UMCES

UNIVERSITY OF MARYLAND CENTER for ENVIRONMENTAL SCIENCE

CHESAPEAKE BAY
WATER QUALITY MONITORING PROGRAM
ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT #18 (INTERPRETIVE)

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1. INTRODUCTION

Almost two decades ago an historic agreement led to the establishment of the Chesapeake Bay Partnership whose mandate was to protect and restore the Chesapeake Bay ecosystem. Last year the signing of *Chesapeake 2000* incorporated very specific goals addressing submerged aquatic vegetation (SAV) restoration and protection and the improvement and maintenance of the water quality of Chesapeake Bay and its tributaries.

The first phase of the Chesapeake Bay Program was undertaken during 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 to the identification of problem areas. During this phase of the program 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 bay sediments. 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, 1997, 1998, 1999 and 2000). 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 program 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 that 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 were dominant followed by forest and urban sources; the "controllable" fraction of nutrient loads was about 47% for nitrogen and 70% for phosphorus; point source reductions were ahead of schedule and diffuse source reductions were close to projected reductions; further efforts were 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 indicated 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 to the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay. During this portion of the program, EPC has been further modified to include intensive examination of SAV habitat conditions in several regions of the Chesapeake Bay in addition to retaining long-term monitoring of sediment processes in the Patuxent estuary.

Chesapeake 2000 involves the commitment of the participants *"to achieve and maintain the water quality necessary to support aquatic living resources of the Bay and its tributaries and to protect human health."* More specifically, this Agreement focuses on: 1) living resource protection and restoration; 2) vital habitat protection and restoration; 3) water quality restoration and protection; 4) sound land use and; 5) stewardship and community engagement. Our current program, the Ecosystems Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring program, has activities that are aligned with the habitat and water quality goals described in this agreement.

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. A description of the complete monitoring program is provided in Magnien *et al.* (1987) and the Chesapeake Bay program web page (*http://www.chesapeakebay.net* and *http://www.dnr.state.md.us/bay/monitoring/eco/index.html*). In addition to the EPC program portion, the monitoring program also has components that measure:

1. Freshwater, nutrient and other pollutant input rates,
2. chemical and physical properties of the water column,
3. toxicant levels in sediments and organisms,
4. phytoplankton and zooplankton community characteristics (abundances, biomass and primary production rates) and
5. benthic community characteristics (abundances and biomass).

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

During the past two decades 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 distribution 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, especially light availability.

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 hypoxic or anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative and large short-term 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 that 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 of organic and nutrients 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 1-1. summarizes this conceptual eutrophication model where increased nitrogen (N) and phosphorus (P) loads result in a water quality degradation trajectory and reduced N and P loads lead to a restoration trajectory.

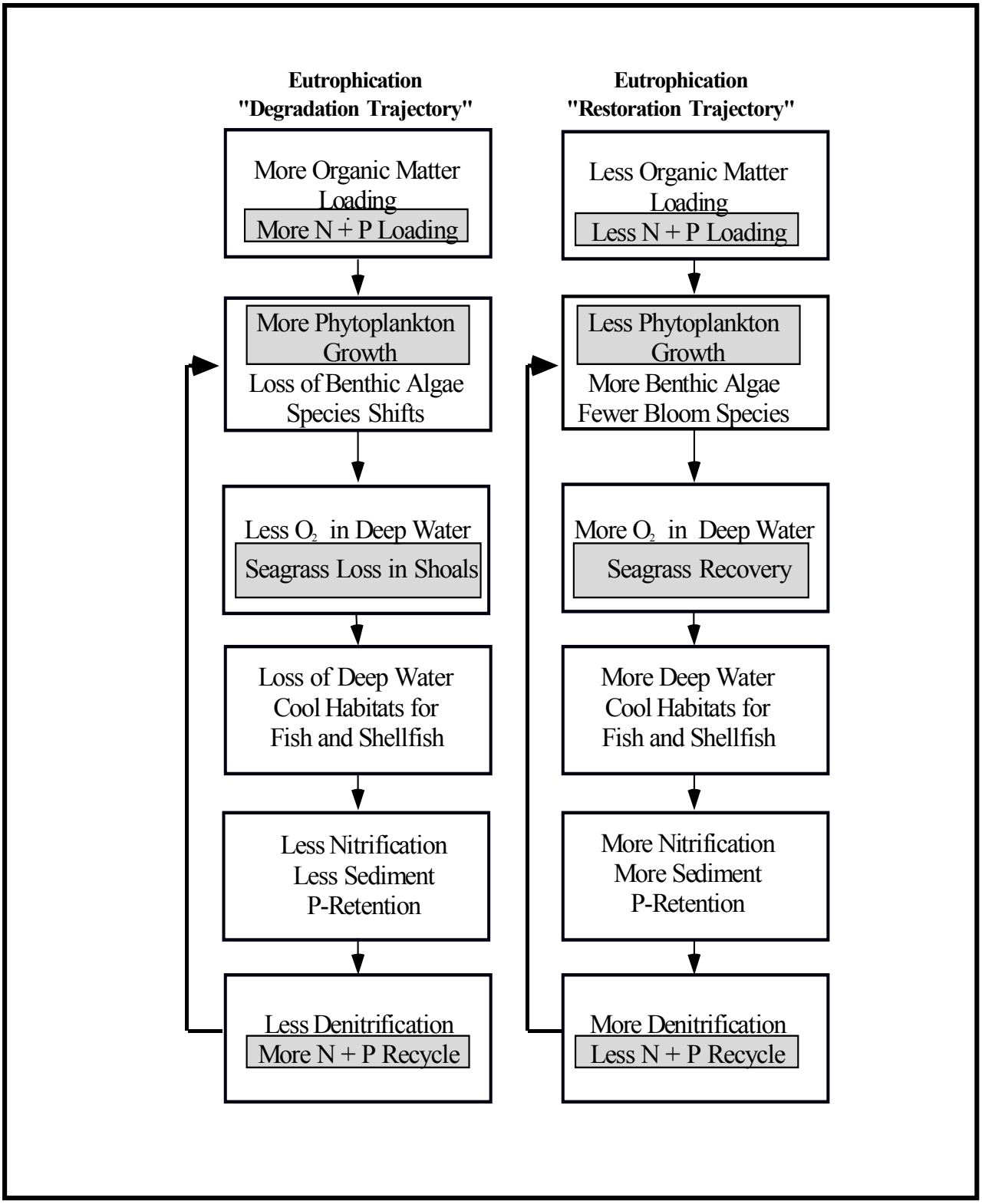

Figure 1-1. A simplified schematic diagram indicating degradation and restoration trajectories of an estuarine ecosystem. Lightly shaded boxes in the diagram indicate past and present components of the EPC program in the Patuxent River and Tangier Sound. (Adapted from Kemp, *pers. comm.*, HPEL)

Within the context of this model a monitoring study of sediment processes and SAV habitat conditions has been developed. The EPC has been gathering information since 1985. Initial program components included monitoring of Sediment-Water Oxygen and Nutrient Exchanges (SONE; 1985-1997) at multiple locations (8-10) in the bay and tributaries and monitoring of the vertical flux of sediments and organic particulates at one location in the mainstem bay (VFX; 1985-1992). More recently the SONE program was modified to a more spatially intensive effort focused on the Patuxent River (MINI-SONE program; 1996-1999). In 1992, 1995-1997 a small program was instituted at one location in the Patuxent River to monitor, at high measurement frequencies, dissolved oxygen conditions. Finally, extensive SAV habitat evaluations were initiated in the Patuxent River (1997-1999), were expanded to Tangier Sound during 1999 and further expanded in 2000 to also include the Magothy River. In all of these monitoring activities the working hypothesis is if nutrient and organic matter loadings decrease, the cycle of high organic deposition rates to sediments, sediment oxygen demand, release of sediment nutrients, continued high algal production, and high water column turbidity will also decrease. As a result, the potential for SAV recolonization will increase and the status of deep water habitats will improve.

1.2 Objectives of the Water Quality Monitoring Program

The EPC of the Maryland Chesapeake Bay Water Quality Monitoring Program conducted monitoring of sediment-water oxygen and nutrient exchanges (MINI-SONE), and evaluated habitat conditions relative to SAV reintroduction. The Patuxent and Magothy River estuaries and Tangier Sound, where EPC efforts were concentrated during the year 2000, are areas of particular interest because substantial reductions in nutrient loading rates have been achieved in one system and SAC community status is of high concern in the others.

The EPC has undergone program modification since its inception in 1984 but its overall objectives are consistent with those of other Monitoring Program Components:

1. Characterize the present status of the Patuxent River estuary (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and sediment oxygen consumption rates.

2. Determine the long-term trends that develop in sediment-water nutrient exchanges and sediment oxygen consumption rates in response to pollution control programs in the Patuxent River estuary.

3. Evaluate near-shore water quality conditions relative to SAV habitat across a range of spatial and temporal scales in the Patuxent and Magothy River estuaries and Tangier Sound.

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

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2. SEDIMENT-WATER OXYGEN AND NUTRIENT EXCHANGES: MINI-SONE

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

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2.1 Introduction and Background

More than a decade of monitoring has shown that nutrient regeneration and release by sediments in many estuaries can be a significant internal source of nutrients to the water column (*e.g.* Boynton *et al*., 1995; Boynton *et al*., 1998). Moreover, sediment nutrient releases have significant potential to negatively affect water quality and living resources. The utilization and regeneration of nutrients within an estuary is governed by processes that are both spatially and temporally variable. The EPC program has focused sediment flux monitoring on monthly temporal scales but more recently, also on finer spatial scales (1-10 km between stations). To evaluate an estuary's response to changes in external nutrient loading (especially reductions), it is important to collect data on appropriate spatial and temporal scales. Previous studies have shown that the highest nutrient releases by sediments occur during the summer months (Boynton *et al.*, 1988). Sediment-water oxygen and nutrient exchange (SONE) measurements were made at monthly intervals during warm periods of the year at fixed-location stations thereby providing reasonable temporal resolution but only a limited indication of spatial variability.

Beginning in 1996, the EPC adopted new techniques that increased the spatial resolution of measurements in the Patuxent River. Six additional sediment-water exchange stations were added to four long-term stations to provide a better assessment of the range of conditions found within the Patuxent River estuary. In order to be cost effective, sediment-water exchanges at these new stations were measured with an abbreviated technique called MINI-SONE, in which a single sediment core was monitored instead of the traditional SONE technique, in which three

replicate cores and a blank core were monitored. Previous studies had shown that variation among replicate cores from a single location was small compared to variation among sites. Therefore, it was believed additional stations would provide a more accurate assessment of sediment-water exchanges across the estuary as a whole, and thus be more useful for evaluating the river's response to nutrient management strategies.

In 1998, 1999 and 2000 traditional SONE measurements (with replication) were not made at the four long-term monitoring stations (BUVA [Buena Vista], MRPT [Marsh Point], BRIS [Broomes Island], and STLC [St. Leonard Creek]) on the Patuxent River. Instead, these stations were measured with the abbreviated MINI-SONE technique. These data were then merged with previous data sets for the calculation of status and trends at the four long-term monitoring stations.

2.2 Station Locations for MINI-SONE Long-term Patuxent River Station Locations

Four stations, St. Leonard Creek (STLC), Broomes Island (BRIS), Marsh Point (MRPT) and Buena Vista (BUVA) were previously monitored using the full suite of measurements referred to as SONE. These sites are now referred to as the long-term monitoring stations and are monitored using an abbreviated MINI-SONE approach. Station locations sampled during 2000 are shown in Figure 2-1 (See also Table 2-1) as are nearby water quality monitoring stations.

2.3 Sampling Frequency for MINI-SONE

The sampling frequency for MINI-SONE 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). Previous studies also indicated 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 and shallow *vs.* deep areas). In light of these results, the monitoring design adopted for MINI-SONE studies involves three monthly measurements at four stations in July, August and September 2000. Sampling dates for these cruises together with alpha-numeric cruise identification codes can be found in Table 2-2.

2.4 Field Methods for MINI-SONE

2.4.1. Water Column Profiles

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

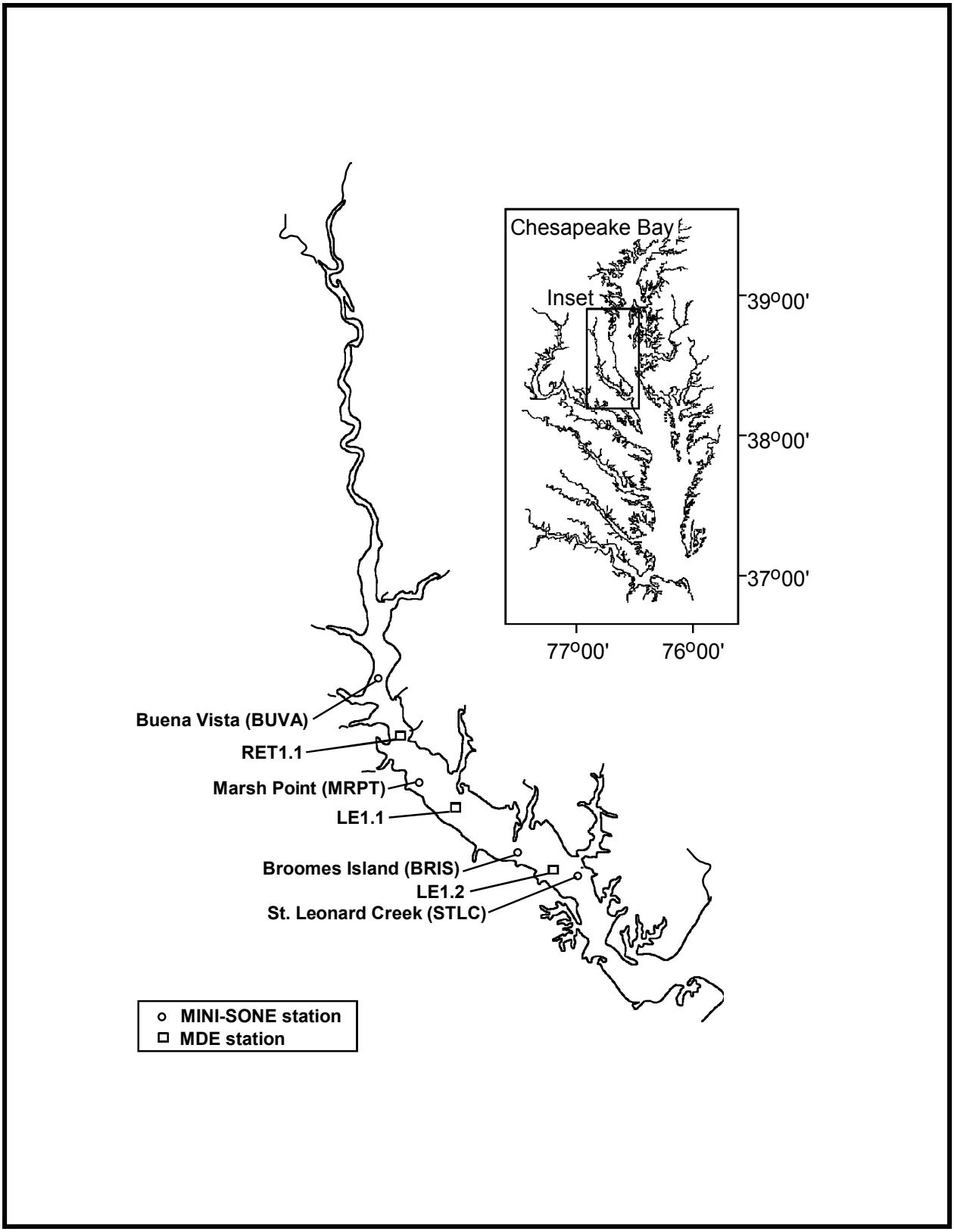


Figure 2-1. Location of four MINI-SONE Stations sampled in the Patuxent River, MD.
Location of stations shown here do not reflect exact geographic locations (See Table 2-1)..

Table 2-1. MINI-SONE Station Code, Grid Location and Nearest MDE Station

STATION CODE	LATITUDE (DGPS) NAD 83	LONGITUDE (DGPS) NAD 83	STATION DEPTH (m)	CHESAPEAKE BAY STATION	BAY SEGMENT
Patuxent River					
BUVA	38° 31.050’	76° 39.783’	5.8	RET1.1	RET1
MRPT	38° 26.767’	76° 37.900’	5.2	LE1.1	LE1
BRIS	38° 23.600’	76° 33.067’	15.0	LE1.2	LE1
SLTC	38° 22.817’	76° 30.067’	7.0	LE1.2	LE1

Table 2-2. MINI-SONE Cruise Identifier

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
MINI-SONE 17	JUN 2000	JUN 12	JUN 16	Orion
MINI-SONE 18	JUL 2000	JUL 7	JUL 19	Orion
MINI-SONE 19	AUG 2000	AUG 8	AUG 14	Orion
MINI-SONE 20	SEP 2000	SEP 9	SEP 13	Orion

2.4.2 Water Column Nutrients

Near-bottom (approximately 1/2 meter above the bottom) 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 ($NO_2^- + NO_3^-$) and dissolved inorganic phosphorus corrected for salinity (DIP or PO_4^{-3}).

2.4.3 Sediment Profiles

At each MINI-SONE station an intact sediment core is used to measure the redox potential (Eh) of the sediment porewater. Sediment redox (mV) is measured at the sediment surface, one and 2 centimeters below the surface and every 2 centimeters thereafter to 10 cm depth. Additionally, surficial sediments are sampled for total and active sediment chlorophyll-*a* to a depth of 1 cm. Particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), are sampled to a depth of 1 cm.

2.4.4 Sediment Flux Measurements

The protocols used in MINI-SONE flux estimates are an abbreviated set of measurements of the standard SONE techniques. MINI-SONE stations use a single sediment core with no blank.

Intact sediment cores constitute a benthic microcosm where changes in oxygen, nutrient and other compound concentrations are determined.

A single intact sediment core is 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 from 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 2-2). 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.

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 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 ($NO_2^- + NO_3^-$) 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.

2.4.5. Chemical Analyses used in MINI-SONE Element

Methods for the determination of dissolved and particulate nutrients are as follows: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), and dissolved inorganic phosphorus (DIP or PO_4^-) are measured using the automated method of EPA (1979); particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using an 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 Parsons *et al.* (1984) are followed for chlorophyll-*a* analysis.

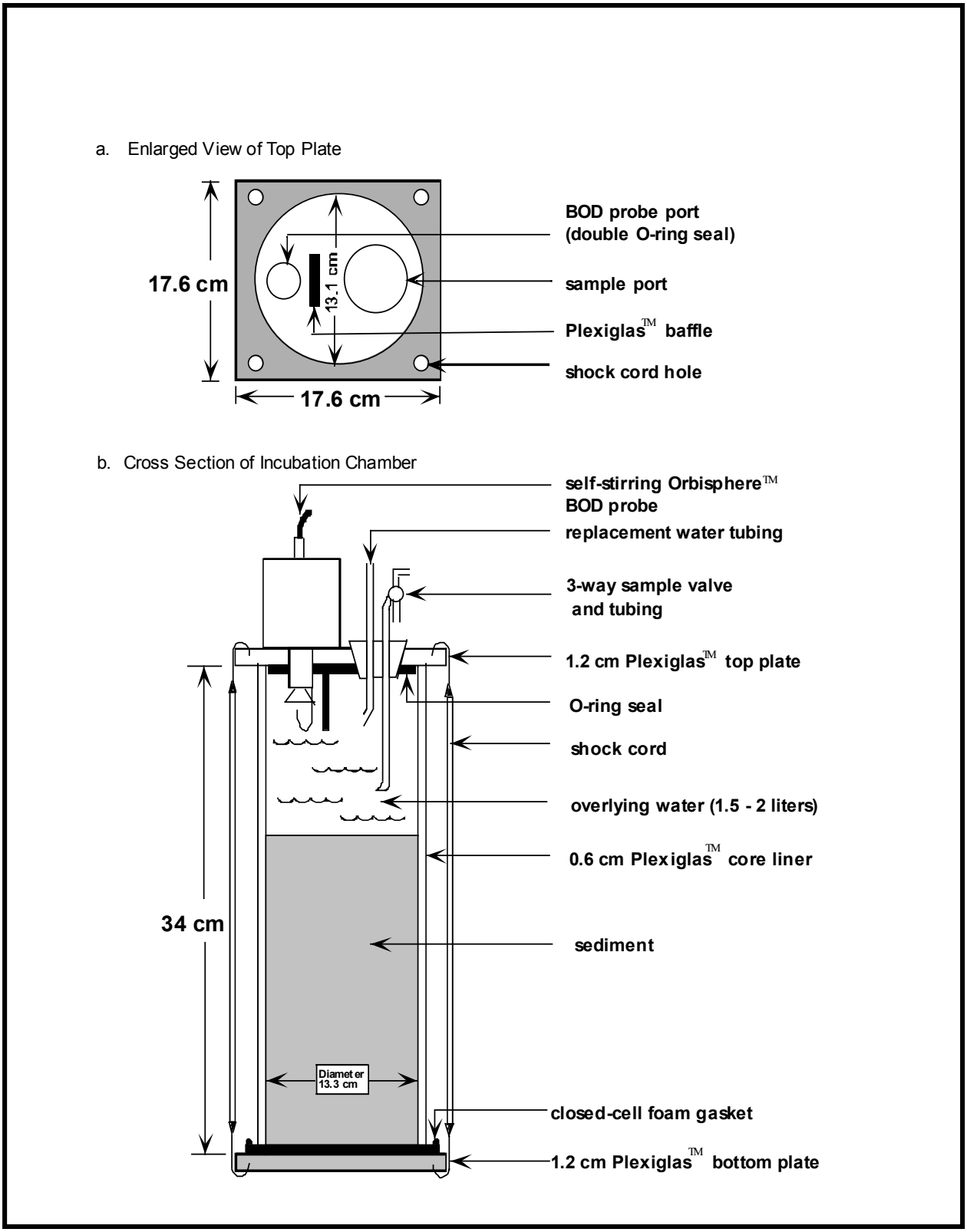


Figure 2-2. Schematic Diagram of the Incubation Chamber
a. Enlarged View of Top Plate.
b. Cross Section of Incubation Chamber

2.5. River Flow

In the Patuxent River, and in other coastal plain estuaries, river flow is often a good indicator of several important external forcing functions that influence estuarine conditions. River flow influences temperature and salinity patterns, circulation and nutrient loading rates. However, not only is the magnitude of river flow important, but also the timing of flow events that can affect such processes as nutrient uptake and subsequent deposition of phytodetritus. An examination of inter-annual and monthly flow patterns helps explain variation in estuarine processes such as sediment-water exchanges. Annual average Patuxent river flow was 315 cfs in 2000, 280 cfs in 1999, 437 cfs in 1998, 412 cfs in 1997 and 704 in 1996; all but 1999 and 2000 were higher than the long-term average of 375 cfs (Figure 2-3.a.). The patterns of monthly average river flow differed significantly during recent years.

Late-winter and spring flows during 2000 were modest compared to a wet spring such as 1998. In 1998 peak monthly river flow occurred in March (1131 cfs), while in 2000 the peak flow occurred in April (581 cfs, Figure 2-3.b.). Because many estuarine processes respond to nutrient loading on time scales of weeks to months, the timing of flow events can be an important consideration. For example, Patuxent river flow was higher during the spring of 1998 compared to 1999 or 2000. In addition, differences in flow also affect the spatial variation found in the river. High flow conditions tend to transport important processes, such as the chlorophyll-*a* maximum, down river compared to lower flow years (Boynton and Kemp, 2000). This may also affect the deposition of labile material to the sediment surface, which in turn affects sediment-water exchanges.

