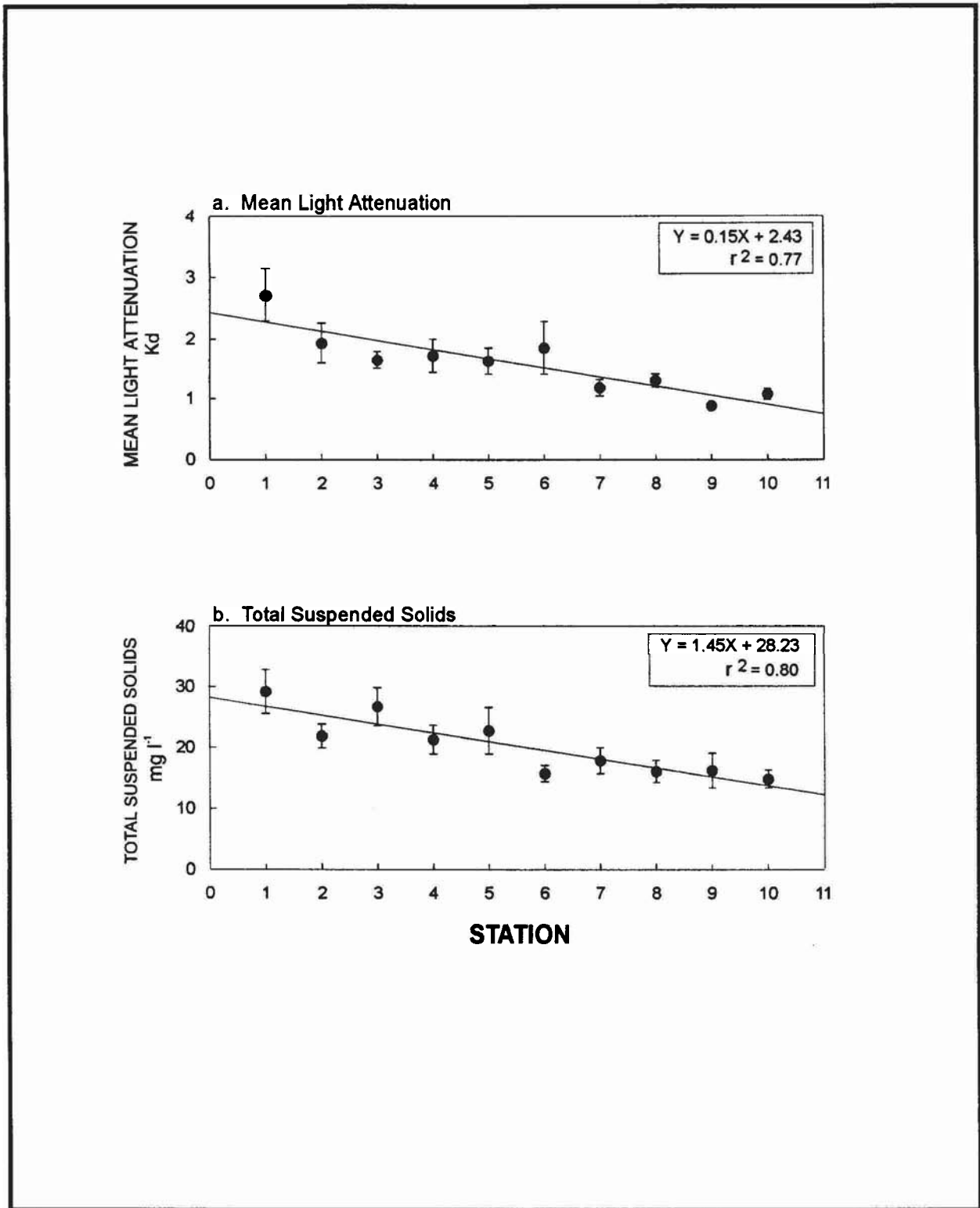


Figure 9-7. Seasonal mean values (\pm 1 SE) at 10 Submerged Aquatic Vegetation (SAV) stations on the Patuxent River during March through October, 1997 for two water column parameters: a. Light Attenuation [Kd]; and b. Total Suspended Solids (TSS).

along the length of the river, with up-river locations having significantly higher TSS concentrations than down-river locations (Figure 9-7). Mean TSS concentrations ranged from 29.2 mg l⁻¹, at SV1A, to 14.80 mg l⁻¹, at SV10.

9.1.8 Light Attenuation

Light attenuation coefficients (Kd) among all ten stations ranged from a minimum of 0.09 m⁻¹ at station SV06 to a maximum of 5.89 m⁻¹ at SV1A over the entire sampling season (Figure 9-5, Table 9-2). For much of the sampling season, Kd values at stations SV1A through SV06 were above 1.5 m⁻¹, the value established as the SAV habitat upper limit for Kd (Batuik *et al.* 1992). Like TSS, Kd values at all stations were lowest in June. There was an increase in Kd values as the summer progressed, being more pronounced at stations SV1A to SV5A, while all values fell below or close to the habitat requirement limit by early October. A significant (P<0.001, r²=0.77) correlation between station location and water column light attenuation (Kd) was found with decreasing mean Kd values for each station moving down river (Figure 9-7). Mean station Kd values ranged from 2.72 m⁻¹, at SV10, to 1.08 m⁻¹, at SV1A.

9.1.9 Near shore Water Quality Evaluation: Discussion and Conclusions

Strong seasonal and spatial gradients were found in near shore SAV habitats along the Patuxent River for a variety of water quality parameters. In general, water quality conditions relative to SAV habitat requirements tended to be much poorer at up-river compared to down-river locations. For example, station SV1A, the most up-river station, consistently experienced the worst overall water quality (e.g. mean Kd = 2.72 m⁻¹), while station SV09, one of the most down-river stations, consistently had the best (e.g. mean Kd = 0.89 m⁻¹). On a seasonal basis, mean light attenuation, TSS, and chlorophyll-a all had significant decreasing values moving down the axis of the river. Since light attenuation (Kd) is well correlated with total suspended solids (TSS) and chlorophyll-a (Figure 9-8) it is not surprising that similar spatial patterns were observed. In addition, temporal variability was similar among Kd, TSS and chlorophyll-a.

In regard to water quality temporal variability, most stations at least some of the time failed to meet minimum SAV habitat requirements for tier II restoration (Batuik *et al.* 1992). However, SAV was observed growing at depths to at least one meter at several stations for a portion of the SAV growing season. For example, *Zannichellia palustris* was found at station SV02 at depths up to one meter despite water quality conditions that rarely met minimum habitat requirements. In fact live SAV was observed growing at 8 of the 10 sampling stations in 1997. In contrast, no SAV was found growing at station SV09 (CBL) despite having the best overall water quality conditions compared to all of the other stations. Since water column light attenuation at station SV1A (Buzzard Island) remained above 1.5 m⁻¹ for most of the season it was not surprising that no growing SAV was observed at that station. Since *Z. palustris* is an early spring species that usually senesces when water temperatures reach 24 C, it may complete its life-history before water quality conditions deteriorate in mid-summer. However, other species that require more stable water quality conditions over a longer period, such as *Potamogeton pectinatus*, may not be able to survive at many of the more upriver locations on the Patuxent River. Although the water quality data collected along the Patuxent River presents a fairly

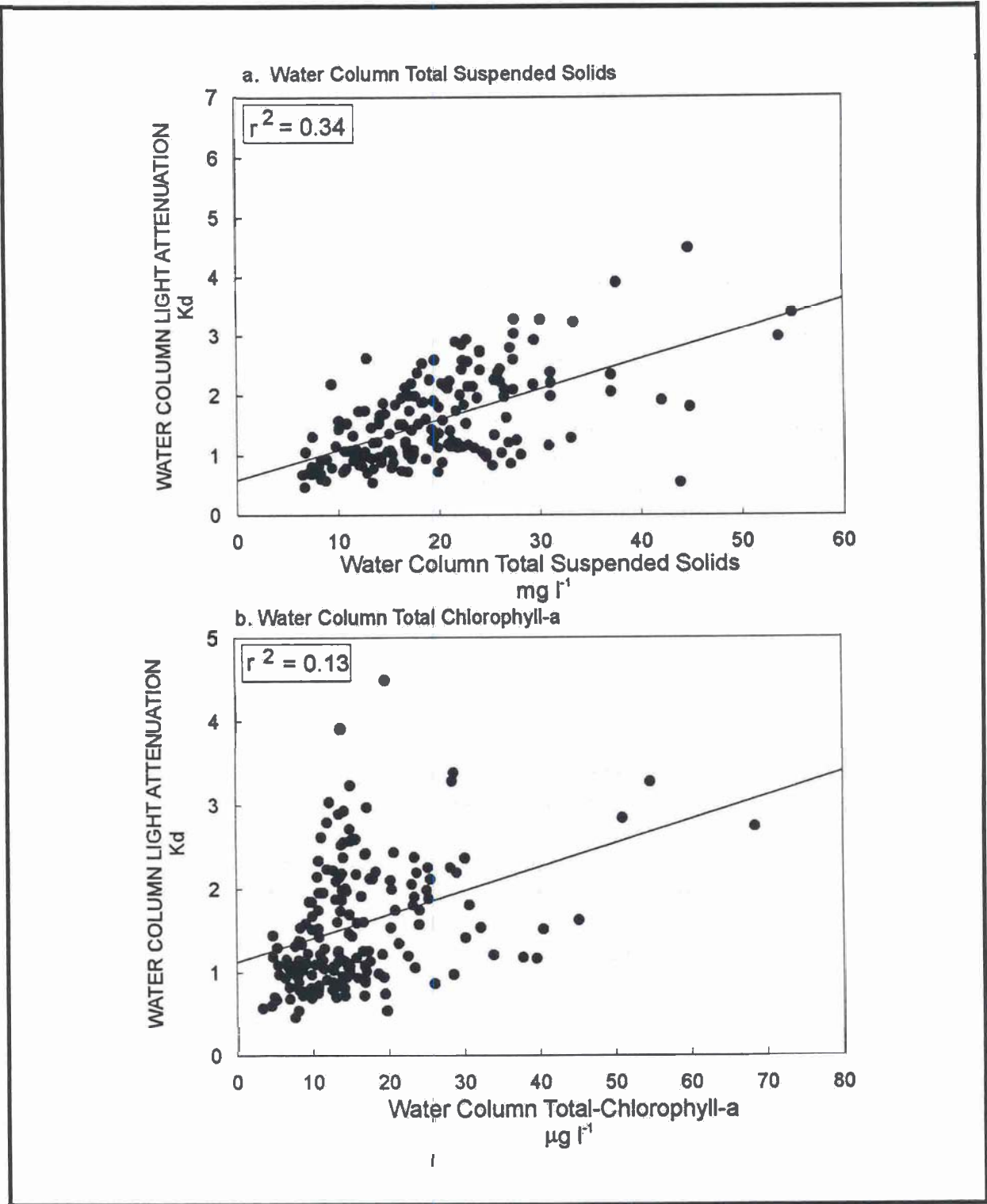


Figure 9-8. Near shore water column light attenuation vs. (a). Water column total suspended solids and (b). Water column total chlorophyll-a.
 Values collected from the Patuxent River SAV monitoring stations SV1A through SV10 from April through September, 1997.

comprehensive view of both temporal and spatial patterns along the river in 1997, it nevertheless represents a fairly short snapshot of SAV habitat conditions. In order to accurately evaluate potential SAV habitats along the Patuxent River additional monitoring is needed to assess the influence of inter-annual variability and obtain a better estimate of longer term conditions.

9.2 Channel-shoal water quality comparison

The channel-shoal water quality comparison was conducted to evaluate the applicability of water quality data collected during the routine monitoring of the river channel relative to near-shore SAV habitats. In this study, water quality measurements were made along two transects arranged perpendicular to the shoreline at stations SV1A (Buzzard Island) and SV05 (Jefferson-Patterson Park) on the Patuxent River (Figure 3-4). Water quality measurements were made at four locations along each transect beginning at the near-shore station and ending at the river channel location. At each location, water quality parameters were measured at 0.5 meters below the water surface. While a large suite of water quality parameters were measured at each location, (see Section 3.2.3 for a full list) five particularly relevant parameters, dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), total chlorophyll-a (TCHLA), total suspended solids (TSS) and water column light attenuation (K_d) are presented in this report. Since water quality measurements were made several weeks apart it was assumed that sampling events were independent of each other. Therefore data from all sampling dates and locations were independent and could be pooled for a three-way analysis of variance (ANOVA). Significance was determined at an alpha level of 0.05.

9.2.1 Dissolved Inorganic Nitrogen

For dissolved inorganic nitrogen (DIN) there was no significant difference among locations on either transect. Mean DIN concentrations in the mid-channel were $11.35 \mu\text{mol}$ compared to $11.06 \mu\text{mol}$ at the near shore locations. In addition, there was no significant difference in DIN concentration between transects. However, there was a significant ($p < 0.001$) difference among sampling dates as might be expected. Late spring DIN concentrations at all locations were between $50\text{-}60 \mu\text{mol}$ but rapidly dropped to around $10 \mu\text{mol}$ by the middle of May (Figure 9-9) where they remained until October when sampling was terminated.

9.2.2 Dissolved Inorganic Phosphorus

Analysis of dissolved inorganic phosphorus (DIP) concentrations indicate there was a significant difference ($p < 0.05$) between mid-channel and the near shore stations of each transect. Mean DIP concentrations in the mid-channel were $0.56 \mu\text{M}$ compared to $0.45 \mu\text{M}$ found near the shoreline. In addition, there was a significant overall difference ($p < 0.001$) in DIP concentrations between the transects and among sampling dates (Figure 9-10).

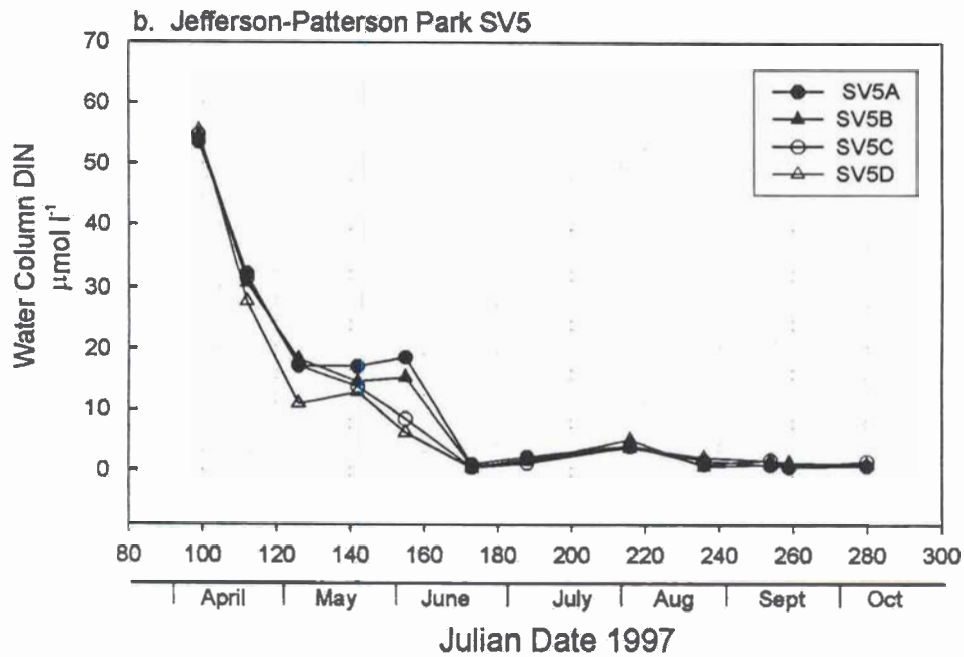
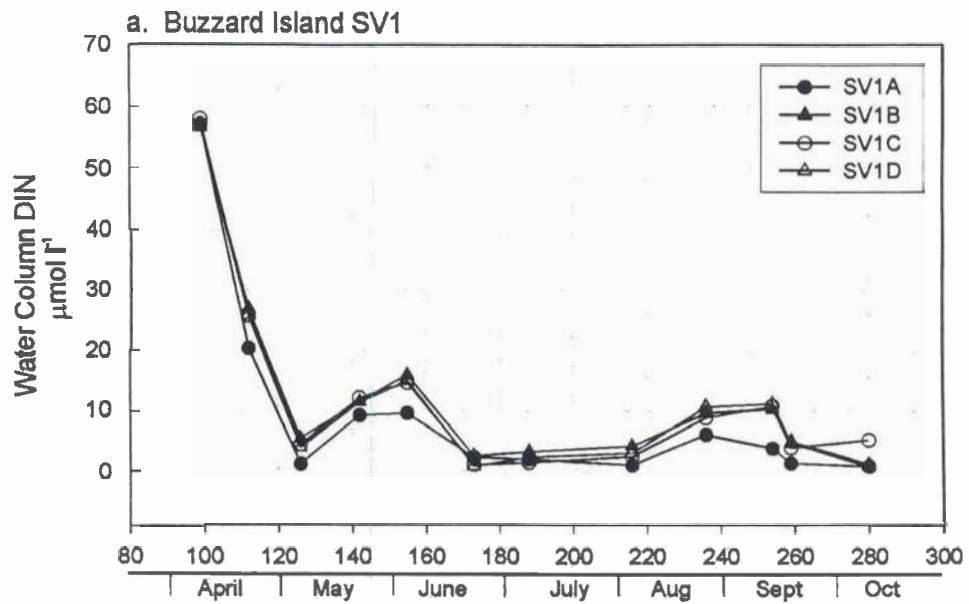


Figure 9-9. Dissolved Inorganic Nitrogen (DIN) in surface waters in the Patuxent River for the period April through October, 1997 along two transects located at (a). Buzzard Island, SV1; and (b). Jefferson-Patterson Park, SV5.

Stations A of each transect represent the most near shore location (SAV habitat), while stations D were located in the river channel.

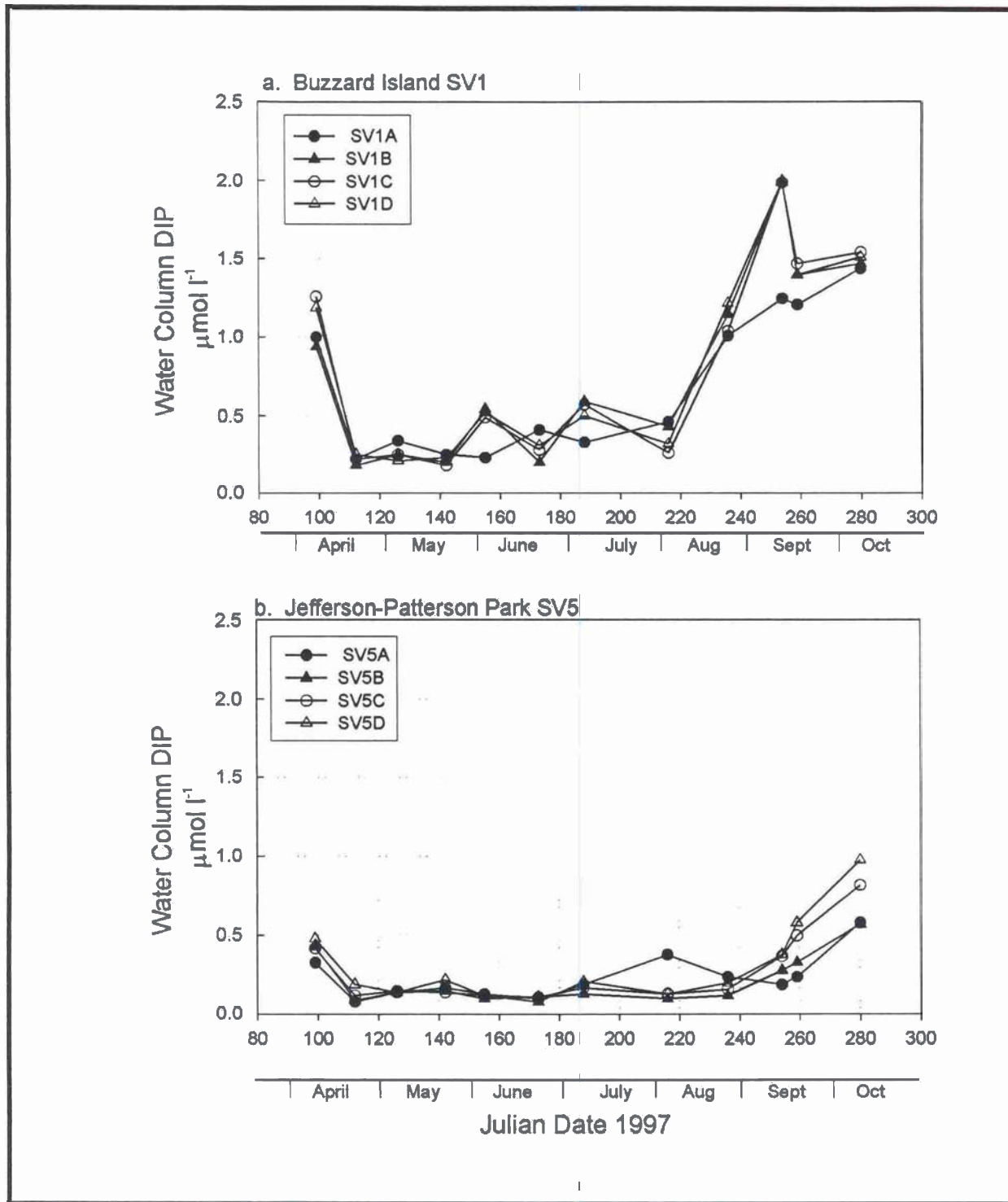


Figure 9-10. Dissolved Inorganic Phosphorus (DIP) in surface waters in the Patuxent River for the period April through October, 1997 along two transects located at (a). Buzzard Island, SV1; and (b). Jefferson-Patterson Park, SV5.
Stations A of each transect represent the most near shore location (SAV habitat), while stations D were located in the river channel.

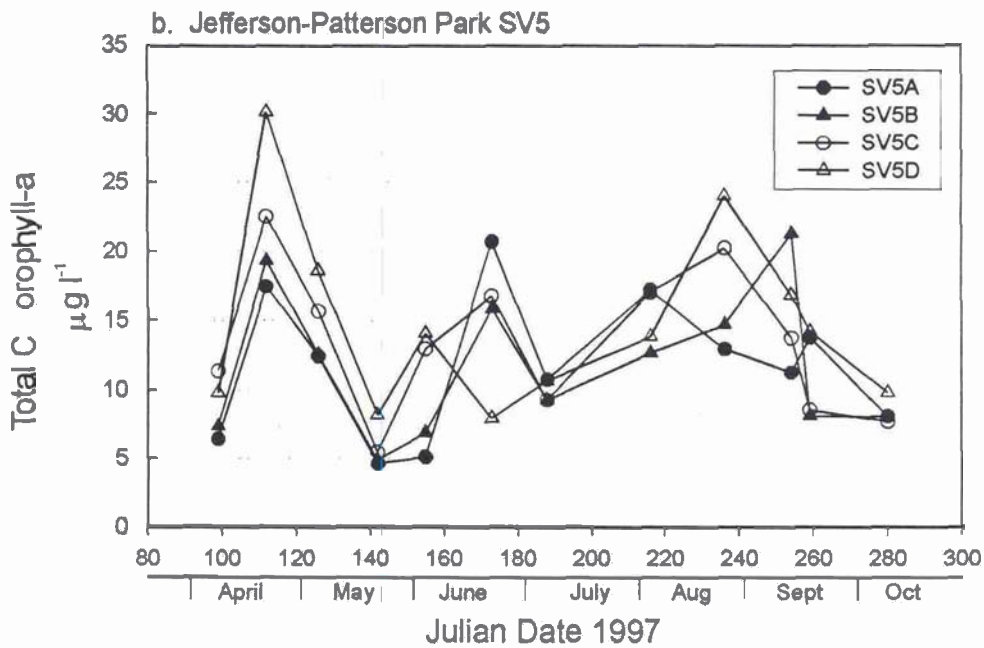
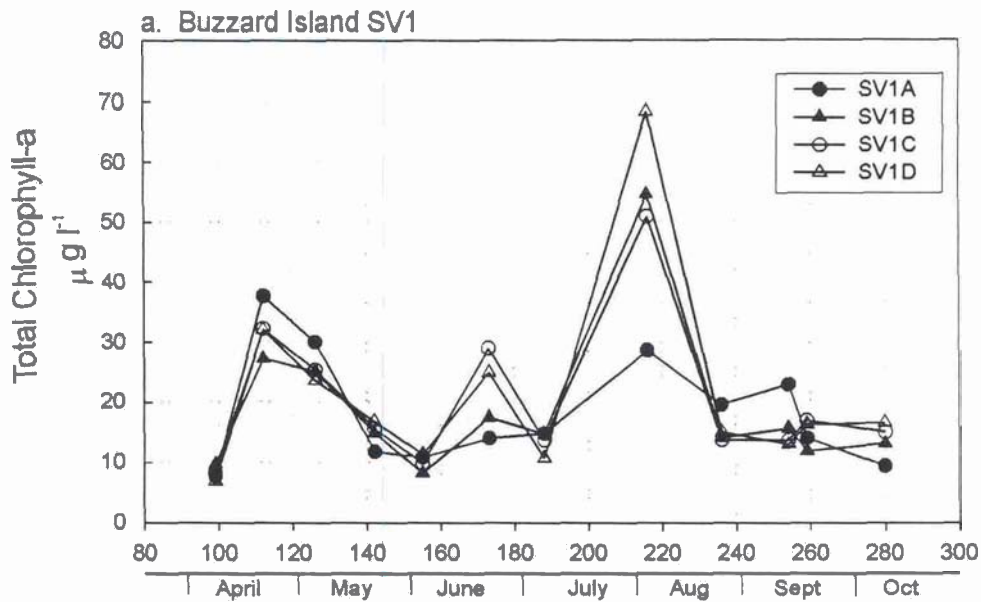


Figure 9-11. Total Chlorophyll-a in surface waters in the Patuxent River for the period April through October, 1997 along two transects located at (a). Buzzard Island, SV1; and (b). Jefferson-Patterson Park, SV5.

Stations A of each transect represent the most near shore location (SAV habitat), while stations D were located in the river channel.

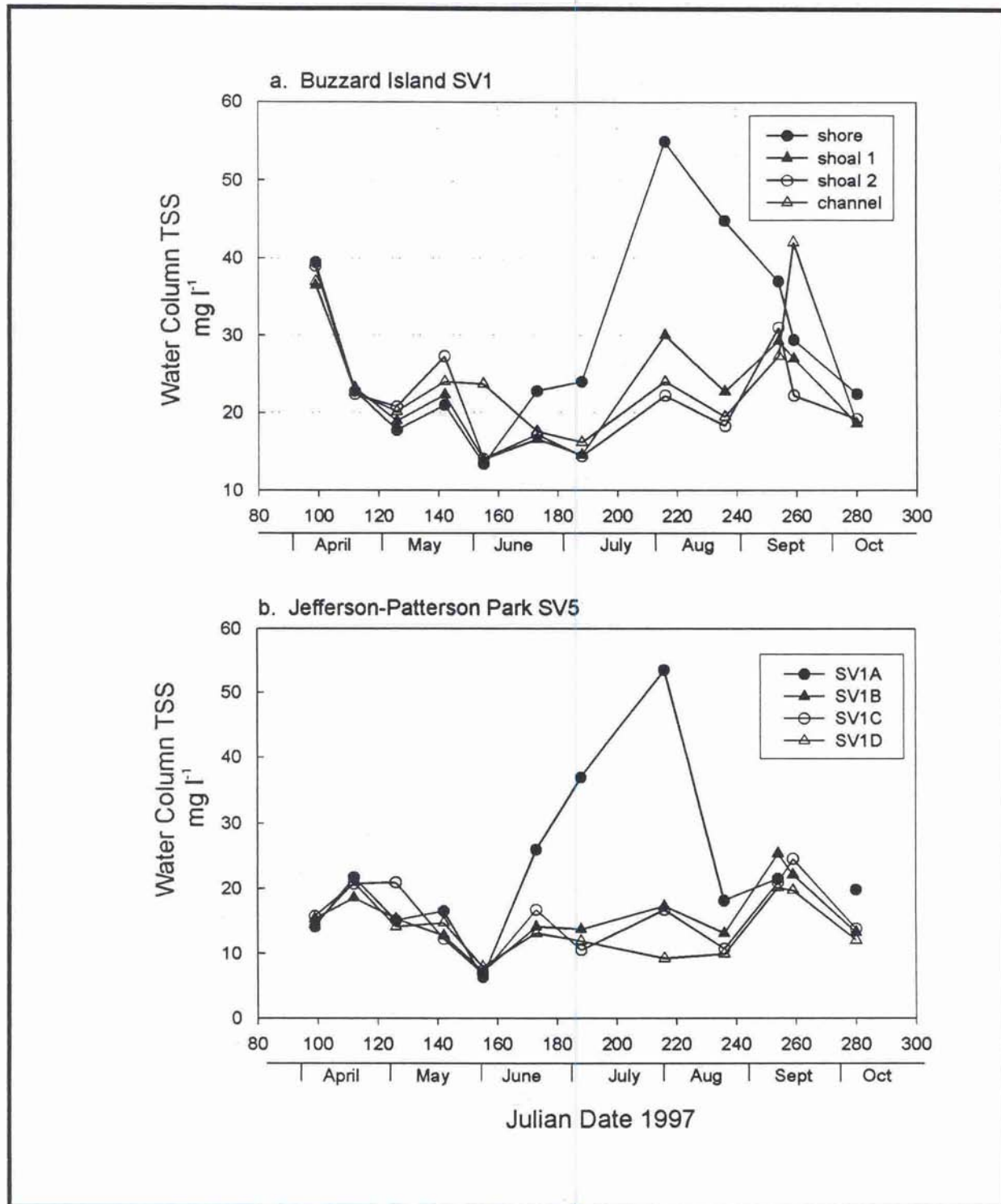


Figure 9-12. Total Suspended Solids (TSS) in surface waters in the Patuxent River for the period April through October, 1997 along two transects located at (a). Buzzard Island, SV1; and (b). Jefferson-Patterson Park, SV5.