2.6 MINI-SONE Sediment-Water Oxygen and Nutrient Fluxes: 2000 Patuxent River Study

Monthly average sediment-water fluxes derived from the complete sediment-water oxygen and nutrient exchanges (SONE) data set (1985 - 1997) are summarized using box and whisker plots (Figures 2-4.1 through 2-4.4) for four flux variables: sediment oxygen consumption (SOC), ammonium (NH_4^+), nitrite plus nitrate ($NO_2^- + NO_3^-$), and phosphate (PO_4^-). Data collected at four stations in the Patuxent River were used to construct these plots. Two stations, Buena Vista (BUVA) and St Leonard Creek (STLC) were sampled during a period of thirteen calendar years (1985 through 1997) while the remaining two stations, Marsh Point (MRPT) and Broomes Island (BRIS), were sampled during a period of nine years (1989 through 1997). 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 mouth (St. Leonard Creek [STLC]). Superimposed on these graphs are the single MINI-SONE flux measurements made at these four stations during 2000.

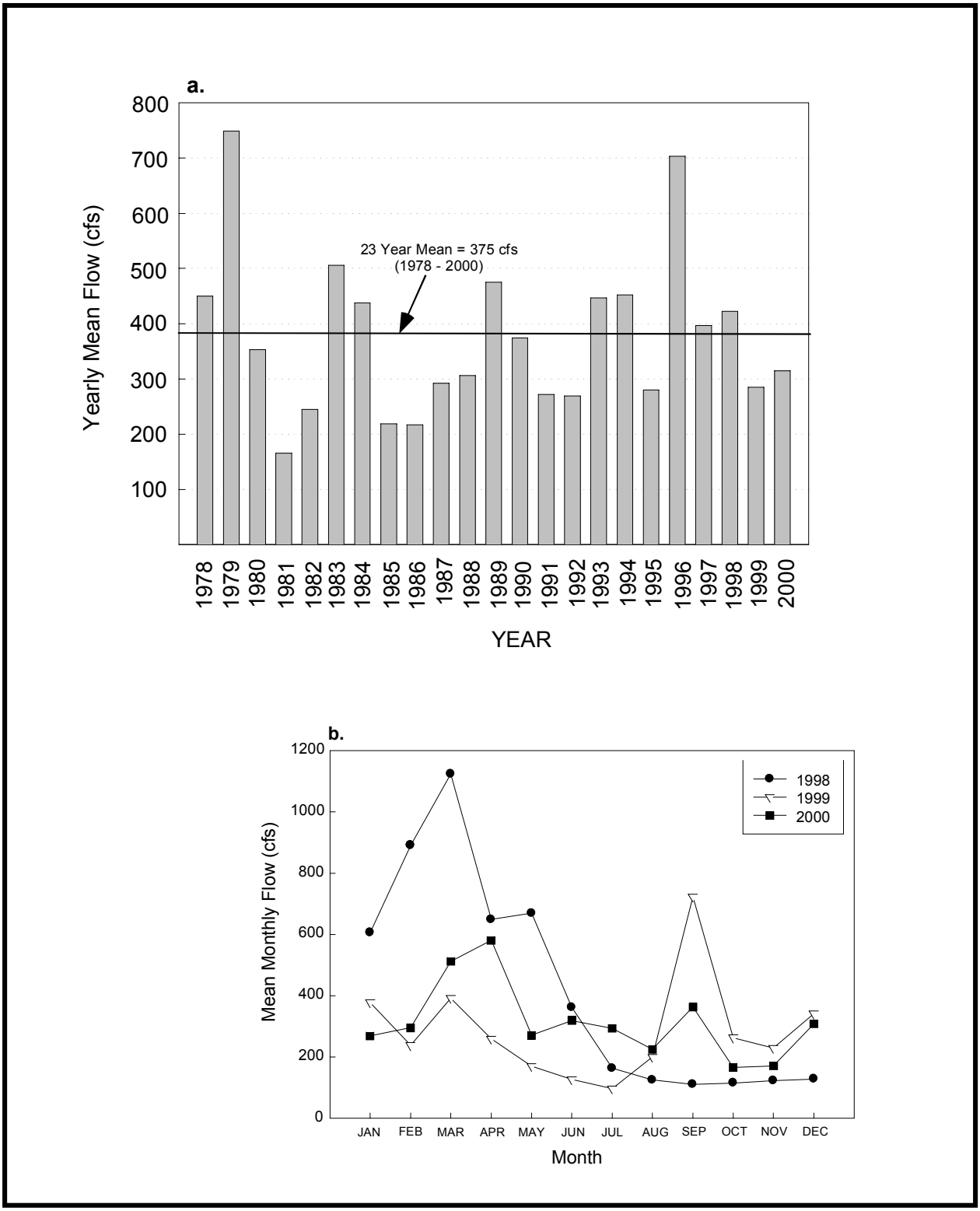


Figure 2-3. (a) Patuxent River average annual river flow for the period 1978 through 2000 (calendar year), at USGS station, 01594440 Patuxent River near Bowie, MD.

(b) Patuxent River average monthly river flow from 1998 through 2000 (calendar year), at USGS station, 01594440 Patuxent River near Bowie, MD.

Construction of 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 (0) 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. In Figure 2-4 the complete SONE flux data set was used to produce the box and whisker plots. The bold solid dots indicate a single flux measured during the MINI-SONE study 2000.

2.6.1 Sediment Oxygen Consumption (SOC)

The magnitude of 2000 SOC observations was generally similar to those observed in previous years. Specifically, at stations where bottom water dissolved oxygen concentrations tend to be depressed during summer months, SOC rates are also generally depressed, as expected due to the influence of low dissolved oxygen concentrations (< 2.0 mg l^{-1}) on SOC rates (*e.g.* July, August and September at MRPT). The year 2000 was an intermediate flow year. In dry years, with low river flow, dissolved oxygen concentrations in deep waters tend to be more elevated than usual. Relatively elevated summer bottom water dissolved oxygen conditions result from a complex interaction between water column stratification (less in years of low flow thereby allowing for more atmospheric reaeration of bottom waters via mixing) and more limited amounts of organic matter reaching deep waters and sediments (because of reduced nutrient delivery from diffuse sources and hence lower rates of algal biomass accumulation and subsequent deposition). Higher than normal dissolved oxygen concentrations in bottom waters (> 1.0 mg l^{-1}) were observed at Buena Vista (BUVA) and St. Leonard Creek (STLC) during June through September, 2000 and SOC rates were elevated at St. Leonard Creek (STLC).

2.6.2 Ammonium (NH_4^+) Fluxes

Ammonium fluxes recorded in 2000 generally followed temporal trends exhibited in previous years but higher than normal releases were noted at several stations. Fluxes tended to peak in July or August and decline during the latter portion of the summer. The general magnitude of ammonium fluxes during 2000 tended to be above the long-term mean at all Patuxent stations. Fluxes were particularly large at BUVA and MRPT, the two stations most proximal to the fall line nutrient sources. Ammonium fluxes were closer to average but still high at the more down river stations (BRIS and STLC). Increased ammonium fluxes suggests a increase in the organic matter supply rate to sediments which probably reflects nutrient loading rates during the winter and spring of 2000.

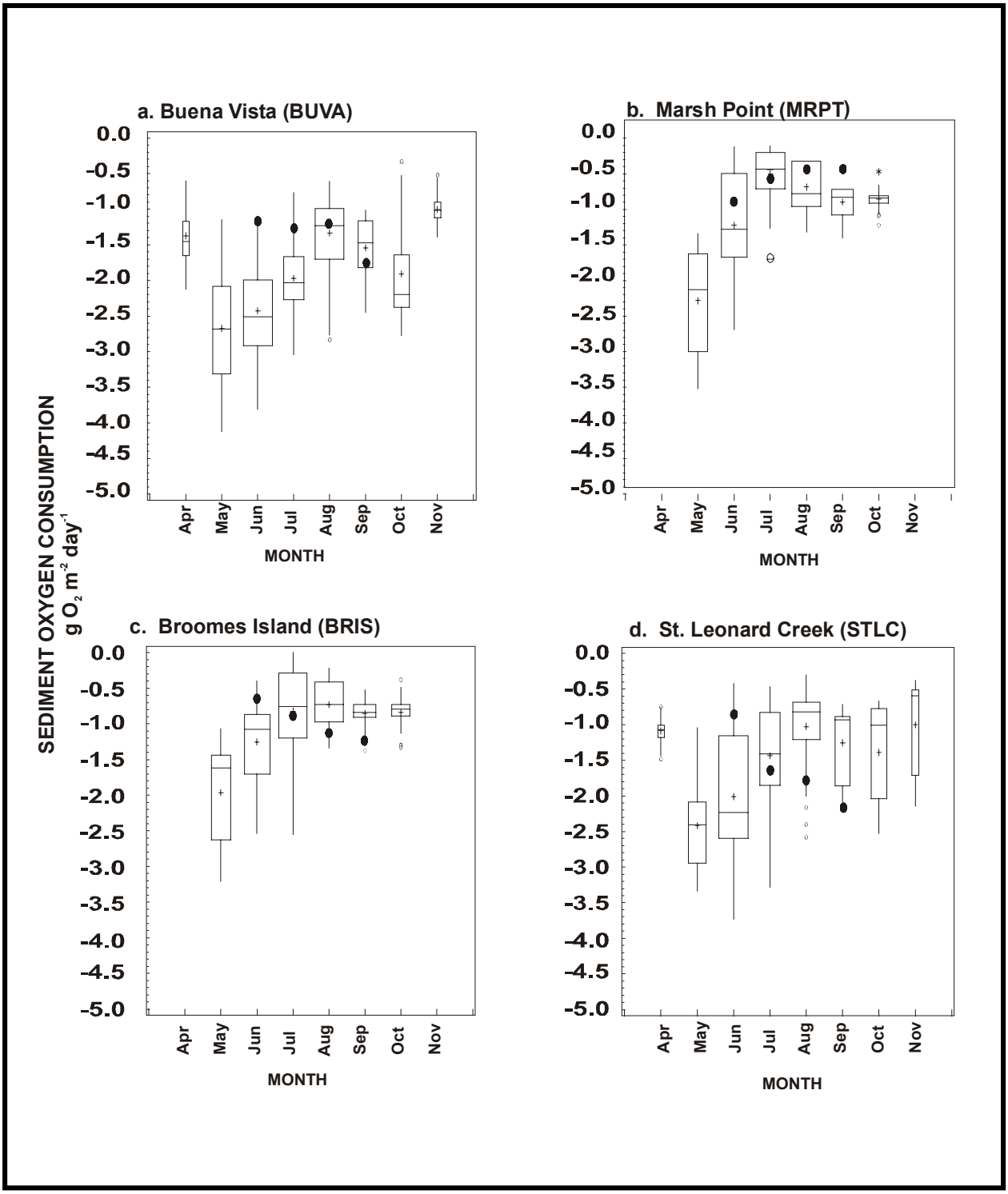


Figure 2-4.1. Box and whisker plots for sediment oxygen consumption (SOC) rates for April to November at four SONE stations located in the Patuxent River.
(a) Buena Vista [BUVA] (b) Marsh Point [MRPT] (c) Broomes Island [BRIS] and (d) St. Leonard Creek [STLC].

The complete SONE flux data set was used to produce 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 of data (1991 through 1997). The bold solid dots indicate a single flux measured during the MINI-SONE study 2000. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined here as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

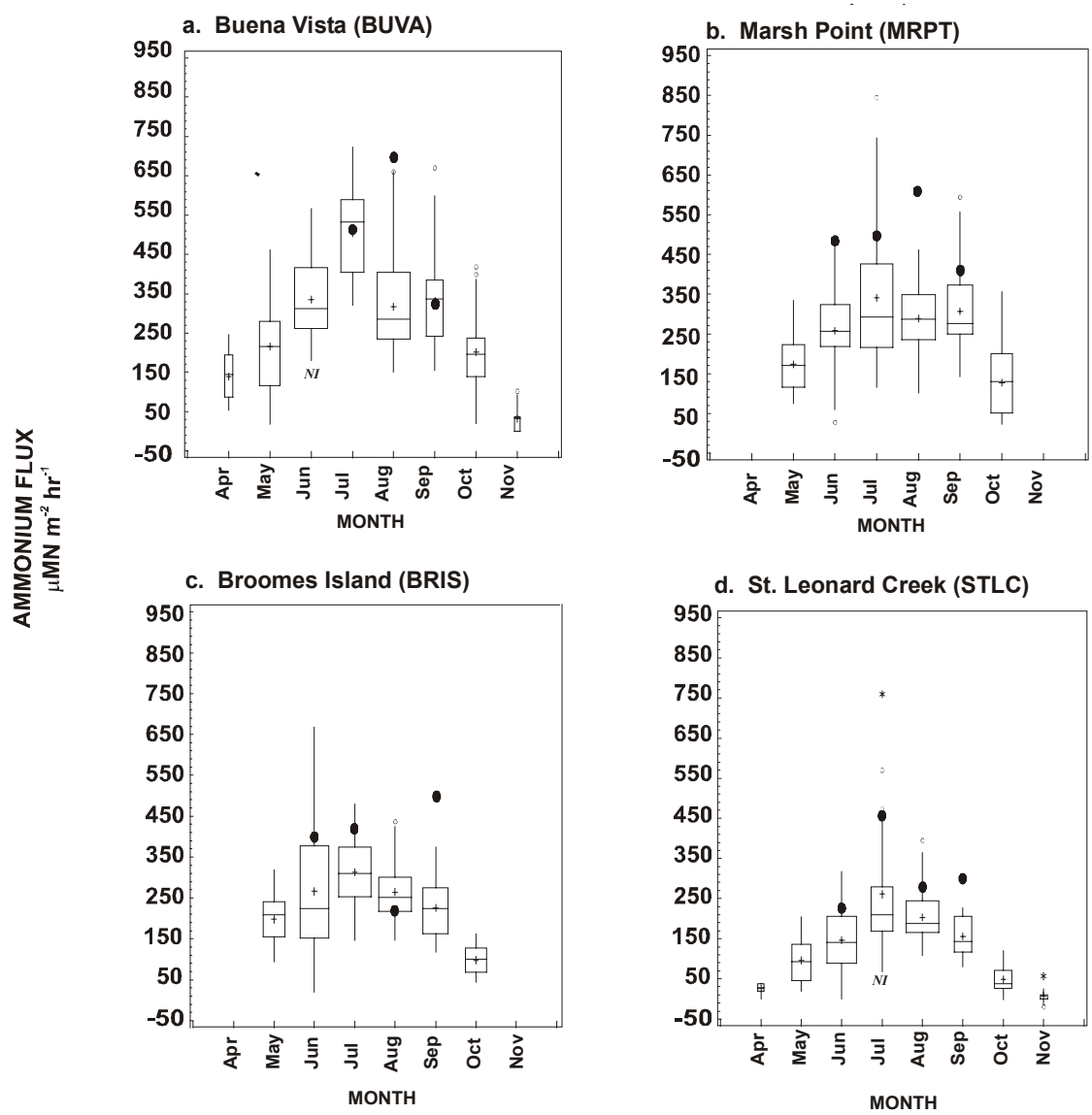


Figure 2-4.2. Box and whisker plots for ammonium (NH_4^+) flux rates for April to November at four SONE stations located in the Patuxent River.
(a) Buena Vista [BUVA] (b) Marsh Point [MRPT] (c) Broomes Island [BRIS] and (d) St. Leonard Creek [STLC].

The complete SONE flux data set was used to produce 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 a single flux measured during the MINI-SONE study 2000. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined here as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.
NI indicates that the data were not interpretable.

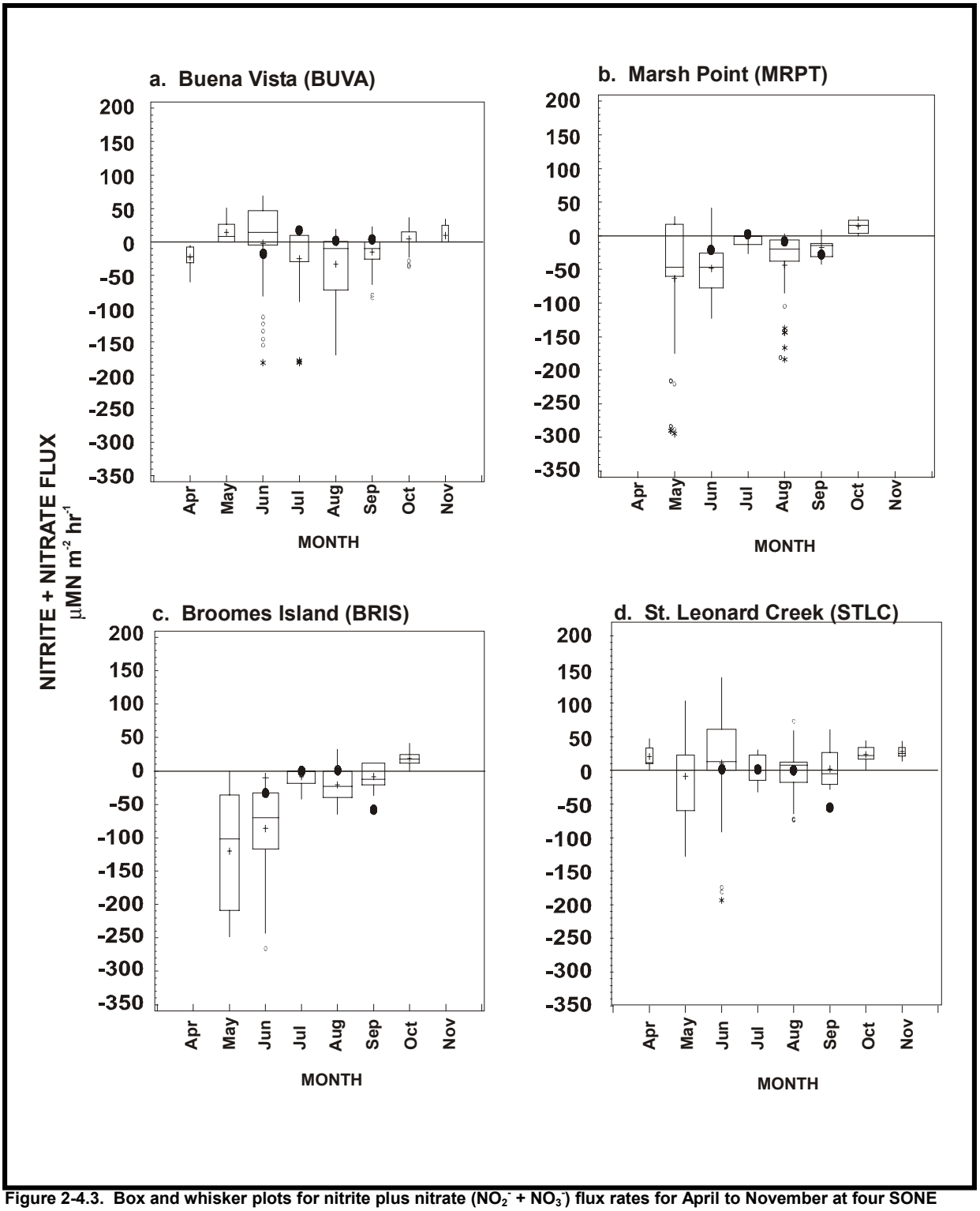


Figure 2-4.3. Box and whisker plots for nitrite plus nitrate (NO_2^- + NO_3^-) flux rates for April to November at four SONE stations located in the Patuxent River.
(a) Buena Vista [BUVA] (b) Marsh Point [MRPT] (c) Broomes Island [BRIS] and (d) St. Leonard Creek [STLC].

The complete SONE flux data set was used to produce 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 a single flux measured during the MINI-SONE study 2000. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined here as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.

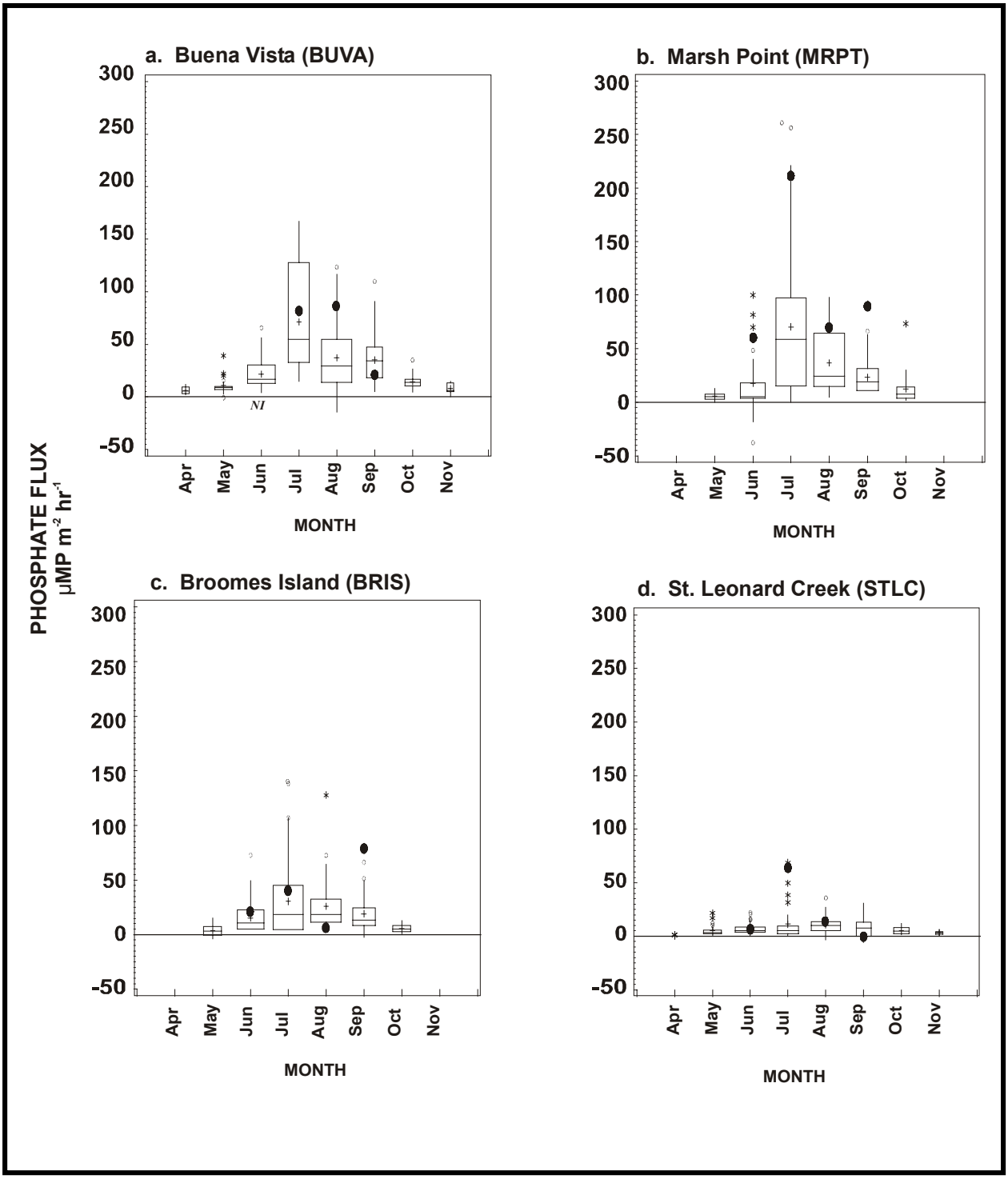


Figure 2-4.4. Box and whisker plots for phosphorus (PO_4^{-3} or DIP) flux rates for April to November at four SONE stations located in the Patuxent River.
(a) Buena Vista [BUVA] (b) Marsh Point [MRPT] (c) Broomes Island [BRIS] and (d) St. Leonard Creek [STLC].

The complete SONE flux data set 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 a single flux measured during the MINI-SONE study 2000. Negative values indicate fluxes from water to sediment. Occasionally hypoxic stations are Broomes Island (BRIS) and Marsh Point (MRPT). Hypoxia is defined here as less than 1.0 mg l^{-1} dissolved oxygen in bottom waters.
NI indicates that the data were not interpretable.

2.6.3 Nitrite plus Nitrate ($NO_2^- + NO_3^-$) Fluxes

In general, nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes do not constitute a large fraction of the nitrogen exchange between estuarine sediments and bottom waters. On occasion, large fluxes from water to sediments or from sediments to water do occur. Most fluxes during 2000 were small or zero, while in September at three of the four stations moderate negative flux from water to sediment was observed.

Even small nitrite + nitrate ($NO_2^- + NO_3^-$) fluxes from sediments to overlying waters provide a useful indication of sediment conditions. Specifically, production and release of nitrite plus 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 2000 (an intermediate flow year), most nitrite plus nitrate fluxes were very small and close to the long-term average, indicating moderately good sediment quality conditions. During 1998 (a wet spring) only 5 of 16 flux measurements were indicative of sediment nitrification. To provide additional contrast, during 1996 (an exceptionally high flow year) the overwhelming pattern was nitrite plus nitrate flux ($NO_2^- + NO_3^-$) from water to sediments which was to be expected during a wet year when water column nitrite plus nitrate ($NO_2^- + NO_3^-$) concentrations were high. During 1995, a very low flow year, stations in the Patuxent River exhibited relatively high rates of sediment nitrate release. In fact, at the St. Leonard Creek (STLC) station sediments released nitrite plus nitrate through the entire monitoring period, a pattern never before observed. During 1999 (another very dry year) nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes were predominately positive (12 of 16 fluxes were from sediments to water). These are the types of nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes to be expected under reduced nutrient load conditions (as was the case in 1995 and 1999) both because these conditions favor improved dissolved oxygen conditions in deep waters and sediments and lower concentrations of nitrite plus nitrate ($NO_2^- + NO_3^-$) in overlying waters. The direction and magnitude of nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes between sediments and overlying waters appears to serve quite well as an indicator of sediment quality.

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

The spatial and temporal patterns of phosphorus flux in the Patuxent River in 2000 are consistent with the conceptual model of factors controlling these fluxes. At both BUVA and MRPT fluxes were elevated and about average at the other two stations. During 1999, very low phosphate fluxes were observed at stations having modest to high dissolved oxygen concentrations in bottom waters, emphasizing the strong control dissolved oxygen concentrations have on phosphorus releases from sediments. When bottom water dissolved oxygen concentrations are even somewhat elevated (>1.5 mg l^{-1}) phosphorus is bound by iron oxides at the sediment surface and not released to overlying waters.

2.7 Comparisons Among Sediment-Water Exchanges during 1998-2000

Average summer sediment oxygen consumption (SOC) decreased slightly at two of the four stations (*i.e.* BUVA and BRIS) between 1999 and 2000 although the decrease was small and

probably not environmentally important, however the change was large at one station, MRPT (Figure 2-5.a.). Fluxes in SOC rates during 1998 and 2000 were quite low (0.6 - 09 g O_2 m^{-2} day^{-1}) compared to 1999 (1.7 g O_2 m^{-2} day^{-1}) the large difference in SOC was probably caused by differences in bottom water DO conditions among these years. In 1999, DO was elevated during the summer period probably in response to a severe drought. As we have pointed out in a previous report (Boynton *et al.*, 1998), SOC rates are suppressed by low oxygen levels (1998 and 2000) and enhanced at high oxygen levels (1999). In general, the approximate ranking of SOC rates among stations during 1998 - 2000 was similar to the long term pattern. For example, those stations with higher SOC rates were also those stations having high bottom water DO conditions (*i.e.*, BUVA and STLC). Those stations with low SOC rates had lower DO conditions. Overall, the magnitude of SOC rates was larger in 1999 (- 1.388 mg O_2 m^{-2} day^{-1}) compared to 1998 (- 1.293 mg O_2 m^{-2} day^{-1}) but there was no significant difference found between these two years (paired t-test, $P = 0.57$).

Overall the mean ammonium flux in 2000 was significantly higher than in 1998 and 1999 (Figure 2-5.b.). At all stations, ammonium flux was greater than 1998 and 2000 than in the drought year of 1999 and was likely due to differences in river flow and nutrient loading to the system between years. Not only does river flow affect the magnitude of these fluxes, but it also affects variation among stations. For example, in 1998 (which was a high flow year compared to 1999) the standard error for ammonium flux among stations was 63.6 μM N m^{-2} hr^{-1} compared to 42.1 μM N m^{-2} hr^{-1} in 1999.

Nitrite plus nitrate (NO_2^- + NO_3^-) flux among MINI-SONE stations in 2000 at most stations indicated uptake of nitrogen by the sediments. Summer mean values ranged from a positive flux of 1.7 μM N m^{-2} hr^{-1} out of the sediment at station BUVA to a value of –59.4 μM N m^{-2} hr^{-1} into the sediment at BRIS (Figure 2-5.c). Taking all stations into consideration, mean nitrite plus nitrate flux was more negative (into the sediment) in 2000 (+ 9.109 μM N m^{-2} hr^{-1}) compared to 1998 (-8.028 μM N m^{-2} hr^{-1}; paired t-test, $P < 0.05$). These fluxes were constantly positive (from sediment to water) during the 1999 drought year. This pattern is thought to have resulted because of higher DO concentrations in deep waters typically associated with low flow drought years.

Mean phosphate (PO_4^{-3}) flux increased in 2000 compared to 1999 (Figure 2-5.d). This was likely the result of an increase in river flow and loading to the estuary and a decrease in DO concentrations at the sediment-water interface. The maximum mean phosphate (PO_4^{-3}) flux was 104.85 μM P m^{-2} hr^{-1} at Marsh Point (MRPT) station, which was also the station having low DO conditions (<0.80 mg l^{-1}) during July through September, 2000.

Results of flux measurements made during 1998 - 2000 (*e.g.* Figure 2-5.a.- 2-5.d.) largely support the notion that oxygen conditions near the sediment-water interface play a strong role in regulating the magnitude and characteristics of these exchanges *e.g.* 1998 and 2000 were wet years while 1999 was a drought, as a result of this oxygen conditions in deep waters were generally low in 1998 and 2000 and higher in 1999. Sediment oxygen consumption (SOC; at most stations), ammonium flux (NH_4^+; at all stations), nitrite plus nitrate (NO_2^- + NO_3^-; at all stations) and phosphate (PO_4^{-3}; at most stations) reflected this pattern of flow, associated nutrient load and *in situ* oxygen conditions.

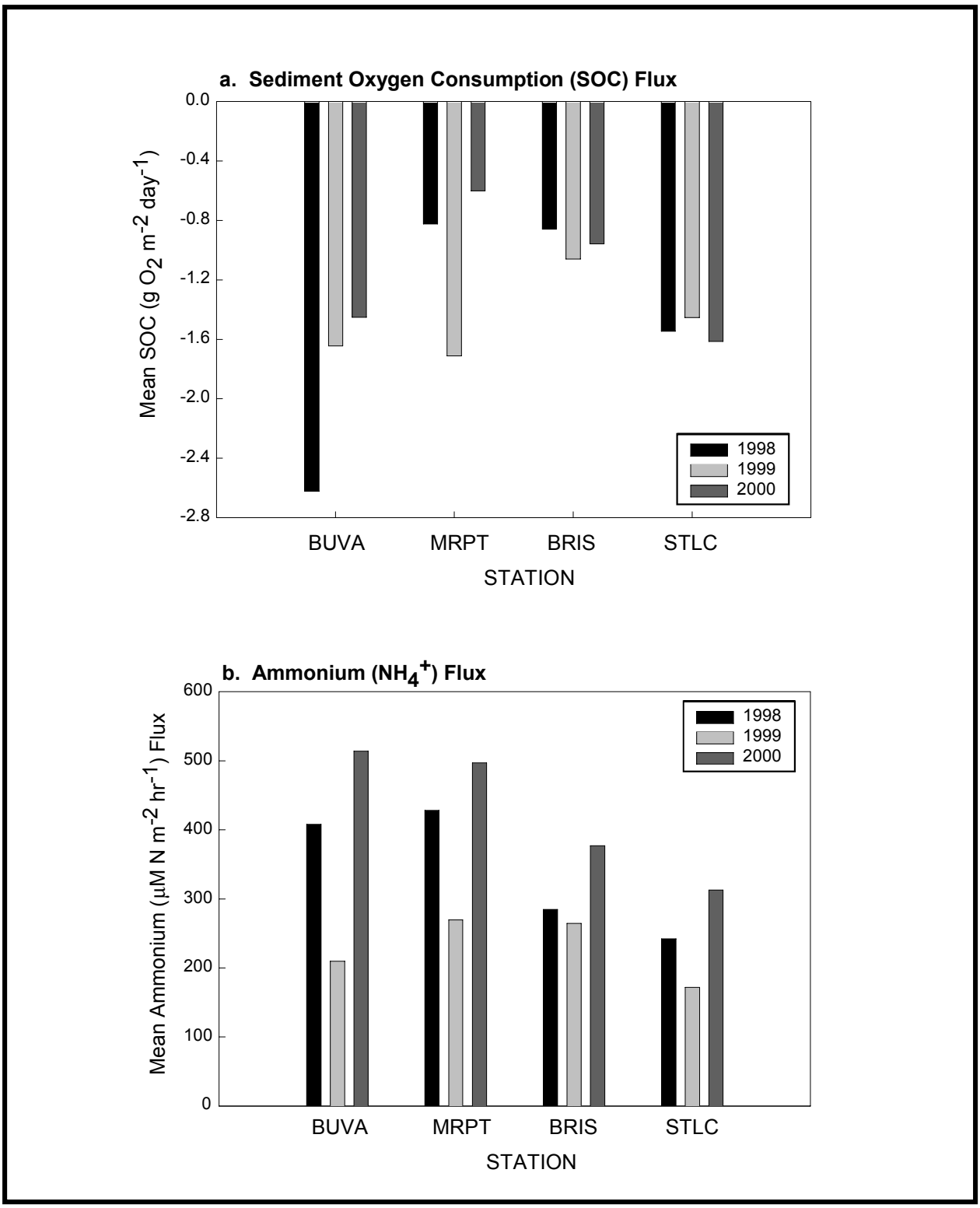
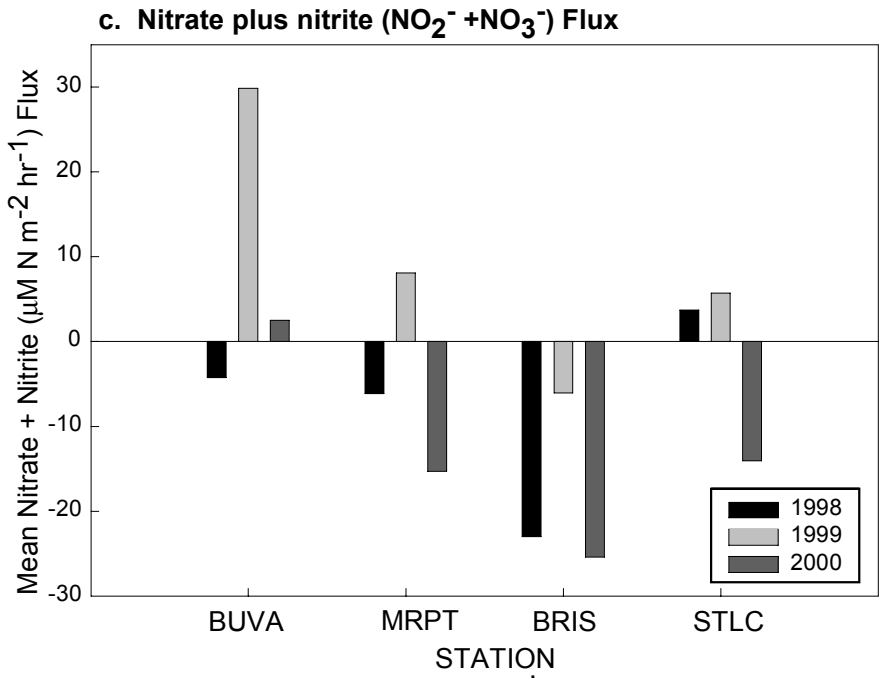


Figure 2-5. Comparison of Patuxent River MINI-SONE mean flux values calculated from monthly measurements from June through September 1998 - 2000 for:

a. sediment oxygen consumption (SOC), and

b. ammonium (NH_4^+) flux.



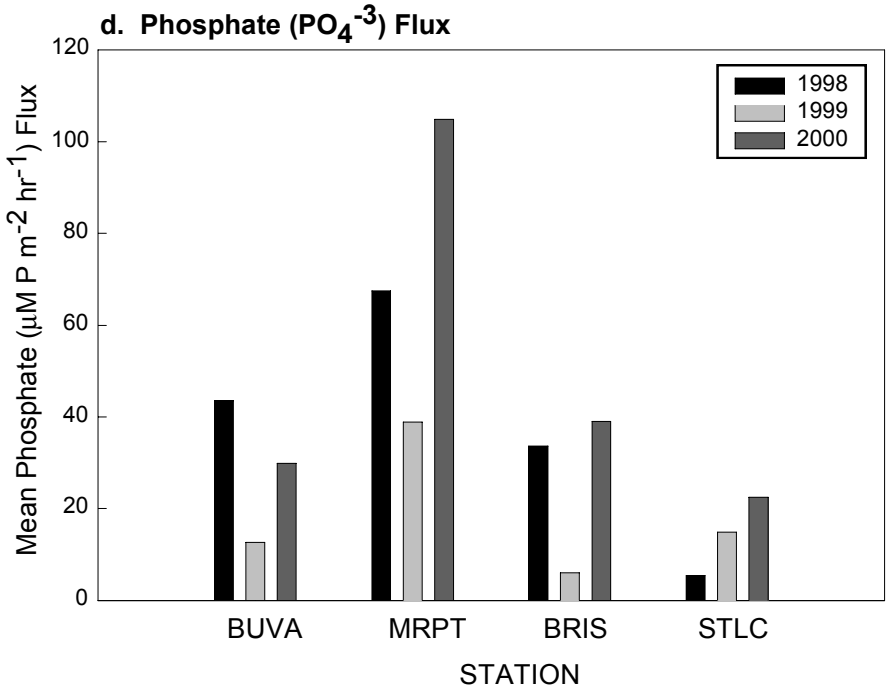


Figure 2-5. Comparison of Patuxent River MINI-SONE mean flux values calculated from monthly measurements from June through September 1998 - 2000 for:
c. nitrite plus nitrate (NO_2^- + NO_3^-), and
d. phosphate (PO_4^{-3}) flux.

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3. SEDIMENT-WATER FLUX STATUS AND TRENDS:

2000 PATUXENT RIVER STUDY

W.R. Boynton and F.M. Rohland

3. SEDIMENT-WATER FLUX STATUS AND TRENDS: 28

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With the signing of *Chesapeake 2000* a commitment was made to continue efforts to achieve and maintain the 40 percent nutrient reduction goal agreed to in 1987, as well as some additional goals which will be adopted for the tributaries south of the Potomac River. Its major goal is " to achieve and maintain the water quality necessary to support the aquatic living resources of the Bay and its tributaries and to protect human health." A part of the Ecosystem Processes Component (EPC) Program was also designed to examine the sediment-water flux data in order to 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.*, 1995). These figures included monthly average data covering the first ten years of the monitoring program (1985 - 1994) collected from 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 (1998) 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 stations and to evaluate the Patuxent River data set for interannual trends.

3.1 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 (Perry, *pers. comm.*). The status of each station is determined by comparison to a benchmark data set comprised of all flux data for the years 1985-1990 collected by the SONE program. The SONE program has no counterpart in the Virginia section of the bay so the data from Maryland are the only data used in the benchmark data set.

Each station is rated as poor, fair, or good relative to the benchmark data. These ratings were obtained as follows.

1. For each parameter in the benchmark data set, a transformation is chosen that yields a distribution that is symmetric and reasonably well approximated by the logistic cumulative distribution function (CDF). For the flux parameters, a signed square root transformation was used for all parameters except SOC for which a signed fourth root transformation was used.

2. A logistic CDF based on the mean and variance of each parameter of the benchmark data set is used to perform a probability integral transform on all data in the most recent 3-year period. This results in data in the interval (0,1) which follows a uniform distribution.

3. The 3 year median of this 0-1 data is computed as an indicator of status in the current three year period. The median of n observations taken from a uniform distribution follows a Beta distribution (a symmetric, two parameter distribution) with parameters (m,m) where m = (n+1)/2.

   The Beta distribution is a two parameter distribution whose density function is defined by the mathematical expression (Patel *et al.*, 1976):

$$f(x;a,b) = \frac{x^{a-1}\ (1-x)^{b-1}}{B(a,b)} \qquad 0 < x < 1,\ a > 0,\ b > 0$$

   The function B(a,b) is a beta function which is defined in terms of the gamma function as follows:

$$B(a,b) = \frac{\Gamma(a) \quad \Gamma(b)}{\Gamma(a+b)}$$

If the argument of the gamma function is a positive integer greater than 1, then the gamma function is define as a factorial:

$$\Gamma(a) = (a-1)!$$

which is the definition needed for this application. On other parts of its domain the gamma function is defined by a definite integral (Abramowits and Stegun, 1972)

If the two parameters a and b are equal, then the beta distribution is symmetric.

The beta distribution arises as the sampling distribution for the median of a sample taken from a uniform distribution (Roussas, 1973). If n observations are taken from a uniform distribution, the median of these n observations will follow a beta distribution with both the a parameter and the b parameter equal to *(n+1)/2*. It is logical that the distribution of the median would be symmetric because the original uniform distribution is symmetric. If for simplicity we define *m = (n+1)/2,* then the median of the uniform data is said to follow a B(m,m) distribution. The mathematical expression is

$$B(x;m,m) = \frac{x^{m-1}\,(1-x)^{m-1}}{B(m.m)}$$

In Chesapeake Bay Program status calculations, the data are transformed to the uniform distribution using the probability integral transform for the log-logistic distribution. The observed median of the transformed data is taken as an indicator of status. The beta density is used to define the probability of observing a similar median from the benchmark population. If the observed median is in the upper 33% of medians from the benchmark population, status is rated as good. If the observed is in the middle 33% status is rated as fair. An observed median in the lower 33% rates as poor.

3.1.1 Notes on the Benchmark

The development of the benchmark for each of the five variables of the EPC-SONE program is different from that used in other portions of the monitoring program. It is most important to note that the stations were not segregated on the basis of salinity zones. As a result of this, every flux measurement made at all four Patuxent River stations was used to develop the benchmark for each parameter. This benchmark is a relative scale, and "good" fluxes can not necessarily be considered to indicate a recovered system. 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 variables; in effect, the variable benchmark is synonymous with the mesohaline benchmark.

3.1.2 Notes on the Current Status for the Patuxent River

A median value for the years 1998, 1999 and 2000 was calculated. The use of the last three years of data provides an "indicator" value of the status of the parameter relative to measurements taken in the benchmark period. The median value of the last three years of 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 1998 was very wet during winter and spring, 1999 was an extremely dry year until September when several hurricanes passed the area, while 2000 exhibited a modest spring peak and low flows through the summer and fall.

3.1.3 Evaluation of the Current Status for the Patuxent River

i. Sediment Oxygen Consumption (SOC)

The current status (median of 1998, 1999 and 2000 data) of sediment oxygen consumption (SOC) fluxes at the four SONE stations in the Patuxent River is indicated in Figure 3-1.a. It seems appropriate to judge higher values of SOC as good in the context of this evaluation for several reasons despite the fact that high SOC rates indicate that sediments are using dissolved oxygen. The main reason for adopting this approach is that SOC rates are responsive to DO concentrations in the water. When dissolved oxygen concentrations in the water are high, SOC rates can be high. 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 in the good range. The pattern of SOC flux in the Patuxent River provides substantiation that the benchmark is appropriate. SOC fluxes progress from good down-river to fair at the head of the deep water channel at station Marsh Point (MRPT). This pattern would be expected based on proximity to nutrient sources and dissolved oxygen conditions. 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 are much reduced at this site.

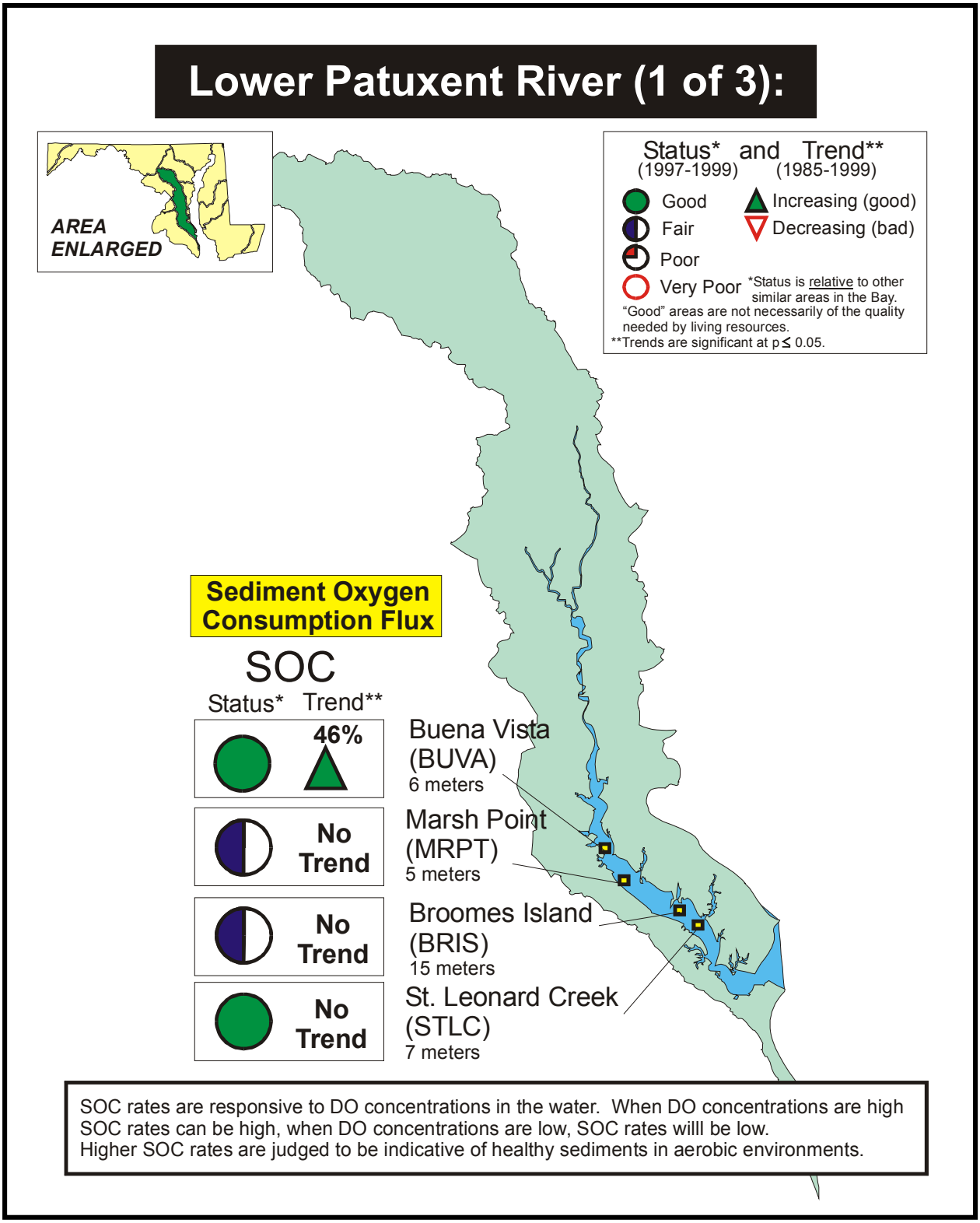

Figure 3-1.a. Map showing status and trends at four stations in the Lower Patuxent River for sediment oxygen consumption (SOC) fluxes (observed data).