Stations A of each transect represent the most near shore location (SAV habitat), while stations D were located in the river Channel.

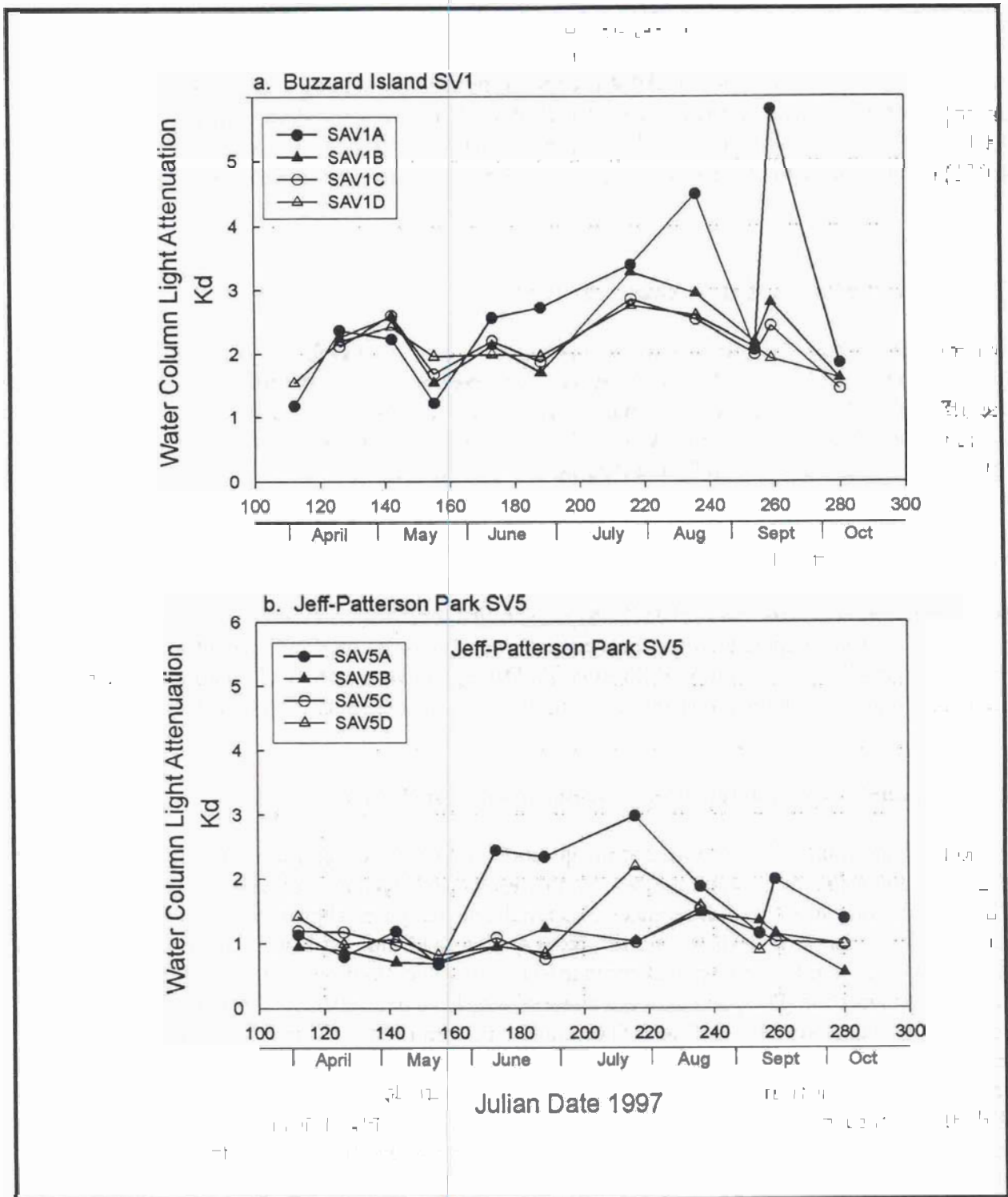


Figure 9-13. Water column light attenuation (Kd) in surface waters in the Patuxent River for the period April through October, 1997 along two transects located at (a). Buzzard Island, SV1; and (b). Jefferson-Patterson Park, SV5.

Stations A of each transect represent the most near shore location (SAV habitat), while stations D were located in the river channel.

9.2.3 Water Column Total Chlorophyll-a

Analysis of total chlorophyll-a (TCHLA) concentrations indicate there was no significant difference among locations on either transect. Mean total chlorophyll-a concentrations in the mid-channel were $18.12 \mu\text{g l}^{-1}$ compared to $15.15 \mu\text{g l}^{-1}$ at the shore. However there were significant differences ($p < 0.001$) in total chlorophyll-a concentrations between the transects and among sampling dates (Figure 9-11).

9.2.4 Water Column Light Attenuation

Water column light attenuation (K_d) at the near shore locations was found to be significantly higher ($p < 0.001$) than any of the off-shore locations. However, no significant difference was found among the off-shore stations. Mean water column light attenuation (K_d) in the mid-channel was 1.63 m^{-1} , while at the near shore locations it was 2.17 m^{-1} . Significant differences ($p < 0.001$) in K_d were also found between transects as well as among sampling dates (Figure 9-12).

9.2.5 Water Column Total Suspended Solids

Water column total suspended solids (TSS) at the near shore locations were found to be significantly higher ($p < 0.001$) compared to the off-shore locations. However, no significant difference was found among the off-shore stations (SV-B through SV-D). Mean water column TSS concentrations were mg l^{-1} at the near shore locations and 26.1 mg l^{-1} at the river channel locations (Figure 9-13).

9.2.6 Channel-shoal: Comparison, Discussion and Conclusions

Although many studies have addressed the question of whether water quality data collected in river channels can be applied to shoreline habitats the results have been inconsistent (Batuik *et al.*, 1992). This may be due in part to differences in spatial and temporal alignment of stations as well as differences in analytical methods and techniques. For the Patuxent River, only limited data were previously available for this type of comparison. Dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP) and light attenuation (K_d) have been evaluated (Parham, *pers. comm.*); however, no data exists for TSS and chlorophyll-a concentrations (Karrh, *pers. comm.*). Among the water quality parameters analyzed, significant differences among transect stations were only found between the near shore and mid-channel locations. For example, both water column light attenuation (K_d) and total suspended solids were found to be significantly greater at the near shore compared to the mid-channel locations. No difference was detected between the river channel location and either of the intermediate stations. Since water column light attenuation (K_d) and TSS are often strongly correlated, it is not surprising that these parameters showed similar results. A possible reason for this difference could be wind driven resuspension at the near shore locations. These results are consistent with previous studies that indicate that, where a significant difference was found, near shore locations generally had higher values (Batuik *et al.* 1992). In contrast, water column chlorophyll-a was found to be higher at the river channel locations but not significantly different from any of the other transect locations. Although dissolved inorganic phosphorus (DIP) concentrations were found to be

significantly higher at the mid-channel locations compared to the near shore locations the actual magnitude of the difference was quite small ($0.11 \mu\text{M P}$) and may not be ecologically significant. No significant differences in dissolved inorganic nitrogen (DIN) were detected between any of the transect stations. This result is also in general agreement with previous studies that rarely found significant differences in DIN concentrations between near shore and mid-channel locations (Batuik *et al.* 1992). However, this study may also suffer from the same limitations imposed by a very large temporal change in DIN values that may mask actual differences. More sophisticated methods of analyzing this data set are being pursued and will be discussed in the final version of this report. While significant differences in several parameters were found between near shore and mid-channel locations in 1997, it is unknown whether these differences will be consistent year to year.

9.3 Tidal-Cycle Water Quality Comparison

The tidal cycle water quality comparisons were conducted to help assess short-term water quality variation as a result of tidal influence in SAV habitats. A variety of water quality parameters were measured hourly for thirteen consecutive hours on July 29, 30, and 31, 1997 at SAV station SV5A (Jefferson-Patterson Park). Measurements began each day at low tide. While a large suite of water quality parameters were measured (see section 3.2.3 Field Methods for a full list) five particularly relevant parameters, dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), total chlorophyll-a (TCHLA), total suspended solids (TSS) and water column light attenuation (K_d) are presented in this report.

9.3.1 Tidal Cycle Results

In order to properly interpret the results of this study several statistical models are currently being evaluated to determine the most appropriate method. Final model choice and interpretation of data will be included in the final report. While a formal statistical analysis has not yet been made, several patterns have emerged from the data.

Dissolved inorganic nitrogen (DIN) concentrations did not appear to vary predictably with tidal cycle (Figure 9-14). For example, on July 29, 1997 dissolved inorganic nitrogen (DIN) increased throughout the day from $3.66 \mu\text{M}$ to $8.91 \mu\text{M}$ twelve hours later. In contrast, during the next two days, DIN concentrations decreased throughout the day from a maximum of $10.97 \mu\text{M}$ in the morning to $4.58 \mu\text{M}$ at the end of the day.

Dissolved inorganic phosphorus (DIP) concentrations remained uniformly low ($< 0.2 \mu\text{M}$) on all three days with the exception of a short one to two hour spike in concentration occurring near mid-day at high tide (Figure 9-14). Excluding these brief excursions in DIP concentration, values remained well below the maximum SAV habitat criteria (Batuik *et al.* 1992). It is unknown why DIP concentrations increased dramatically for such a brief period each day, or why the increase did not happen at the same tidal stage each day. Further investigation may reveal the cause of this anomaly.

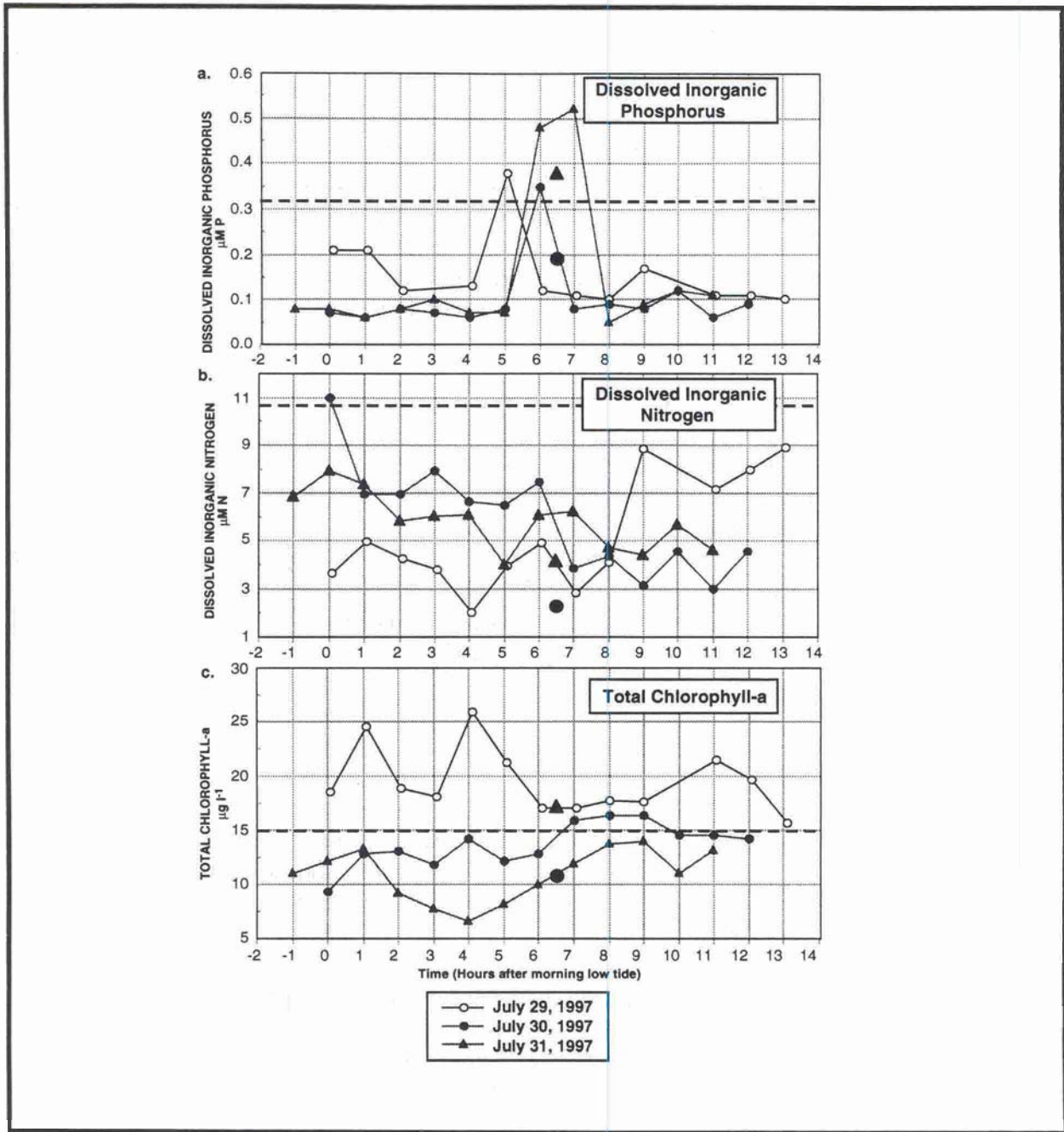


Figure 9-14. Line graphs depicting concentrations of (a) dissolved inorganic phosphorus, (b) dissolved inorganic nitrogen and (c) total chlorophyll-a over thirteen hour periods during three consecutive days of the Tidal Cycle Survey portion of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of the SAV habitat requirement value for each parameter as indicated in Chesapeake Bay Submerged Aquatic Vegetation Habitat Requirements and Restoration Targets: A Technical Synthesis (Batiuk *et al.*, 1992). The solid circle (●) indicated the value for the sample taken during the previous sampling event (July 8, 1997) and the bold triangle (▲) indicates the value for the sample taken during the subsequent sampling event (August 5, 1997). All data have been plotted relative to the time of low tide following sunrise on each sample date.

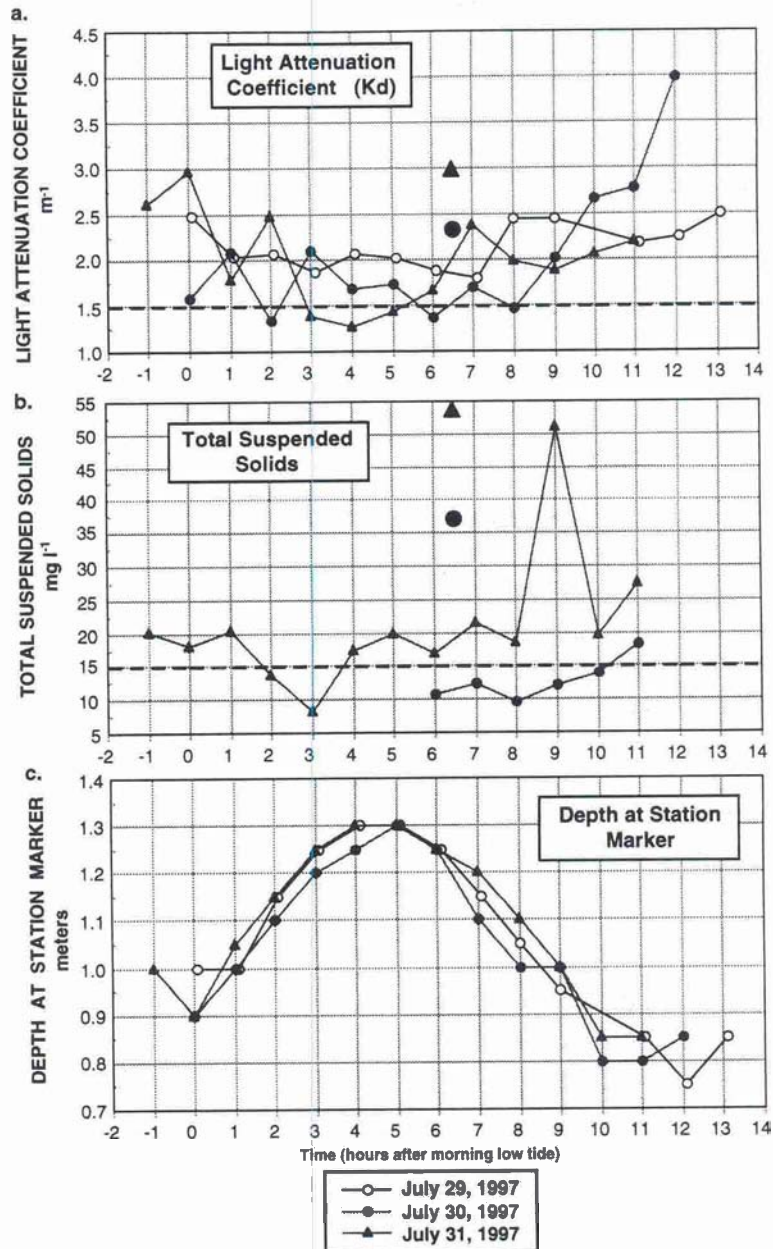


Figure 9-15. Line graphs depicting the (a) Light attenuation coefficient, (b) the amount of total suspended solids and (c) the station depth recorded over thirteen hour periods during three consecutive days of the Tidal Cycle Survey portion of the Patuxent River SAV Habitat Evaluation.

The dashed horizontal line indicates the upper limit of the SAV habitat requirement value for each parameter as indicated in Chesapeake Bay Submerged Aquatic Vegetation Habitat Requirements and Restoration Targets: A Technical Synthesis (Batiuk *et al.*, 1992). The solid circle (●) indicated the value for the sample taken during the previous sampling event (July 8, 1997) and the bold triangle (▲) indicates the value for the sample taken during the subsequent sampling event (August 5, 1997). All data have been plotted relative to the time of low tide following sunrise on each sample date.

Concentrations of water column chlorophyll-a did not appear to vary predictably with tidal cycle (Figure 9-13). However, on a daily basis, the highest mean chlorophyll-a concentration of $19.5 \mu\text{g l}^{-1}$ was found on day 1 (July 29, 1997) followed by $13.7 \mu\text{g l}^{-1}$ found on day 2 (July 30, 1997) and $10.9 \mu\text{g l}^{-1}$ on the last day (July 31, 1997).

Water column light attenuation (K_d) varied substantially within a single tidal cycle (Figure 9.15). Values ranged from a minimum of 1.37 m^{-1} to a maximum of 3.99 m^{-1} on day 2 (July 30, 1997). In general, values were lowest at midday on all three days, but no statistical tests have been run to verify this observation. Much of the data collected for water column total suspended solids (TSS) was lost due to damaged filter pads, however the available data does show a strong correlation with light attenuation as might be expected.

9.4 Epiphyte Growth Study

Various field and laboratory studies indicate that light limitation is a major factor influencing the survival and distribution of submerged aquatic vegetation SAV (e.g. Dennison and Albert 1985; Kemp *et al.*, 1983). In addition to water column light attenuation, epiphytic growth on the leaves of SAV has been recognized as a possible factor limiting the available light reaching the leaves of SAV (e.g. Twilley *et al.*, 1985). Although it has been assumed that increases in nutrient loading are responsible for increases in epiphyte growth and subsequent light attenuation, various field and laboratory studies have had mixed results (e.g. Twilley *et al.*, 1985; Lin *et al.*, 1997). Complex interacting factors such as the presence of epiphyte grazers may mask any effects of increased nutrient loading on epiphyte growth (e.g. Neckles *et al.*, 1993). However the potential for light attenuation from epiphytes can be great, and may influence the growth and survival of SAV. The goal of this study was to examine the potential contribution that epiphytes may make towards attenuating the available light to SAV at various sites along the Patuxent river.

In order to estimate the potential light attenuation caused by epiphytes, artificial substrates in the form of thin Mylar™ strips were deployed at ten stations (Figure 3-4) on the Patuxent River and its tributaries throughout the SAV growing season from May through October, 1997. While artificial substrates may not provide a direct estimate of epiphyte biomass on actual SAV leaves, they can be used on a comparative basis to evaluate various sites relative to each other, and to obtain a first order approximation of light attenuation. Additional advantages of artificial substrates are that they can be used to sample areas that are devoid of living SAV at a fraction of the effort needed to transplant living plants and they can be used to accurately measure epiphyte light attenuation which is not possible with actual SAV.

In this study, Mylar™ strips were sampled concurrently with the water quality component of the larger SAV habitat evaluation. Individual epiphyte collection strips were typically exposed to *in-situ* fouling for 14 days; however, some intervals were as short as 5 or as long as 28 days. Three parameters were measured in order to assess the impact of epiphytic fouling on SAV leaves. Light attenuation as a result of fouling was measured from replicate strips, while epiphyte chlorophyll (total and active) and total accumulated solids were each measured from single representative strips collected at each station. Epiphyte chlorophyll-a, and total suspended solids (TSS) accumulation rates were standardized to daily accumulation rates in order to facilitate seasonal and inter-site comparisons.

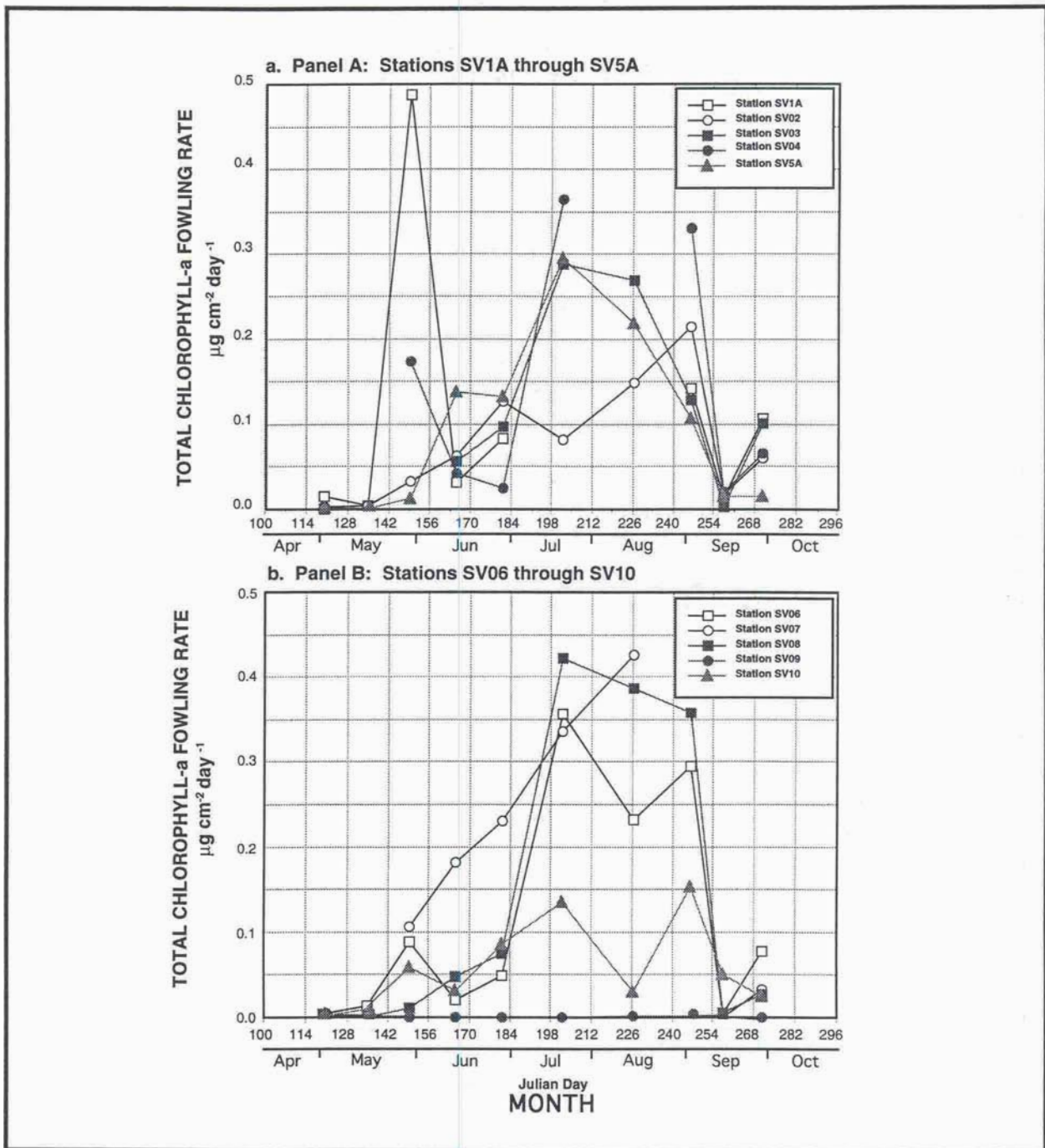


Figure 9-16. Line graphs of epiphytic fowling rates of total chlorophyll-a between April and October, 1997 as a component of the Patuxent River SAV Habitat Evaluation
a. Panel A represents stations SV1A through SV5A and
b. Panel B represents stations SV06 through SV10.

Rates were based on weight of materials collected on Mylar™ strips suspended in water column at specific sites in the Patuxent River. Rates are expressed as weight of material per area of artificial substrate per time of exposure. Total chlorophyll-a values are plotted at Julian day number that corresponds with the middle point of the deployment period. Incomplete lines indicate data were not collected or not interpretable.