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

ii. Ammonium (NH_4^+)

The current status (median of 1998, 1999 and 2000 data) of ammonium fluxes at the four SONE stations in the Patuxent River is indicated in Figure 3-1.b. In the case of ammonium fluxes it appears appropriate to judge high values as poor because of the well-established direct relationship between ammonium availability and excessive phytoplankton biomass accumulation. In 1999 the four SONE stations in the Patuxent River had two stations with ammonium fluxes in the fair range, and two were in the poor range. It should be noted that high river flow years have a particularly strong influence on ammonium fluxes (fluxes increase) and one of the three years, 1998, was a high flow year. All four SONE stations in the Patuxent River had ammonium fluxes in the poor range in 2000. It was predicted that the two down river sites that were in the fair category last year, 1999, (St. Leonard Creek [STLC] and Broomes Island [BRIS]), may be expected to move towards the good category when river flows, and associated nutrient loads, return to lower levels.

iii. Nitrite (NO_2^-)

The current status (median of 1998, 1999 and 2000 data) of nitrite flux at the four SONE stations in the Patuxent River is indicated in Figure 3-1.c. In the case of nitrite fluxes it appears appropriate to judge high values (positive values) as good because of the well-established linkage between nitrite evolution from sediments and oxidized sediment conditions. Among the SONE stations, three had nitrite fluxes in the good range and one was in the fair range. Stations are expected to change from poor to fair or fair to good when dissolved oxygen (DO) conditions in bottom water improve, even if only enough to allow some nitrification activity to occur. The poor status at Broomes Island (BRIS) in 1999 changed to good in 2000.

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

The current status (median of 1998, 1999 and 2000 data) of nitrite plus nitrate fluxes at the four SONE stations in the Patuxent River is indicated in Figure 3-1.c. 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 judged to be good, Buena Vista (BUVA). Broomes Island (BRIS) and Marsh Point (MRPT) changed from poor to fair but the St. Leonard Creek (STLC) station went from good to fair.

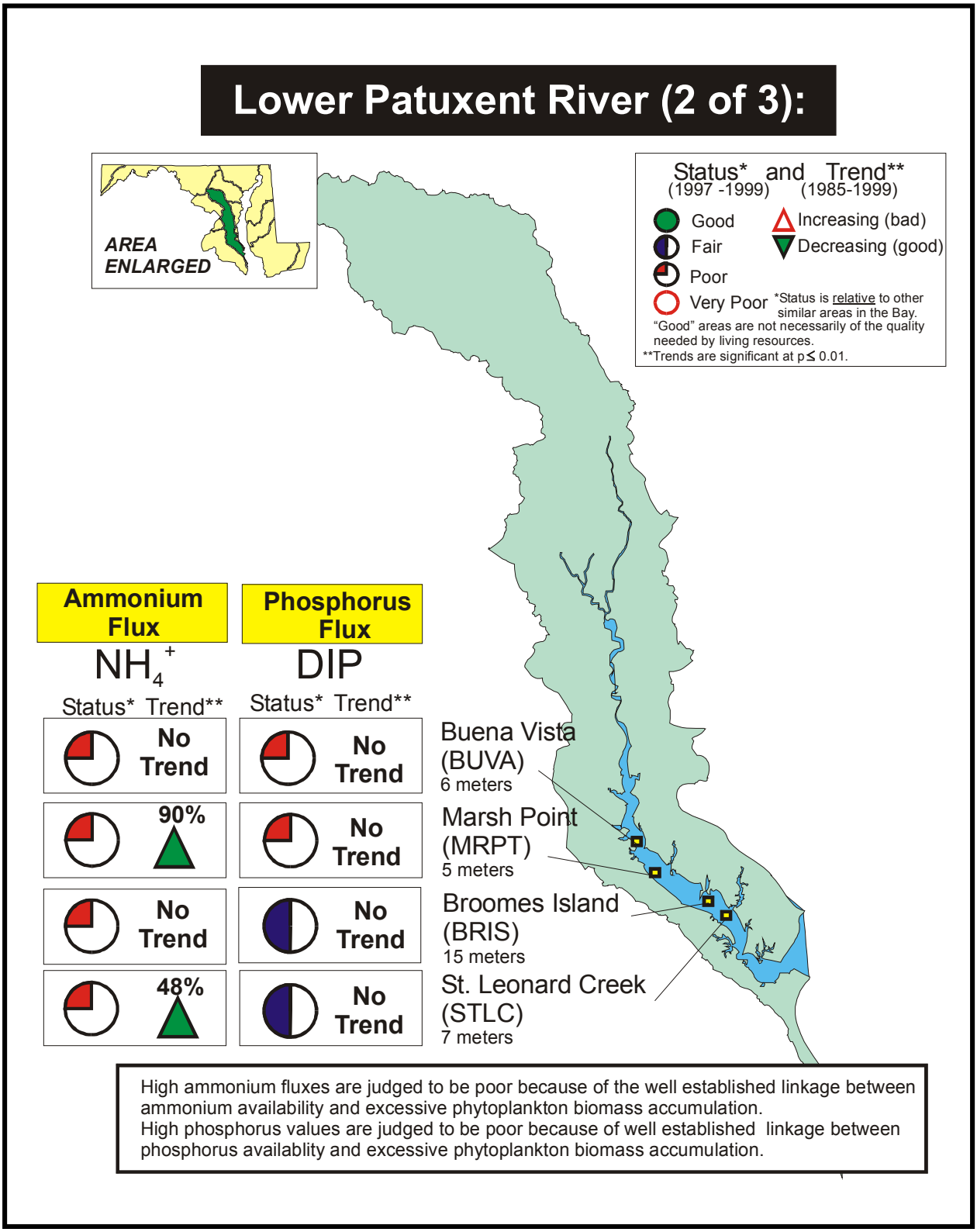

Figure 3-1.b. Map showing status and trends at four stations in the Lower Patuxent River for ammonium (NH_4^+) and phosphorus (PO_4^{-3}) fluxes (observed data).

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

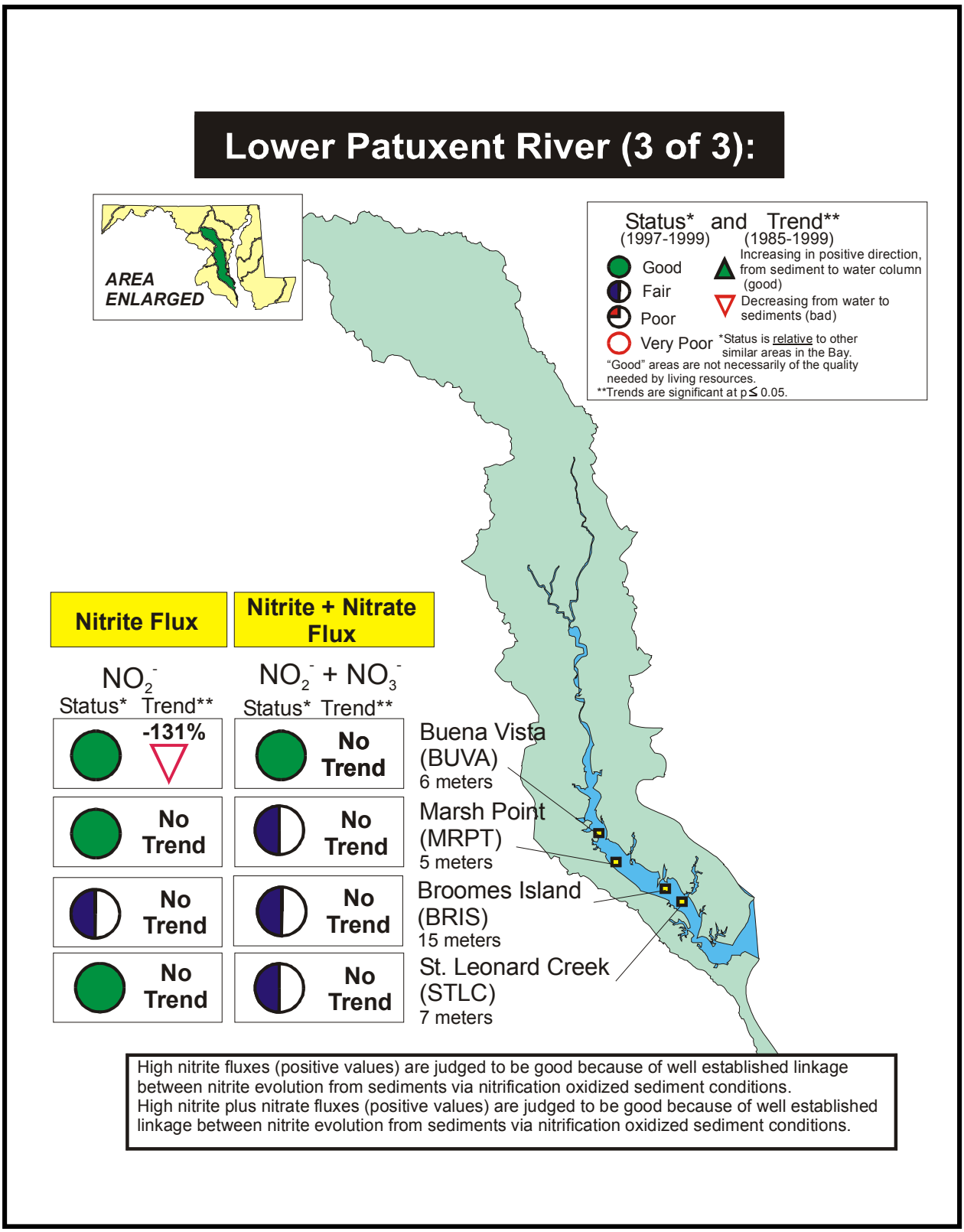

Figure 3-1c. Map showing status and trends at four stations in the Lower Patuxent River for nitrite (NO_2^-) and nitrite plus nitrate (NO_2^- + NO_3^-) fluxes (observed data).

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

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

The current status (median of 1998, 1999 and 2000 data) of dissolved inorganic phosphorus fluxes at the four SONE stations in the Patuxent River is indicated in Figure 3-1.b. 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, two stations had phosphorus fluxes in the fair range, Marsh Point (MRPT) and St. Leonard Creek (STLC). Two stations were in the poor category. St. Leonard Creek (STLC), the station farthest downstream, went from good to fair. It should be noted that high river flow years have a particularly strong influence on phosphorus fluxes (fluxes increase) and one of the three years considered, 1998, was an exceptionally high flow year.

3.2 Sediment-Water Oxygen and Nutrient Exchanges (SONE) Trends: 2000 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 used the non-parametric seasonal Kendall test. In results presented here, sediment oxygen and nutrient (SONE) flux data were NOT adjusted for river flow, as is the case for testing other variables for trends within the monitoring program. This adjustment was not attempted because the temporal and spatial linkages between flow and sediment responses have not been clearly established.

3.2.1 Current Testing (Seasonal Kendall Test) for Seasonal Trends: 1985 - 2000 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 program design to restore optimum conditions in the Bay as well as prevent 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).

3.2.2 Flux Data Set for Four Patuxent River

Flux data were collected over a period of sixteen years (1985 - 2000) 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 that may increase the variance of the data. In order to characterize the data initially, manual QA/QC checks were completed. 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 2.2.3.1). 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 analyzes were performed for each sediment oxygen and nutrient exchange (SONE) variable. A probability level of 0.01 was used to assess the significance of the results using observed data (data not "corrected" for river flow effects).

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

Three graphics (Figures 3-1.a., 3-1.b. and 3-1.c.) summarize results of the five flux variables, indicating sediment oxygen consumption (SOC), ammonium (NH_4^+), inorganic phosphorus, nitrite (NO_2^-) and nitrite plus nitrate ($NO_2^- + NO_3^-$) fluxes, 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 3-1. Annual values for observed data are presented in Table 3-2.

Testing for trends at the annual time scale resulted in few statistically significant results ($p < 0.01$). In the Patuxent River estuary the sediment oxygen consumption (SOC) fluxes continue to have a slightly significant increasing trend at the upper estuary station at Buena Vista (BUVA). It is important to note that increasing 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 marginally significant increasing trend (at probability level $p < 0.05$) was indicated for ammonium (NH_4^+) at St. Leonard Creek (STLC) and Marsh Point (MRPT) and for nitrite (NO_2^-) at St. Leonard Creek (STLC). All of these were degrading trends.

There were no significant annual trends for dissolved inorganic phosphorus or nitrite plus nitrate fluxes in the Patuxent River estuary. During the last sixteen years both wet and dry years have been recorded (relatively high and low diffuse source loading years, respectively) 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 several years.

Table 3-1. A condensed summary of significant trends (observed data) detected for sediment-water exchange data using seasonal Kendall Test statistic.

More details can be found in Table 3-2 and Table 3-3.

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

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

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

Station	Month								ANNUAL
	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	
a. Sediment Oxygen Consumption (SOC; g O_2 m^{-2} day^{-1} yr^{-1})									
BUVA					* ↑				* ↑
BRIS					* ↑				
b. Ammonium (NH_4^+; μM N m^{-2} hr^{-1} yr^{-1})									
BUVA					* ↑				* ↑
MRPT		* ↓			*				* ↓
STLC					* ↑				
c. Nitrite (NO_2^-; μM N m^{-2} hr^{-1} yr^{-1})									
BUVA		* ↑							* ↑
d. Nitrite plus Nitrate (NO_2^- + NO_3^-; μM N m^{-2} hr^{-1} yr^{-1}) No significant trends									
e. Dissolved Phosphorus (PO_4^{-3}; μM Pm^{-2} hr^{-1} yr^{-1}) No significant trends									

Table 3-2. 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. Annual Trends

STATION	SOC	NH_4^+	NO_2^-	$NO_2^- + NO_3^-$	PO_4^{-3}
St. Leonard Creek (STLC)					
Sign	-60	89	31	-16	27
p value	0.11	0.02*	0.29	0.69	0.49
Slope	-0.026	3.275	0.318	-0.334	0.106
Marsh Point (MRPT)					
Sign	-23	56	30	48	50
p value	0.43	0.05*	0.27	0.09	0.08
Slope	-0.013	14.120	0.033	1.283	1.625
Broomes Island (BRIS)					
Sign	-54	4	-16	43	-18
p value	0.06	0.91	0.58	0.11	0.54
Slope	-0.038	0.233	-0.008	0.358	-0.167
Buena Vista (BUVA)					
Sign	-78	45	60	11	-31
p value	0.04*	0.23	0.04*	0.78	0.40
Slope	-0.047	5.967	0.711	0.000	-0.403

3.2.4 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 3-3). 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 3-3. The *n* value indicates the number of observations used in the analysis**.**

i. Sediment Oxygen Consumption (SOC)

Two significant negative (improving trends) were indicated for sediment oxygen consumption (SOC) fluxes at $p < 0.05$ at Buena Vista (BUVA) for August and at Broomes Island (BRIS; Table 3-3.a) for August.

ii. Ammonium (NH_4^+)

A significant trend was indicated for ammonium (NH_4^+) fluxes at $p < 0.05$ in August at Buena Vista (BUVA; degrading trend), in May and August at Marsh Point (MRPT; degrading trend) and at St. Leonard Creek (STLC) in August (degrading trend; Table 3-3.b).

iii. Nitrite (NO_2^-)

A positive (improving) significant trend was indicated for nitrite (NO_2^-) fluxes at $p < 0.05$ in the Patuxent River at Buena Vista (BUVA) in May (Table 3-3.c).

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

No significant trends were observed for nitrite plus nitrate fluxes (Table 3-3.d).

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

A positive (improving) significant trend was found for phosphorus (PO_4^{-3}) fluxes at $p < 0.01$ at Marsh Point (MRPT) in June (Table 3-3.e).

Table 3-3. 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 - 2000								
Sign	3	-10	6	-20	-46	1	-9	-3
p value	.	0.28	0.82	0.19	0.04*	1.00	0.24	.
N	3	8	16	12	16	10	7	3
Marsh Point (MRPT): 1989 - 2000								
Sign		-3	8	-20	-13	8	-3	
p value		0.72	0.58	0.19	0.41	0.60	1.00	
n		6	11	12	12	10	6	
Broomes Island (BRIS): 1989 - 2000								
Sign		5	11	-8	-32	-19	-11	
p value		0.47	0.44	0.63	0.03*	0.11	0.06	
n		6	11	12	12	10	6	
St. Leonards Creek (STLC): 1985 - 2000								
Sign	3	-10	28	-21	-30	-22	-5	-3
p value	.	0.28	0.22	0.17	0.15	0.07	0.56	.
n	3	8	16	12	15	10	7	3

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

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER: Buena Vista (BUVA): 1985 - 2000								
Sign	-3	10	-7	14	48	-15	-3	1
p value	.	0.28	0.77	0.37	0.03*	0.22	0.77	.
n	3	8	15	12	16	10	7	3
Marsh Point (MRPT): 1989 - 2000								
Sign		13	3	8	32	-9	9	
p value		0.02*	0.88	0.63	0.03*	0.48	0.14	
n		6	11	12	12	19	6	
Broomes Island (BRIS): 1989 - 2000								
Sign		-3	3	18	-26	11	1	
p value		0.72	0.87	0.24	0.09	0.38	1.00	
n		6	11	12	12	10	6	
St. Leonards Creek (STLC): 1985 - 2000								
Sign	1	-4	23	9	52	3	5	0
p value	.	0.72	0.32	0.53	0.02*	0.86	0.56	.
n	3	8	16	11	16	10	7	3

Table 3-3. 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^-; μM N m^{-2} hr^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER: Buena Vista (BUVA): 1985 - 2000								
Sign	0	13	-8	30	14	5	6	0
p value	.	0.02*	0.62	0.05	0.43	0.73	0.23	.
n	1	6	12	12	13	10	5	1
Marsh Point (MRPT): 1989 - 2000								
Sign		3	-5	14	12	-5	11	
p value		0.72	0.74	0.27	0.45	0.73	0.06	
n		6	11	11	12	10	6	
Broomes Island (BRIS): 1989 - 2000								
Sign		-3	-7	-12	3	-1	4	
p value		0.72	0.63	0.44	0.89	1.00	1.00	
n		6	11	12	12	10	6	
St. Leonards Creek (STLC): 1985 - 2000								
Sign	0	1	-10	18	19	0	3	0
p value	.	1.00	0.54	0.18	0.27	1.00	0.72	.
n	1	6	12	11	13	10	6	1

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

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER: Buena Vista (BUVA): 1985 - 2000								
Sign	-3	-10	3	24	-2	7	-8	0
p value	.	0.28	0.93	0.11	0.96	0.60	0.38	.
n	3	8	16	12	15	10	7	3
Marsh Point (MRPT): 1989 - 2000								
Sign		-5	21	14	14	1	3	
p value		0.47	0.12	0.35	0.71	1.00	0.72	
n		6	11	12	12	10	6	
Broomes Island (BRIS): 1989 - 2000								
Sign		-3	23	12	11	-1	1	
p value		0.72	0.09	0.36	0.49	1.00	1.00	
n		6	11	12	12	10	6	
St. Leonards Creek (STLC): 1985 - 2000								
Sign	-3	2	-22	14	-22	9	7	-1
p value	.	0.90	0.34	0.31	0.68	0.48	0.38	.
n	3	8	16	11	16	10	7	3

Table 3-3. 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}; μM Pm^{-2} hr^{-1} yr^{-1})

STATION	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV
PATUXENT RIVER: Buena Vista (BUVA): 1985 - 2000								
Sign	-3	2	-19	-10	16	-9	-9	1
p value	.	0.90	0.32	0.54	0.50	0.48	0.24	.
n	3	8	14	12	16	10	7	3
Marsh Point (MRPT): 1989 - 2000								
Sign		1	33	8	-4	1	11	
p value		1.00	0.01**	0.63	0.84	1.00	0.06	
n		6	11	12	12	10	6	
Broomes Island (BRIS): 1989 - 2000								
Sign		3	1	2	-32	5	3	
p value		0.72	1.00	0.95	0.03	0.73	1.00	
n		6	11	12	12	10	6	
St. Leonards Creek (STLC): 1985 - 2000								
Sign	-2	4	6	24	11	-18	1	1
p value	.	0.72	0.82	0.11	0.65	0.16	1.00	.
n	3	8	16	12	16	10	7	3

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4. SUBMERGED AQUATIC VEGETATION (SAV) HABITAT EVALUATION

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4.1 Introduction

Declines in submerged aquatic vegetation (SAV) populations during the last half of the twentieth century have been well documented in a variety of shallow coastal estuaries worldwide (Den Hartog and Polderman, 1975; Kemp *et al*., 1983; Orth and Moore, 1983; Cambridge *et al*., 1986; and Orth and Moore, 1984). In response to these changes, a variety of studies have suggested that increased anthropogenic inputs of dissolved nutrients and particulate matter have been primarily responsible for degraded water quality conditions and reduced light availability to rooted macrophyte populations (*e.g.*, Sand-Jensen, 1977; Cambridge *et al*., 1986; Kemp *et al*., 1983; Twilley *et al*., 1985; and Silberstein, 1986). While light availability is generally agreed to be the most critical

resource limiting the extent and distribution of SAV populations, an understanding of what conditions are necessary and sufficient to provide adequate light has proven to be most elusive. For example, a number of studies have demonstrated that epiphytes can substantially reduce the amount of available light reaching the leaf surface (*e.g.*, Burt *et al*., 1995; Boynton *et al.*, 1999). However, epiphyte loads can be modified to a great extent by a variety of factors such as: epiphyte grazer density (*e.g.* Neckles *et al*., 1993 ; Williams and Ruckelshaus, 1993), light availability (Boynton *et al.*, 1999), nutrient availability (Kemp *et al*., 1983; Burt *et al*., 1995), wave action (*e.g.* Koch, 1996) and leaf turnover rates, *etc*.

Due to this inherent complexity and the difficulties of determining mechanisms and causal factors, field monitoring of water quality remains an important tool for understanding why SAV thrives, survives or declines at specific locations. In Chesapeake Bay, field monitoring is particularly important because of the large range of conditions found within the Bay and it's tributaries. For example, in some Chesapeake Bay tributaries, modest reductions in nutrient loading has been achieved in recent years resulting in improved water quality conditions (*e.g.* Boynton *et al*., 1995). However, many of these tributaries, including the Patuxent River, that were historically populated with SAV beds, have not shown significant recovery. While in other areas, such as Tangier Sound, SAV acreage has declined significantly in recent years despite a general increase in SAV coverage the previous decade.

In 1997, the EPC began an ambitious and diversified study of the near-shore water quality conditions important to SAV growth and survival. With information gathered during the first several years of investigation, this study was refined and modified for the 2000 investigation. These changes included the addition of selected locations in Tangier Sound and a modification of overall sampling frequency. As in past years, the SAV habitat evaluation was composed of two discrete but complimentary study elements: the near-shore water quality evaluation and the epiphyte growth study.