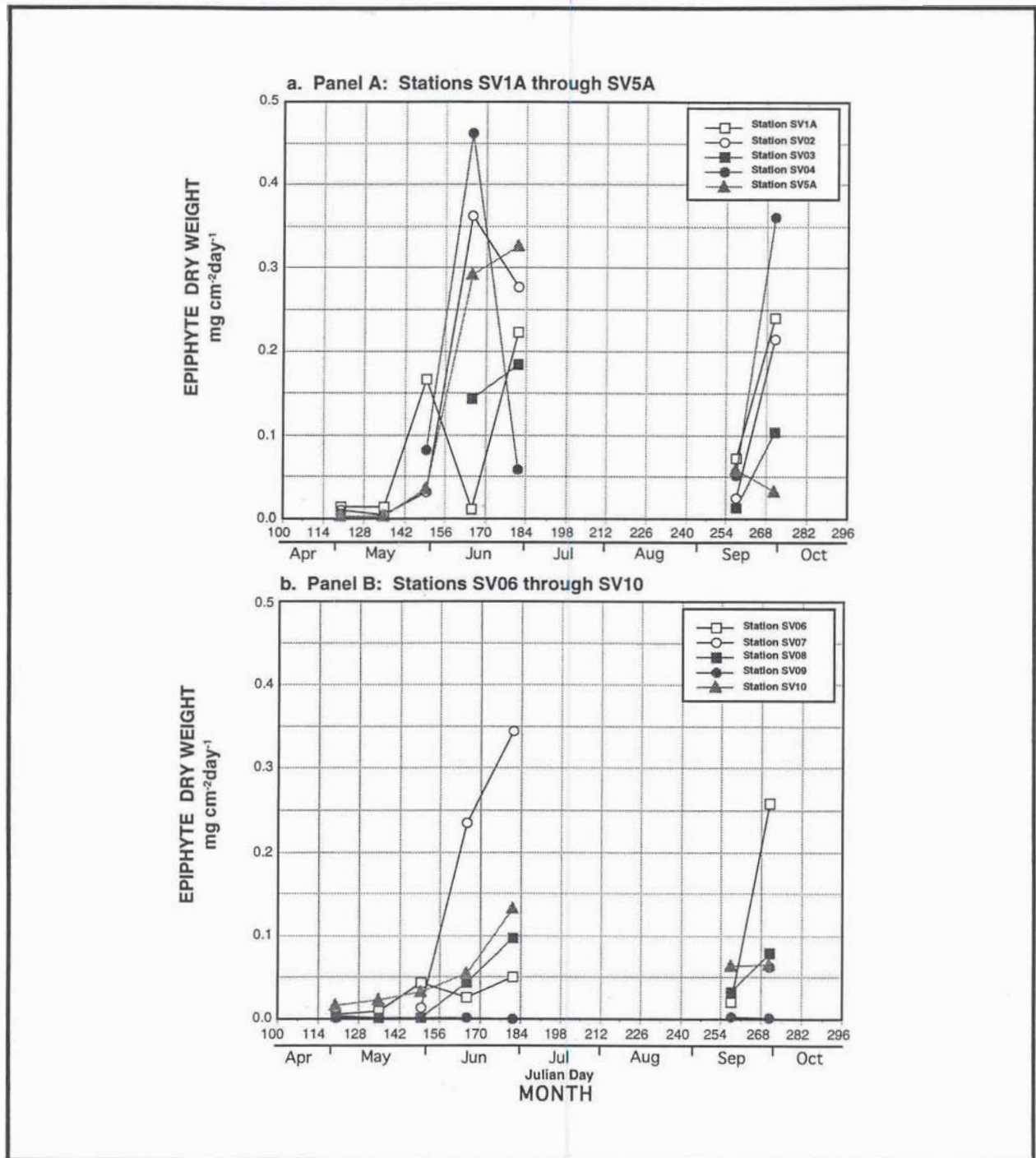


Figure 9-17. Line graphs of epiphytic fouling rates of total epiphytic dry weight between April and October, 1997 as a component of the Patuxent River SAV Habitat Evaluation

a. Panel A represents stations SV1A through SV5A and

b. Panel B represents stations SV06 through SV10.

Rates were based on weight of materials collected on Mylar™ strips suspended in water column at specific sites in the Patuxent River. Rates are expressed as weight of material per area of artificial substrate per time of exposure. Total chlorophyll-a values are plotted at Julian day number that corresponds with the middle point of the deployment period. Incomplete lines indicate data were not collected or not interpretable.

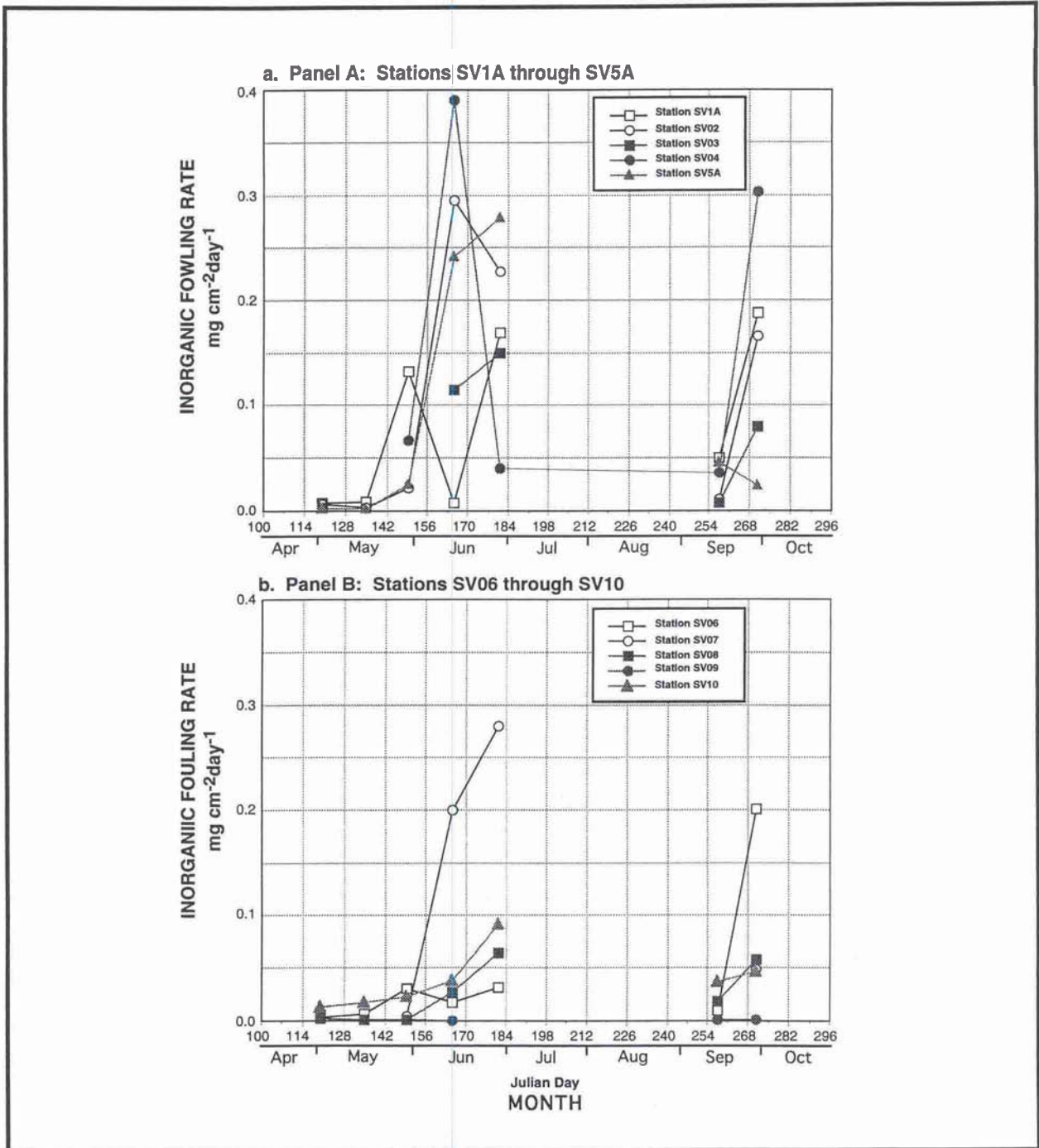


Figure 9-18. Line graphs of epiphytic fouling rates of epiphytic inorganic weight between April and October, 1997 as a component of the Patuxent River SAV Habitat Evaluation
a. Panel A represents stations SV1A through SV5A and
b. Panel B represents stations SV06 through SV10.

Rates were based on weight of materials collected on Mylar™ strips suspended in water column at specific sites in the Patuxent River. Rates are expressed as weight of material per area of artificial substrate per time of exposure. Total chlorophyll-a values are plotted at Julian day number that corresponds with the middle point of the deployment period. Incomplete lines indicate data were not collected or not interpretable.

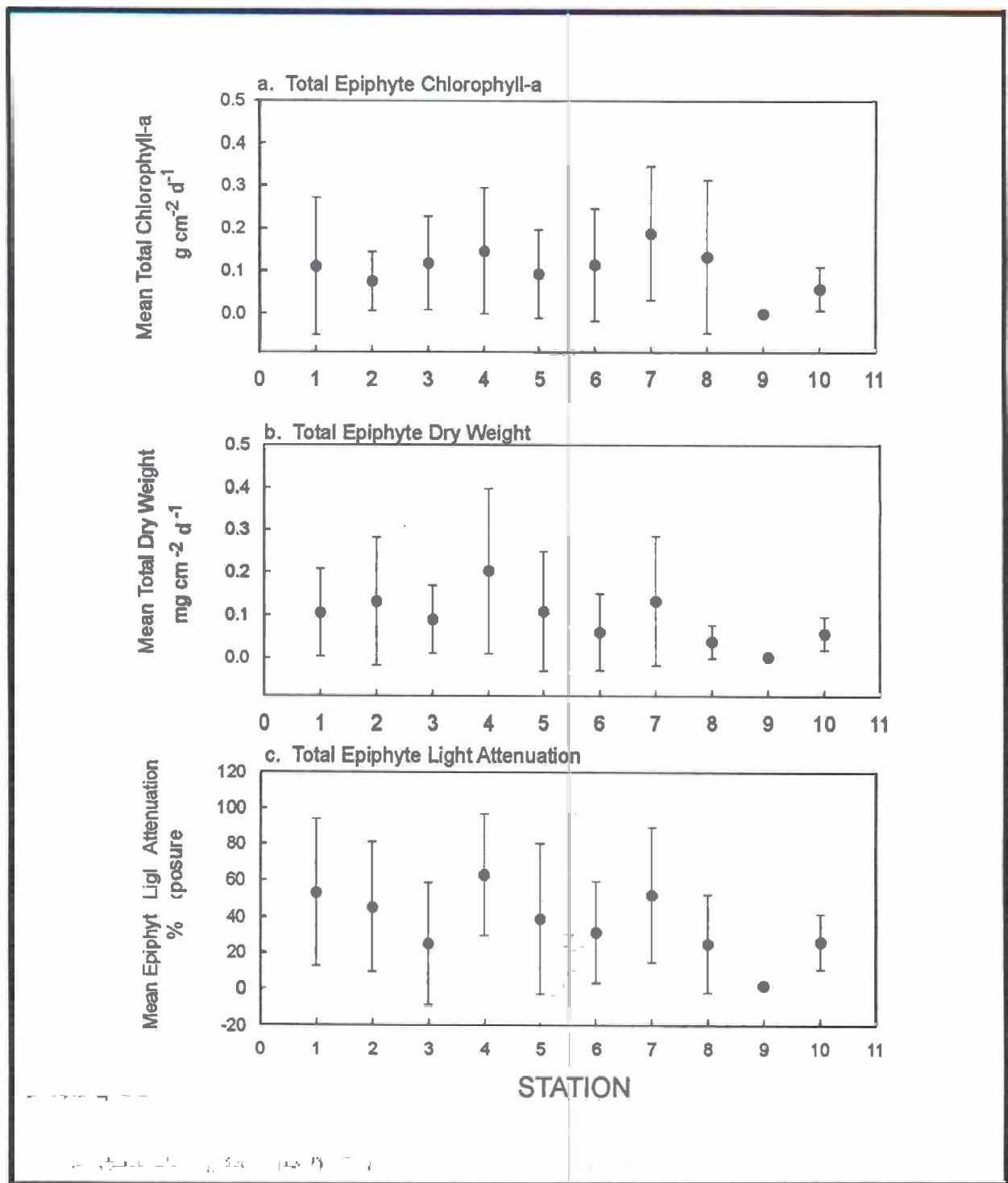


Figure 9-19. Seasonal mean values for epiphytic growth study on artificial substrates at 10 stations on the Patuxent River for the period May through October, 1997.

Error bars represent ± 1 SE.

- a. Total Epiphyte Chlorophyll-a
- b. Total Epiphyte Dry weight and
- c. Total light attenuation due to epiphytes.

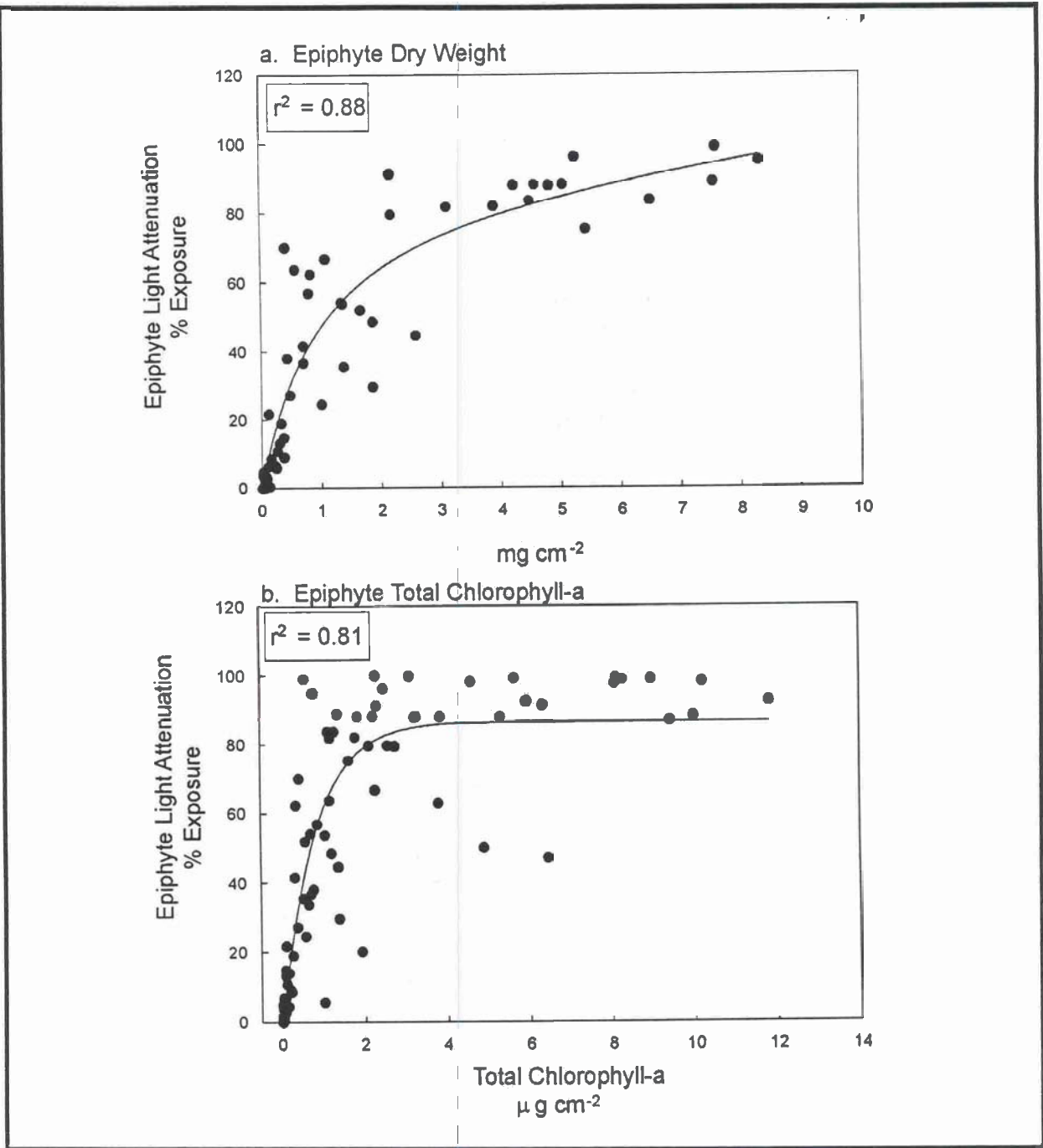


Figure 9-20. Submerged Aquatic Vegetation (SAV) epiphyte light attenuation vs. (a). Epiphyte dry weight and (b). epiphyte total chlorophyll-a collected from artificial substrates deployed in the Patuxent River during 1977.

The regression equation for (a) epiphyte dry weight is:

$$LA = (89.22 \cdot DW) / (0.97 + DW) + 2.02 \cdot DW,$$

where LA=light attenuation and DW=epiphyte dry weight.

The regression equation for (b) epiphyte total chlorophyll-a is:

$$LA = 86.62 \cdot (1 - 0.293^{Tchla})$$

where Tchla is total epiphyte chlorophyll-a.

9.4.1 Results and Conclusions

Epiphytic fouling rates were highly variable throughout the sampling season (Figure 9-14 through 9-16). Epiphytic chlorophyll-a fouling rates ranged from nearly zero at station SV09 (CBL) to as high as $4.8 \mu\text{g cm}^{-2} \text{day}^{-1}$ at station SV1A (Buzzard Island). In April at a mean water temperature of 11.4°C , the mean chlorophyll accumulation rate across all stations was $0.003 \mu\text{g cm}^{-2} \text{d}^{-1}$. However, by late May, mean water temperatures had reached 16.6°C , and the mean chlorophyll-a fouling rate had increased dramatically to $0.10 \mu\text{g cm}^{-2} \text{d}^{-1}$. While much of the temporal variation in fouling rates can be explained by increases in temperature, a significant portion of this variation is likely the result of differences in the length of *in-situ* deployment. For example the apparent rapid decrease in fouling rates in September (Figure 9-14) is likely an artifact of an unusually short deployment (5 days), since chlorophyll-a accumulation rates increased again in October. Since the growth and accumulation of epiphytes is probably not a linear process, some unknown error is incurred when converting the total accumulation of unequal deployment intervals to a daily rate. While this approach may present a limitation for temporal comparisons, it has less of an effect on spatial comparisons. However it does contribute to high variance among the data making differences among stations more difficult to detect. Of all the stations sampled, only station SV09 had uniformly low epiphyte accumulation rates throughout the season. On a seasonal mean basis, with the exception of station SV09, no significant differences in chlorophyll-a accumulation rates were found among the stations (Figure 9-19).

Measurement of epiphyte dry weight accumulation rates also followed a pattern similar to epiphyte chlorophyll-a fouling rates (Figure 9-17). However, due to extended lengths of *in-situ* deployment during July and August, many strips were so extensively fouled they were rendered unusable. During this time, a wide range of encrusting bryozoans and hydroids were recruiting onto the Mylar™ strips creating a three dimensional structure much greater than what would be found with epiphytic growth alone. Although not measured, these strips would most assuredly have attenuated 100% of the available light. The epiphyte dry weight (organic and inorganic components) rates of fouling were also dependent on ambient temperature and length of deployment. A maximum measured mean accumulation of $0.22 \text{ mg cm}^{-2} \text{day}^{-1}$ was found at station SV04 (Broomes Island) and a minimum of $0.00 \text{ mg cm}^{-2} \text{day}^{-1}$ at station SV09 (CBL). Fouling rates at station SV09 were much lower than all the other stations. With station SV09 excluded from the analysis there was no significant difference in dry weight accumulation ($p > 0.10$) among any of the other SAV sampling stations.

Since epiphyte light attenuation is a direct consequence of epiphyte fouling rates and sediment accumulation, the pattern of light attenuation among SAV stations is similar to that found for chlorophyll-a fouling rates and dry weight accumulation (Figure 9-17). Once again, with station SV09 (CBL) excluded, no significant differences in light attenuation were found among the stations.

9.4.2 Discussion

Strong logarithmic relationships were found between light attenuation and epiphyte dry weight ($r^2=0.88$) as well as between light attenuation and epiphyte total chlorophyll-a ($r^2 = 0.78$; Figure 9.18). These relationships indicate that when epiphyte total dry weight approaches 2 mg cm^{-2} , greater than 80% of the available light is attenuated before it reaches the leaves of SAV. Similarly, when

epiphyte total chlorophyll-a approaches $1 \mu\text{g cm}^{-2}$ almost 100% of the available light is attenuated.

While it is impossible, to accurately extrapolate predictions based upon artificial substrates to actual SAV, a first order approximation can be constructed. If we assume as a worst case scenerio the accumulation of epiphytes on actual SAV is approximated by epiphyte accumulation on Mylar™ strips, then given that the mean dry weight fouling rate at most stations was approximately $0.1 \text{ mg cm}^{-2} \text{ day}^{-1}$, it would only take 20 days before epiphytic accumulation would attenuate as much as 80% of the available light. If water column light attenuation already reduces available light to minimum levels, SAV would not survive very long in the Patuxent River. However, this estimate is based upon seasonal means and may be biased by very high values recorded in July and August. Epiphyte accumulation rates were much lower through April, May, and June. In addition, water column light attenuation was much lower during the spring months, compared to July and August, resulting in water quality conditions much more likely to support SAV growth. For a species such as *Zannichellia palustris* that completes its life cycle by mid summer, deteriorating water quality conditions late in the season are not as critical. This is supported by field observations of *Z. palustris* growing at all but two of the monitoring stations through June, even though seasonal estimates of water quality and epiphyte loading would suggest otherwise. However, for other species, such as *Potamogeton pectinatus*, which does not ordinarily senesces until late fall, poor water quality conditions during mid-summer could have severe detrimental effects. This was also supported by the field observation that at station SV07 (Hungerford Creek), a *P. pectinatus* bed was thick and lush through June, deteriorating in July, and virtually gone by late August after two months of poor water quality.

While this study provided baseline information regarding potential epiphytic accumulation on SAV leaves in the Patuxent River further studies promise to shed more light on these relationships. While a variety of factors such as hydrodynamic effects, and allelopathic interactions between SAV and epiphytes, limit our ability to estimate actual epiphyte accumulation rates with artificial substrates it is possible to bridge the gap between the two substrates. By concurrently measuring biomass accumulation on artificial substrates and live on SAV deployed simultaneously we may be able to determine the proper correction factor needed to make accurate light attenuation estimates. With this added information it is possible to develop a useful monitoring tool using artificial substrates to estimate the potential for light attenuation from SAV epiphytes.

9.5. Submerged Aquatic Vegetation (SAV) Propagule Availability Study

The availability of SAV propagules along the margins of the Patuxent River was monitored to test the idea that the slow regrowth of SAV communities in this system was due to a lack of viable SAV material.

The mean number of propagules were plotted against time (date of sample) and indicated a dramatic increase in number towards the end of May and beginning of June and followed by a noticeable decline in July. At the station located at Solomons Island, CBL, very few propagules, and in most cases none were found in collection traps throughout the study period (Figure 9-21.a).

The mean length of the propagules collected was also plotted against time (date of sample; Figure 9-21.b). The samples were predominantly monospecific and in most cases *Zanichellia palustris* was the only species present. At station SV1, trap 2 and trap 3, on May 7th, 1997 *Potamogeton pectinatus* was recorded.

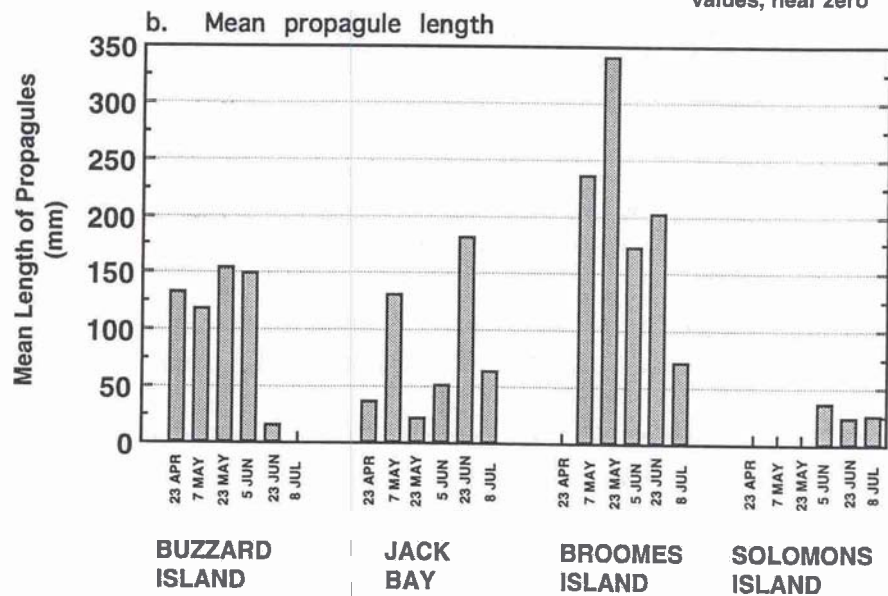
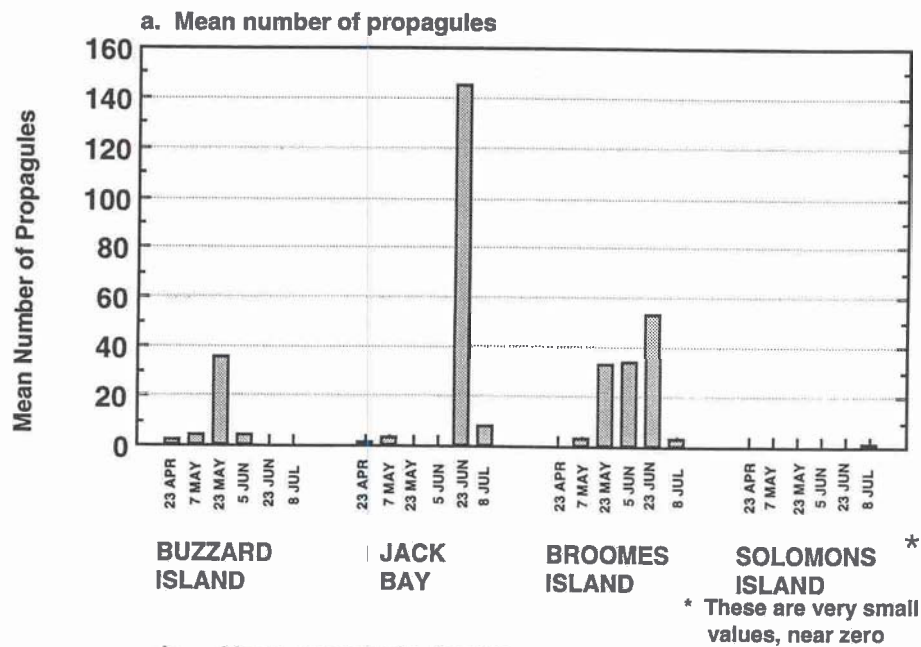


Figure 9-21. Bar graphs showing results of submerged aquatic vegetation (SAV) propagules collected at four sites between April and July, 1997
 a. Mean number of propagules.
 b. Mean propagule length (mm).

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10. PATUXENT RIVER HIGH FREQUENCY MONITORING

N.H. Burger and J. D. Hagy III

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.*, 1982; 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 (hours to days) 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 the violation of this assumption. 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.

10.1. 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 increases 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 persistently low dissolved oxygen concentrations 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.

Several years ago the Ecosystem Processes Component (EPC) Program was able to obtain a data record collected from the bridge at Benedict (Maryland 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 Robert Cory of the U. S. Geological Survey maintained a monitoring station on the bridge (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 a good deal can be learned about the performance of the Patuxent River during a period (1964 - 68) when water quality conditions were better and nutrient loads to the system were lower than in recent decades.

With the availability of continuous data in the Patuxent River prior to water quality deterioration, a new study was initiated to similarly measure and quantitatively assess current water quality conditions and contrast current observations to earlier conditions. The procedure described by Odum and Hoskins, 1958) for measurement of community metabolism with the diurnal curve method was adapted to analyze both the earlier data collected by Cory and contemporary measurements to represent current conditions for comparative analysis. Sampling at the same site and following the same regimen used by Cory during the 1960's was repeated from April through October in 1992 and from June through October 1996 using a modern temperature, salinity and dissolved oxygen instrument (Hydrolab DataSonde-3). 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 (every 3 - 4 days) was followed.

The Cory data set and the 1992 data set were analyzed by Sweeney (1995) and the 1996 data by the EPC Program (Boynton *et al.*, 1997). Figure 10-1 shows 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 (P_a^*) in 1992 exceeded those in 1964 by a factor of three (300%) while estimates of community respiration at night (R_n) in 1992 were greater than those in 1964 by a factor of two (200%). Analyses by Sweeney (1995) indicate a statistically significant trend towards higher values for both daytime net community production (P_a^*) and community respiration at night (R_n) between 1964 and 1969 and significant differences between the data collected in the 1960's and 1992. Furthermore, there were changes in the seasonal pattern of metabolism between the 1960's and 1992. In the 1960's, daytime net community production (P_a^*) 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 (P_a^*) 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

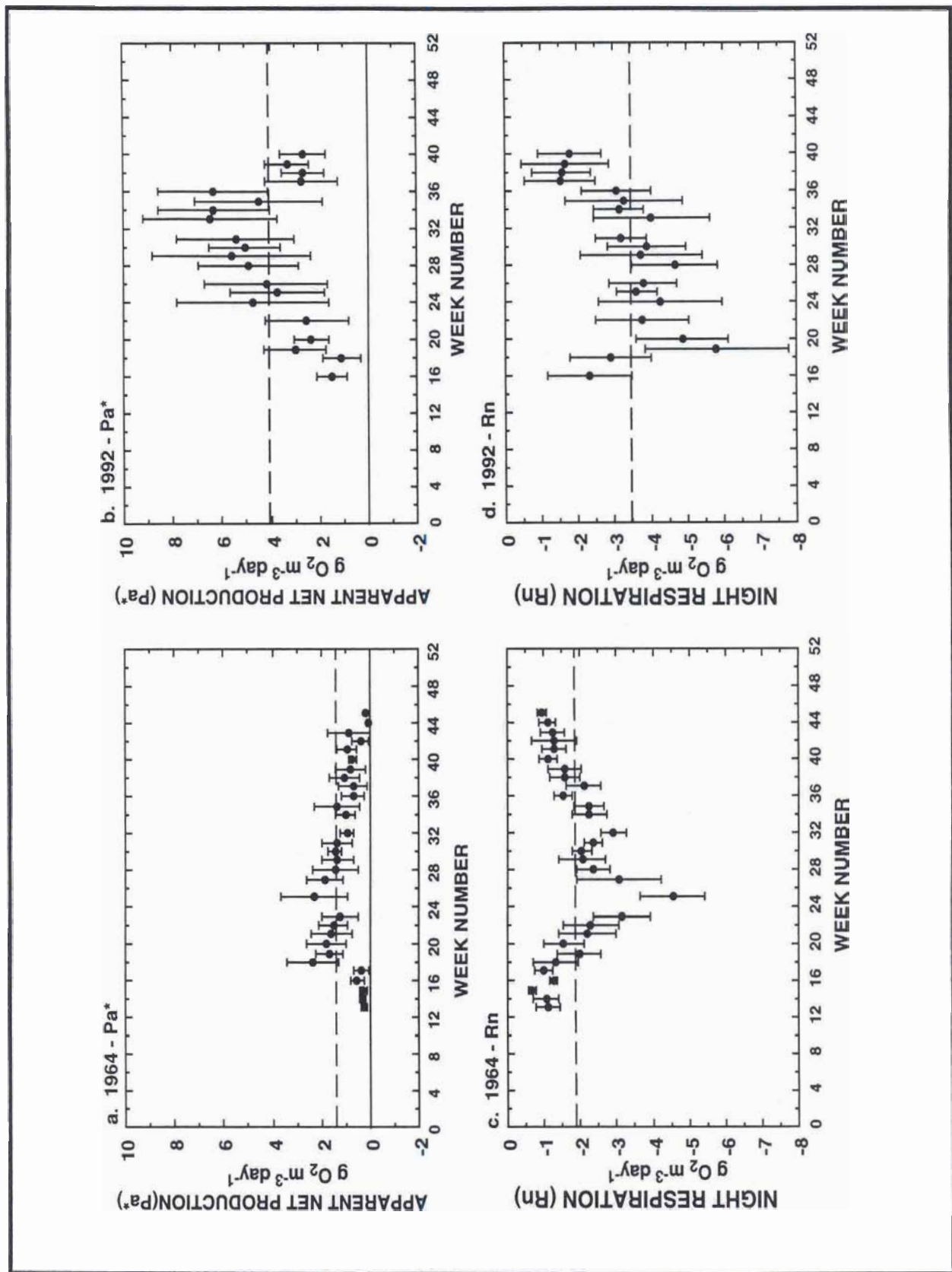


Figure 10-1. A comparison of rates (week averages and standard deviations) of daytime net community primary production (Pa*) and community night respiration (Rn) measured during 1964 and 1992 at the Benedict Bridge (MD Route 231 bridge), Patuxent River. Rates were based on diel measurements of dissolved oxygen and converted to estimates of metabolism using the technique of Odum and Hoskins (1958).

The 1996 data were collected by Cory (pers. comm.) and the 1992 data were collected by Sweeney (1995).

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 (see Chapter 11, this report). Rates of oxygen consumption (R_n) 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 1960's, 1992 and 1996 data sets demonstrated the utility of the diel oxygen technique for measuring community production and respiration as a powerful and cost effective complement to monitoring efforts in the Patuxent River estuary and possibly other sites as well. Preliminary results indicated a clear association of historical nutrient loading to community metabolism responses inferred from continuously measured water quality data. It appears the technique can quantify temporal changes in the community metabolism rates which are known to be strongly impacted by nutrient supply rates, and therefore provide a genuine and measurable dynamic linkage between the effectiveness of nutrient reduction in the watershed coupled to water quality in receiving waters. This chapter presents results from continued high frequency measurements during 1997 and further comparative analyses utilizing the fine-scale temporal measurements to characterize the associations between metabolism rate processes and estuarine eutrophication.

10.2 High Frequency Monitoring during 1997

Submersible self-recording environmental monitoring instruments were deployed from May 20 through October 22, 1997 from the Maryland Route 231 bridge at Benedict, a crossing in the mesohaline portion of Patuxent River where continuous water quality monitoring has been conducted during portions of recent years and throughout the year during most of the 1960's. In addition to continuous water temperature, salinity and dissolved oxygen measurements by sensors, water samples were collected each week throughout the 1997 deployments for a variety of laboratory analyses. One analysis provided dissolved oxygen concentrations for *in-situ* sensor calibration, another provided total and active chlorophyll-*a* concentrations and a third procedure provided plankton respiration rates. Synoptic data from high frequency meteorological instruments, including photosynthetically active radiation (PAR), air temperature, wind velocity and rainfall measured at Solomons, Maryland were also collected. Procedures are detailed in the Methods section of this report.

The major objectives of this effort are:

1. To examine dissolved oxygen data to determine if dissolved oxygen habitat criteria are achieved at current loading regimes,
2. To use 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 metabolism rates from contemporary measurements to those observed at this same site when nutrient loads were considerably lower, as was the case in the mid 1960's.

10.3 Examination of 1997 Data

10.3.1 Database Compilation

All raw data is retained for permanent storage. Copies of raw data were formatted for later retrieval as a "meta-file", which includes synoptic measurements of water quality sensor data, corresponding results of water sample analyses and meteorological data. Continuous sampling for 21 weeks from May through October yielded a total of 14,689 observations for each water quality variable (water temperature, conductivity, salinity, dissolved oxygen percentage saturation and dissolved oxygen concentration) at 15 minute intervals. Included in the synoptic database compiled for analysis were an equal number of observations for PAR (photosynthetically active radiation), air temperature, wind velocity and rainfall. From the 63 water samples collected are 23 *in-situ* Winkler determinations for instrument calibration, 20 total and active chlorophyll-a concentrations and 20 Winkler determinations from dark bottle experiments for independent weekly community respiration estimates, each corresponding to the beginning and end of a sensor deployment.

The resulting continuous data set consists of uninterrupted time series for all data on 150 days out of the total 155 days that sensors were deployed. Brief data gaps occurred on 2 of the days (1 hour and 1¾ hours) when low internal batteries caused temporary instrument power failures. The same problem also occurred over a 2½ day period which resulted in data gaps of several hours. The intermittent data (44 observations) was retained to provide an estimate of the range of measurements over that period. The resulting time series data stream includes 98.6% of total observations possible over the 5 month sampling period.

10.3.2 Data Evaluation

Before the high frequency data could be utilized for analysis, it was necessary to verify the accuracy of the observations. The first step in the time series analysis was to plot the observations against time (Chatfield, 1989). The plots of temperature, salinity and dissolved oxygen would reveal important features of each series, such as trend, seasonality, discontinuities and outliers.

The temperature portion of the sensor is certified to ± 0.25 degrees Celsius by the manufacturer and requires no calibration or maintenance. Time series plots showed the continuous temperature trace with no perturbations even when sensors were exchanged, therefore all temperature data was considered to be acceptable in the raw form.

The conductivity portion of the sensor was calibrated with a conductivity standard each week. The time series plots of salinity measurements, that are computed by the sensor internally, showed no perturbations associated with exchanging instruments, so these data were also considered to be acceptable for analysis in raw form.

Strong agreement between sensors calibrated in air with *in-situ* Winkler determinations is further validated by a strong statistical relationship $r^2 = 0.90$; $P \ll 0.01$; Figure 10-2). The regression further indicated a tendency for sensors to read slightly higher (by a factor of 0.07) than corresponding Winkler determinations. Over the season, 3 of the Winkler determinations departed significantly from

either beginning or ending sensor measurements. These large discrepancies were likely the result of measurement error and were removed from the analysis (Table 10-1).

In contrast to the accuracy found at the beginning of each deployment, comparisons of sensor concentrations and *in-situ* Winkler determinations at the end of each sensor deployment did not initially appear to follow consistent patterns. A total of 12 of the 22 deployments appeared to be acceptable due to close agreement of end point sensor measurements with Winkler determinations. End point sensor measurements of 5 time series ranged from 1.96 to 2.80 below respective Winkler determinations (Table 10-1). The remaining 5 time series could not be similarly assessed due to outlier Winkler determinations or missing data. In order to optimize data for analysis, further action was needed to distinguish acceptable time series data from that which could be either corrected or eliminated.

10.3.3 Data Compensation

Due to varying rates of biofouling observed on sensors and the apparently corresponding effect of fouling on dissolved oxygen measurements by sensors in comparison to Winkler determinations at the end of 10 of the 21 week-long deployments, it became necessary to quantitatively assess DO probe performance using the various independent *in-situ* calibration measurements available.

Winkler dissolved oxygen determinations, sensor measurements and respective values assigned to indicate biofouling observed on dissolved oxygen membranes at the end of respective deployments are listed in Table 10-1. In all 4 cases where sensor data was greater than 1 mg l⁻¹ lower than Winkler data at the end of the deployment, fouling was moderate to heavy, as expected. However, there were 3 cases where sensors with moderate to heavy fouling were in close agreement (± 0.37 mg l⁻¹) with Winkler concentrations. The remaining 7 cases for which low fouling values were recorded were within acceptable range of Winkler determinations (≤ 0.86 mg l⁻¹). Speculation is that the inconsistent relationship between observed fouling, sensor readings and Winkler determinations may be due to different effects on sensor performance by different species of fouling organisms.

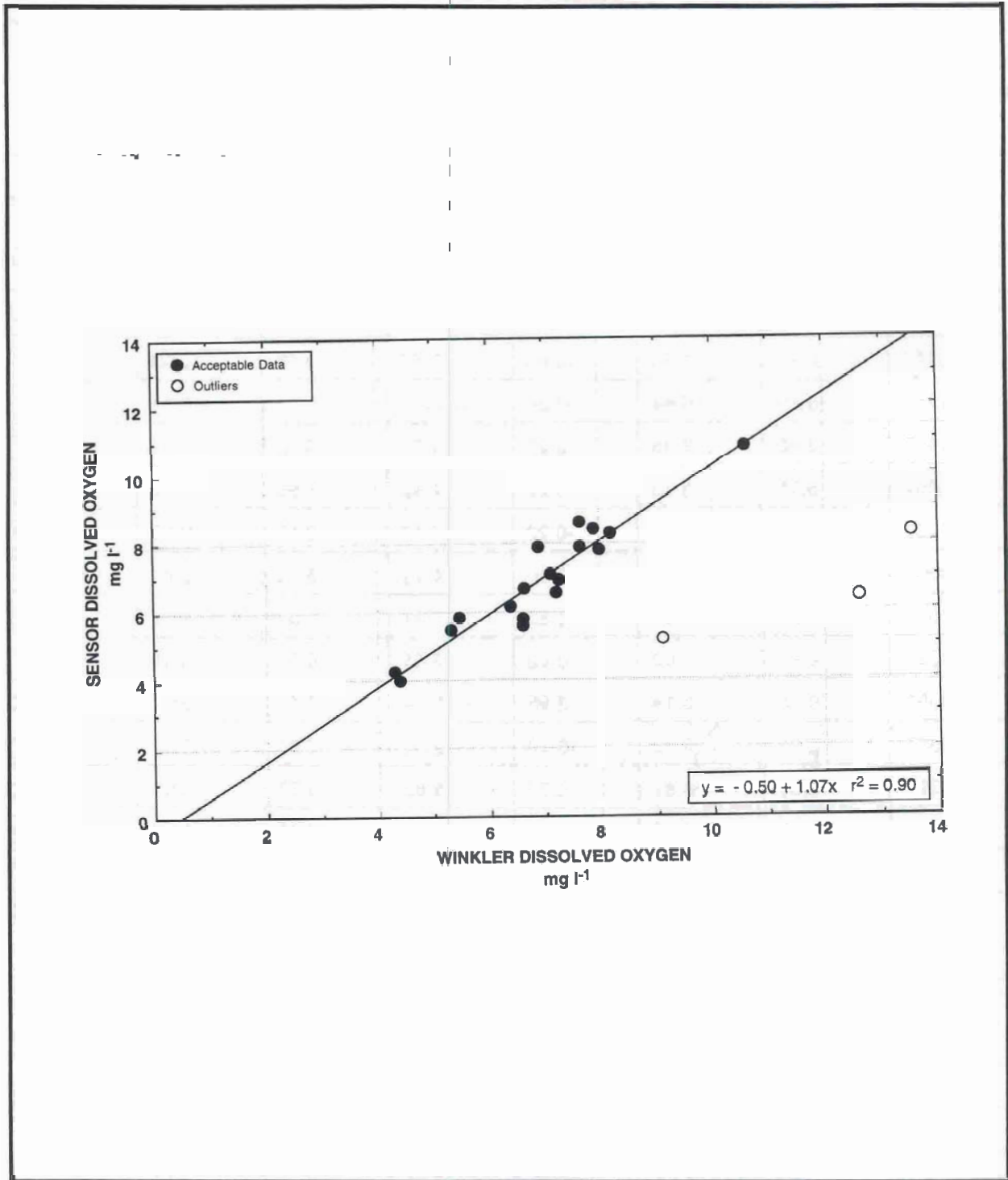


Figure 10-2. A scatter plot of dissolved oxygen concentrations measured at the beginning of a deployment using Winkler titrations (x-axis) and dissolved oxygen sensors (y-axis; Hydrolab DataSonde 3 and YSI model 6920). Measurements were made at the MD Route 231 Bridge at Benedict MD between May 20 and October 22, 1997. Several observations (shown as open circles) were obviously outliers; they are indicated in the diagram but not included in the regression equation.

Table 10-1. The corresponding dissolved oxygen concentrations from *in-situ* Winkler determinations and dissolved oxygen probe measurements at the beginning and end of each sensor deployment from the MD Route 231 bridge over the Patuxent River near Benedict.
 Week long deployments from May 20 through October 22, 1997.

Date (mmddyy)	DO (mg l ⁻¹) Winkler	DO (mg l ⁻¹) Sensor Beginning	dDO (mg l ⁻¹) Wink-Sensor Beginning	Do (mg l ⁻¹) Sensor End	dDO (mg l ⁻¹) Wink-Sensor End	dDO (mg l ⁻¹) Sensor Beginning-End	Fouling Index (1=Low) (10=High)
52097	8.20	8.29	-0.09				
52897	8.00	7.79	-0.09	7.24	0.76	0.55	2
60497	6.62	6.68	-0.06	5.76	0.86	0.92	2
61197	10.60	10.84	-0.24	malfun		10.84	3
61997	12.60	6.38	6.22	4.30	8.30	2.08	4
62697	6.38	6.16	0.22	4.42	1.96	1.74	5
70297	7.65	7.87	-0.22	7.48	0.17	0.39	na
70997	7.20	6.54	0.66	4.10	3.10	2.44	na
71697	7.25	6.92	0.33	5.91	1.34	1.01	na
72397	4.40	4.00	0.40	3.55	0.85	0.45	2
73097	9.10	5.14	3.96	26.24	-17.14	-21.1	na
80697	5.30	5.49	-0.19	2.50	2.80	2.99	6
81397	6.60	5.81	0.79	5.82	0.78	-0.01	2
82097	4.30	4.27	0.03	4.02	0.28	0.25	6
82797	5.45	5.85	-0.40	5.01	0.44	0.84	4
90397	6.60	5.59	1.01	3.96	2.64	1.63	6
91097	6.20	malfun	na	5.53	0.67	-5.53	4
91697	6.90	7.89	-0.99	6.53	0.37	1.36	5
92497	7.10	7.07	0.03	6.78	0.32	0.29	6
100297	7.65	8.61	-0.96	5.66	1.99	2.95	5
100997	13.55	8.30	5.25	7.93	5.62	0.37	3
102097	7.90	8.41	-0.51	8.24	-0.34	0.17	6
102297	7.85	Finished		8.40	-0.55	-8.40	1

The question of whether to accept, reject or compensate for a portion of the 9 deployments which ended with sensor dissolved oxygen data more than 1.00 mg l^{-1} lower than Winkler dissolved oxygen was resolved using linear correction to compensate data based on the following considerations. Conventional use of monitoring sensors for attended overboard measurements (spot sampling) relies, at a minimum, on proper adherence to laboratory procedures specified by the manufacturer for calibration of the dissolved oxygen sensor in air. For long-term unattended deployments, air calibration is recommended prior to and following each deployment. Of the 2 monitors used, one (YSI Model 6920) provides software to compensate the data for any sensor drift which may occur, by a linear correction of data between accepted values from pre-deployment and post-deployment air calibration or from independent measurements. The other type of sensor used (Hydrolab DataSonde 3) does not provide software for drift compensation, so to maintain consistency, all data was retained in raw form.

A routine was developed to compensate data for sensor drift as needed using a linear interpolation correction for each dissolved oxygen value between accepted sensor end and beginning values (as done by YSI software) based on the following criterion:

1. All sensor data from deployments with both **beginning and end** point measurements within $\pm 1 \text{ mg l}^{-1}$ of respective Winkler concentrations are retained unchanged. This condition accounted for 13 of the 22 deployments.
2. If end point sensor measurements exceeded the Winkler concentration by more than 1 mg l^{-1} , the *difference* between that and the corresponding beginning point concentration of the replacement sensor was computed, then added to the end point concentration. All preceding measurements were similarly compensated by addition of a linearly decreasing value from end to beginning of that deployment, where correction was zero for the first dissolved oxygen measurement. Then, compensated percent saturation dissolved oxygen was computed from each temperature observation and compensated dissolved oxygen concentration. This procedure was used for 7 deployments.
3. Deployments with **beginning** point sensor measurements that exceeded the acceptable $\pm 1 \text{ mg l}^{-1}$ range of respective end point sensor data *and* Winkler dissolved oxygen concentrations were also similarly compensated. For 2 deployments in which that condition occurred, the beginning point was compensated to equal the respective end point concentration, followed by a decreasing linear interpolation correction to the subsequent end point.

Unaltered and compensated water quality sensor was then integrated with simultaneous meteorological data and archived in a (nearly) continuous time series format suitable for analysis.

10.4 Qualitative Description of 1997 High Frequency Data

The time series plots of high frequency measurements at Benedict during 1997 (Figure 10-3) generally demonstrate what are commonly accepted as normal seasonal patterns that are depicted by conventional lower frequency measurements throughout Chesapeake Bay tributaries. A seasonal pattern in salinity was predictable based on the average annual Patuxent River flow and typical distribution of monthly river flow observed in 1997 (Figure 5-1.).

Data were first examined in the context of both long term and short term signals to provide evidence of water quality suitability for living resource habitat conditions defined by specific water quality standards. Further quantitative analyses of high frequency measurements focus in particular on short-term changes in dissolved oxygen during each day that, by inference, provide an estimated measure of daily open water metabolism. The following is a general overview of water temperature, salinity measurements and more specific assessment of dissolved oxygen observations.

10.4.1 Temperature

Water temperature during the May 20 through October 22 period of record followed a typical seasonal pattern, from a low of 16 °C at the beginning and end of the study to a maximum of 32 °C in mid-July. Shorter term temperature variations of approximately 5 °C reoccur on a fortnightly frequency that appear to correspond to lunar spring tides. Diurnal and semidiurnal temperature variations ranging from 1 to 3 °C suggest that a combination of tidal advection, vertical mixing and longitudinal temperature gradients may at times be fairly significant.

As would be expected by the proximity of sensors to the air-water interface, water temperature patterns followed closely with air temperature and solar radiation (photosynthetically active radiation: PAR). The response of water temperature to meteorological forcing of sunlight, air temperature and wind clearly demonstrate expected fundamental patterns both over long-term, as well as short-term.

10.4.2 Salinity

Salinity showed a typical season pattern, increasing steadily over the 5-month period from a minimum of 4.4 ppt on 31 May to a maximum of 14.6 ppt on 17 October. The average of all salinity observations is 9.8 ppt. As seen in the water temperature record, there appears to be an approximately fortnightly effect expressed by an average salinity decline following peak spring tides, as well as a semidiurnal variation ranging from 1 to 3 parts per thousand. Further resolution of these salinity gradient patterns are of interest in assessing the influence of advection and vertical mixing processes on observations at the sample location, but are beyond the scope of this study.

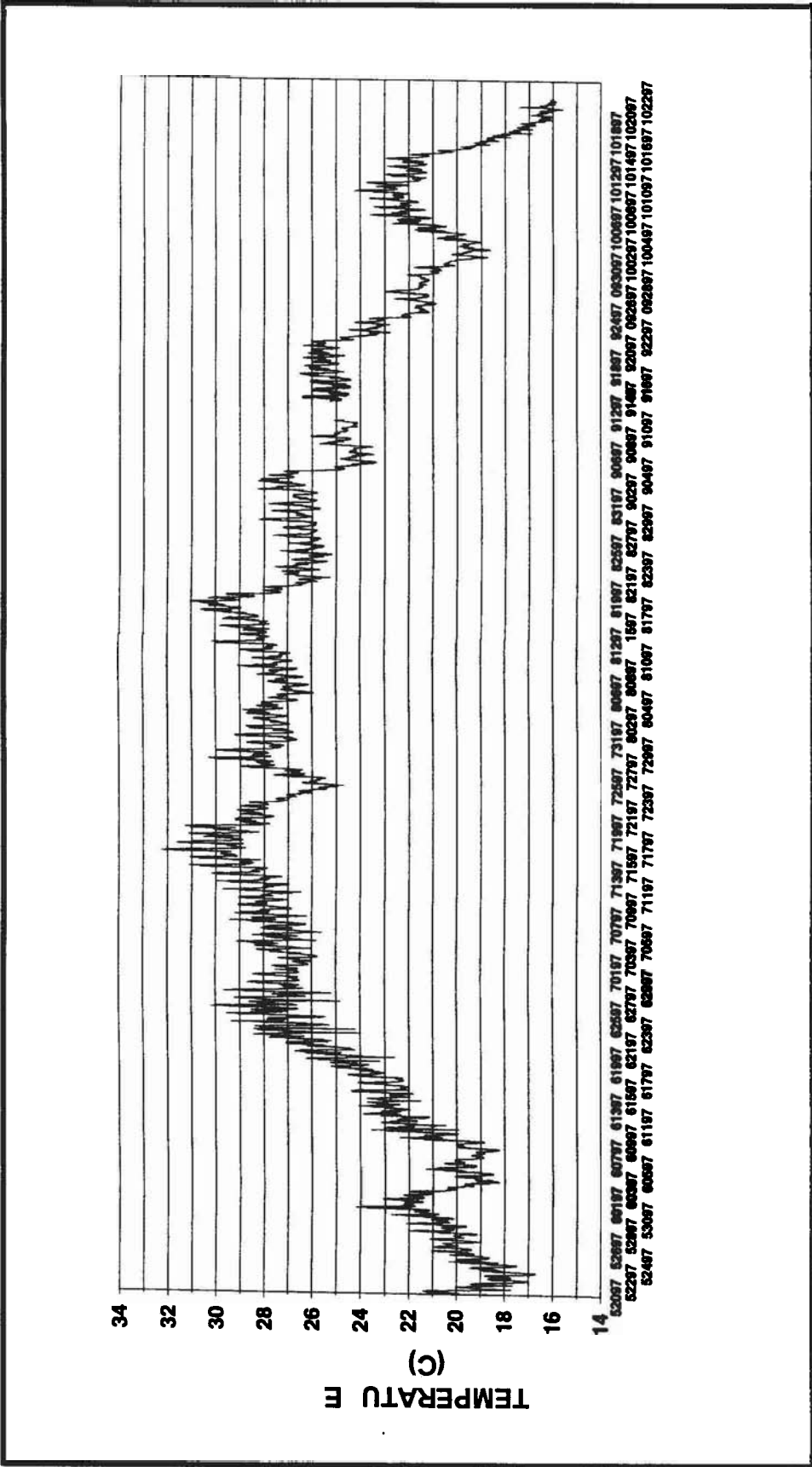


Figure 10-3.a. A time series plot of water temperature measured from the MD Route 231 bridge over the Patuxent River near Benedict. Measurements were recorded every 15 minutes between May 20 through October 22, 1997. Date (mmdyy) is on the x-axis.

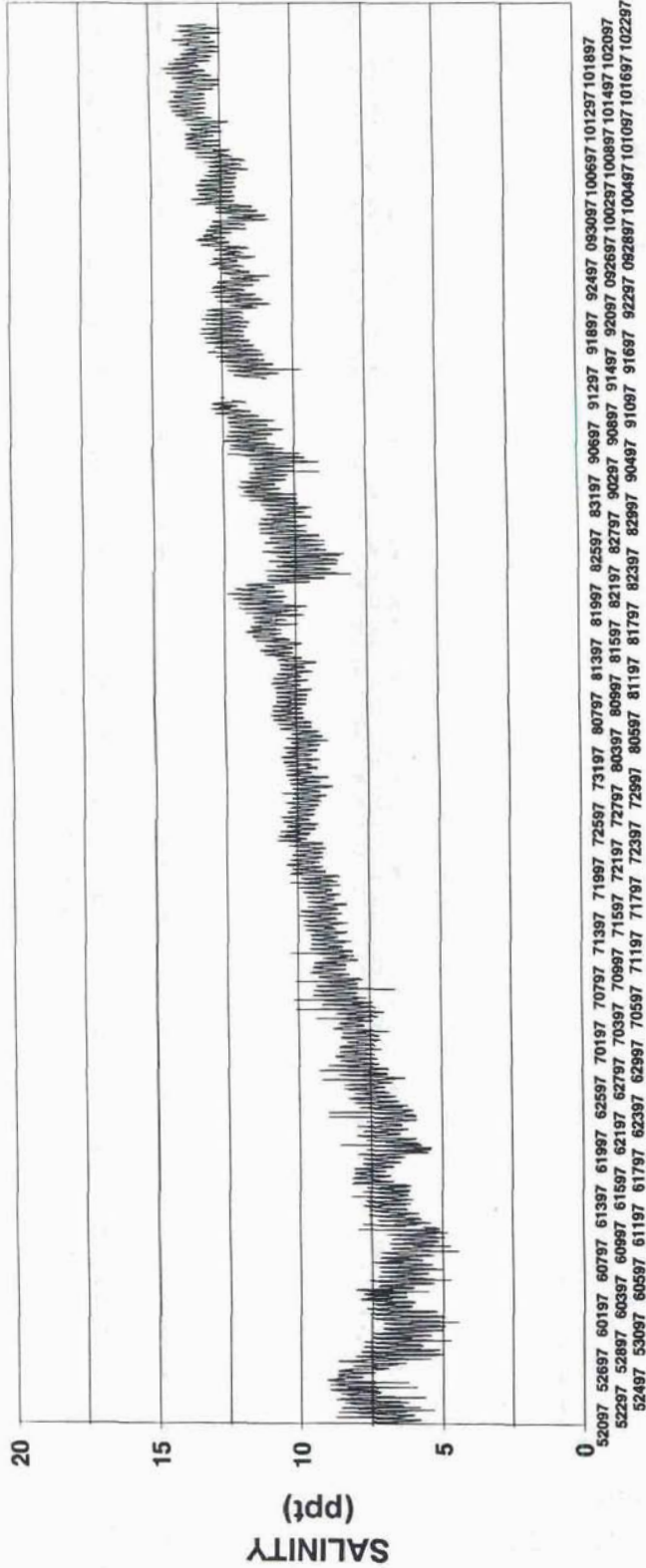


Figure 10-3.b. A time series plot of salinity measured from the MD Route 231 bridge over the Patuxent River near Benedict. Measurements were recorded every 15 minutes between May 20 through October 22, 1997. Date (mmddyy) is on the x-axis.