4.1.1 Near-shore Water Quality Evaluation

The primary goal of the near-shore water quality evaluation was to measure a suite of water quality parameters directly in the shallow near-shore habitat to assess compliance with established SAV habitat requirements (Batuik *et al*., 1992; USEPA, 2000). The five water quality parameters thought to be most important for SAV growth and survival are water column dissolved inorganic nitrogen (DIN), dissolved inorganic phosphorus (DIP), water column light attenuation (Kd), water column total suspended solids (TSS), and water column chlorophyll-*a* (Tchl-*a*). At present, the vast majority of routine water-quality monitoring is done at channel locations often distant from actual SAV habitats. These data may not reflect near-shore conditions due to a variety of localized conditions such as: resuspension of sediments, point source discharges, or existing macro algal communities. Therefore, data for this study, collected directly in near-shore SAV habitats, will provide more accurate information about water quality conditions in these locations. The secondary goal of this study was to provide corresponding water quality

data to be used in the evaluation of the epiphyte growth study, where water quality affects light attenuation through the stimulation of epiphytic growth.

4.1.2 Epiphyte Growth Study

The epiphyte growth study was designed to compare epiphyte accumulation rates to water quality data at various locations along the axis of the Patuxent River and at selected sites in Tangier Sound. This comparison will provide field data for calibration of models predicting epiphyte biomass based upon simple, water quality data. In 1998, a comparison of epiphyte fouling rates on live SAV and Mylar® strips was conducted to compare epiphytic growth rates on transplanted live SAV with the artificial substrates to help calibrate and interpret results obtained using artificial substrates. The results of this study suggested that Mylar® strips could be used as an acceptable surrogate for live plants in order to estimate light attenuation from epiphytic fouling (Boynton *et al*., 1999). While a number of comparisons of epiphyte accumulation rates have been made between live SAV blades and artificial substrates (seagrass mimics) with conflicting results (*e.g.* Lin *et al*., 1995; Pinckney and Micheli, 1998) such comparisons are made more difficult because of differences in technique, geographic region, length of exposure, and SAV species. Despite potential limitations, artificial substrates can be used effectively to compare the effects of differing water quality conditions on epiphyte accumulation rates and light attenuation when live plants are not available (*e.g.*, Burt *et al*., 1995, Boynton *et al.*, 1999). In addition, artificial substrates can be standardized between sites, and provide a quick assessment of epiphyte growth potential at SAV restoration sites.

4.2 Location of SAV Stations and Sampling Frequency

4.2.1 Near-shore Water Quality Evaluation

4.2.1.1 Location of Water Quality Stations

In 2000, six mesohaline stations on the Patuxent River and six stations in the lower Tangier Sound were monitored. The Patuxent River stations were also monitored from 1997 to 1999, and were selected to reflect a variety of nutrient, salinity and wave exposure regimes (Figure 4-1.a; Table 4-1). Six stations in Tangier Sound were selected to provide a variety of water quality and wave exposure conditions (Figure 4-1.b; Table 4-2).

4.2.1.2 Water Quality Sampling Frequency

Sampling was conducted in three seasonal time blocks: spring, summer and fall. Three weekly samples were collected during each seasonal block for a total of 9 SAV sampling cruises.

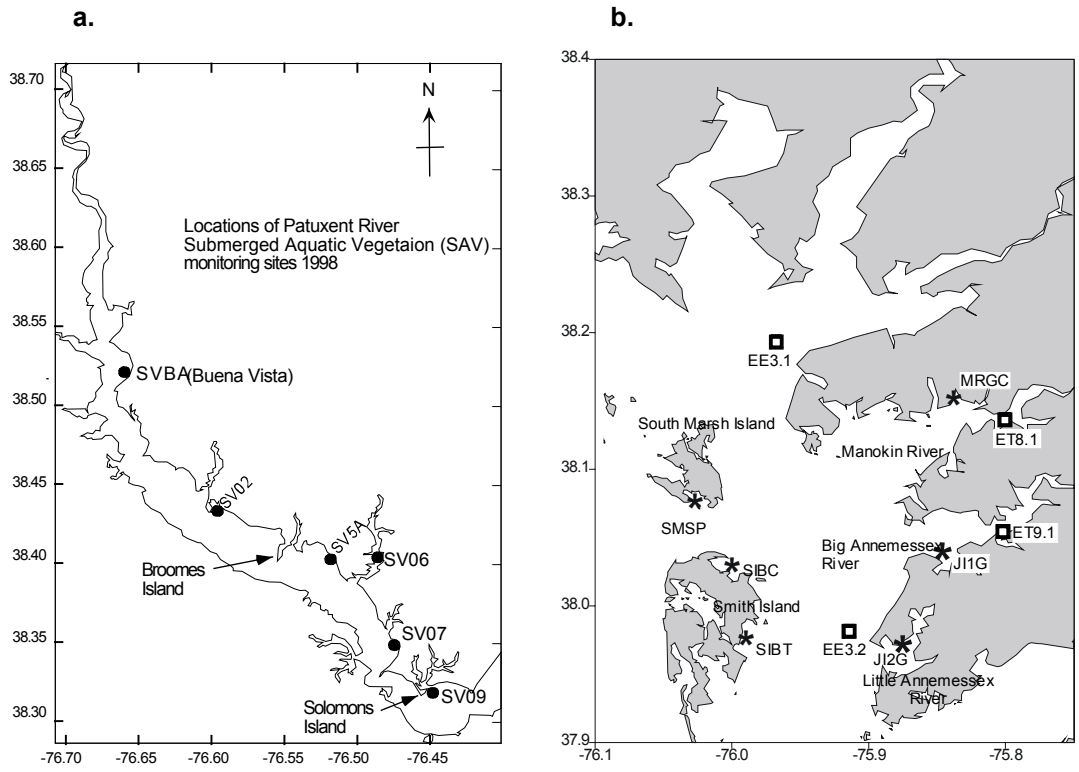

Figure 4-1. Maps of 2000 Submerged Aquatic Vegetation (SAV) monitoring stations as well as nearest DNR monitoring sites in (a) Patuxent River and (b) Tangier Sound.
Latitude and longitude are in decimal degrees.

Table 4-1. Patuxent River: Submerged Aquatic Vegetation (SAV) Station Abbreviations and Locations: Latitude and Longitude (DGPS).

Geographic Location of Station	Station Abbreviation	Latitude NAD83	Longitude NAD83
Jefferson Patterson Park Station 1	SV5A	38° 24.534'	76° 31.299'
St Leonard Creek	SV06	38° 23.709'	76° 29.105'
Hungerford Creek	SV07	38° 20.982'	76° 28.307'
Point Sandy	SV09	38° 19.016'	76° 27.119'

Table 4-2. Tangier Sound: Submerged Aquatic Vegetation (SAV) Station Code, Grid Location and Nearest MDE Station.

Geographic Location of Station	Station Abbreviation	Latitude (DGPS)	Longitude (DGPS)	MDE Station	Bay Segment
Tangier Sound					
Janes Island - North	JI1G	38° 01.620’	75° 50.509’	ET9.1	BIGMH
Janes Island - South	JI2G	37° 58.249’	75° 52.609’	EE3.2	TANMH
Little Deal Island	LDIS	38° 07.531’	75° 57.775’	EE3.1	
Manokin River Geoquaking Creek	MRGC	38° 08.835’	75° 50.349’	ET8.1	MANMH
Smith Island - Big thoroughfare	SIBT	37° 58.147’	75° 59.553’	EE3.2	TANMH
Smith Island- Back Cover	SIBC	38° 01.262’	76° 00.133’	EE3.2	TANMH
South Marsh - South Point	SMSP	38° 04.571’	76° 01.653’	EE3.2	TANMH

4.2.1.3 SAV Water Quality Field Methods

At each of the near-shore 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.

4.2.1.3.1 Physical Parameters

Temperature, salinity, conductivity, and dissolved oxygen measurements were collected with a Yellow Springs International (YSI) 600R or YSI 6920 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 (Kd). 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.

4.2.1.3.2 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 ($NO_2^- + NO_3^-$) and phosphate (PO_4^{-3}). Whole water portions were filtered in the laboratory using 47 mm 0.7 µm (GF/F) glass fiber filters and were analyzed by NASL for the following particulate nutrients: total suspended solids (TSS), and total and active chlorophyll-*a* concentrations where total chlorophyll-*a* includes chlorophyll-*a* plus breakdown products.

4.2.1.3.3 Chemical Analysis Methodology

Methods for the determination of dissolved and particulate nutrients are as follows: ammonium (NH_4^+), nitrite (NO_2^-), nitrite plus nitrate ($NO_2^- + NO_3^-$), and dissolved inorganic phosphorus (DIP or PO_4^-) are measured using the automated method of EPA (1979); particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using an 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 Parsons *et al.* (1984) are followed for chlorophyll-*a* analysis.

4.2.2 Epiphyte Growth Survey

4.2.2.1 Location of Epiphyte Survey Stations and Sampling Frequency

The epiphyte growth survey was completed concurrently with the SAV water quality element at all 12 sites, six Patuxent River and six Tangier Sound sites. The sampling schedule is given in Table.

4.2.2.2 Epiphyte Growth Measurement Method

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 10 near-shore stations for periods of one to two 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.

4.2.2.3 Description of Epiphyte Collector Arrays

Each collector array (Figure 4-2) consists of a square PVC frame situated horizontally with a vertical PVC shaft oriented in the center of the square. To this shaft is attached a line with a small surface float that allows for easy location of the collector. Each collector array holds up to eight strips per deployment. Mylar® strips (2.5 cm wide x 51 cm long and 0.7 mil thick) are attached to the frame so that the top is allowed to move freely in the water column. Small foam floats (~3.5 x 3.3 cm) are attached to the top of the strip to help maintain a vertical position in the water column at all times.

4.2.2.4 Sampling the Epiphyte Collector Arrays

To retrieve the epiphyte collector strips the entire collector array was removed from the water and suspended from the washboard of the vessel, 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.

On each sampling date, an additional strip was haphazardly chosen for chlorophyll-*a* 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.

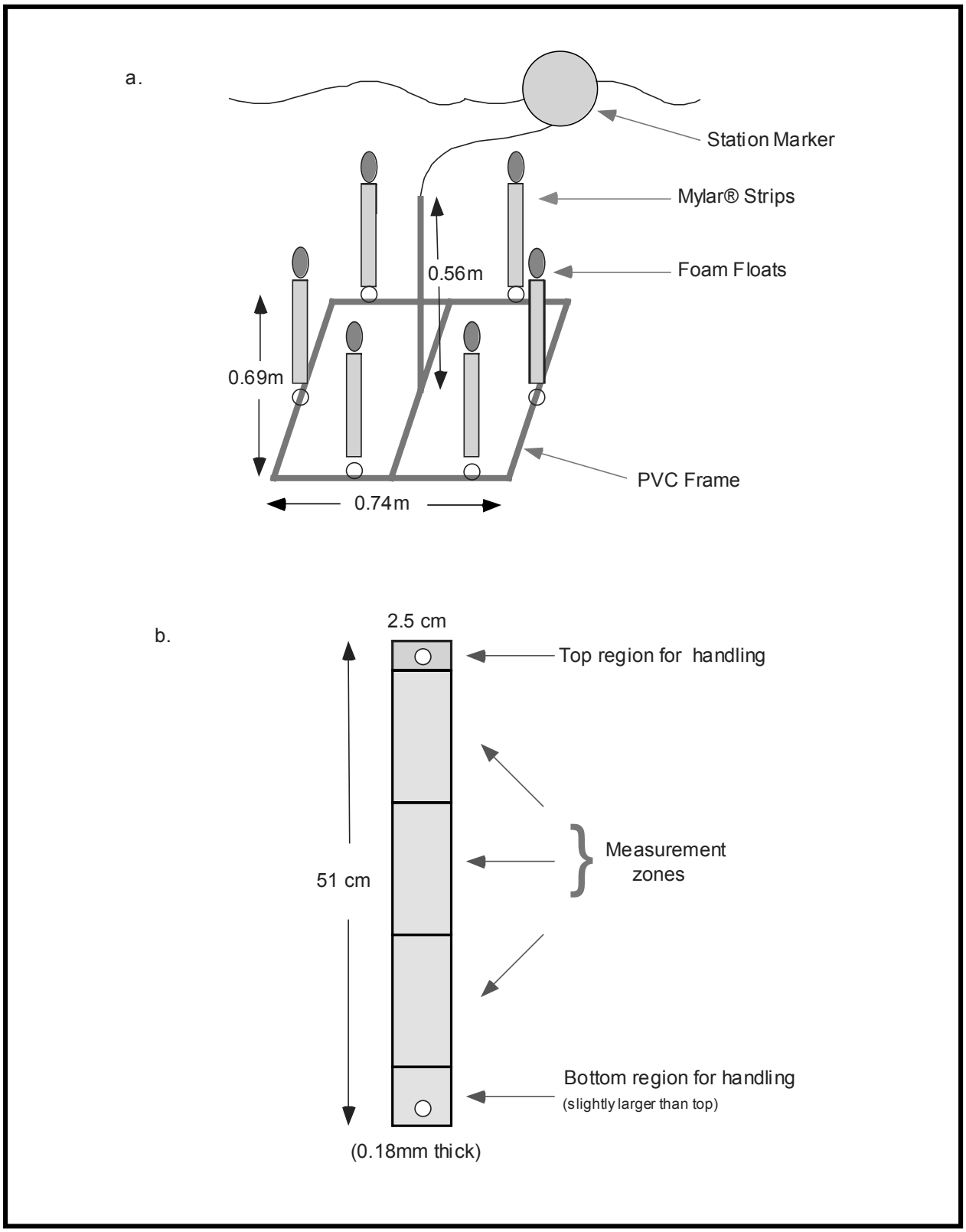

Figure 4-2. Diagram of SAV Epiphyte Collector Array.
a. Epiphyte Collector Array
b. Mylar® strips

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

4.2.2.5 Processing Inorganic Epiphyte Material

The middle third of Mylar® strips collected for TSS/TVS analysis were scraped of all material and rinsed with distilled water. Water from the transport tube was added to the scraped material and both were diluted to a fixed volume (400 - 500 ml). The solution was mixed as thoroughly as possible on a stir plate until homogenized. A small aliquot (10 to 50 ml) was then extracted with a glass pipette and filtered through a 47 mm 0.7 µm (GF/F) glass fiber filter. Once filtered, the pads were immediately frozen and delivered to NASL for analysis.

4.2.3 Estimation of Light Attenuation, PLW and PLL

Estimates of epiphyte light attenuation were calculated using measurements of epiphyte dry mass and existing relationships between dry mass and light attenuation (Figure 4-3.a and 4-3.b). These relationships were developed using direct measurements of epiphyte light attenuation and dry mass accumulated on Mylar® strips deployed at a number of locations from 1997 to 1999 (Boynton *et al*. 1998; Stankelis *et al*., 1999; Stankelis *et al*., 2000). These estimates along with corresponding measurements of water column light attenuation (Kd) allow us to calculate the percent of surface light reaching the depth of the SAV blade through the water column (PLW) and the percent surface light reaching the blade of SAV through the epiphyte layer at the leaf surface (PLL). Calculations of these metrics defined by the Chesapeake Bay Program (USEPA, 2000) are shown below in Table 4-3.

Table 4-3. Calculation of % Surface Light Reaching Leaf Surface (PLL)

$PLW = (I_Z/I_0)*100 = 100*[e^{-kd*Z}]$	Where: Iz = Light flux (PAR) at depth
$PLL = [e^{-kd*Z}][1-LA/100]$	I_0 = Light flux (PAR) at surface
	LA = Epiphyte light attenuation
	Z = Observation depth (m)

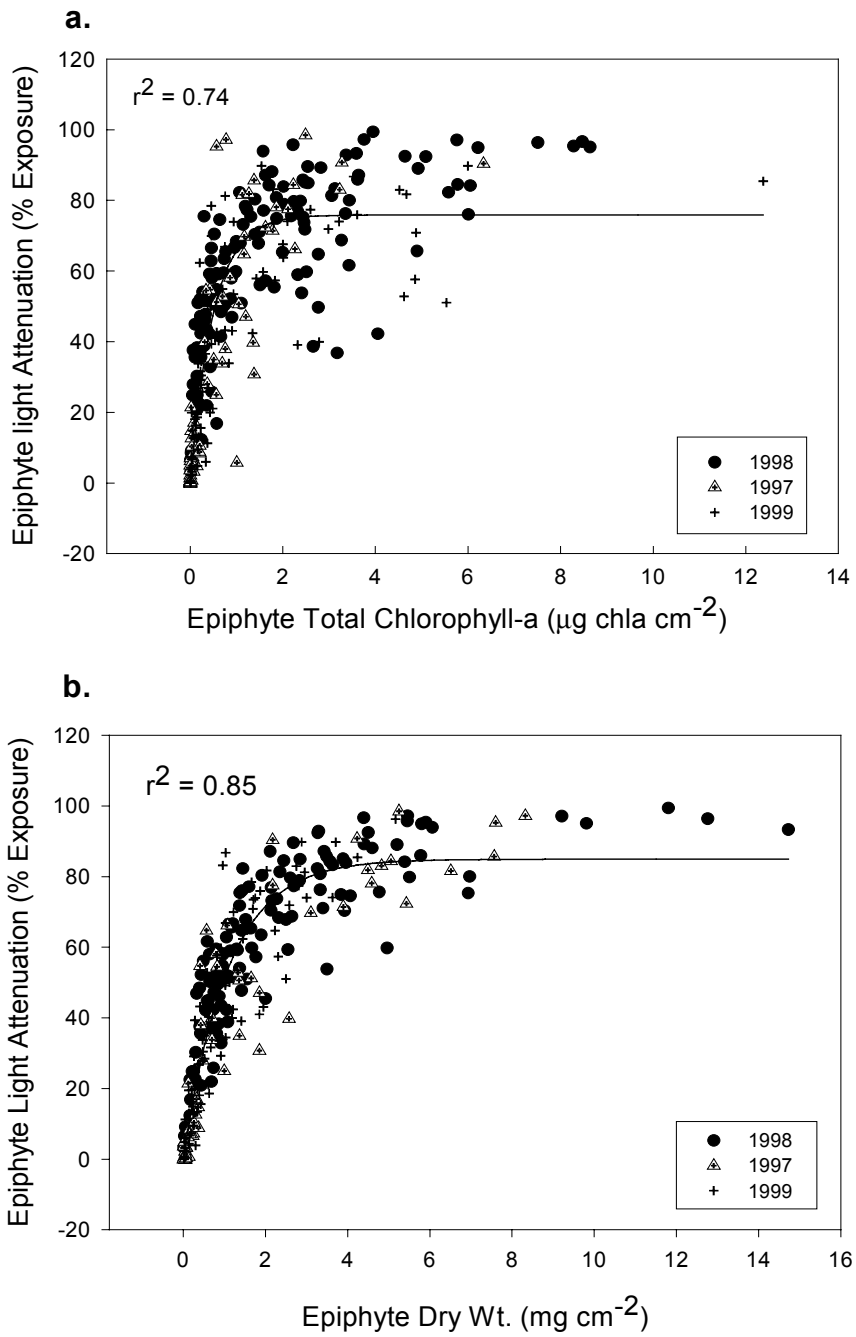

Figure 4-3. (a) Epiphyte light attenuation vs. epiphyte chlorophyll-a, where light attenuation = 77.36*(1-$e^{-2.082 * Epi\ Chla}$) and (b) epiphyte light attenuation vs. epiphyte dry mass where Light Attenuation = 84.634*(1-$e^{-0.963 * Epi\ drywt}$) .

4.3 Results

4.3.1 Results of Near-shore Water Quality Evaluation

Due to the limited frequency of sampling, *i.e.* three weekly blocks of time in spring, summer and fall, only limited comparisons can be made between sampling done in previous years when sampling was completed on a regular basis throughout the SAV growing season. However, comparisons were made among seasons and regions in 2000.

4.3.1.1 Physical Parameters

The full data set is available in Ecosystems Processes Component Level One Report #18, Data and Progress Report (Boynton *et al*., 2000).

4.3.1.2 Dissolved Nitrogen Concentrations (DIN)

During the spring, summer and fall of 2000, dissolved inorganic nitrogen (DIN) concentrations typically remained well below the 10.7 μM N mesohaline SAV habitat limit (USEPA, 2000; Figure 4-4). During the spring season, differences in DIN concentrations were observed among sites within each region. During this time, DIN concentrations were highest at the most down-river sites of the Patuxent River and the island sites in Tangier Sound. However, no significant overall difference was found in DIN concentrations between Patuxent River and Tangier Sound. During the summer season, DIN concentrations were consistently low in Tangier Sound, but were variable in the Patuxent River. No clear pattern was observed between upriver and downriver locations. In the fall, DIN concentrations were also more variable among sites in the Patuxent River than in Tangier Sound, however there was no overall statistical difference between the two regions (t-test $p > 0.05$).

4.3.1.2 Dissolved Phosphorus Concentrations (DIP)

Overall, dissolved phosphorus concentrations were below the 3.2 μM P Tier II mesohaline habitat limit (USEPA, 2000) with the exception of one sample collected at South Marsh Island (SMSP) during the spring (Figure 4-5.a). With this observation excluded no significant difference in DIP concentrations were found among the sites in Tangier Sound. Dissolved phosphorus concentrations were significantly higher in the Patuxent River compared to Tangier Sound throughout the entire year (Mann-Whitney rank test $p < 0.001$). A gradient in DIP concentrations was also found along the axis of the Patuxent River with higher concentrations recorded at upriver stations compared to downriver stations (Figure 4-5).

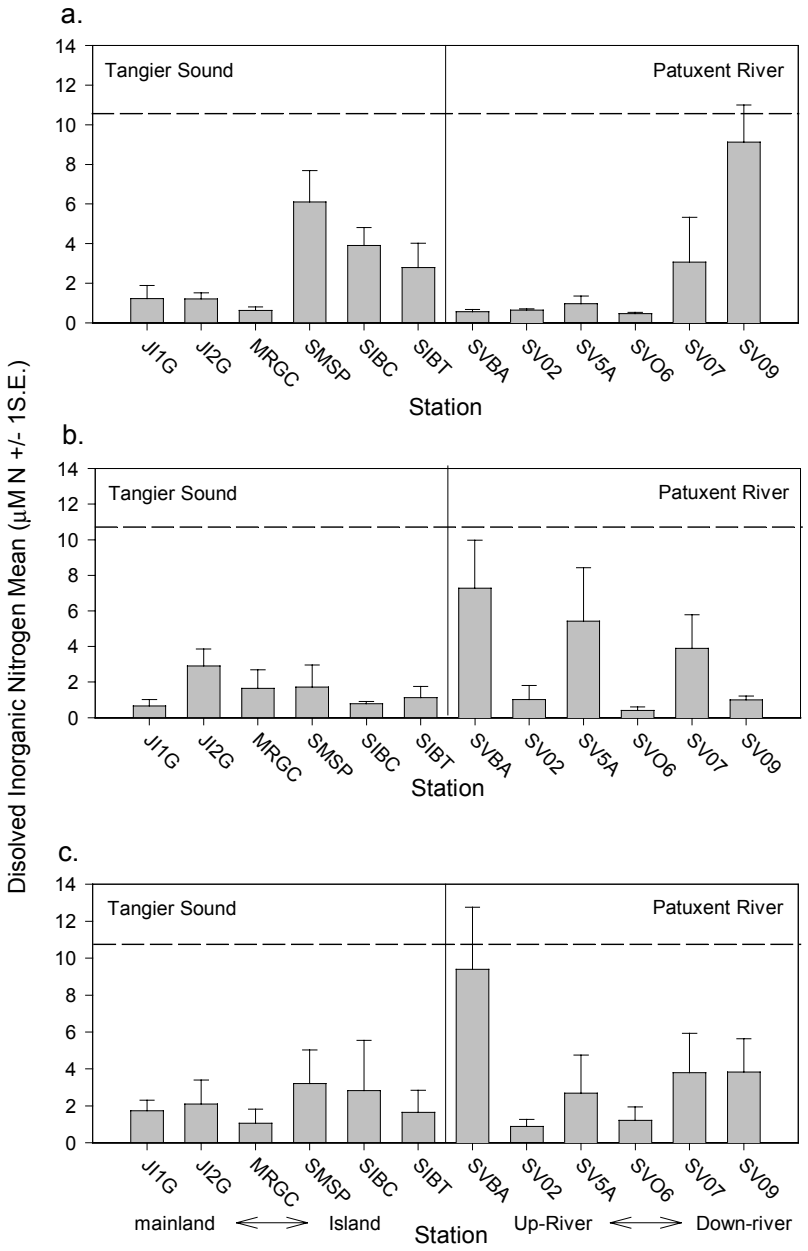

Figure 4-4. Mean (+/- 1SE) dissolved inorganic nitrogen (DIN) concentrations for (a) spring, (b) summer, and (c) fall in the Patuxent River and Tangier Sound 2000.
Dashed lines represent minimum Tier II mesohaline SAV habitat requirement (USEPA, 2000).