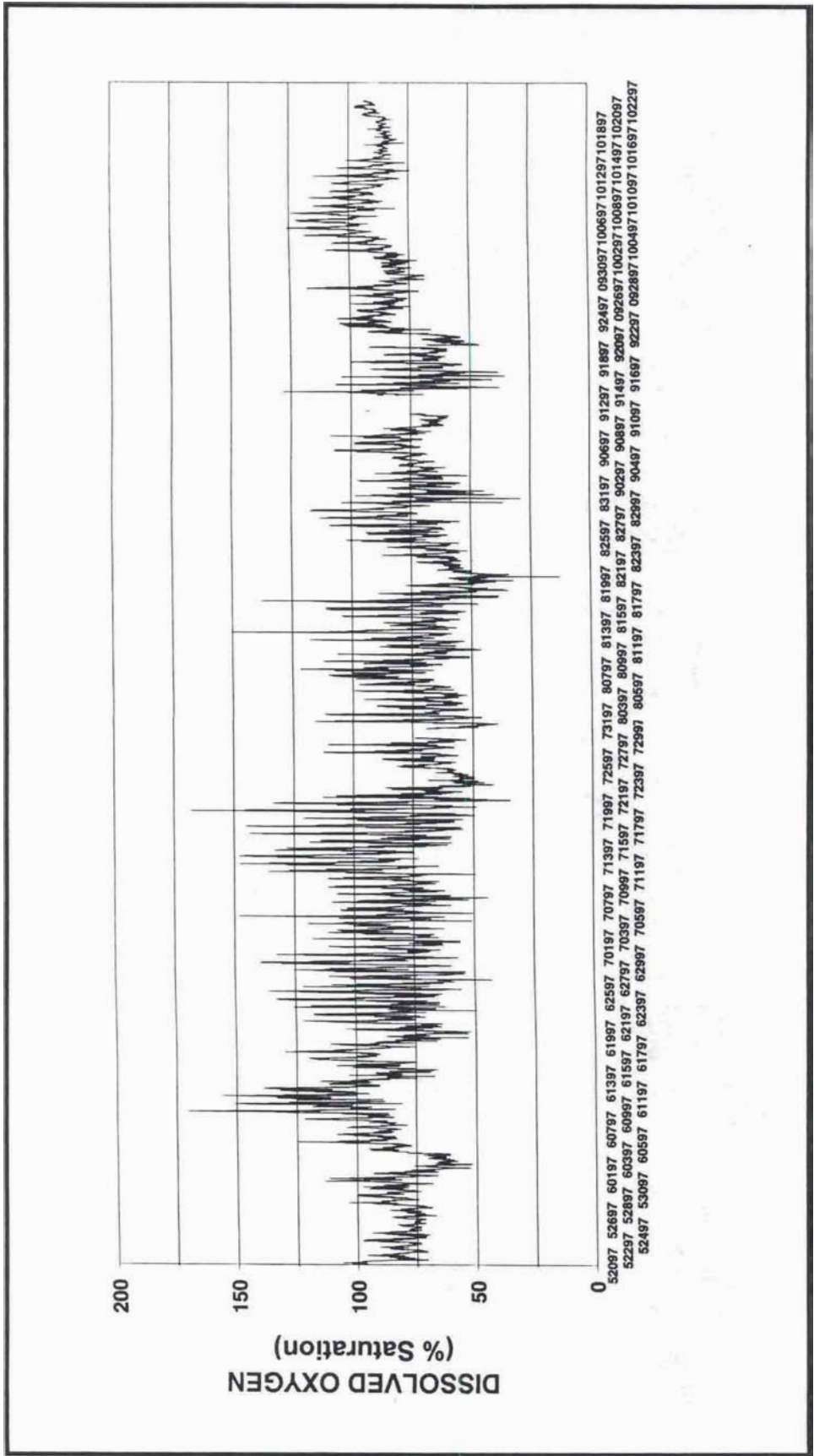


Figure 10-3.c. A time series plot of dissolved oxygen percent saturation measured from the MD Route 231 bridge over the Patuxent River near Benedict. Measurements were recorded every 15 minutes between May 20 through October 22, 1997. Date (mmddyy) is on the x-axis.

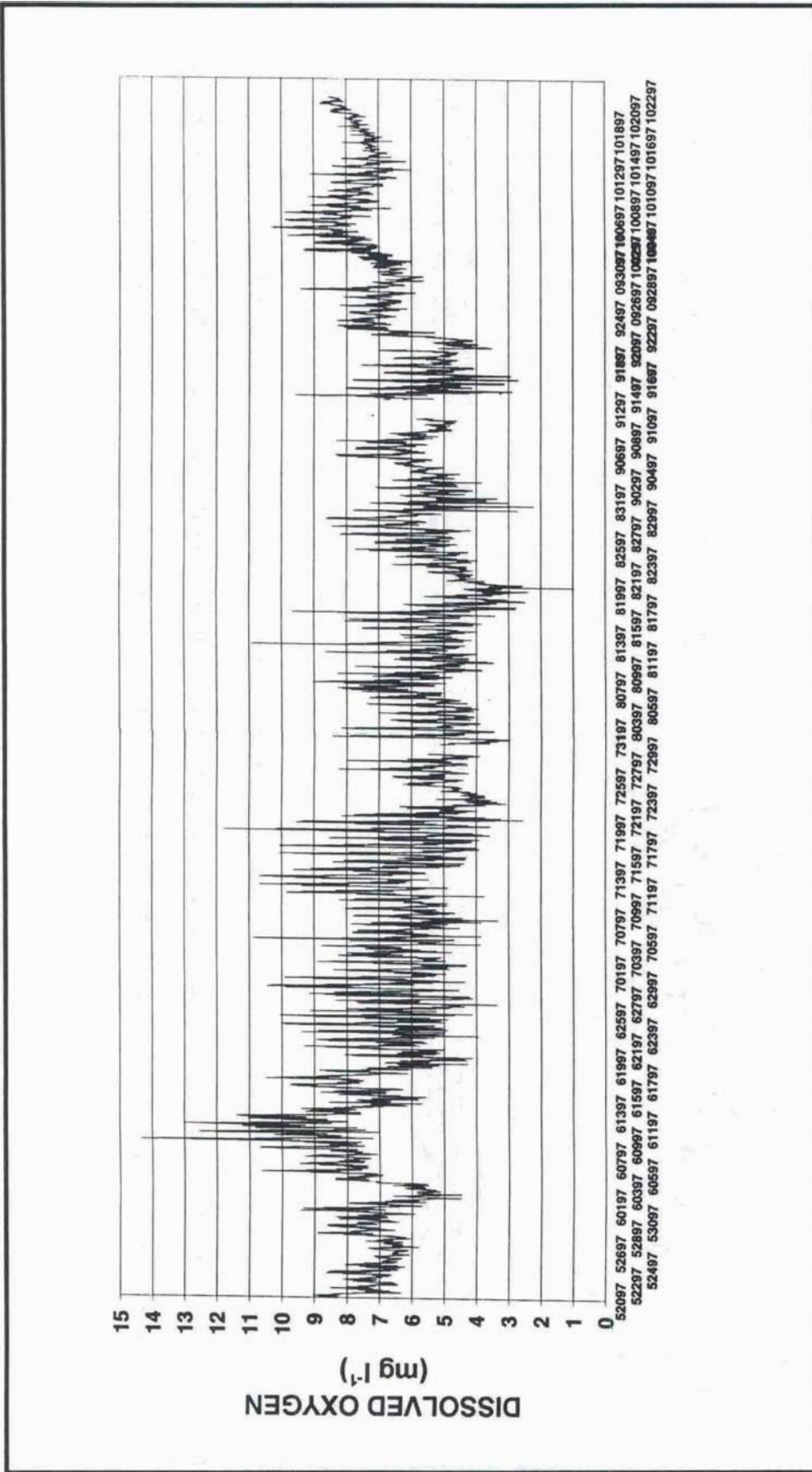


Figure 10-3.d. A time series plot of dissolved oxygen concentration measured from the MD Route 231 bridge over the Patuxent River near Benedict. Measurements were recorded every 15 minutes between May 20 through October 22, 1997. Date (mmddy) is on the x-axis.

10.4.3 Dissolved Oxygen

The range of dissolved oxygen concentrations and percentage saturation observed was large on a seasonal, as well as a daily basis from the lowest value (0.95 mg l⁻¹; 12.8 percentage saturation) recorded was on 20 August to the highest (14.36 mg l⁻¹; 170.5 percentage saturation) on 9 June. The average of all dissolved oxygen observations from May through October was 6.21 mg l⁻¹ (81.3 percentage saturation). Diurnal fluctuations ranged from 1 to 7 mg l⁻¹.

On two occasions, there were excursions which peaked at 20 and 27 mg l⁻¹. These temporary excursions were well beyond any previous measurements in Patuxent River and could not be validated. The dissolved oxygen concentration and percent dissolved oxygen saturation measurements judged to be excursions were retained in the raw data set, but were excluded from statistical and metabolism computations.

10.4.4 Compliance with Dissolved Oxygen Habitat Criteria

Recognizing the need to manage the Chesapeake Bay as an integrated ecosystem, living resource and water quality goals were sought as a commitment to the 1987 Chesapeake Bay Agreement. Dissolved oxygen conditions deemed to provide viable habitat conditions for reproduction, growth and survival of fish, mollusc, crustacean, benthic and planktonic species indigenous to Chesapeake Bay were conjured from known tolerance levels of various species. Because of the natural fluctuations of dissolved oxygen in the water column and the varied ability of different species to tolerate low dissolved oxygen conditions (hypoxia), habitat requirements could not be expressed as a single critical concentration (Jordan *et al.*, 1992). Rather, criteria were established to provide a systematic way to assess the degree to which dissolved oxygen conditions in Chesapeake Bay are sufficient to support growth and survival of important living resources. The conditions cited reflect recognition that detrimental levels of oxygen stress can be compounded by prolonged or repeated exposure to sub-lethal concentrations and ultimately, acute mortality following exposure to lethal concentrations (Table 10-2). Based on tolerances of certain species, the criteria demarcate acceptable dissolved oxygen means over specified time intervals between hypoxic excursions to address exposure of organisms to the inherent fluctuations above and below threshold dissolved oxygen levels.

The 1997 high frequency data collected from the bridge at Benedict were evaluated to assess compliance with living resource habitat criteria for dissolved oxygen as defined in Table 10-2. Patuxent River tidal reaches (and all tidal reaches of tributaries in Chesapeake Bay) are designated anadromous fish spawning river and nursery areas (Funderburk *et al.*, 1991), and the sample depth (1 meter) at Benedict is indicative of conditions for *above pycnocline* waters at the sample location. As such, water quality conditions in that tributary region and water column portion are evaluated following the more stringent criteria for dissolved oxygen.

Table 10 - 2. 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 anadromous 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* (Funderburk *et al.*, 1991).
- e. In addition, where dissolved oxygen conditions presently exceed the requirements, these conditions should be maintained.

Dissolved oxygen averaged over the entire 3,672 hour period from May 20 through October 22, 1997 was 6.21 mg l⁻¹. Although mean monthly dissolved oxygen concentrations were all greater than the 5 mg l⁻¹ minimum (Table 10-2), excursions below 5 mg l⁻¹ frequently occurred between 2 June and 21 September. Dissolved oxygen concentrations in the above pycnocline waters were below or equal to 5 mg l⁻¹ for a total of 19% (689 hours) of the 5 month period of record (Figure 10-3d). Excursions below 3 mg l⁻¹ totaled 11 hours, but were distributed over nine days and were relatively short-lived. The most persistent hypoxia was during a 3-day period, 18 - 20 August, when excursions remained below 3 mg l⁻¹ on 5 separate occasions, ranging from 15 minutes to 2¾ hours. Although several reoccurrences of excursions slightly below 3 mg l⁻¹ within 48 hour periods were observed over the 5-month period of record, none persisted longer than 2¾ hours. There was only a single observation below 1 mg l⁻¹ on 20 August at 00:15.

The most distinct finding from assessment of the 1997 high frequency data, in the context of each provision of the overall dissolved oxygen goal (Table 10-2.), is that this representative portion of the Patuxent River exhibited conditions that were frequently *not sufficient* for anadromous fish spawning reaches and nursery areas. That condition occurred when dissolved oxygen was below 5 mg l⁻¹ for 30% of summertime observations, which also accounted for 19% of all observations including spring and fall portions. The single observation below 1 mg l⁻¹ does not constitute a persistent violation of the provision for habitat requirements. These findings represent 2 provisions that could be literally interpreted by the standards of the criteria as not providing sufficient dissolved oxygen for restoration of living resource habitats. Although the dissolved oxygen excursions below 3 mg l⁻¹ were brief, infrequent and punctuated by daily dissolved oxygen fluctuations reaching saturation concentrations, the overall low monthly means in July (5.88 mg l⁻¹; 78% saturation), August (5.28 mg l⁻¹; 70% saturation) and in particular, the month-long period between 21 July to 21 August (5.05 mg l⁻¹ mean; (67% saturation) do not adequately convey the persistently marginal conditions that many species are able to tolerate only over short term (Funderburk *et al.*, 1991). Accumulative stress on tolerances of organisms is likely during the large proportion of July and August, when excursions below 5 mg l⁻¹ lasted from 12 to 15 hours on a majority of days.

Any sense that these data represent adequate habitat conditions should be tempered with the awareness that an overly optimistic bias may be projected by time-averaged dissolved oxygen values, since concentrations at the 1 meter depth from which all data was measured represent the highest dissolved oxygen value in the water column for that time. The fact that the low dissolved oxygen conditions in this study persisted *near the water surface* for nearly half of most days during the summer attest to what could only be lower dissolved concentrations with increasing depth to the pycnocline (typically 3 - 4 meters at the Benedict location). The density gradient at the pycnocline effectively restricts vertical oxygen diffusion and thereby further limits reaeration of subpycnocline waters. Thus, even though utilization of the long term high frequency data provides important insight on fine scale temporal dynamics of dissolved oxygen at the water surface, proper assessment of the dissolved oxygen goal should further optimize available spatial data. Additional work is underway to formulate an acceptable method to integrate corresponding water column profile data with time series data.

10.5 Open Water Metabolism Measurements in the Patuxent River

Each day as the sun rises and retires the beautiful green bays like great creatures breathe in and out. By day photosynthetic production of food and oxygen by plants is plentiful, but day and night there is also a furious feasting. The animals, the consumer parts of plants, and the bacteria remove the food and oxygen previously created from the sunlight. On some days the production exceeds the respiratory consumption, and organic food matter accumulates, but at other times respiration dominates so that the waters and their bottom ooze lose their store of energy. Just as the life in single organisms is driven by the metabolism of the body cells, so many marine phenomena of theoretical or practical interest to man can be related to the composite metabolism of the environment (excerpt from Odum and Hoskins, 1958).

10.5.1 Background and Definitions

Measurements of both 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.

The high frequency time series of dissolved oxygen from the bridge over the Patuxent River at Benedict (Maryland Route 231) were used to generate daily estimates of surface water (top 1 m) metabolism for the period of record from late spring through early fall 1997. The open water technique used relies on the daily excursions in dissolved oxygen caused by the diel cycle of incident irradiance (sunlight). While certain 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.

Surface water dissolved oxygen typically increases over the course of a sunny day as oxygen is produced by phytoplankton photosynthesis. The combination of phytoplankton respiration, oxygen-consuming processes by all marine organisms and other chemical reduction and oxidation processes throughout the water column lead to an overall dissolved oxygen decline during low sunlight conditions and at night. 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. The pattern is affected by oxygen exchange (diffusion) across the air-sea interface from air-to-sea when water is lower than 100% dissolved oxygen saturation (under-saturated), or in the opposite direction, from sea-to-air, when water is over-saturated. 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 used for community metabolism estimates are defined as follows:

Rn Night Respiration ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$): oxygen consumption between sunset and sunrise.

Rn/hr Night Respiration Rate ($\text{g O}_2 \text{ m}^{-3} \text{ hr}^{-1}$): mean hourly oxygen consumption rate between sunset and sunrise.

SRm Metabolic Sunrise: time of dissolved oxygen minimum during daylight hours.

SRm Metabolic Sunset: time of dissolved oxygen maximum during daylight hours.

Pa Net oxygen production ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$) between sunrise and sunset.

Pa* Net oxygen production during period of net autotrophy ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$), which occurs between times of dissolved oxygen minimum (SRm) and maximum (SSm).

Pg Gross oxygen production ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$) between sunrise and sunset, assuming daytime respiration rate is equal to nighttime respiration rate (Rn hr^{-1}) during subsequent night.

Pg* Gross oxygen production during period of net autotrophy ($\text{g O}_2 \text{ m}^{-3} \text{ day}^{-1}$), assuming daytime respiration rate is equal to nighttime respiration rate (Rn hr^{-1}) during subsequent night.

10.5.2 Estimation Algorithms

All of the metabolic parameters can be calculated routinely using SAS once several operations are performed on the entire time series. Operations are as follows:

- (1) Times of sunset and sunrise were obtained from the US Naval Observatory (<http://riemann.usno.navy.mil/AA/>) for each day. Supplemental dissolved oxygen concentration (DO) and percent oxygen saturation (POSAT) were computed by interpolation for times when sunrise or sunset did not correspond to measured observations. Using times of sunrise and sunset, DAYPART labels were assigned to distinguish each observation measured during either daylight or nighttime.
- (2) Change in DO (ΔDO), mean POSAT and time interval in hours (Δt) were computed between each observation and preceding observation.
- (3) Air-sea oxygen exchange (ASEXCH) during each interval was computed, assuming a constant exchange coefficient of $0.5 \text{ g O}_2 \text{ m}^{-2} \text{ hr}^{-1}$ at 100% saturation deficit (Kemp and Boynton, 1980). This equation is:

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

Resulting units are $\text{g O}_2 \text{ m}^{-2}$.

- (4) Corrected net oxygen production (CNOP) was computed by subtracting ASEXCH from Δ DO. ASEXCH is multiplied by 1 m to obtain identical units, since this metabolism calculation represents processes across the dimensions of the 1 meter near-surface water.
- (5) Minimum and maximum DO observations for each day were identified. A METPART label was then assigned to each daytime observation *preceding the minimum* as "Pre-dawn"; or daytime observations *following the maximum* as "Pre-dusk". Remaining daytime observations were assigned METPART labels "Day"; and all night-time observations labeled "Night".
- (6) A date variable (METDAY) was assigned to designate observations during each "metabolic day", defined as one daytime period and the entire following night (sunrise to the following sunrise) rather than the usual 24 period. (Note that this "metabolic day" may encompass slightly more or less than 24 hours.)

Once the above operations were completed, daily metabolic parameter values were computed by summation of all values in each METPART group for that METDAY. The parameters $R_n \text{ hr}^{-1}$, P_g and P_g^* were calculated using the formulas in Table 10-3. Once all of these parameters were calculated, any daily observations for which insufficient data was available were eliminated.

10.5.3 Preliminary Results and Discussion of Metabolism Calculations

10.5.3.1 Validity of Observations

Summary statistics for the principle metabolic parameters and the duration of the components of the metabolic day are shown in Table 10-4. Estimates were obtained for 147 days out of the 155 day study period, 8 days were eliminated due to missing or incomplete data. Values fell within expected ranges, with a few exceptions. The exceptions included four negative values for P_a^* and for P_g , which all (except one negative P_g value) depicted conditions on days at the end of several three to four day northeasters that were characterized by prolonged low sunlight and sustained strong northeast winds. The lowest production values during the 147 day period of record all occurred during days with the lowest sunlight. It is probable that the four negative P_a^* values resulted from measurements within a heterogeneous water characterized by a longitudinal dissolved oxygen gradient on those days that by model assumptions, were interpreted as a negative rate of change of production.

The three negative P_g values could also have resulted from factors not accounted for by model assumptions. One possibility is that extrapolation of night respiration rate ($R_n \text{ hr}^{-1}$) throughout the hours of the previous day resulted in computed respiration rates which exceeded actual community respiration that occurred on those days. Dissolved oxygen conditions that remain under-saturated through the day indicate dominance of heterotrophic energy support (Odum, 1958). Community respiration which greatly exceeds photosynthesis may indicate support of the community from imported organic matter from river inflow or tidal advection.

Table 10-3. The formulas for calculating Rn /hr, Pg and Pa* and resulting units.

Parameter	Method of Calculation	Units
Rn/hr	Rn/Night	gO ₂ m ⁻³ hr ⁻¹
Pg	Pa + (Rn/Night)*(Pre-Dawn + Day + Pre-Dusk)	gO ₂ m ⁻³ day ⁻¹

Table 10-4. Summary statistics for the computed daily metabolic parameters for Patuxent River near bridge at Benedict between May 20 through October 22, 1997.

The units of Pa, Pa*, Pg, Pg* and Rn are g O₂ m⁻³ day⁻¹. The units of Rn/hr are g O₂ m⁻³ hour⁻¹. The units of Pre-Dawn, Day, Pre-Dusk and Night are hours.

Parameter	Pa	Pa*	Pg	Pg*	Rn	Rn/hr	Pre-Dawn	Day	Pre-Dusk	Night
Mean	0.13	2.36	3.36	5.59	2.35	0.23	3.0	8.1	2.6	10.4
Median	0.01	2.22	3.06	5.18	2.20	0.22	2.5	8.5	2.2	9.9
Minimum	-3.58	-1.78	-2.47	0.54	4.51	0.45	0.0	0.4	0.0	9.1
Maximum	4.46	7.45	8.38	12.25	0.10	0.01	10.1	14.3	11.7	13.1

10.5.3.2. 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. For approximately 10% of the 150 days, this period was less than 1 hour. For a majority of days, an interval of 1 to 4 hours was observed between sunrise and the onset of positive net production. The monthly averages of pre-dawn periods showed an inverse relationship with daylight period. The pattern is likely to result from a variety of other factors which affect water clarity and light attenuation.

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 existence of pre-dawn and pre-dusk periods on the majority of days indicates that net production calculated over the sun-rise to sun-set period (P_a) under-represents the autotrophic activity during the day. A better representation of community photosynthetic production may therefore be the metabolic parameter P_a^* , which records the maximum amount of positive production during the day. All subsequent references to net production will refer to P_a^* .

10.5.3.3. Respiration

Nighttime respiration averaged $2.35 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$ over the period of record, ranging from a maximum of $4.51 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$ on August 26 to a minimum of $0.10 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$ on September 22. More than 95% of observations were larger than $1 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$, while the median respiration was $2.20 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$. The broad pattern in the respiration estimates is an increase from early June through late August, followed by a decrease through fall (Figure 10-4.a). This is very close to the Q_{10} reported for middle Chesapeake Bay surface waters ($2.36 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$) by Smith and Kemp (1995). The respiration estimates, however, are much greater than those reported by Smith and Kemp (1995).

There are a number of possible explanations for the larger respiration estimates from the measurements at Benedict relative to those from middle Chesapeake Bay. The most obvious is that the area of Patuxent River near Benedict 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 factors contributes to some extent.

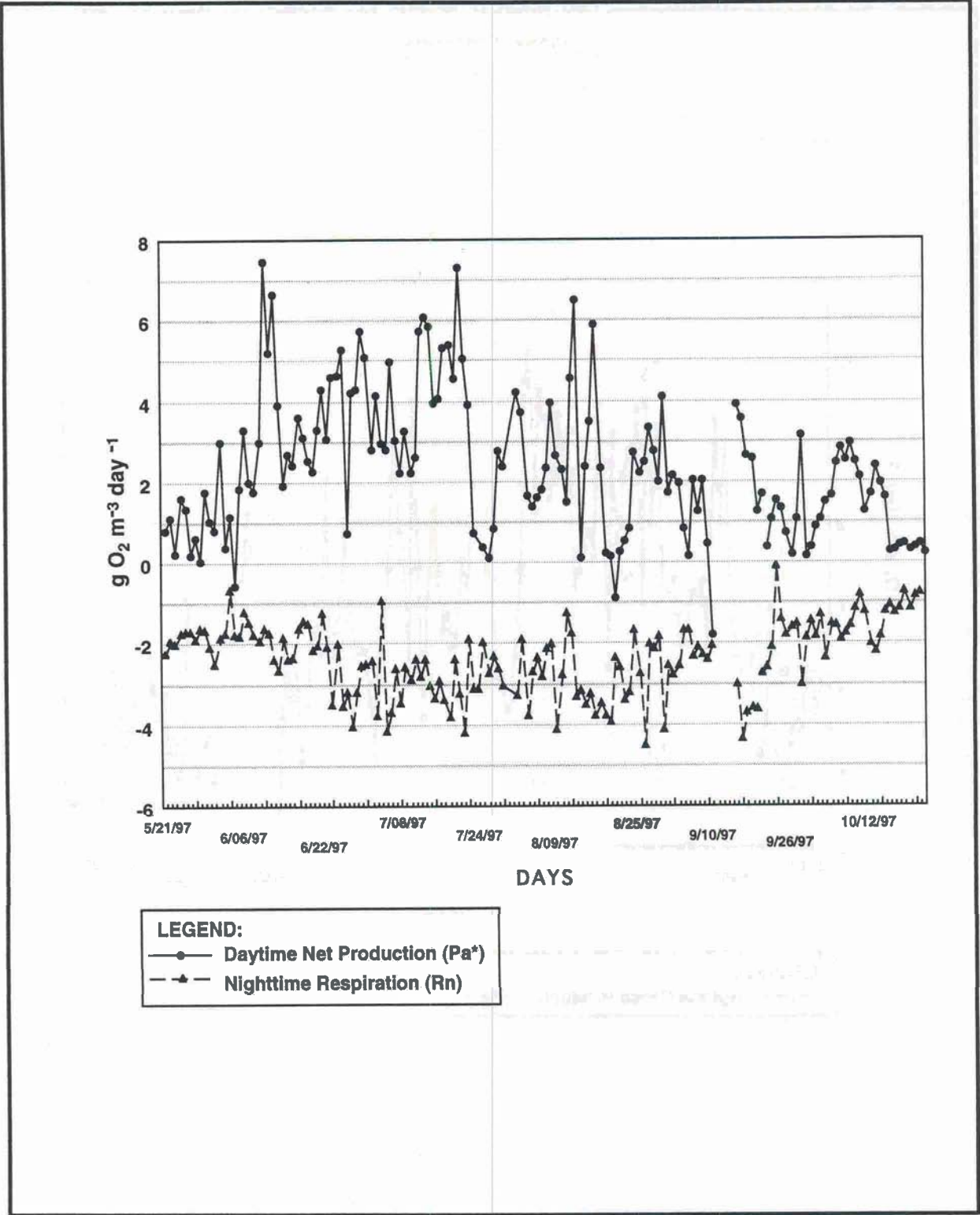


Figure 10-4.a. The time series plot of daytime net production (Pa*) and respiration at night (Rn) in the Patuxent River near Benedict. Date (mmddyy) is on the x-axis.

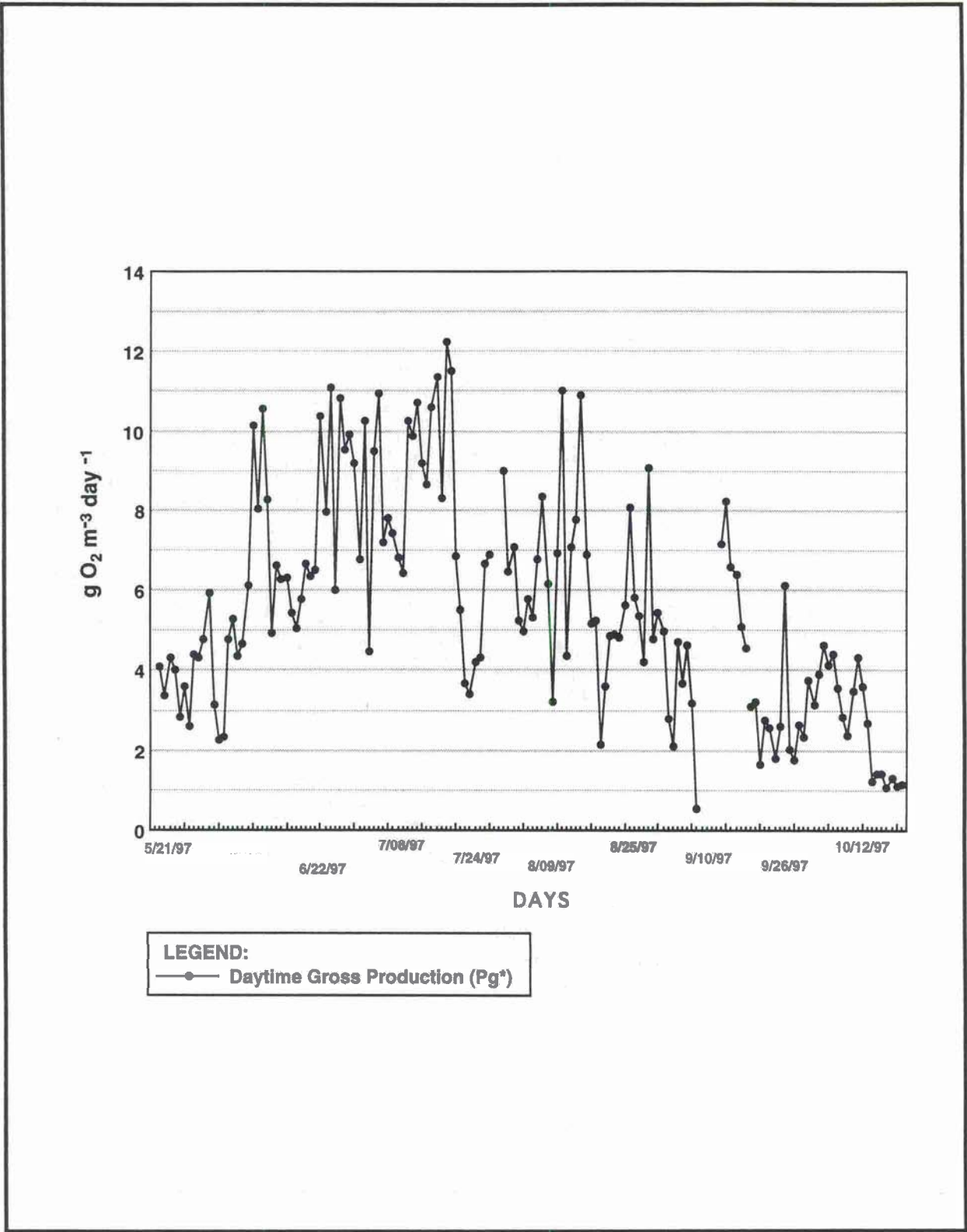


Figure 10-4.b. The time series plot of daytime gross production (Pg*) in the Patuxent River near Benedict.
 Date (mmddyy) is on the x-axis.

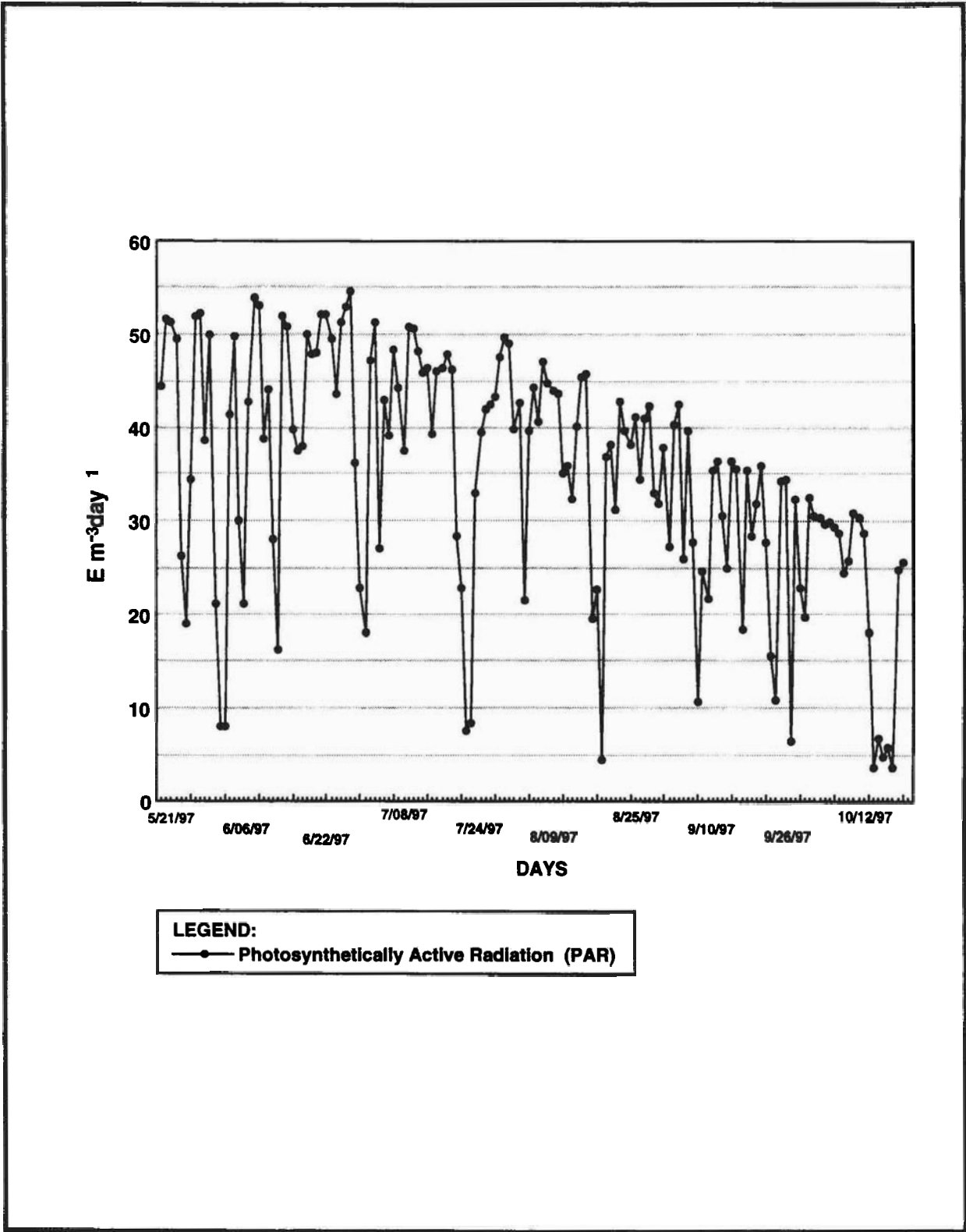


Figure 10-4.c. The time series of integrated daily PAR (photosynthetically active radiation) measured near the mouth of the Patuxent River at Solomons, Maryland. Date (mmddyy) is on the x-axis.

10.5.3.4. Net Daytime Production (P_n^*)

The period of net autotrophic production ("Day" in Table 10-4.) ranged in duration from 30 minutes to nearly the entire daytime period. P_n^* varied between 0.06 on May 27 and 7.45 g O₂ m⁻³ day⁻¹ on June 9 and averaged 2.36 g O₂ m⁻³ day⁻¹ over the period of record (Table 10-4.). Net daytime production was highly variable from day to day (Figure 10-5a) and was highest during July and August. Like respiration, daytime net production appears to be positively related to water temperature (Figure 10-4.f), each increasing from May to an overall peak in mid-August, followed by a decline to October. Further analysis will be conducted to test correlations of daily net production with 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.

10.5.3.5. Gross Production (P_g^*)

Gross production (P_g^*) averaged 5.59 g O₂ m⁻³ day⁻¹; values ranged from a minimum of 0.54 g O₂ m⁻³ day⁻¹ on September 9 to a maximum of 12.25 g O₂ m⁻³ day⁻¹ on July 19 (Table 10-4.). Further analysis will be conducted to test correlations of daily net production with 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.

10.6. Preliminary Characterization and Comparative Metabolism Calculations

Metabolic rates were calculated for estuarine community metabolism parameters using the methodology described by Odum (1958), which was adapted for conventional high frequency measurements. Data for a total of 8 years have been used to generate daily community production and respiration rates at a single location on the Patuxent River near Benedict. The historical range of available data is especially significant for comparative analysis of both water quality and living resource impacts, since the record includes years prior to water quality deterioration (early 1960's), followed by a period during which nutrient enrichment to the Patuxent River continued to increase and water quality declined significantly (1970 - 1980). Phosphorus loads started to sharply decrease by 1980 (possibly a few years earlier) (Figure 11-8) at the Patuxent River fall line and reached a minimum by 1990. The pattern in nitrogen loadings (Figure 11-5) is similar, with a rapid increase beginning in the late 1960's but not beginning a decline until later, in the late 1980's. Both nitrogen and phosphorus loading rates appear, by 1997, to be approaching the relatively lower levels that existed in the 1960's.

Preliminary comparisons of the range of community production and respiration calculated for years of available data suggest an analogous pattern in community metabolism (Table 10-5). The lowest production rates are during 1964, when nutrient loading were at the lowest level. The average net production rate was exceeded by respiration rate, which indicates that all available organic matter produced within the community ecosystem was metabolized by autotrophic and heterotrophic activities. Among the four years (1964, 1992, 1996 and 1997) presented in Table 10-5, seasonally averaged peak production and respiration rates occurred during 1992, when nitrogen loading rates were the highest of those years. Metabolism rates and loading rates were at intermediate levels during 1996. Production exceeded respiration during both 1992 and 1996, a possible indication of

net export of organic matter. Metabolism rates and nutrient loading rates are relatively low during 1997, with net production and respiration rates approximately in balance on a seasonal basis. Respiration rates in 1997 and 1964 are approximately equal. Additional analyses are planned to further characterize and contrast data measured in 1997 with available historical data.

10.7. Summary of Community Metabolism and Living Resource Habitat Suitability in Estuaries

Comparisons of current community metabolism with historical data at a single location in Patuxent River appears to support the overall reverse of water quality declines in the Patuxent River that has been achieved through declining nutrient loading rates at the fall line. However, the pattern of higher weekly averaged net production rates which increased earlier and persisted longer during 1997 (Figure 10-5) and 1992 relative to 1964 (Figure 10-1) still suggest a pattern of community response caused by relatively high nutrient loading rates and the positive feedback effects associated with high loads.

Assessment of dissolved oxygen in the Patuxent River surface waters based on the criteria for living resource habitat conditions during 1997 did not indicate persistent conditions that could be distinctly classified as unsuitable. However, the persistence of borderline dissolved oxygen concentrations during most of July and August did indicate that the portion of the Patuxent River monitored at times does not meet the criteria considered adequate for above pycnocline waters of anadromous fish spawning reaches and nursery areas of Chesapeake bay tidal tributaries. The persistence of this condition is particularly notable, since the depth measured at Benedict, only 1 meter below the water surface, likely represents the *highest* dissolved oxygen concentration at that point in the water column, below which dissolved oxygen excursions are certain to have persisted at concentrations and over time periods more distinctly unacceptable for living resource habitat conditions. Any sense that these data represent adequate habitat conditions should be tempered with the awareness that an overly optimistic bias may be projected by time-averaged dissolved oxygen values, since concentrations at the 1 meter depth at which all data were collected represent the highest dissolved oxygen value in the water column for that time.

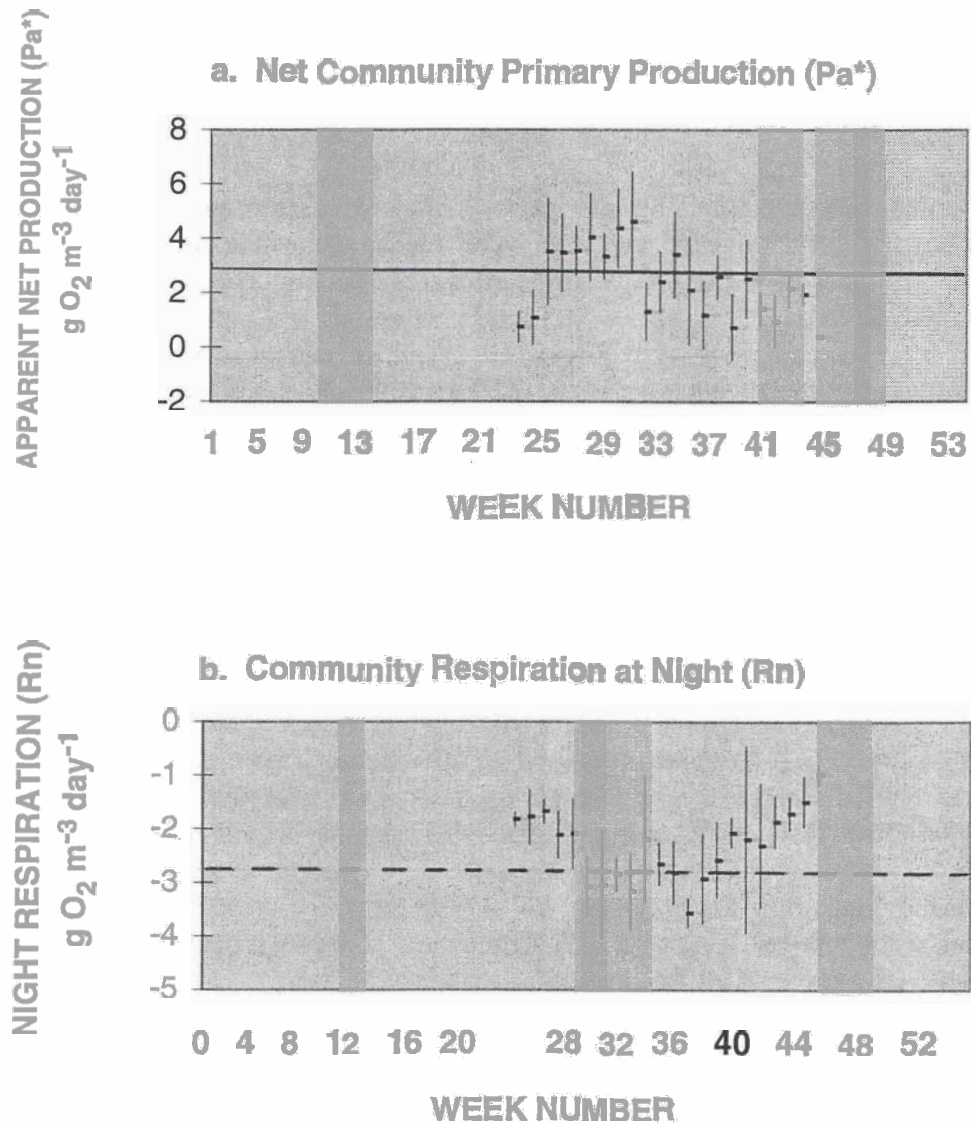


Figure 10-5. A comparison of rates (week averages and standard deviations) of net community primary production (P_a^*) and community respiration at night (R_n) measured from the bridge over the Patuxent River near bridge at Benedict between May 20 through October 22, 1997. The units on the y-axis for P_a^* and R_n are $gO_2\ m^{-3}\ day^{-1}$.

Table 10-5. Summer average daytime net production and respiration at night computed from daily metabolic parameters for Patuxent River near the Bridge at Benedict for the years 1997, 1996, 1992 and 1964.

YEAR	AVERAGE (June 21 - September23)	
	Summer Average Daytime Net Production (Pa*) gO ₂ m ⁻³ day ⁻¹	Summer Average Nighttime Respiration (Rn) gO ₂ m ⁻³ day ⁻¹
Patuxent River (Benedict)		
1997	2.8	2.8
1996	3.6	2.9
1992	4.9	4.1
1964	1.6	2.6

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11. ESTIMATING NITROGEN AND PHOSPHORUS LOADS FOR PATUXENT RIVER, 1960-1977

J. D. Hagy III, W. R. Boynton and M. M. Weir

The loading rates of nitrogen and phosphorus to an estuary are among the most important determinants of water quality and ecosystem health for estuaries. In general, extremely high loading rates are associated with poor water quality and degraded ecosystems. One way to establish a goal for nutrient load reduction is to identify historical nutrient loading levels that were known to have been associated with a desirable level of estuarine water quality and ecosystem health. There is evidence that water quality and other indicators of ecosystem health in the Patuxent River estuary were satisfactory in the early 1960's; however, the corresponding nutrient loading rates have not been estimated. This reflects in part the relative paucity of data prior to 1977. For example, the Patuxent fall line gauging station at Bowie, MD did not begin operation until 1977, nor was the current United States Geological Survey (USGS) fall line input monitoring program in place.

However, there is not a complete lack of data. A small number of nutrient measurements are available. Flow estimates are available for other gauging stations on Patuxent River back to 1960 and earlier. Using the available data and the most defensible assumptions possible, we estimate monthly mean total nitrogen, nitrate plus nitrite, total phosphorus and dissolved inorganic phosphorus loading rates at the fall line of Patuxent River for 1960-1977. Combined with the modern records collected by the USGS, this completes a 37-year record of loading rates, quantifying a dramatic increase in nutrient loads and a subsequent decline under a coordinated nutrient management effort. Ultimately, we hope we will be able to relate both the decline and partial recovery of the Patuxent River estuary to changes in nutrient loading rates.

11.1 Nutrient Loading Rate Estimation and Discussion

We estimated monthly mean total nitrogen (TN), total phosphorus (TP), nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$), and dissolved inorganic phosphorus (DIP) loading rates for 1960-1977 as the product of monthly mean river discharge rates and monthly mean nutrient concentrations. Both the river discharge rate and nutrient concentrations were estimated via empirical models fit to the available data. Different models were used to estimate concentrations at different points in the record, reflecting changes in the relative strengths of the data record. All but one of the models are analysis of covariance (ANCOVA) models, combining continuous variables such as "time" and "river flow" with discrete variables such as "month." Additionally, most of the models are so-called "joint-point" regressions, meaning that the model incorporates a discontinuity where a slope abruptly changes. An example is a point in time where the rate of change of nutrient concentrations changes. The correct locations of the joint points were determined from among the candidate locations by selecting the locations that minimized the error sums of squares. Finally, several of the models are constructed on the natural logs of nutrient concentrations. This reflects two aspects of the data. Since nutrient concentrations must be positive, are often very small, and are only occasionally very large, they tend to be log-normally distributed about mean levels. Secondly, seasonal variations in nutrient concentrations vary in amplitude with the average concentration. In other words, the seasonal effect

is “multiplicative.” By modeling the natural logs of concentration, we can fit an additive model with normally distributed errors, the usual assumptions of ordinary least-squares regression.

All of the models estimating nutrient concentrations use estimates of monthly mean nutrient concentrations at Bowie (Figures 11-1 and 11-2). These concentrations were obtained by dividing the monthly mean nutrient loading estimates obtained from the USGS by the corresponding monthly mean Patuxent River discharge rate at Bowie. The strength of this approach is that the model used by the USGS (Cohn *et al.*, 1989) accounts for flow related effects on nutrient concentrations, providing a mean concentration for the month that does not depend randomly on the river discharge level on the particular days water samples were collected.

The Cohn model shares many similarities with the models used here to describe the concentrations, accounting to some extent, and potentially a large extent, for the excellent fit obtained to the recent concentration data. A seasonal pattern, a flow dependence, and a linear time trend are all components of the Cohn model and are imposed on the concentration estimates obtained as described above. In contrast, the nutrient concentrations prior to 1978 are individual water samples, not monthly means. These observations therefore have a larger variance and a poorer fit to the models presented here. Our objective is not to model the variability in the recent concentration estimates since this variability is imposed by the Cohn model that generated them. In contrast, we use the recent data to capture in our model the patterns of variability with respect to year, season, and river flow, thereby placing the few historical observations in a better defined context.

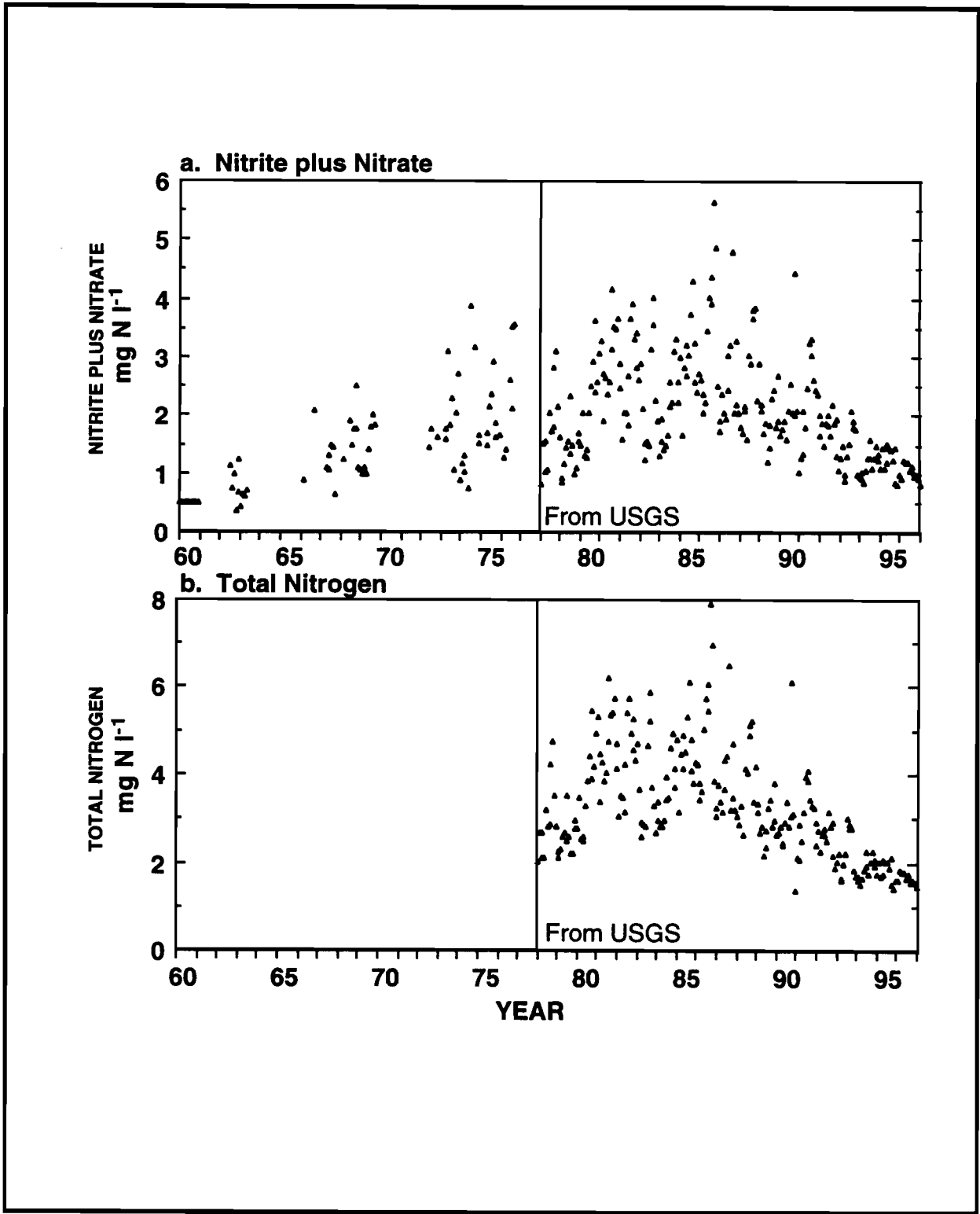


Figure 11-1. The nitrate plus nitrite ($\text{NO}_2^- + \text{NO}_3^-$) and total nitrogen (TN) concentrations calculated from USGS-estimated nutrient loading rates and the historical $\text{NO}_2^- + \text{NO}_3^-$ concentration collected from a variety of sources as described in Table 11-1.

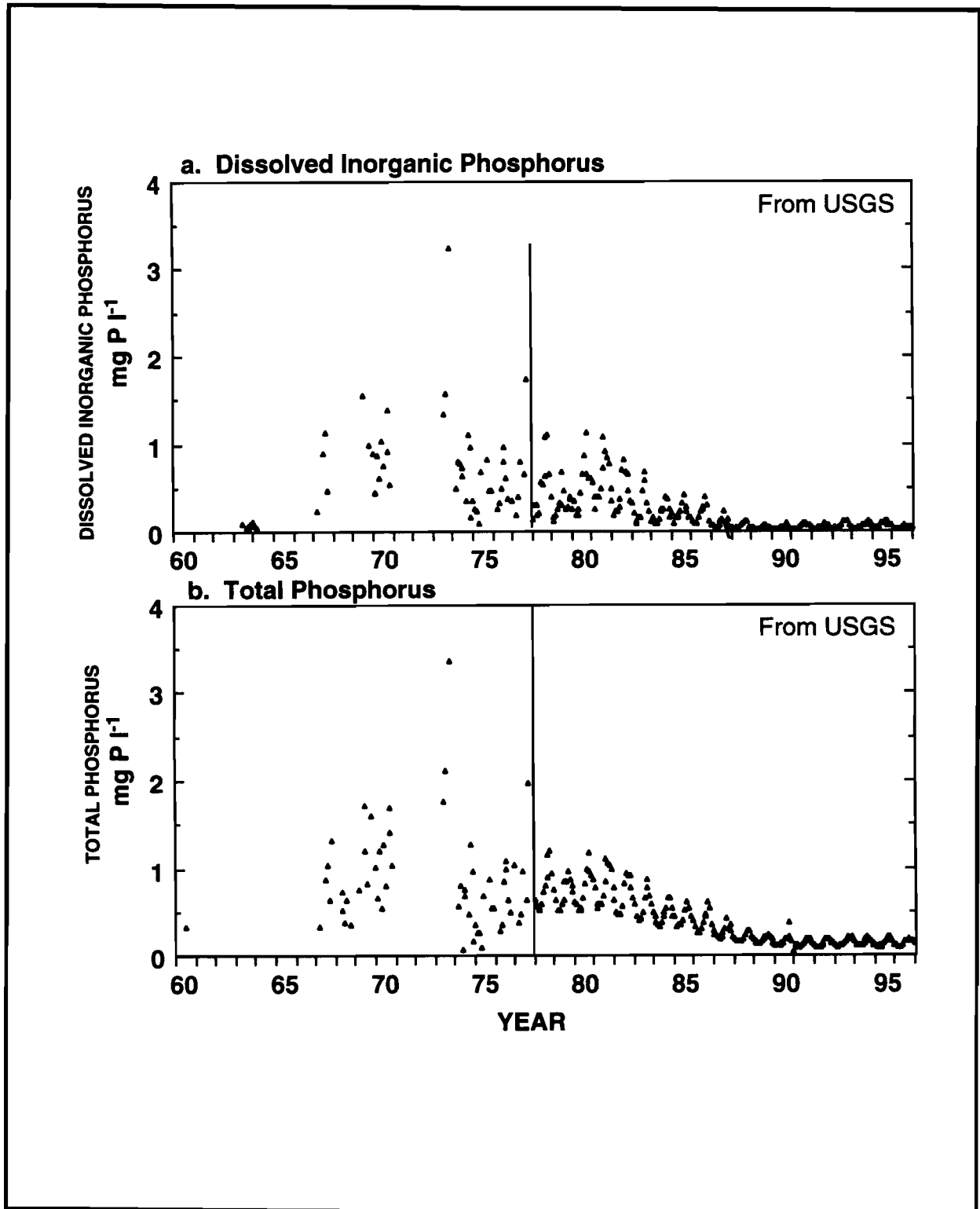


Figure 11-2. The dissolved inorganic phosphorus (DIP) and total phosphorus (TP) concentrations calculated from USGS-estimated nutrient loading rates and the historical DIP and TP concentrations collected from a variety of sources as described in Table 11-2.

11.1.1 Estimating Patuxent River Discharge at Bowie

While measurements of Patuxent River discharge at Bowie did not begin until mid-1977, a record of daily average discharge for Patuxent River at Laurel, the next USGS gauging station upriver, is available beginning in 1944 and overlapping the record at Bowie through the present. The Laurel gauge has a watershed area of 342 km², 40% of the watershed area for the Bowie gauge. Because its flow is highly regulated by the dams for the T. Howard Duckett and Triadelphia reservoirs, the daily mean flows are much less variable than the Bowie flows. Seasonal regulation of water level in the reservoirs (James *et al.*, 1994) affects the flow at Laurel more than the flow at Bowie, generating seasonal variation in the relationship between the Laurel and Bowie flow rates. To accommodate these effects, an ANCOVA model incorporating a discrete “month” effect was fit to monthly average flows at Laurel and Bowie for June 1977 through December 1996. Taking monthly means from daily means removed the daily variability in the Bowie flow such that the pattern of variability better matched that of the Laurel flows, which were already less variable from day to day.

The ANCOVA model has the following form:

$$\beta_{y,m} = (\beta_0 + M_m) + \beta_1 L_{y,m} + \varepsilon_{y,m} \quad (11.1)$$

where $\beta_{y,m}$ and $L_{y,m}$ are the monthly mean flows at Bowie and Laurel, respectively, in year y and month m , M_m is the effect of month m , and $\varepsilon_{y,m}$ is the residual error. The parentheses emphasize that this is a linear regression where the y-intercept varies according to the month of the year. The model predicts 87% of the variability in the monthly mean flow at Bowie from 1977-1996. The slope β_1 is 2.27 ± 0.07 (\pm S.E.), slightly less than 2.50, the slope predicted by the relative watershed areas of the gauges (901 km² vs. 360 km²). The sum of β_0 and M_m for each month (Table 11-1, Column B) shows that as the Laurel flow approaches zero, there always remains some flow at Bowie. This reflects municipal water withdrawal from the reservoir which averaged 1.69 m³s⁻¹ during the late 1980s (James *et al.*, 1994 and similar publications for other years), and probably also evaporative losses from the reservoirs plus other small differences. There was a relative accumulation of water in the reservoirs during the wetter seasons and a release during the drier seasons (James *et al.*, 1994), which was reflected in negative values for M_m during late summer and early fall (Table 11-1).