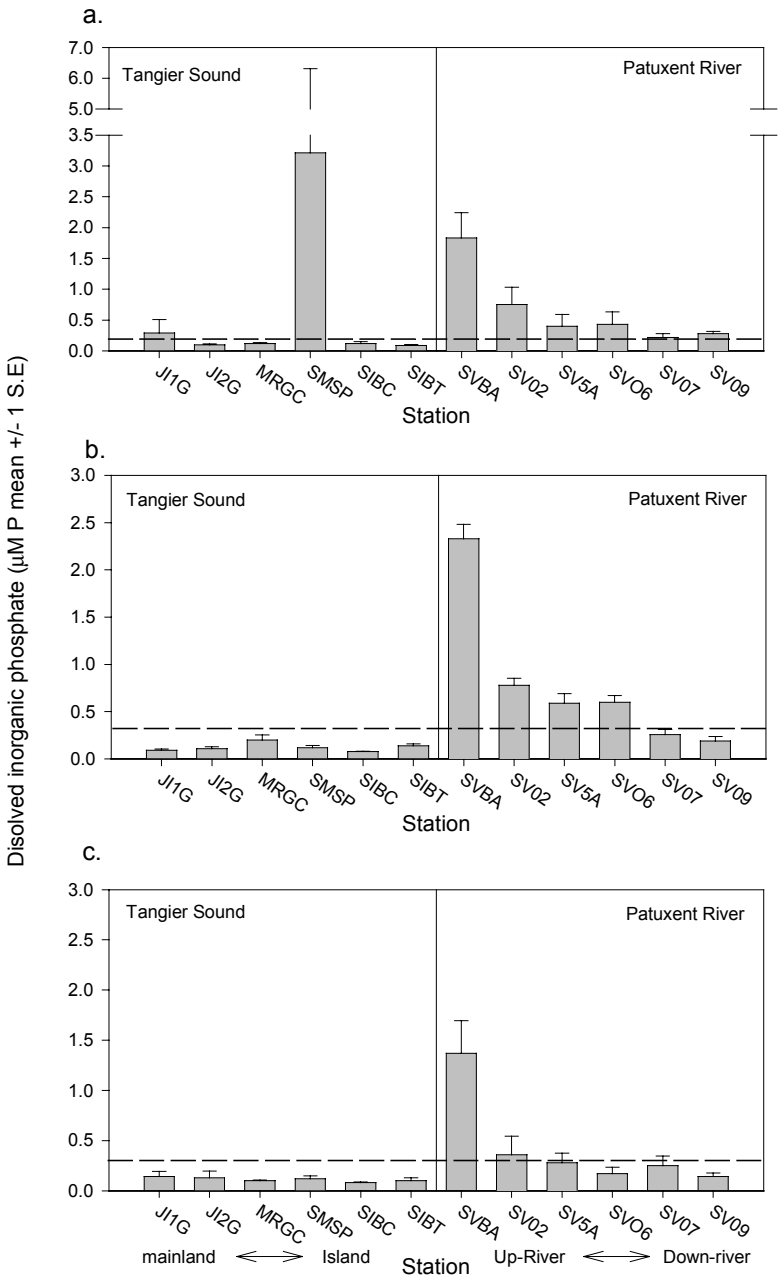

Figure 4-5. Mean (+/- 1SE) dissolved inorganic phosphorus (DIP) concentrations for (a) spring, (b) summer, and (c) fall for the Patuxent River and Tangier Sound 2000.
Dashed line represents upper limit Tier II mesohaline SAV habitat requirement (USEPA, 2000).

4.3.1.3 Water Column Light Attenuation

Water column light attenuation (Kd) values at most stations remained very close to the Tier II mesohaline habitat limit (1.5 m^{-1}) throughout the year (Figure 4-6). No significant differences were found overall between sites located in Tangier Sound compared to the Patuxent River (Mann-Whitney rank test $p > 0.05$). However, subtle spatial and temporal patterns were observed within each region. For example, as in past years, the most upriver stations along the Patuxent were more turbid compared to down-river stations (Figure 4-6). The highest mean light attenuation coefficient (Kd) was found at the most up-river station SVBA (3.69 m^{-1}), while the lowest was found near the mouth of the river at station SV09 (1.13 m^{-1}). Differences in light attenuation were also found among the stations in Tangier Sound (ANOVA, $p < 0.05$). In this region, the highest Kd was found at the Manokin River station (MRGC, 2.27 m^{-1}) while the lowest was found at the northern Janes Island station (JI1G, 1.46 m^{-1}). In both Tangier Sound and the Patuxent River, light attenuation was significantly lower in the fall compared to either the spring or summer seasons (ANOVA, $p < 0.05$).

4.3.1.4 Water Column Total Suspended Solids

The spatial and temporal patterns in water column suspended solids (TSS) were very similar to those for light attenuation. In the Patuxent River, in all three seasons, a spatial gradient was found along the axis of the river with highest concentrations found at the most up-river sites compared to downriver locations (Figure 4-7). During the spring, TSS concentrations at the two sites furtherest up-river in the Patuxent (SVBA, and SV02) were among the highest recorded all year. In addition, median TSS concentrations in the Patuxent River were significantly higher in the spring (28.5 mg l^{-1}) compared to either the summer or fall (14.8 mg l^{-1} and 14.4 mg l^{-1}, sign rank test, $p <0.01$). In Tangier Sound, median TSS concentrations were highest in the spring (27.5 mg l^{-1}), however, no significant seasonal differences were found among the seasons (sign rank test, $p >0.05$). Overall, TSS concentrations in Tangier Sound were significantly higher than in the Patuxent River (sign rank test, $p < 0.01$).

4.3.1.5 Water Column Chlorophyll-*a*

The spatial and temporal patterns in water column chlorophyll-*a* concentrations were different from many of the other measured parameters (Figure 4-8). Overall, median water column chlorophyll-*a* concentrations were significantly higher (sign rank test, $p < 0.001$) in the Patuxent River (14.98 μg l^{-1}) compared to Tangier Sound (9.11 μg l^{-1}). On a seasonal basis, in Tangier Sound there were no significant differences in chlorophyll-*a* concentrations. However, in the Patuxent River, median chlorophyll-*a* concentrations were significantly higher ($p < 0.01$) in the spring (34.32 μg l^{-1}) compared to either the summer (14.4 μg l^{-1}) or fall (12.2 μg l^{-1}) season.

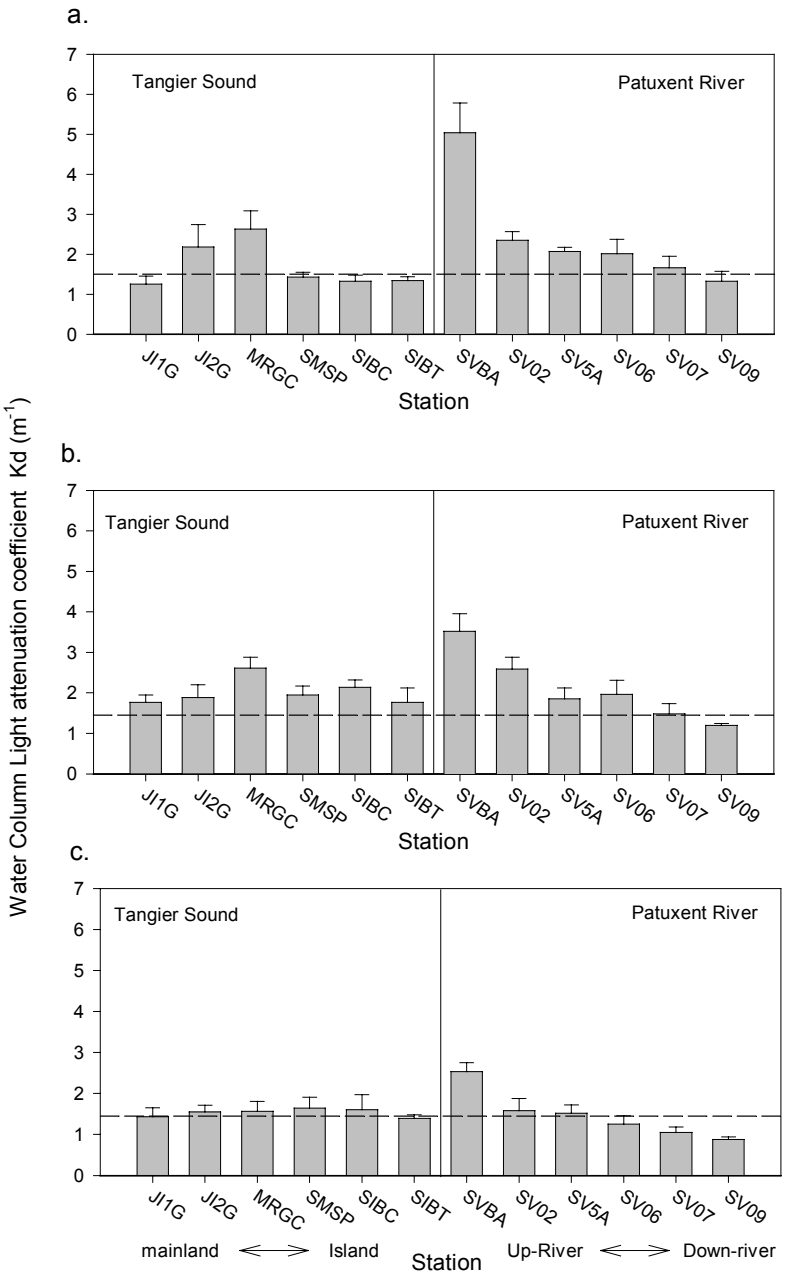

Figure 4-6. Mean (+/- 1SE) water column light attenuation coefficient (Kd) for (a) spring, (b) summer, and (c) fall for the Patuxent River and Tangier Sound 2000. *Dashed line represents the upper limit Tier II mesohaline SAV habitat requirement (USEPA, 2000).*

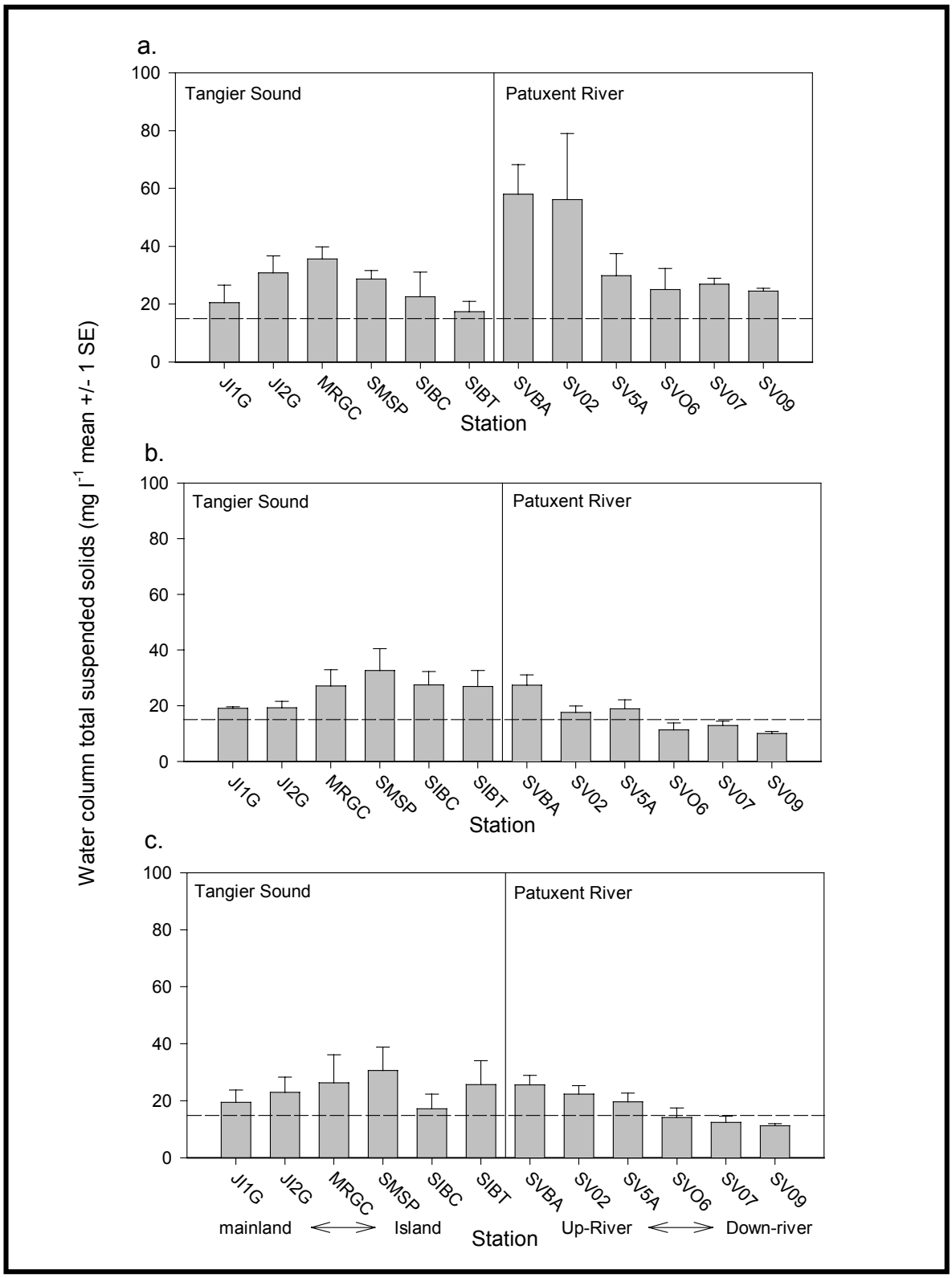

Figure 4-7. Mean (+/- 1SE) water column total suspended solids (TSS) concentrations for (a) spring, (b) summer, and (c) fall for the Patuxent River and Tangier Sound 2000.
Dashed line represents the upper limit Tier II mesohaline SAV habitat requirement (USEPA, 2000).

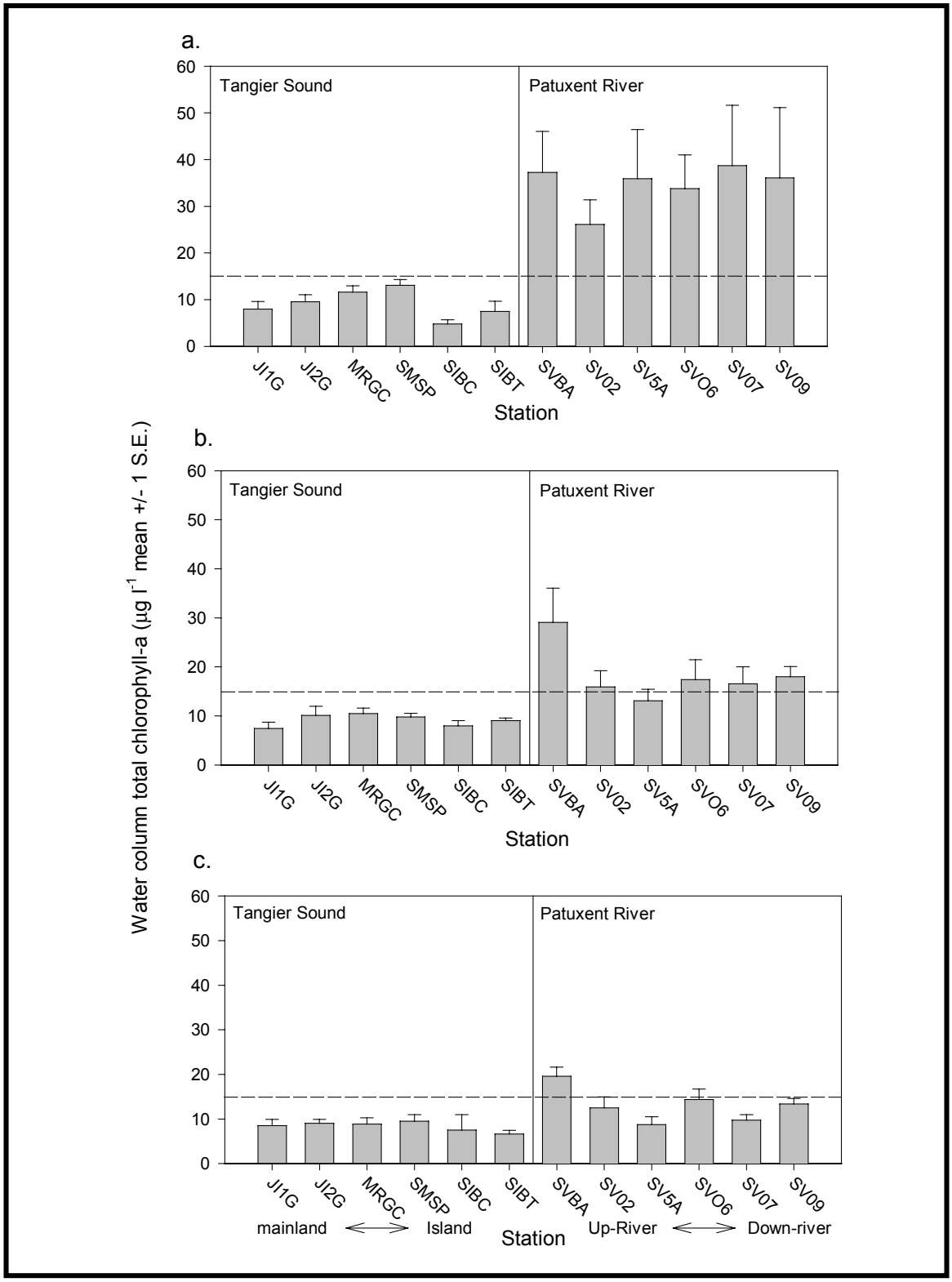

Figure 4-8. Mean (+/- 1SE) water column total chlorophyll-*a* (Tchl*a*) concentrations for (a) spring, (b) summer, and (c) fall for the Patuxent River and Tangier Sound 2000. *Dashed line represents the upper limit Tier II mesohaline SAV habitat requirement (USEPA, 2000).*

4.3.2 Results of Epiphyte Growth Study

4.3.2.1 Epiphyte Dry Mass

Epiphyte dry mass accumulation rates varied with season and were significantly higher in summer compared to either the spring or fall ($p < 0.01$, Figure 4-9). Dry mass accumulation rates also varied considerably within each region. This was especially true during the summer. In the Patuxent River, for example, the mean dry mass accumulation rate varied from 0.07 mg cm^{-2} day^{-1} (station SVBA) to 0.32 mg cm^{-2} day^{-1} (station SV09). In Tangier Sound the mean dry mass accumulation rate varied from 0.05 mg cm^{-2} day^{-1} (station SIBT) to 0.41 mg cm^{-2} day^{-1} (station SIBC). No significant difference was found in dry mass accumulation between Tangier Sound and Patuxent River in either the spring or summer season. However, dry mass accumulation was higher in Tangier Sound compared to the Patuxent River in the fall (sign rank test, $p< 0.001$).

4.3.2.2 Epiphyte Chlorophyll-*a*

Epiphyte total chlorophyll-*a* accumulation rates varied with season and were significantly higher in summer compared to either the spring or fall ($p < 0.01$, Figure 4-10). Epiphyte chlorophyll-a accumulation rates also varied considerably among stations within each region as well. In the Patuxent River the maximum mean summer chlorophyll-*a* accumulation rate was 0.264 µg cm^{-2} day^{-1} at station SV09 while the minimum was 0.035 µg cm^{-2} day^{-1} at station SVBA. Due to large difference in fouling rates among stations, there was no statistical difference in chlorophyll-*a* accumulation between Tangier Sound and the Patuxent River in any season.

4.3.2.3 Epiphyte Light Attenuation (PLW and PLL)

Calculating the PLW and PLL statistics allows the comparison of the relative contribution that epiphyte fouling will make towards light attenuation among sites, regions and seasons and a comparison of true light availability among stations. In the spring, while fouling rates were fairly low, results suggest SAV at all locations in the Patuxent River, except the most up-river station (SVBA), would experience light conditions similar to those stations in Tangier Sound (Figure 4-11.a). In fact PLL at station SV09 (44 %) in the Patuxent was slightly better than any station surveyed in Tangier Sound. During the summer season, water column light attenuation in the Patuxent was lower than in Tangier Sound, but epiphyte fouling rates in the Patuxent resulted in PLL levels at most stations similar to those found in Tangier Sound (Figure 4-11.b). No significant differences were found in mean PLL levels between the Patuxent River and Tangier Sound during the summer season ($p > 0.05$). In the fall however, PLL levels at most stations in the Patuxent were actually higher than those found in Tangier Sound ($p < 0.05$).

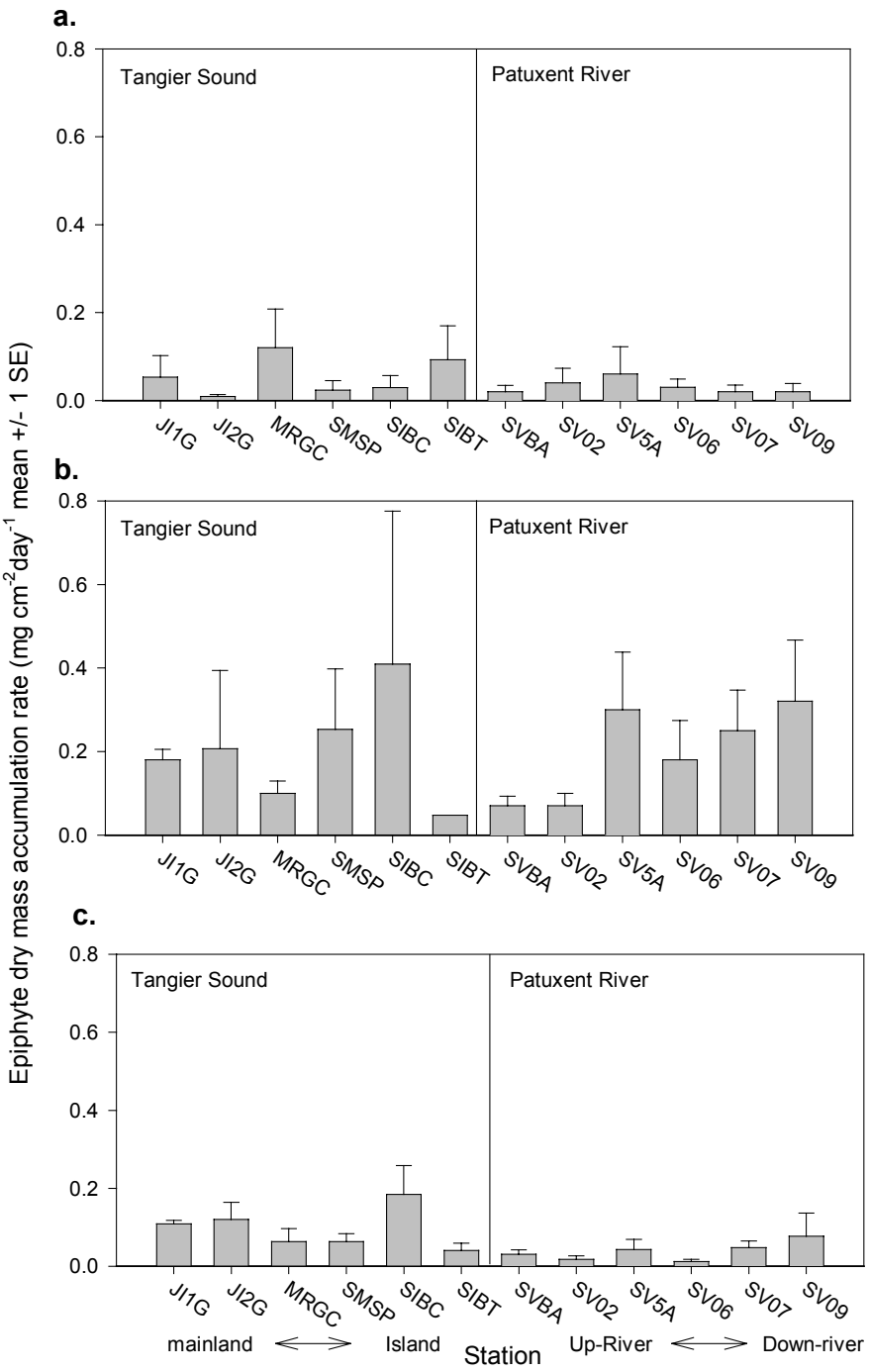

Figure 4-9. Mean (+/- 1SE) epiphyte dry mass accumulation rate on Mylar® strips deployed for exposures of 6-8 days in a) spring, b) summer and c) fall along the Patuxent River and Tangier Sound 2000.

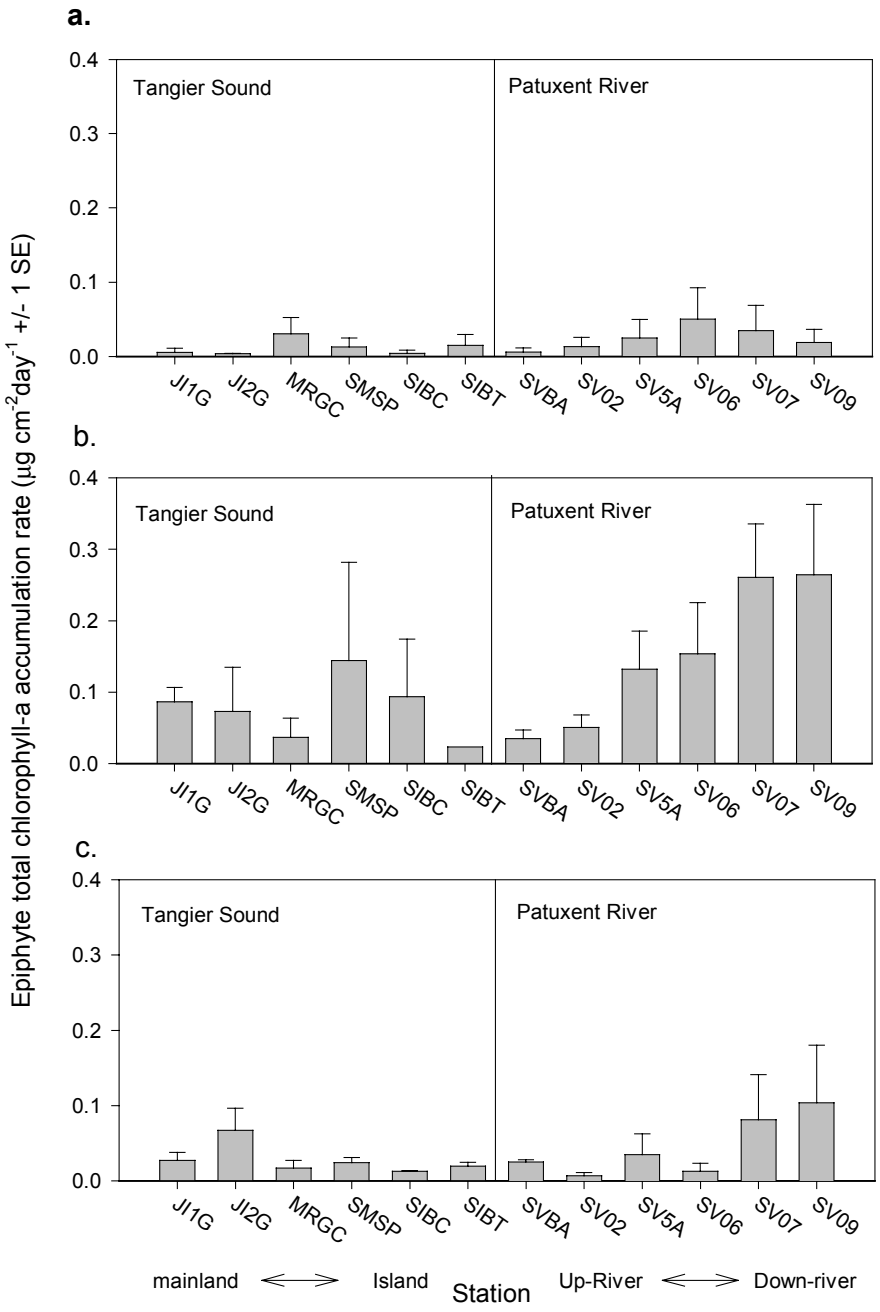

Figure 4-10. Mean (+/- 1SE) Epiphyte total chlorophyll-*a* accumulation rates on Mylar® strips deployed for *in situ* exposures of 6-8 days in a) spring, b) summer and c) fall in the Patuxent River and Tangier Sound 2000.

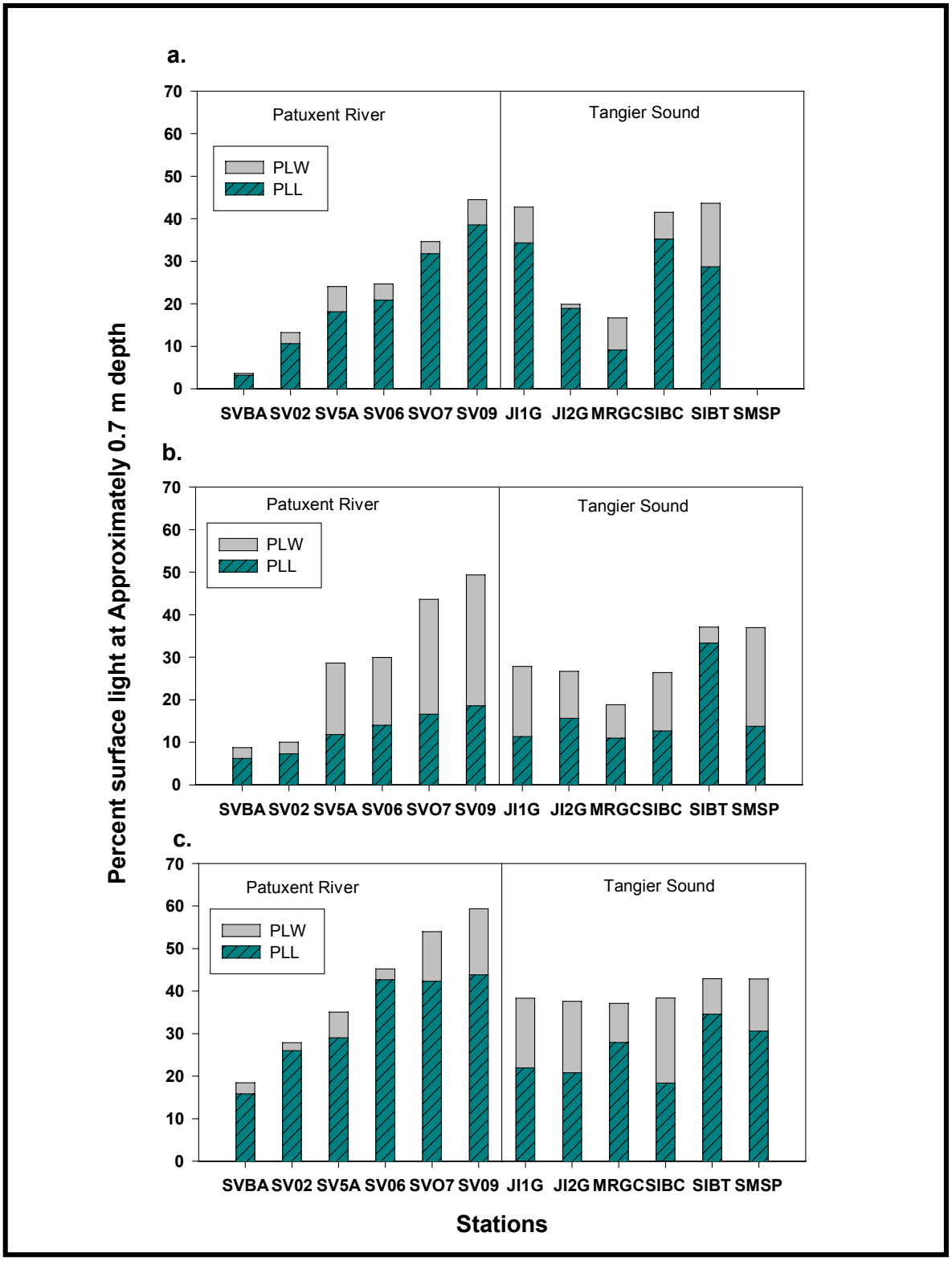

Figure 4-11. Mean light available through the water column (PLW) at approximately 0.7m depth and light at the leaf surface (PLL) in the Patuxent River and Tangier Sound for a) spring, b) summer and c) fall 2000 calculated from epiphyte accumulation on Mylar® strips.

4.4 Discussion and Conclusions

4.4.1 Near-shore Water Quality Evaluation

Dissolved nutrient concentrations (DIN and DIP) in both Tangier Sound and Patuxent River generally fell below the mesohaline habitat limits established by the Chesapeake Bay Program (USEPA, 2000). However, concentrations differed significantly among stations within each region. In addition, the ranking of these stations by nutrient concentration also changed with season reflecting differences in the source of these nutrients. For example, during the spring season, the highest DIN concentrations were found at sites influenced most by Chesapeake Bay waters rather than river water in both the Patuxent and Tangier Sound. These differences were not found in the other seasons. Dissolved phosphorus concentrations were uniformly low in Tangier Sound and were consistently lower than concentrations found in the Patuxent River in all seasons. Water column chlorophyll-*a* concentrations did exhibit some dramatic differences between regions. During the spring season, chlorophyll-*a* concentrations were significantly higher in the Patuxent than in Tangier Sound. These differences between regions, while not as great, were also found in the summer and fall seasons. Water column chlorophyll-a concentrations in Tangier Sound were consistently below the mesohaline habitat limit ($15\mu g^{-1}$), while in the Patuxent concentrations only fell below that limit in the fall season. Concentrations of total suspended solids (TSS) overall were highly variable among stations within each region, but were slightly higher in Tangier Sound compared to the Patuxent River and in general exceeded the habitat limit of 15 mg^{-1} most of the time. Only the most down-river stations in the Patuxent were below this limit during certain times of the year (Figure 4-7). Water column light attenuation (Kd) was somewhat more variable among stations in the Patuxent than among stations in Tangier Sound. For example, light attenuation at some stations never fell below the mesohaline Tier II habitat limit (1.5 m^{-1}; USEPA, 2000), while at other stations Kd values were very close or consistently lower than the habitat limits throughout the season (Figure 4-6). Considered together, these results suggest that water quality conditions within the down-river locations of the Patuxent should be adequate for SAV survival. Water quality conditions at these Patuxent locations appear to be equivalent in many ways to conditions found in Tangier Sound where SAV is healthy and thriving. Therefore, it further reinforces the notion that other factors may be limiting SAV recovery in the lower Patuxent River.

4.4.2 Epiphyte Growth Study

The measurement of epiphyte fouling rates and the calculation of PLW and PLL statistics allow for a further refinement of the habitat conditions experienced by SAV in these two regions. During the spring season, epiphyte fouling rates were quite low and contributed little to light attenuation to the leaf surface in both Tangier Sound and Patuxent River. Light available to the leaf surface at sites in Tangier Sound was very comparable to sites in the Patuxent River and were not very different from estimates using water column light attenuation alone. In the summer, fouling rates were higher and resulted in light available at the leaf surface much lower than would be expected using water column light

attenuation alone. For example, in the down-river sites of the Patuxent (SV5A, SV06, SV07, and SV09), light availability was reduced from 38% surface irradiance using water column estimates alone (PLW) to 15% at the leaf surface (PLL) with epiphyte light attenuation considered. In Tangier Sound, epiphytes reduced the light available from 28% of surface irradiance using water column estimates alone (PLW) to 16% at the leaf surface (PLL). However, the interpretation of these statistics must be made carefully. In this study, epiphyte biomass estimates were made using artificial substrates rather than live SAV. While previous studies have shown that fouling rates on Mylar® strips are similar to certain species of SAV for short time intervals (7-10 days; Boynton *et al*., 1999), shoots of SAV are composed of blades of varying age with a range of epiphyte biomass covering them. As a consequence, light attenuation to the whole plant would depend on a variety of factors such as leaf growth rates, position in the water column and morphological similarity to the Mylar® strips. In addition, these data reflect only a few weeks of sampling in the spring, summer, and fall of 2000. As a result of this limited sampling, caution must be used when comparing these data to habitat limits that have been established for medians throughout the whole SAV growing season (April – October).

4.4.3 Observations regarding SAV transplant success on the lower Patuxent River

In the lower Patuxent River natural recruitment of some SAV species has been sufficient to establish small, but ephemeral, populations in recent years. Since the 1980s, a number of SAV species have been observed in small patches at several different locations within this region of the estuary (Moore, 2000; personal observation). However, these populations have rarely persisted for more than a single season, and in many cases only a few months. For example, in 1997 a bed of *Potamogeton pectinatus* (Sago Pondweed) was found near Hungerford Creek (SV07), in the lower mesohaline region. However, this bed did not survive beyond summer. Similarly, *R. maritima* was observed, in small patches (up to several square meters each), along shoreline areas near the mouth of the Patuxent River in the summer of 1999. These isolated patches also did not persist into the next season (*personal observation*). An exception to this generalization has been the frequent appearance of the early spring annual *Zannichellia palustris*, which has been found in many of the smaller tributaries, and along the lower 25 km of the main estuary (*personal observation*). However, each spring, this species germinates from seed and completes its life cycle by mid-June as water temperatures reach 25 C. After June, these plants naturally senesce and thereby avoid periods of high epiphytic fouling.

Several hypotheses may explain why these small populations or patches have not persisted. These include poor water quality conditions, waterfowl grazing, disturbance by cownose rays (*Rhinoptera bonasus*), storm events or a combination of these. Secchi depth measurements collected in recent years (1985 – present) indicate that water transparency in the lower mesohaline region should be sufficient to support SAV to the one meter depth contour (USEPA, 2000). However, our studies indicate that especially in the lower mesohaline portion of the estuary, epiphytic fouling during the summer season can be a significant component of light attenuation to SAV. During summer

periods epiphyte accumulation can reduce the amount of light reaching SAV blades from approximately 30% of surface irradiance to less than 10% within a week. While an exact determination of light availability to a whole plant would depend on many variables (*e.g.*, leaf age, water depth, and hydrodynamics around the blade), these data suggest a possible mechanism contributing to the loss of SAV from this area and potential limitations to recovery.

SAV recovery may also be affected by grazing pressure from waterfowl or disturbance by cownose rays. Small, newly established beds, may be particularly sensitive to these types of disturbances. Evidence from transplant experiments in the lower mesohaline portion of the estuary suggests these mechanisms may also be important. Several test plots (1.0 m^2) of eelgrass initially survived for more than a year before they were grazed by waterfowl. Following this success, two larger plantings were completed in the spring of 2000 in the lower Patuxent River. At one site just upriver of Point Patience 5000 shoots each of *R. maritima*, *P. pectinatus*, and *Z. marina* were planted by the Alliance for the Chesapeake. Subsequent surveys indicated that the mixed species transplants suffered severe losses due to foraging by cownose rays and were destroyed only a few months after planting (R. Murphy, *pers. comm.*). The other planting at Sandy Point (SV09) survived to the fall 2000 but suffered extreme waterfowl (mute swans, *Cygnus olor*) grazing pressure in early 2001. Currently, several small isolated patches of eelgrass continue to grow at Sandy Point despite both high epiphyte loads and grazing pressure. We will continue to track the success of these transplants and add new transplants to this area to determine if larger scale efforts would be successful.

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5. HIGH RESOLUTION MAPPING OF SURFACE WATERS IN TANGIER SOUND AND MAGOTHY RIVER

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

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5.1 Introduction

An evaluation of potential gradients in water quality parameters was made using the DATAFLOW IV mapping system in the Magothy River and Tangier Sound in 2000. The DATAFLOW mapping system, when deployed from a small research vessel, allowed for the estimation of several water quality parameters with high spatial resolution in both shallow (approximately 1.0 m) and deeper waters. This is important because of the importance of shallow littoral zone habitats and the concern that monitoring of water quality in deeper channel waters may not adequately represent these shallow zones. The DATAFLOW system allowed us to collect water quality data in both habitats with high spatial resolution. As a result, the extent of any gradients in water quality parameters can be detected and mapped thus providing more information to help plan and design monitoring strategies for a more accurate assessment of near-shore habitats.

5.2 Methods, Locations and Sampling Frequency

5.2.1 DATAFLOW IV

DATAFLOW IV is a system of sensors, pumps, and dataloggers configured to collect a variety of water quality parameters while underway from a small research vessel. A schematic of this system is shown in Figure 5-1. This system collects data for the following parameters: temperature, salinity, conductivity, transmittance, and fluorescence. The flow rate of water through the system along with a time stamp and GPS coordinates are also logged. Water column turbidity is measured with a Wetlabs transmissometer. This unit provides a voltage output linearly proportional to the transmittance of light through a 10cm column of water with a voltage range of 0.0 V for a blocked path reading to 4.85 V for air. This voltage output must be regressed against more universally recognized units such as secchi depth and Kd, collected at fixed calibration stations in order to be of comparative use. Fluorescence is measured with a

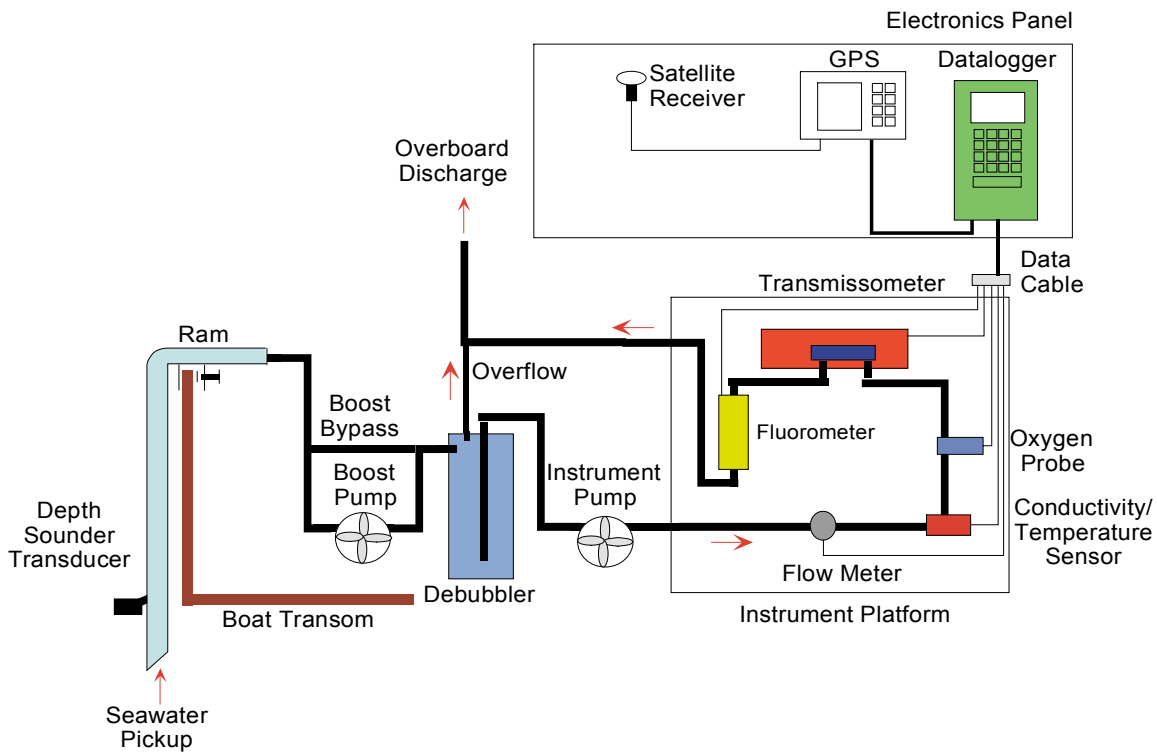


Figure 5-1. Schematic diagram of DATAFLOW IV illustrating the path of water through the instrument. *Seawater is picked up behind the transom of the research vessel through the "ram." At speeds in excess of 10 knots, hydrostatic pressure pushes water through the boost bypass to the debubbler. At slower speeds, the bypass is closed off and the boost pump is activated to ensure adequate flow of water to the instrument. The flow rate generated by either hydrostatic pressure or the boost pump is greater than that of the instrument pump, resulting in an overflow of water and any air bubbles through the debubbler overflow. The instrument pump draws water from the bottom of the debubbler at a rate of approximately 7.5 l* m^{-1}*. This flow rate is monitored by the flow meter to detect any malfunctions either during system use, or in post-processing of the data. Subsequently, the water flows past the conductivity/water temperature sensor, the dissolved oxygen probe, the transmissometer and finally the fluorometer before being discharged overboard. The global position system (GPS) is located in the electronics panel, directly above instrument array. The depth sounder transducer is located on the ram. Readings from all sensors are conveyed directly to the instrument controller units and to the datalologger, also located on the electronics panel.*

Wetlabs fluorometer and must be compared to discrete samples at fixed calibration stations to be converted to water column chlorophyll-*a*. A detailed explanation of all field and laboratory procedures is given in Rohland *et al*. (1999).

5.2.2 Sampling Locations and Frequency

DATAFLOW cruises were completed twice in the spring and twice in the fall of 2000 on both the Magothy River and Tangier Sound (Table 5-1). Cruise tracks were chosen to provide a reasonable coverage of each water body, sampling both near-shore and off-shore waters. A sample cruise track is shown for each region in Figure 5-2. In the Magothy River, a total of 8 calibration stations were sampled during each cruise and in Tangier Sound, a total of 18 calibration stations were sampled per cruise. The selection of calibration station locations in each region was made to sample the greatest possible range of water quality conditions found during each cruise and to sample a broad spatial area. Therefore, the location of most calibration stations in each region may not have varied between cruises. However, the location of several calibration stations were chosen where possible to correspond to Chesapeake Bay Program water quality monitoring stations within each region and every effort was made to sample at those locations during each cruise. The coordinates for those stations are listed below in Table 5-2.