Table 11-1. M_m parameter estimates (eq. 11.1) for the ANCOVA model relating Patuxent River discharge at Laurel to Patuxent River discharge at Bowie.
At the bottom is the overall intercept, β_0 .

Month	M_m ($\text{m}^3 \text{s}^{-1}$)
1	2.18
2	1.58
3	1.98
4	-0.24
5	0.29
6	-0.60
7	-1.57
8	-2.06
9	-2.54
10	-1.51
11	1.01
12	1.44
β_0	4.94

11.1.2 Estimating TN and NO₂⁻ + NO₃⁻ Concentrations at Bowie, 1960-1978

Total nitrogen (TN) and nitrate plus nitrite (NO₂⁻ + NO₃⁻) concentration estimates for 1978-1996 obtained from the USGS loading estimates as described above show a pronounced seasonal pattern, a clear increase in concentration between 1978 and sometime in the mid-1980's, and a subsequent decrease through 1996 (Figure 11-1). Initial TN and NO₂⁻ + NO₃⁻ concentration estimates for 1960-1978 were estimated by fitting a joint-point ANCOVA model to the natural logs of the 1978-1996 concentration estimates, then extrapolating the initial increasing trend backward from 1978 through 1960. Subsequently, the estimated concentrations were compared with the available concentration measurements for 1960-1978.

The ANCOVA model has the form

$$\ln(N_{y,m}) = (\alpha_i + M_m) + \beta_1 Y + \beta_Q Q_{y,m} + \varepsilon_{y,m} \quad (11.2)$$

where subscripts *i*, *y*, and *m* refer to model segment *i*, year *y* and month *m*, $N_{y,m}$ is the TN or NO₂⁻ + NO₃⁻ concentration, M_m is the seasonal effect, α_i and β_1 are the slope relative to year and the intercept for each model segment, *Y* is the year, β_Q is the effect of river flow on concentration, $Q_{y,m}$ is the monthly mean river flow and $\varepsilon_{y,m}$ is the residual error. The model fits a separate linear trend to the observations before and after the point when concentrations stopped increasing and began to decrease (the joint-point) On the basis of the graph of the concentration time series (Figure 11-1), the years 1982-1990 were identified as possible years for the joint-point. The TN and NO₂⁻ + NO₃⁻ models were each fitted for each possible joint-point year, then the joint-point year that minimized the error sums of squares was selected.

The joint-point was estimated to occur in January 1986. The ANCOVA confirmed an initial positive trend in nitrogen concentrations from 1978-1986, followed by a decline through 1996. The flow effect indicated a significant negative relationship between concentration and river flow (b_Q), while the seasonal effects indicated that in an average year both TN and NO₂⁻ + NO₃⁻ were lower during November through June than other times of the year (Table 11-2).

Nitrite plus nitrate (NO₂⁻ + NO₃⁻) measurements for 1960-1977 were in the same range as the predicted concentrations, except for those in the early 1960's (Figure 11-3.; Table 11-3.). For that period, the measurements appear slightly lower than the model predictions. It was decided, however, that the differences were not sufficient to merit revising the NO₂⁻ + NO₃⁻ concentration estimates downward. While there are no measurements of TN near Bowie for 1960-1977, there was a strong relationship between NO₂⁻ + NO₃⁻ and TN for 1978-1996 (Figure 11-4). Using this relationship to estimate TN concentrations from the 1960-1977 NO₂⁻ + NO₃⁻ concentrations, TN concentrations were obtained that approximately reflect the trend predicted by the ANCOVA model for TN (Figure 11-3).

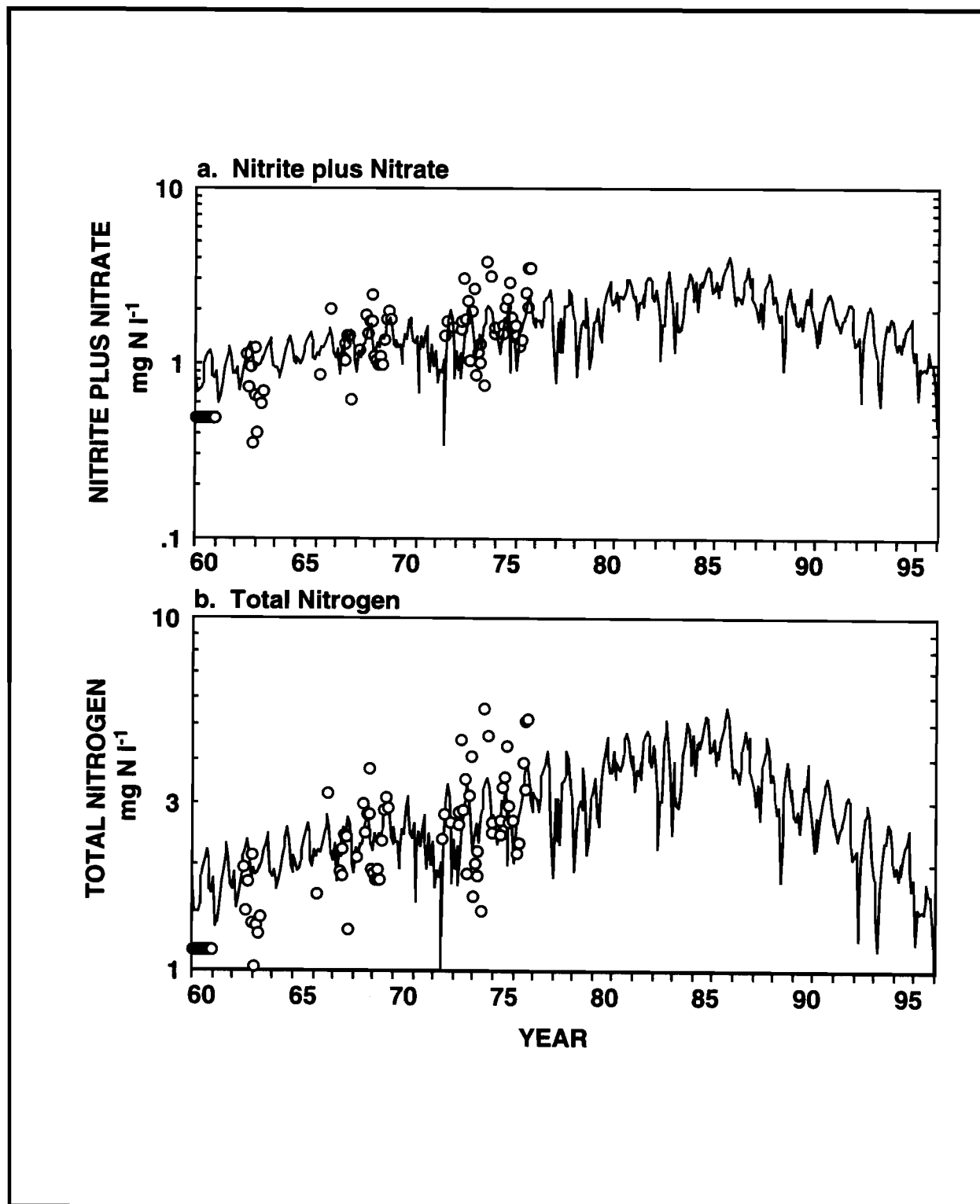


Figure 11-3. Nitrite plus nitrate ($\text{NO}_2 + \text{NO}_3$) and total nitrogen (TN) concentrations predicted by the ANCOVA model (continuous line) and observed concentrations for 1960-1977 (open circles). The open circles in the lower panel are TN concentrations estimated from the $\text{NO}_2 + \text{NO}_3$ concentrations via the regression in Figure 11-4.

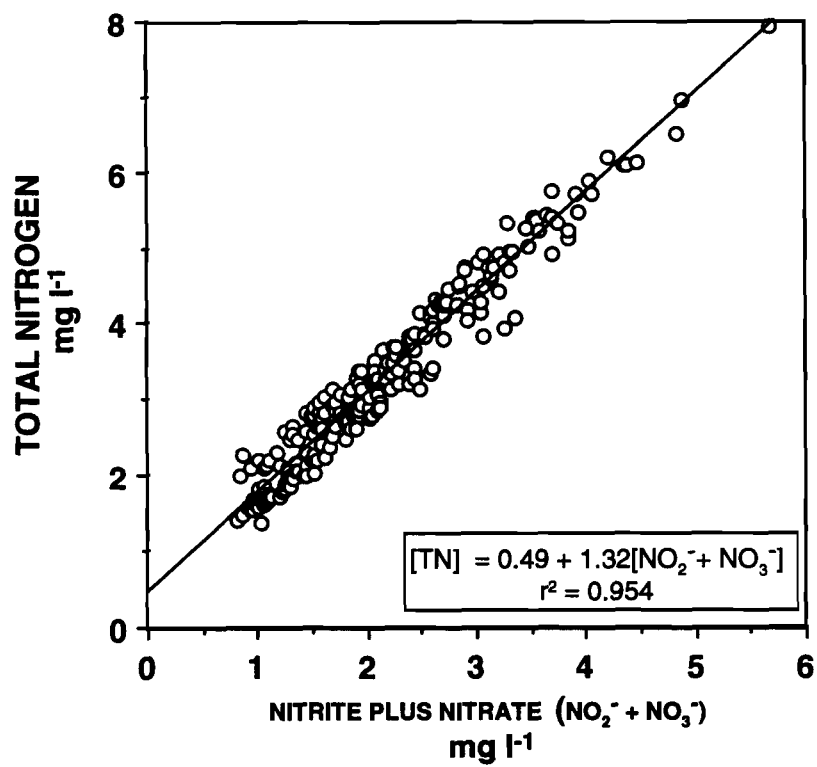


Figure 11-4. The relationship between nitrite plus nitrate (NO₂⁻ + NO₃⁻) and total nitrogen (TN) concentrations in the Patuxent River fall line at Bowie 1978-1996.

11.1.3 Estimation of the TN and $\text{NO}_2^- + \text{NO}_3^-$ Loading Rates, 1960-1977

Total nitrogen (TN) and nitrate plus nitrite ($\text{NO}_2^- + \text{NO}_3^-$) loading rates for 1960-1977 were estimated as the product of the estimated monthly mean concentration and river flow. The monthly mean TN and $\text{NO}_2^- + \text{NO}_3^-$ loading estimates are shown in Figure 11-5. The estimates of the annual mean $\text{NO}_2^- + \text{NO}_3^-$ loads ranged from 528 kg N d⁻¹ in 1963 to 1,658 kg N d⁻¹ in 1975 (Table 11-4). Annual mean TN loading ranged from 984 kg N d⁻¹ in 1963 to 3,124 kg N d⁻¹ in 1972. The minimum TN loading rate is 2 to 4 times the TN loading rate expected if the entire watershed consisted of mixed deciduous hardwood forest and was not subject to NO_x -enriched precipitation (0.1 to 0.2 g TN m⁻² y⁻¹; Boynton *et al.*, 1995). Given that the watershed in 1960 was far from this pristine condition, this suggests that extrapolating the 1978-1986 TN loading trend back to 1960 has not resulted in an excessively low TN loading estimate.

Table 11.2. Parameter estimates for the model in equation (11.2) fitted for total nitrogen (TN) and nitrate plus nitrite ($\text{NO}_2^- + \text{NO}_3^-$).

Month	Total Nitrogen, M_m , ln(mg l ⁻¹)	$\text{NO}_2^- + \text{NO}_3^-$, M_m , ln(mg l ⁻¹)
1	0.003	-0.036
2	-0.052	-0.087
3	-0.032	-0.040
4	-0.043	-0.026
5	-0.045	-0.020
6	-0.015	0.018
7	0.036	0.073
8	0.075	0.106
9	0.129	0.137
10	0.069	0.059
11	-0.048	-0.083
12	-0.076	-0.101
α_1 (year<1986)	-1.51	0.10
α_2 (year ≥ 1986)	9.03	8.52
β_1 (year<1986)	0.04	0.05
β_2 (year≥1986)	-0.09	-0.08
β_Q	-0.02	-0.03

Table 11-3. Nitrate plus nitrite (NO₂ + NO₃) or nitrate (NO₃) concentrations (mg N l⁻¹) near the fall line of Patuxent River, 1960-1977.

NO₂⁻ + NO₃⁻ and NO₃⁻ are used interchangeably. The data were collected from a variety of report sources which are listed below. All values are as mg N l⁻¹. Conversions of original data to units of mg N l⁻¹ have been made when needed. All data were collected at Bowie, MD or at Queen Annes Bridge in the riverine portion of Patuxent River.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1960	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600	0.600
1961												
1962												
1963						1.150	1.150	0.830	1.000	0.370	0.680	1.260
1964	0.410	0.660	0.600	0.710								
1965												
1966							1.900	2.870				
1967			0.882				1.478		0.627			
1968				1.078	1.305	1.052	1.478					
1969		1.224			1.905	1.905	3.496	1.750		1.750		1.070
1970		0.890	1.090		1.400	2.200	1.930		2.680	2.540	1.270	
1971												
1972							1.442	1.751		1.638		
1973							1.820	2.287		2.030	2.725	0.870
1974			1.600	1.773	3.105	1.820	2.287		1.070			
1975	1.170	1.300	1.038	1.680	0.758	3.890	2.350	2.933	3.167	1.640	1.503	1.645
1976				1.261	1.397	2.148	2.350	2.933	1.640	1.867		
1977						2.607		3.546	3.569			

References:

- Heidel and Frenier (1965): Jun, 1963 - Apr, 1964 (Queen Anne Bridge @ Hardesty, MD)
- Marks et al. (1967): Mar, Jul, Aug, 1967 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al. (1968): Apr, May, Jun, Jul, Sep, 1968 (Rt 50/301 Bridge @ Bowie, MD)
- Patuxent River water Quality Managt Tech Evaluation (1969): Mar, Aug, 1967 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al. (1969): Feb, Jun, Jul, Aug, Oct, Dec 1969 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al. (1970): Feb, Mar, May, Jun, Jul, Sep, Oct, Nov 1970 (Rt 50/301 Bridge @ Bowie, MD)
- Pfeiffer and Lovelace (1974): Jun, Jul, 1973 (Rt 50/301 Bridge @ Hardesty, MD)
- Pfeiffer and Lovelace (1974): Oct, 1973 (Queen Anne Bridge @ Hardesty, MD)
- Jaworski and Helling (1996): Jan-Dec, 1960 (estimated from concentrations at fall line of Potomac in 1960)
- Olson (1998): Jul, 1968; Mar, Apr, May, Jun, Jul, Sep, Oct, Nov, Dec, 1974; Jan, Feb, Mar, May, Jun, Sep, Nov, Dec, 1975; Apr, May, Jun, Jul, Aug, Sep, Oct, Dec, 1976; Mar, Apr, Jun, Aug, Sep, 1977 (Rt 50/301 Bridge @ Bowie, MD)

Table 11.4. The 1960-1977 annual means based on the estimated monthly mean $\text{NO}_2^- + \text{NO}_3^-$ and TN loading rates for Patuxent River at Bowie, MD.

Year	Nitrate plus Nitrite Loading Rate (kg d⁻¹)	Total Nitrogen Loading Rate (kg d⁻¹)
1960	572	1129
1961	680	1370
1962	591	1139
1963	528	984
1964	663	1263
1965	622	1150
1966	579	1051
1967	770	1425
1968	808	1493
1969	702	1250
1970	976	1780
1971	1447	2834
1972	1516	3124
1973	1399	2671
1974	1166	2080
1975	1658	3117
1976	1358	2455
1977	1189	2073

11.1.4 Estimation of Phosphorus Loading Rates, 1960-1977

11.1.4.1 Dissolved Inorganic Phosphorus (DIP) Concentrations, 1963-1977

DIP concentrations for the period 1963-1977 were estimated using a four-segment ANCOVA model fit to the natural logs of all of the available DIP concentration data (Figure 11-6). The four segments are 1963-1969, 1970-1982, 1983-1990 and 1991-1996. The model fits a monthly effect for the entire model and a separate slope and y-intercept for each segment. A DIP concentration in month m , year y , and model segment i is estimated as

$$\ln(P_{y,m}) = (M_m + I_i) + S_i Y + \varepsilon_{y,m} \quad (11.3)$$

where M_m is the seasonal effect for month m , I_i is the y-intercept for segment i , S_i is the slope with respect to year for segment i , and $\varepsilon_{y,m}$ is the residual. The model has units of $\ln(\text{mg l}^{-1})$ for M_m and I_i and $[\ln(\text{mg l}^{-1})] \text{ y}^{-1}$ for S_i . DIP concentrations were less than average from December through May, reached their lowest in March and increased to the seasonal maximum in August (Table 11-7). DIP concentrations increased at $0.499 [\ln(\text{mg l}^{-1})] \text{ y}^{-1}$ from 1963-1969, decreased slightly or remained the same from 1970-1982, then decreased at a rate of $0.310 [\ln(\text{mg l}^{-1})] \text{ y}^{-1}$ from 1983-1990 (Table 11-8).

Table 11-5. Dissolved inorganic phosphorus concentrations (mg P l⁻¹) near the fall line of Patuxent River.

The data were collected from a variety of report sources which are listed below. Conversions of original data to units of mg P l⁻¹ have been made when needed. All data were collected at the Bowie, MD station or at Queen Annes Bridge in the riverine portion of the Patuxent.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1960												
1961												
1962												
1963						0.085						
1964	0.070	0.050	0.020					0.050	0.060	0.056	0.090	0.110
1965												
1966												
1967			0.240				0.900	1.120	0.460			
1968												
1969							1.560			1.000		0.884
1970		0.450	0.880		0.620	1.040	0.750		1.380	0.920	0.530	
1971												
1972												
1973							1.330	1.574		3.243		
1974			0.500	0.810	0.770	0.630	0.740		0.350	1.113	0.960	0.160
1975	0.350	0.250	0.230		0.100	0.685			0.830		0.480	0.470
1976				0.270	0.330	0.490	0.800	0.960	0.620	0.380		0.350
1977			0.185	0.410		0.810		0.650	1.750			

References:

- Heidel and Frenier (1965): Jun, 1963-Mar, 1964 (Queen Anne Bridge @ Hardesty, MD)
 Marks et al.(1969): Jul, Oct, Dec 1969 (Rt 50/301 Bridge @ Bowie, MD)
 Marks et al.(1970): Feb, Mar, May, Jun, Jul, Sep, Oct, Nov 1970 (Rt 50/301 Bridge @ Bowie, MD)
 Pfeiffer and Lovelace (1974): Jun, Jul, 1973 (Rt 50/301 Bridge @ Bowie, MD)
 Pfeiffer and Lovelace (1974): Oct, 1973 (Queen Anne Bridge @ Hardesty, MD)
 Olson (1998): Mar, Apr, May, Jun, Jul, Sep, Oct, Nov, Dec, 1974; Jan, Feb, Mar, May, Jun, Sep, Nov, Dec, 1975; Apr, May, Jun, Jul, Aug, Sep, Oct, Dec, 1976; Mar, Apr, Jun, Aug, Sep, 1977 (Rt 50/301 Bridge @ Bowie, MD)

Table 11-6. Total phosphorus concentrations (mg P l⁻¹) near the fall line of Patuxent River.

The data were collected from a variety of report sources which are listed below. Conversions of original data to units of mg P l⁻¹ have been made when needed. All data were collected at the Bowie, MD station or at Queen Annes Bridge in the riverine portion of the Patuxent.

Year	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
1960							0.340					
1961												
1962												
1963												
1964												
1965												
1966												
1967			0.330				0.860	1.030	0.636	1.312		
1968				0.506	0.736	0.382	0.627		0.364			
1969		0.754				1.199	1.710	0.835		1.601		1.016
1970		0.650	1.210		0.540	1.270	0.810		1.690	1.400	1.040	
1971												
1972												
1973						1.772	2.129			3.355		
1974			0.570	0.810	0.060	0.680	0.760		0.460	1.280	0.970	0.170
1975	0.350	0.250	0.260		0.100	0.685			0.860		0.530	
1976				0.280	0.360	0.855	1.000	1.090	0.630	0.505		
1977			0.380	0.480		0.953		0.637	1.970			

References:

- Marks et al.(1967): Mar, Jul, Aug, Sep, Oct 1967 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al.(1968): Apr, May, Jun, Jul, Sep, 1968 (Rt 50/301 Bridge @ Bowie, MD)
- Patuxent River Water Quality Managt Tech Evaluation (1969): Jul, 1955 (used for 1960 in above table); Mar, Aug, Sep, Oct, 1967 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al.(1969): Feb, Jun, Jul, Aug, Oct, Dec 1969 (Rt 50/301 Bridge @ Bowie, MD)
- Marks et al.(1970): Feb, Mar, May, Jun, Jul, Sep, Oct, Nov 1970 (Rt 50/301 Bridge @ Bowie, MD)
- Pfeiffer and Lovelace (1974): Jun, Jul, 1973 (Rt 50/301 Bridge @ Bowie, MD)
- Pfeiffer and Lovelace (1974): Oct, 1973 (Queen Anne Bridge @ Hardesty, MD)
- Olson (1998): Jul, 1967; Jul, 1968; Mar, Apr, May, Jun, Jul, Sep, Oct, Nov, Dec, 1974; Jan, Feb, Mar, May, Jun, Sep, Nov, Dec, 1975; Apr, May, Jun, Jul, Aug, Sep, Oct, Dec, 1976; Mar, Apr, Jun, Aug, Sep, 1977 (Rt 50/301 Bridge @ Bowie, MD)

Table 11-7. The seasonal pattern (M_m) in natural log dissolved inorganic phosphorus [ln(DIP)] concentration (mg l^{-1}) in Patuxent River at Bowie as estimated by the ANCOVA model. The coefficients have been re-coded such that they sum to zero. The remainder was incorporated into the segment intercepts (Table 11-4.). As noted in eq. 11.3, the intercept for any observation includes both M_m and I_p , the values of which are in Table 11-4.

Month	$M_m, \ln(\text{mg l}^{-1})$
1	-0.329
2	-0.494
3	-0.603
4	-0.372
5	-0.319
6	0.193
7	0.460
8	0.575
9	0.570
10	0.356
11	0.200
12	-0.236

Table 11-8. The slope and segment intercept for each of the four model segments.
As indicated by equation 11.3, the intercept for any observation is the sum of the segment intercept and the monthly intercept (Table 11-3).

Model Segment	Intercept ln(mg l ⁻¹)	Slope [ln(mg l ⁻¹)] y ⁻¹
1963-1969	-34.415	0.499
1970-1982	2.199	-0.038*
1983-1990	24.483	-0.310
1990-1996	-3.047	0.001*

11.1.4.2 Dissolved Inorganic Phosphorus (DIP) Concentrations, 1960-1962

Since there are no DIP observations prior to 1963, it was assumed that the DIP concentrations in 1960-1962 averaged the same as in 1963 and varied seasonally in the way described in Table 11-3 (Figure 11-6).

11.1.4.3 Estimating Total Phosphorus (TP) Concentrations, 1960-1969

Since there are not sufficient total phosphorus (TP) concentrations prior to 1969 to establish the trend in TP concentrations, the TP concentrations were estimated via an empirical relationship between DIP and TP concentrations (Figure 11-7). This relationship is

$$TP = 1.13DIP^{0.60} \quad (11.4)$$

indicating that as the DIP concentration increases, the DIP fraction of TP increases. However, this fraction reaches 100% at a DIP concentration well above the maximum concentration observed.

11.1.4.4 Estimating Total Phosphorus (TP) Concentration, 1970-1977

For the period 1970-1977, total phosphorus concentrations were estimated by fitting the 1970-1996 TP data (Figure 11-5) to the ANCOVA model described in Section 11.2.4.1 (Figure 11-6). The seasonal pattern was similar to that for DIP, with total phosphorus lower than average during December through May and higher than average during June through November (Table 11-9). The annual minimum concentration was observed in May, while the maximum was observed in October, later in the year than for DIP. A large decrease in TP concentrations occurred between 1983 and 1990, while there were no significant trends in other periods (Table 11-10).

11.1.5 Dissolved Inorganic Phosphorus (DIP) and Total Phosphorus (TP) Loading Rates

Dissolved inorganic phosphorus and total phosphorus loading rates were estimated by multiplying the estimated monthly mean concentration (Figure 11-8) by the corresponding estimate of monthly mean river discharge at Bowie. The annual mean loading rates for 1960-1977 are shown in Table 11-11. The annual mean loading rates through the 1990's are in the same range as those in the early 1960's, demonstrating the dramatic success of phosphorus abatement efforts. However, an all-forest watershed might be expected to yield approximately $0.004 \text{ g P m}^{-2} \text{ y}^{-1}$ (Boynton *et al.*, 1995), which for the Patuxent River watershed is an average load of 10 kg d^{-1} .

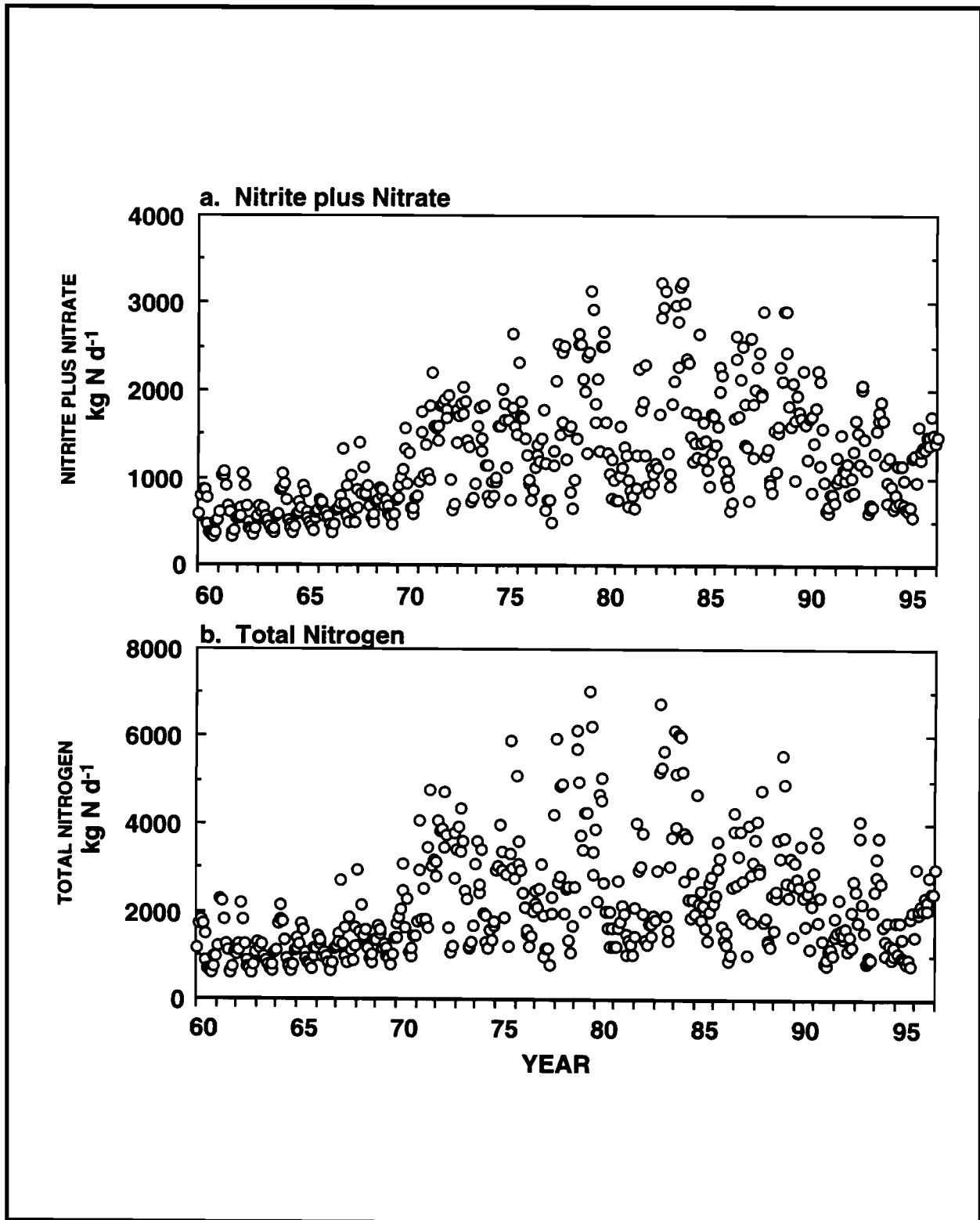


Figure 11-5. Estimated monthly mean nitrite plus nitrate ($\text{NO}_2^- + \text{NO}_3^-$) and total nitrogen loading rates at the fall line of the Patuxent River, 1960-1996. The loading estimates for 1978-1996 are from the USGS, while those for 1960-1977 are from this study.

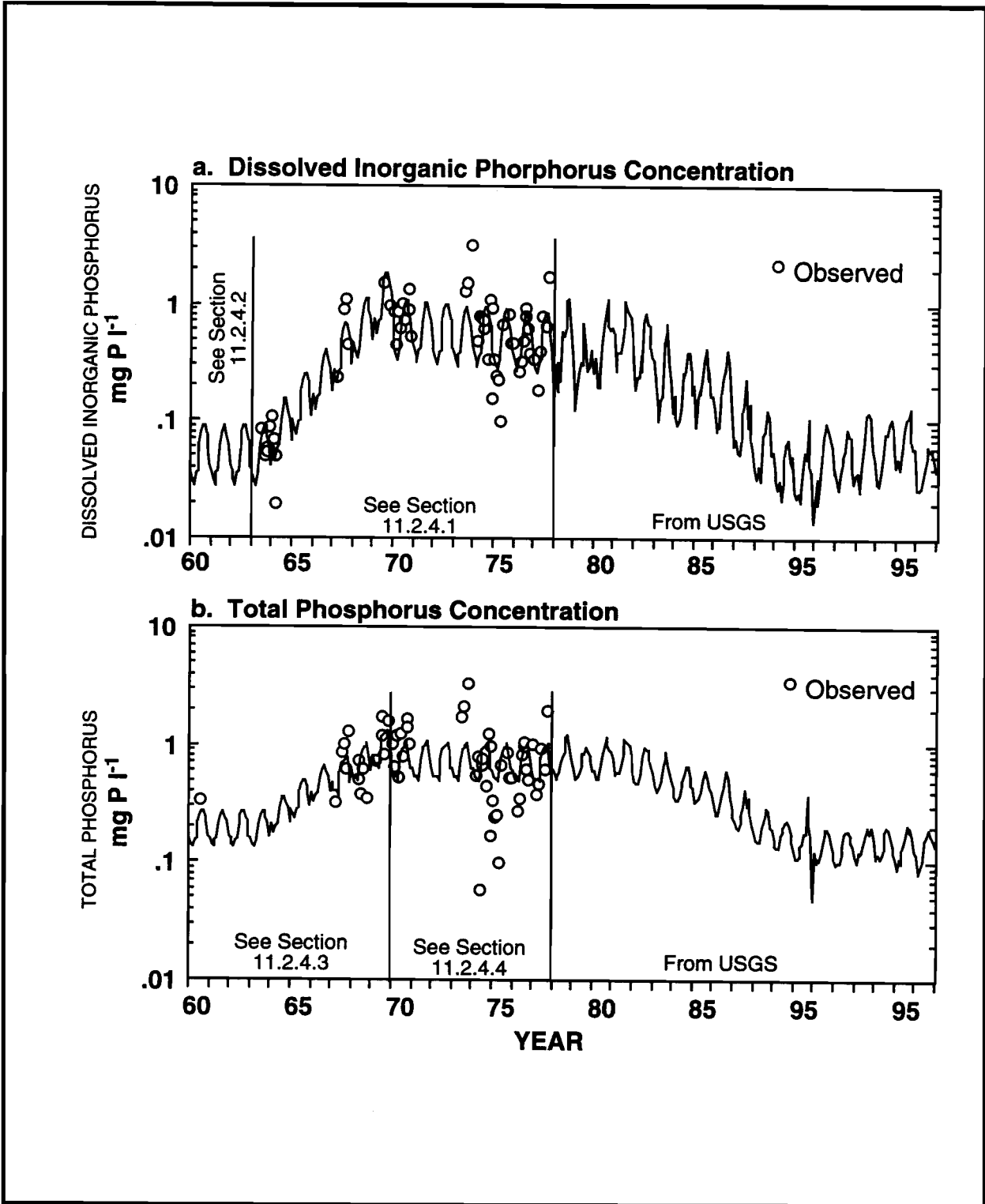


Figure 11-6. The predicted dissolved inorganic phosphorus (DIP) and total phosphorus (TP) concentrations and the observed concentrations prior to 1978. Predicted concentration from 1978 and later were directly calculated from the loading rates. For the remainder of the time series, the method of estimating the predicted values is described in the indicated section in the text.

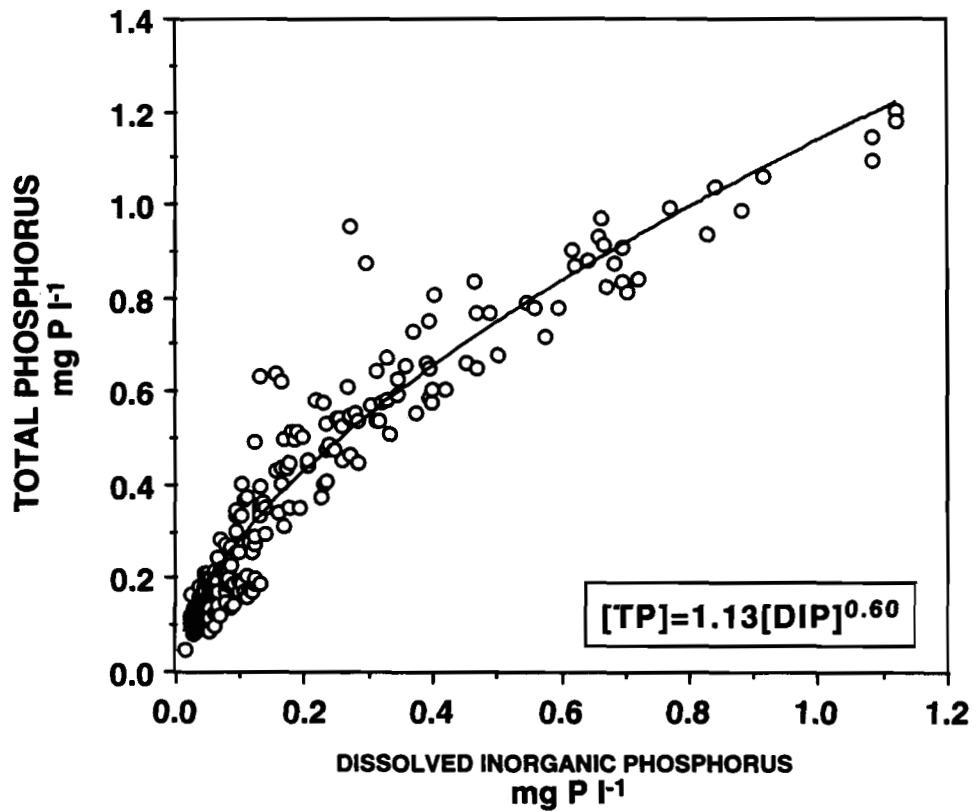


Figure 11-7. The relationship between dissolved inorganic phosphorus (DIP) and total phosphorus (TP) in the Patuxent River at Bowie, 1978-1996.
The line was fitted with non-linear least squares regression.

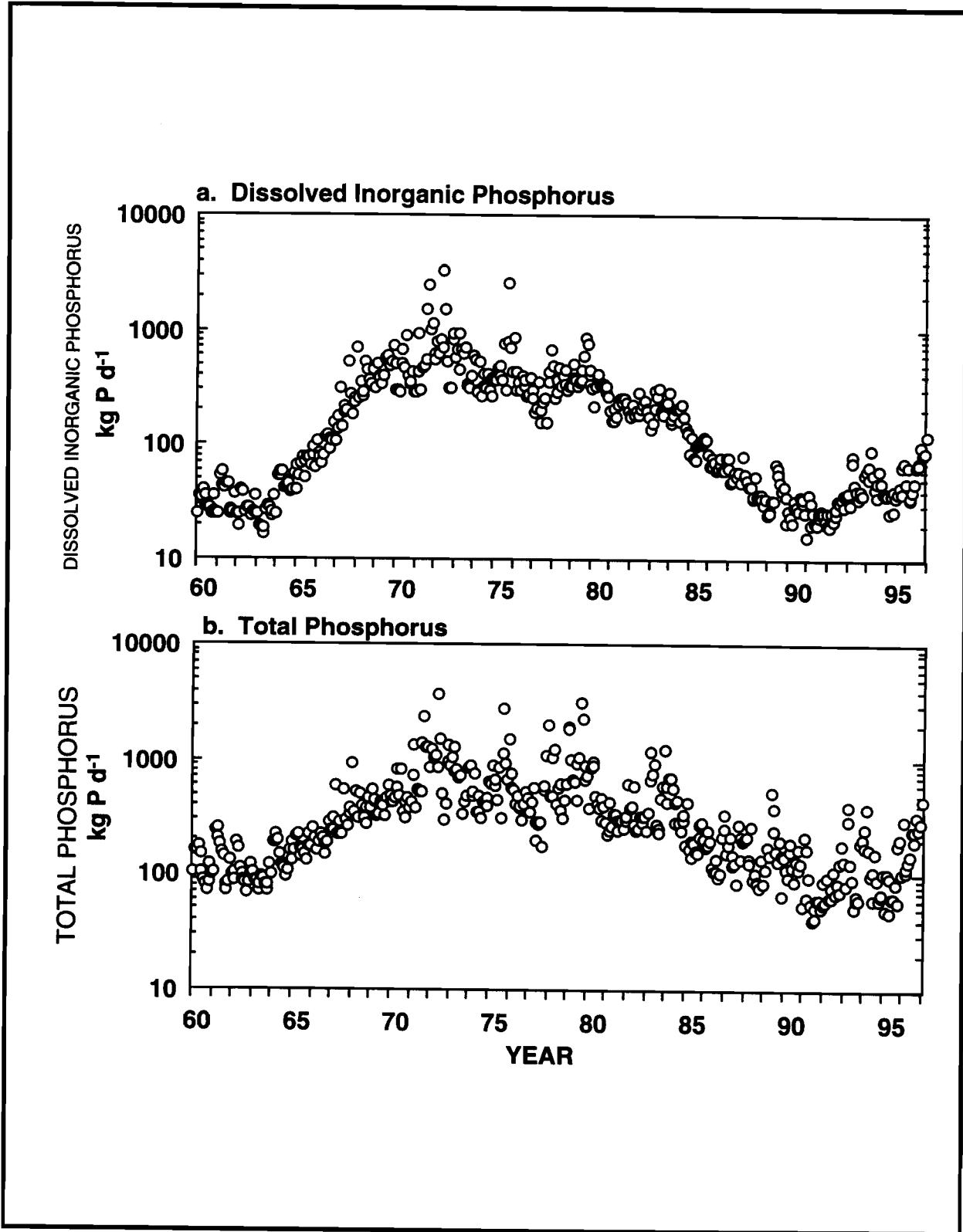


Figure 11-8. Monthly mean dissolved inorganic phosphorus (DIP) and total phosphorus loading rates at the fall line of Patuxent River.
Loading estimates for 1978-1996 are from the USGS, while the estimates for 1960-1977 are from this study.

Table 11-9. The seasonal pattern (M_m in equation 11.3) in natural log total phosphorus [LN(TP)] in the Patuxent River at Bowie estimated by the ANCOVA model.

The coefficients have been re-coded such that they sum to zero; the average value has been incorporated into the segment intercepts (Table 11-4). As noted in equation 11.3, the intercept for any observation includes both M_m and I_i , the values for which are in Table 11-4.

Month	M_m ln(mg l ⁻¹)
1	-0.135
2	-0.292
3	-0.312
4	-0.315
5	-0.468
6	0.132
7	0.278
8	0.292
9	0.379
10	0.383
11	0.160
12	-0.102

Table 11-10. The slope and segment intercept for each of the three total phosphorus (TP) model segments.

As indicated by equation 11.3, the intercept for any observation is the sum of the segment intercept and the monthly intercept (Table 11-5).

Model Segment	Intercept, ln(mg l ⁻¹)	Slope, [ln(mg l ⁻¹)] y ⁻¹
1970-1982	-1.527	0.014*
1983-1990	16.1224	-0.202
1991-1996	-0.295	-0.007*

Table 11-11. The estimated annual mean dissolved inorganic phosphorus (DIP) and total phosphorus (TP) loading rates at the fall line of Patuxent River from 1960-1977.

Year	DIP Loading Rate kg P d⁻¹	TP Loading Rate, kg P d⁻¹
1960	25	102
1961	25	102
1962	25	102
1963	25	102
1964	41	136
1965	66	180
1966	109	243
1967	242	382
1968	310	387
1969	509	502
1970	296	390
1971	634	863
1972	960	1352
1973	608	886
1974	269	406
1975	434	678
1976	300	484
1977	674	1127

11.2 Relationship Between Estimated Historical Fall Line Loads and Point Source Discharges

To evaluate whether the estimation procedure used to estimate fall line loading rates for 1960-1977 yielded reasonable estimates, the estimated loads were compared to known point source loads from that period (Figure 11-9). For TP, the point source loads tracked the fall line loads that were observed in years with the lowest river flow rates. On average, the point source TP loads accounted for 60% of the fall line load. However, due to in stream TP losses, the point sources account for something less than 60% of all TP sources. For TN, the point source loads also tracked lowest fall line loads, but accounted for a slightly smaller fraction of the fall line load. On average, the point source TN loads accounted for 50% of the fall line TN load. As with TP, the point source TN loads accounted for somewhat less than 50% of all TN sources because of in-stream TN losses. Prior to 1967, the fall line TN loading rate did not increase as the point source TN loading rate increased (Figure 11-9). This could mean that the estimates for the TN loading rate should be lower through this period. Alternatively, increases in point source TN loads may have been offset by decreases in non-point sources as cities and towns were converted from septic systems to municipal sewage systems.

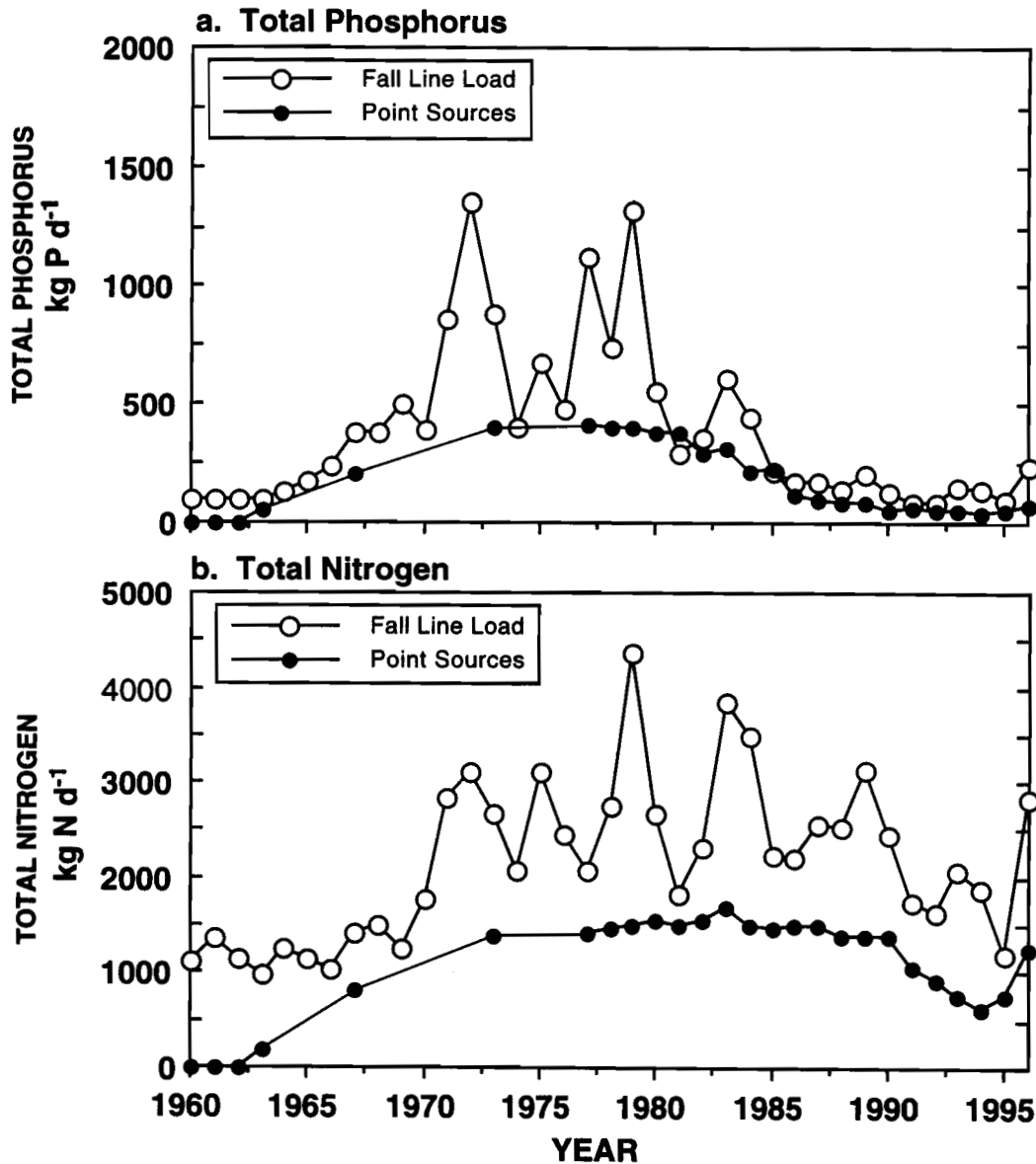


Figure 11.9. Annual mean point source total phosphorus (TP) and total nitrogen (TN) loading rates above the fall line and the annual mean loading rates at the fall line, 1960-1996.

Fall line loading rates for 1960-1977 are from this study, while 1978-1996 fall line loading rates are from the USGS. Point source loading rates for 1960-1988 are from Domotor et al. (1989). Subsequent point source loading rates were calculated from Maryland Department of the Environment data.

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12. MANAGEMENT SUMMARY

Based on a review of previous Ecosystem Processes Component (EPC) Reports (Boynton et al., 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996 and 1997), and the analyzes presented in this report, the following observations are provided which have relevance to water quality management in the Patuxent River estuary.

Nutrient loading data (fall line load of TN and TP; above and below fall line point source loads of TN and TP) for the Patuxent River were reviewed for the period 1984-1996. 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 have been even lower except for relatively high inputs associated with flood events (e.g. May 1989, March 1993 and March 1994 and much of 1996). Fall line TN loads have also decreased over this period but not nearly as much as TP loads; similar increased loads of TN were associated with flood events. 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 $230 \text{ kg day}^{-1} \text{ year}^{-1}$. 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 1997 data when they become available. Given the moderate flows observed during 1997, diffuse source loads were also probably reduced, at least compared to those observed during 1996 and some of the other high flow years observed during the late 1980s (1989) and 1990s (1993, 1994, 1996). It is also 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. Thus, there is ample evidence that substantial nutrient load reductions have occurred in recent years.

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 and the year during which summer dissolved oxygen conditions were the best yet observed in the EPC Program. At both the Broomes Island (BRIS) and Marsh Point (MRPT) locations, summer dissolved oxygen conditions were depressed in July and August, 1997 but rebounded during late summer. Summer average (June-September) concentrations at BRIS and MRPT were 1.8 and 1.7 mg l^{-1} , respectively.

Ammonium (NH_4^+) fluxes at three locations (STLC, BRIS and MRPT) in the Patuxent River were consistently lower than the long-term average and much below the long term average at BRIS and MRPT. Ammonium fluxes at the upper Patuxent River station (BUVA) remained high. The reductions in flux at the three lower river stations may well be a response to nutrient load reductions. The large reductions in ammonium flux between 1996 (a year of high nutrient load and very high river flow) and 1997 further indicates that while sediments are the largest storage of nutrients in these systems, the portion of the stored material that is biologically active is not large enough to support enhanced fluxes in subsequent years. In short, this is evidence for relative limited nutrient memory and the potential for rapid (year rather than decade scale) responses to management actions. The enhanced ammonium flux at the most up river station (BUVA) is part of a statistically significant trend at this site. The reasons for this are not definitely known but several possibilities exist. First, because of reductions in turbidity in the upper river chlorophyll-a stocks have increased. Enhanced ammonium fluxes could be the result of this material being deposited in the vicinity of BUVA. Second, enhanced fluxes could be the result of an expanding benthic invertebrate community;

enhanced ammonium fluxes can result from the excretion of wastes from infauna and from the bioturbating activities of these animals.

Positive *sediment nitrate flux* (fluxes directed from sediments to the water column) is a definite sign of sediment nitrification activity which is a microbial process converting ammonium to nitrate and one that requires that oxygen be present. Positive nitrate fluxes are a sign of good sediment quality. Such positive fluxes were observed during June, 1997 at three stations where bottom water oxygen concentrations were adequate (STLC, MRPT and BUVA). The fact that this did not occur at BRIS where dissolved oxygen concentrations were low is another indication that bay sediments are responsive to nutrient loading rates and resultant DO conditions. We continue to believe that the presence of positive nitrate flux is a good tool for monitoring the biogeochemical health of sediments.

During 1997, *inorganic phosphate (PO₄⁻ or DIP) fluxes* were substantially reduced below the long-term average at two sites (BRIS and MRPT) and similar to the long-term average at the other two sites. 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 (PO₄⁻) flux and dissolved oxygen (DO) conditions 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 (Jasinski, 1995). It appears that sediment phosphorus fluxes have responded to reduced inputs of phosphorus and that sediments do not contain active phosphorus reserves that can sustain high sediment releases beyond the annual time scale.

A method for measuring *total sediment metabolism*, which is consistent with the needs of a monitoring program, was implemented during 1996 and continued during 1997. Recently developed and reliable technology was used to detect small concentration changes in dissolved inorganic carbon (TCO₂) with both accuracy and precision. Data based on TCO₂ 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 TCO₂ 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 Patuxent River stations. Indications of current status (average of fluxes during 1995, 1996 and 1997) 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 year of 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 the Patuxent River stations with the strong exception of the most up river site (BUVA) where there are strong increases in SOC, ammonium and nitrite fluxes. We conclude that nutrient load reductions have not been large enough to allow for detection of interannual trends at other stations which is not surprising given the large interannual differences observed in river flows and loading rates.

Results of *sediment chlorophyll mapping* in the Patuxent River indicated relatively small, but statistically significant, month to month variability in the mass of deposited chlorophyll from March

through June, 1997 and then increasing mass through September. During most of the monitoring period chlorophyll mass tended to be highest in deeper areas (possibly because of particulate material focusing) and in the saltier portion of the mesohaline reach. It is in this reach that water column monitoring data indicate that spring and summer algal blooms occur with regularity. Thus, there is an emerging understanding linking production and deposition of labile organic matter in this system. For the second year, a *MINI-SONE* set of measurements was completed at six stations in the Patuxent River. MINI-SONE measurements are a simplification of SONE measurements (*e.g.* one sediment core per station) and have been added to the EPC program as an interim means of increasing the spatial extent of sediment process measurements and to assist in the development of predictive statistical models of sediment-water exchanges. MINI-SONE flux measurements made in 1997 were almost uniformly smaller in magnitude than those observed during 1996. This is consistent with current understanding of the influence of loading on sediment-water exchanges (loads were higher in 1996 than in 1997). Using sediment chlorophyll mass as one of several key variables (others include sediment Eh and bottom water oxygen and nutrient concentrations), statistically significant *regression models* (linear single and multiple variable models) were developed for SOC, ammonium, phosphorus and nitrite plus nitrate fluxes. This analysis was repeated using 1997 data and repeated again using the combined 1996 and 1997 data sets. Results continued to indicate that this approach has great merit. We recommend that one more year of data (MINI-SONE, sediment chlorophyll-a and bottom water quality conditions) be collected for both traditional monitoring purposes and for verification of statistical sediment-water flux modeling; following this, SONE should be converted to a more spatially inclusive program based on simply and rapidly measured and inexpensive variables which are used in statistical models of sediment-water exchange

The Benedict Bridge *high frequency sampling* effort generated a nearly continuous record of salinity, water temperature and dissolved oxygen from mid-May through late October, 1997. The high frequency sampling is important because extreme values, often observed for only short periods of time, may have large ecological impacts 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 during 1996 to estimate metabolic parameters such as net production and respiration using the high frequency dissolved oxygen observations and this algorithm was used again in 1997 with some improvements. Net daytime production was in the range of -0.5 to $5 \text{ g O}_2 \text{ m}^{-3} \text{ day}^{-1}$, while nighttime respiration was in the same range. These observations indicated generally lower levels of metabolic activity than were observed in 1992 and 1996, but considerably greater than in 1964, 1965 and 1966 when nutrient loading rates to the estuary were lower. Data collected during 1996 were examined for relationships with possible controlling factors; analyzes indicated that about 60% of daily variability in metabolism could be accounted for by temperature and daily insolation. In addition, seasonal average metabolic rates were examined for relationships to nutrient loading rates; initial simple regression analysis did not indicate significant relationships but when seasonal or annual nutrient loads were scaled by water residence time for this sector of the estuary very significant, positive relationships emerged. Again, this indicates the importance of both loading rates and the particular characteristics (residence time in this case) of the estuary being monitored. These analyzes are part of a continuing effort to establish relationships between ecosystem performance and key management objectives (nutrient load reductions in this case).

Average annual load estimates derived for the period 1960 - 1977 ranged between 984 kg N day⁻¹ (1963) and 4100 kg N day⁻¹ (1972) for TN and from 102 kg P day⁻¹ to 1750 kg P day⁻¹ for TP. In general, loads were lower than those observed during the late 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 resulting in 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 3900 kg N day⁻¹ and 1300 kg P day⁻¹, respectively; during the decade of the 1980's TN and TP annual fall line loads averaged about 4300 kg N day⁻¹ and 350 kg P day⁻¹, respectively, and during the first half of the 1990's, TN and TP annual fall line loads averaged about 2500 kg N day⁻¹ and 200 kg P day⁻¹, respectively (Figure 11-9.). This 36-year record of loading rates needs to be carefully examined for relationships with measurements of estuarine ecosystem performance. This will admittedly be a difficult task because records during the 1960's and early 1970's are quite incomplete by today's standards. However, there are observations available concerning dissolved oxygen concentrations in deep waters, fisheries yields, SAV distributions and the like. Significant relationships to loads have already been reported for metabolic rates from one portion of the estuary. The goal of this analysis would be to further refine estimates of load that are compatible with healthy estuarine ecosystem function.

During 1997 an ambitious and broad ***evaluation of littoral zone habitats*** was initiated in the lower 35 km of the Patuxent River estuary (mesohaline zone) concerning the suitability of this region for SAV growth and possible reintroduction. The stimulus for this program was the observation that substantial nutrient load reductions recently achieved in this system have led to improving water quality conditions with little or no resurgence in SAV. The goal of this program element was to accurately measure and characterize many of the complex and interacting parameters necessary for SAV growth and survival in this shallow water habitat. As part of the baseline assessment, a full suite of water quality parameters was measured along the salinity gradient of the estuary from April through October, 1997. Results of near shore water quality sampling indicate substantial temporal and spatial variation along the longitudinal axis of much of the Patuxent River. In general, water quality conditions were much better during the spring months of April, May and June, but deteriorated rapidly through the summer months. Although down river locations appear to have slightly better water quality conditions compared to up-river locations, overall most locations experienced water quality conditions for at least brief periods of time that do not meet estimated minimum habitat requirements for SAV growth and survival. In addition, first order estimates of epiphytic light attenuation during summer months suggested that after 20 days of exposure, epiphytic growth can potentially remove up to 80% of the available light reaching the leaves of SAV. Despite water quality conditions that overall were near or exceeded estimated limits for SAV growth and survival, certain early spring species of SAV were able to exist, and at some locations thrive, on the Patuxent River. These species complete their life cycle before water quality conditions become detrimental. The presence of substantial propagule flux of these early spring species suggest that the lack of SAV beds at historically vegetated sites is limited by water quality conditions not propagule availability, at least for this species. The 1997 monitoring provided baseline information about these near shore habitats; we recommend that additional monitoring be conducted to evaluate inter-annual variability since the success and growth of SAV requires consistent water quality conditions from year to year. Finally, since light availability is a critical requirement for SAV survival, we recommend a

more diversified study of SAV epiphyte light attenuation and hope to develop a simple and useful monitoring tool for SAV habitat evaluation.

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