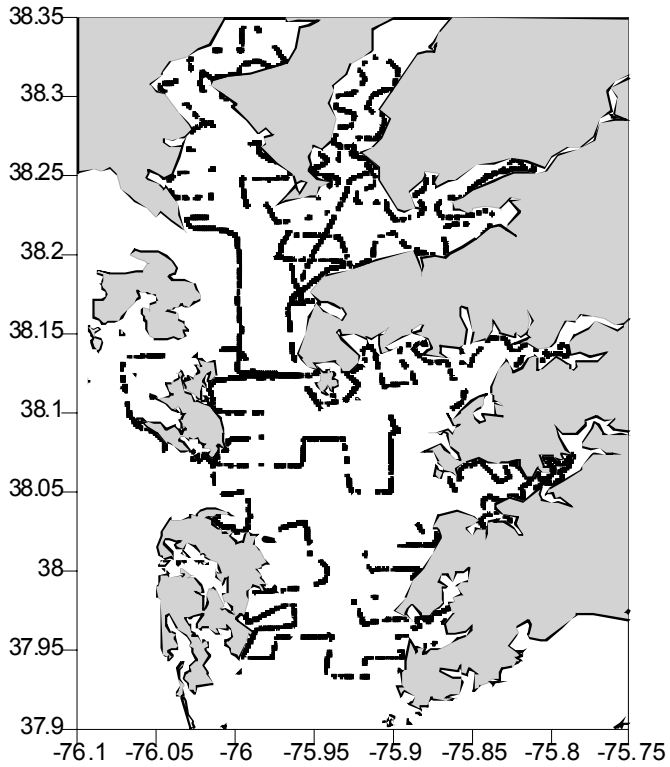
Table 5-1. DATAFLOW cruise dates in 2000. Tangier Sound, cruises typically required 2-3 days of mapping, thus dates listed below represent the initial day of each cruise. Magothy River cruises were completed in a single day.

Region	Spring	Fall
Tangier Sound	5/15, 5/23	9/26, 10/11
Magothy River	5/12, 5/26	9/7, 9/18

Table 5-2. Location of DATAFLOW IV calibration stations coincident with DNR water quality monitoring stations.

Region	DNR Station	Latitude NAD 83	Longitude NAD 83
Tangier Sound	EE3.0	38˚ 17.015'	76˚ 17.974'
	EE3.1	38˚ 11.190'	75˚ 58.377'
	EE3.2	37˚ 58.793'	75˚ 55.495'
	ET6.2	38˚ 20.015'	76˚ 52.959'
	ET7.1	38˚ 16.015'	75˚ 47.458
	ET8.1	38˚ 08.184'	75˚ 48.097'
	ET9.1	38˚ 03.319'	75˚ 48.109'
Magothy River	WT6.1	39˚ 04.538'	76˚ 30.200'

a.



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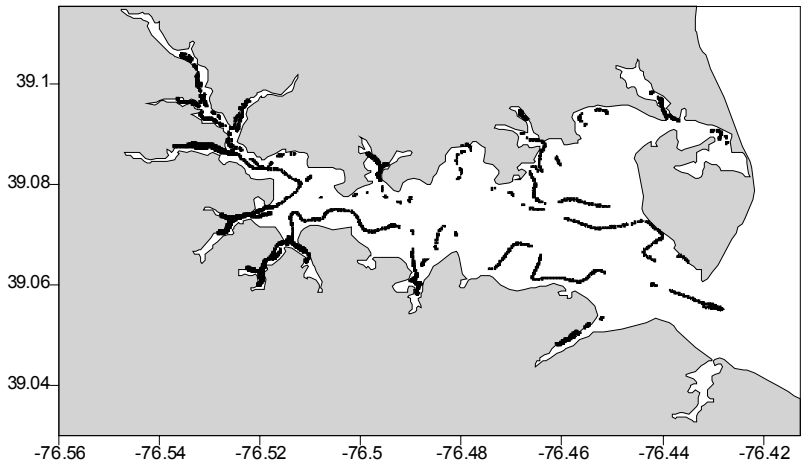

Figure 5-2. Typical DATAFLOW cruise track for:
a. Tangier Sound, September 26, 2000.
b. Magothy River, September 9, 2000

5.3 Results

5.3.1 Sources of Error with Interpolated Maps

The creation of contour maps of various water quality parameters from DATAFLOW data, allows for the visualization of spatial patterns in water quality. However, this process will incur a series of errors from various sources that should be recognized while interpreting these maps. The first source of error is incurred by the sensors themselves. The magnitude of this error will depend on the particular parameter being measured. A detailed explanation of these errors can be found in Rohland *et al*., (2000). The second set of error arises from the interpolation process that creates a regular spatial grid from the actual data points collected along the vessel cruise track. This error depends on many factors including the spacing and density of actual data points and the method of interpolation. This error is likely to increase as the distance from the actual data point increases. Finally, the creation of contour maps of parameters such as Kd, secchi, chlorophyll-*a* that are estimated from regression relationships calculated from data collected at the calibration stations will incur further error in the contour maps. This error will depend on the data collected during each cruise and may vary considerably. A detailed and thorough analysis of these errors has not yet been performed. As such, interpretation of these contour maps should be made with caution. Despite these limitations, the overall general patterns observed should remain valid.

5.3.2 Tangier Sound

Contour maps created from this data can be created with a number of different interpolation methods and thus provide different results and interpretations of the data. The maps provided simply illustrate one possible method used to view the patterns within the data. "Surfer" contouring software (Golden Software) was used to create the contour maps presented in this report. Interpolation using the nearest observations was performed using the default kriging procedures available in the software. Other interpolation methods may generate slightly different results.

A representation of the spatial variability in turbidity found within Tangier Sound on Sept. 26 – 28, 2000 is shown as a contour map of transmissometer voltage in Figure 5-3a. The primary pattern (North – South) of higher turbidity in the northern portion of the sound (Fishing Bay, Nanticoke and Wicomico Rivers) compared to more southerly regions was also found in previous cruises in Tangier Sound (Hagy and Boynton, 2000) and appears to be a permanent feature of Tangier Sound. The second order patterns that show isolated areas of higher turbidity regions located near-shore are likely the results of resuspension of sediments caused by 10 - 15 mph N-NE winds during that time. Patterns of turbidity at spatial scales smaller than these should be viewed with great caution. A contour map of secchi depth in Tangier Sound is shown in Fig. 5-3b. This map was created using estimated secchi depth values obtained from the regression of secchi depth on transmissometer voltage ($r^2 = 0.84$) measured at the 18 discrete calibration stations during this cruise. While the potential error associated with creation of a contour map from estimated values is greater than using direct measurements, the visualization of broad spatial patterns for commonly measured parameters remains valuable. The use of these

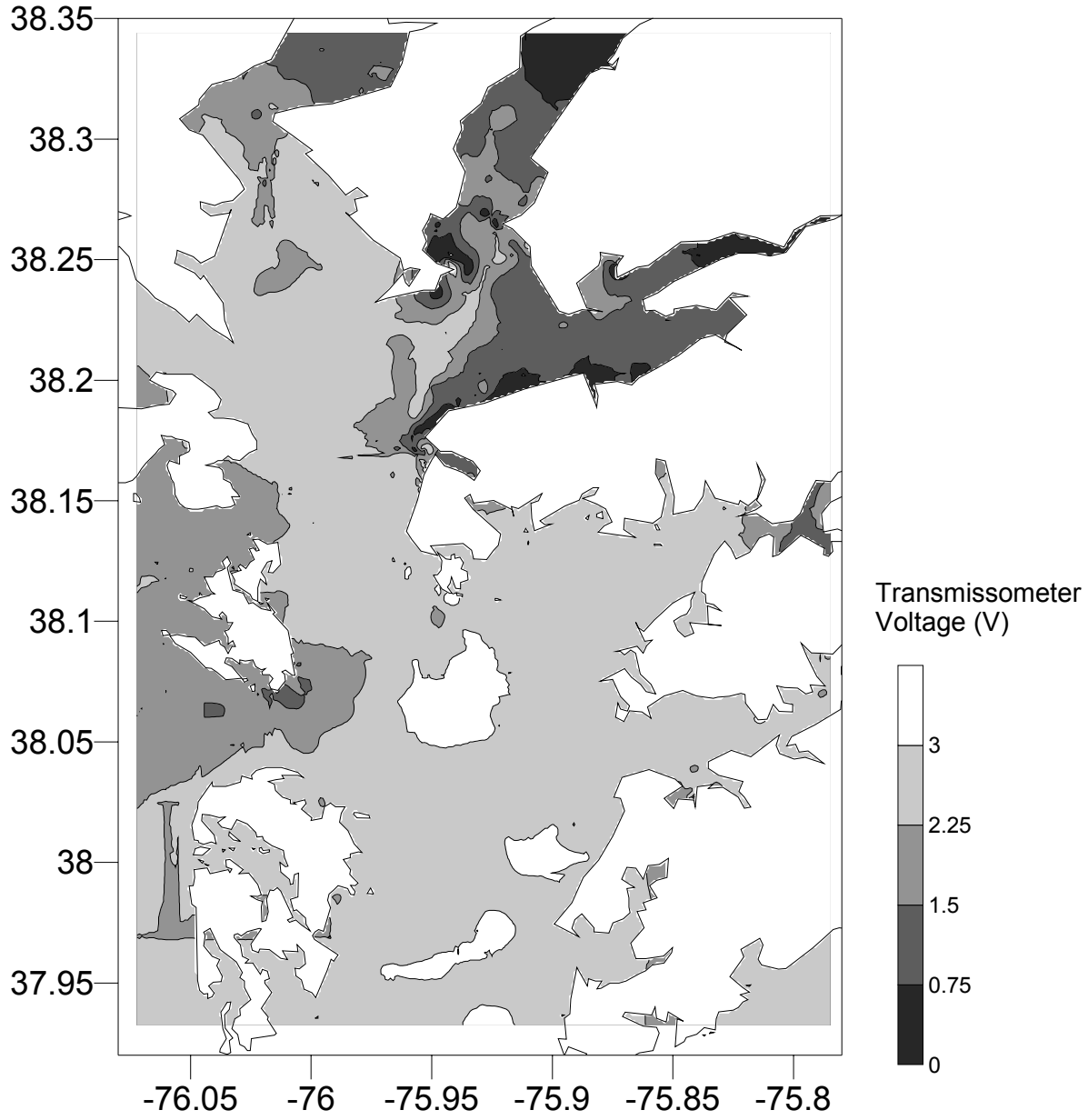

Figure 5-3.a. Contour map of transmissometer values constructed from DATAFLOW data collected in Tangier Sound, September 26 - September 28, 2000.

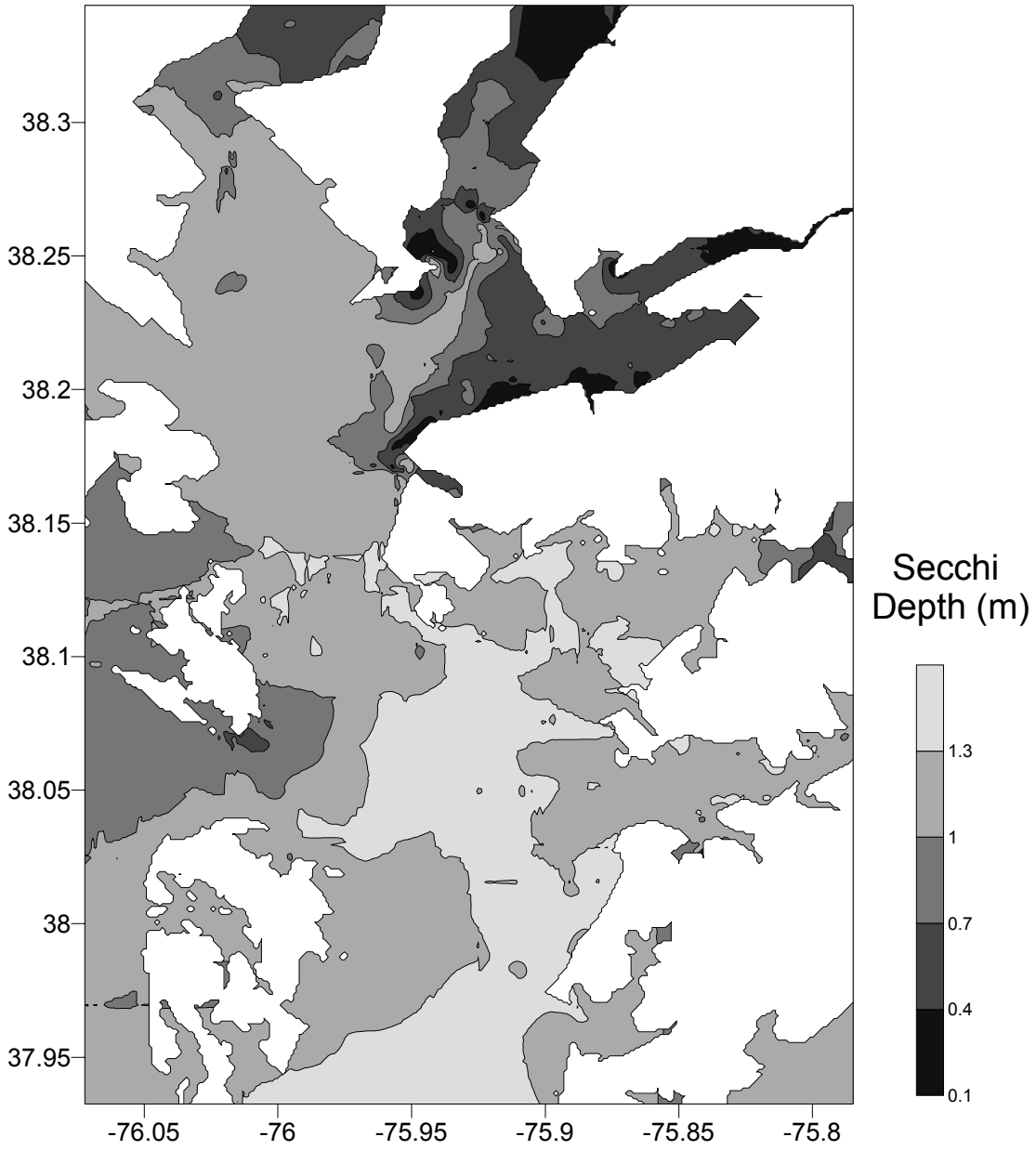

Figure 5-3.b. Contour map of estimated secchi depth constructed from DATAFLOW data collected in Tangier Sound September 26 - September 28, 2000.

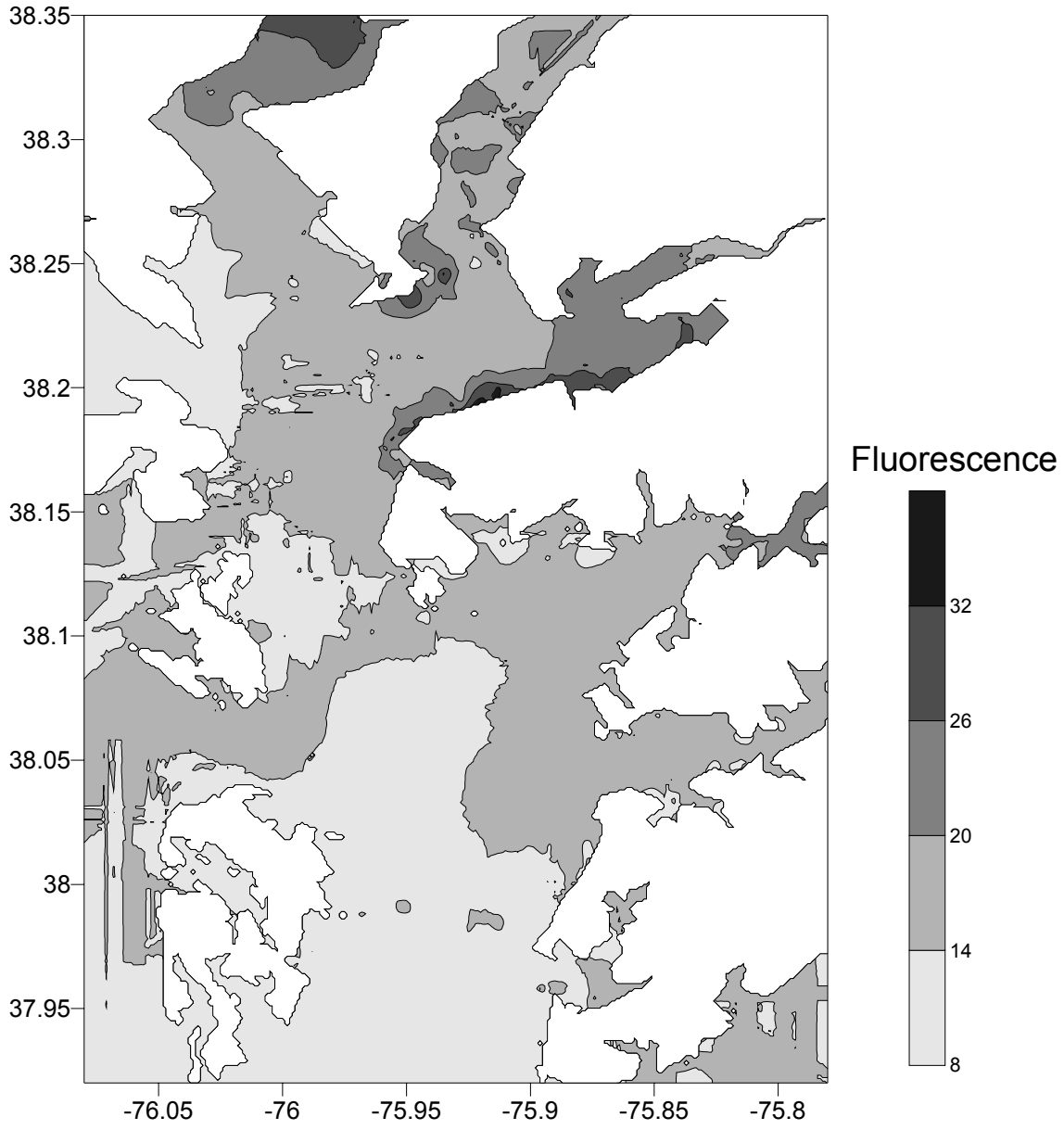

Figure 5-4. Contour map of fluorescence for data collected in Tangier Sound on September 26, 2000 and September 28, 2000 using DATAFLOW IV.

values to assess habitat compliance however should not be made unless a detailed error analysis can be completed.

A contour map of fluorescence values measured in Tangier Sound on Sept. 26 – 28, 2000 is shown in Figure 5-4. The primary patterns are very similar to those for transmittance with higher values found in Fishing Bay, the Nanticoke and Wicomico Rivers compared to other areas of the Sound. This suggests that for those areas of high turbidity, high phytoplankton concentrations were a large contributor.

5.3.3 Magothy River

Contour maps of transmissometer voltage and estimated secchi depth for the Magothy River on Sept. 7, 2000 are shown in Figure 5-5. The primary spatial pattern of higher turbidity near the mouth of the river indicates the large influence Chesapeake Bay water has on this relatively small tributary system. During this particular cruise, measurable gradients in turbidity were found within the waters sampled. For example, secchi depth ranged from 0.6 to 1.3 meters among the 8 calibration stations sampled, and transmissometer voltage ranged from 1.66 to 2.91 volts at those same locations. For this reason, the regression between transmissometer voltage on secchi depth was strong ($r^2 = 0.90$) thus minimizing the error associated with the construction of an interpolated contour map (Figure 5-5b). A similar spatial pattern was also seen for fluorescence. Higher levels of fluorescence found near the mouth of the river compared to more up-river locations suggest that regions of higher turbidity are the result of chlorophyll-*a* and not just suspended sediment. While strong relationships were identified on the September 7, 2000 cruise allowing the translation of transmissometer voltage to other more universal parameters (Kd and secchi depth), virtually no spatial gradients were found during other cruises on the Magothy River. The lack of spatial gradients resulted in very poor regression relationships between transmissometer voltage and the other indicators of water transparency.

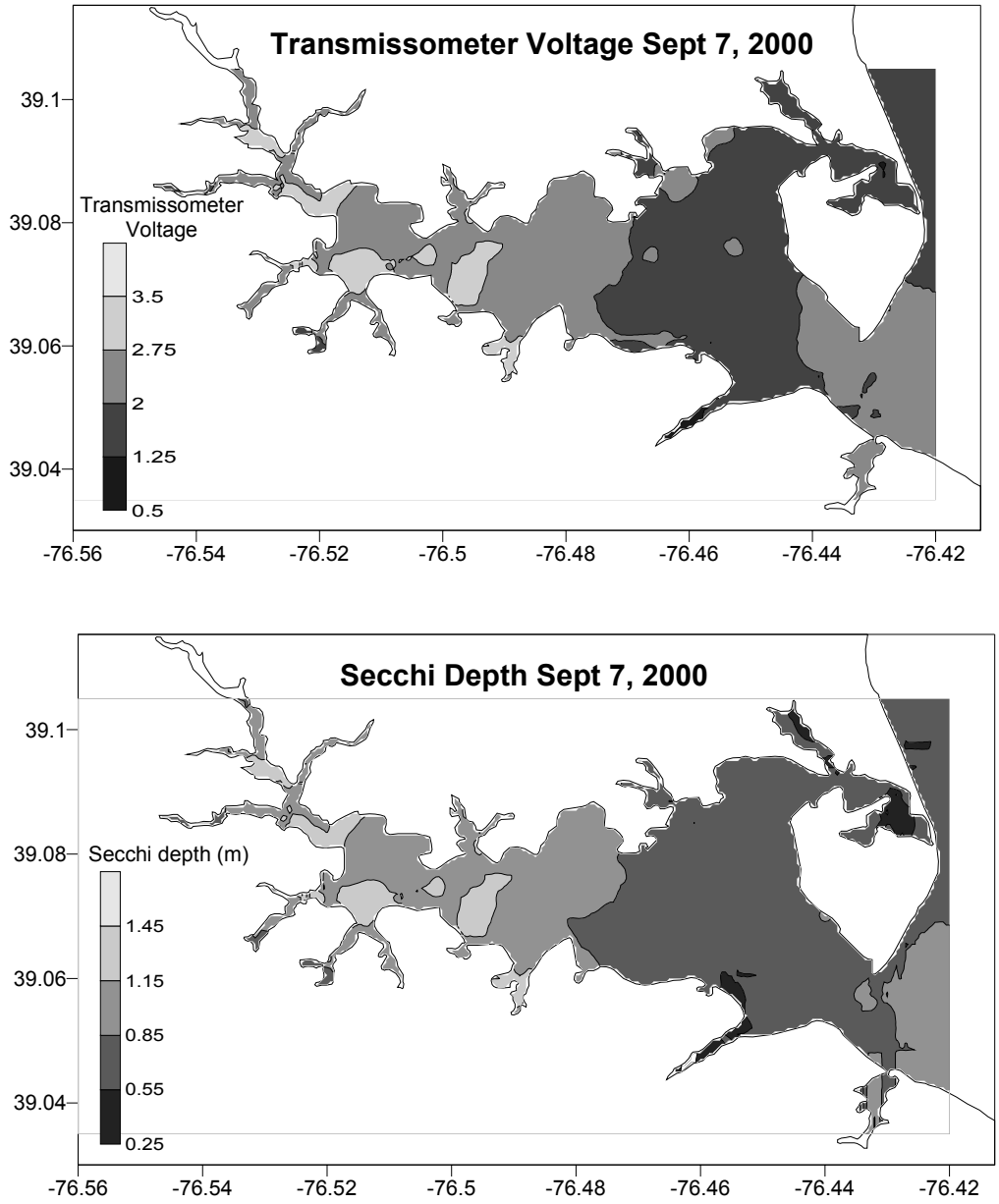

Figure 5-5. Contour maps created from data collected on September 7, 2000 in the Magothy River for a. transmissometer data and b. secchi depth converted from transmissometer data (r^2 = 0.90).

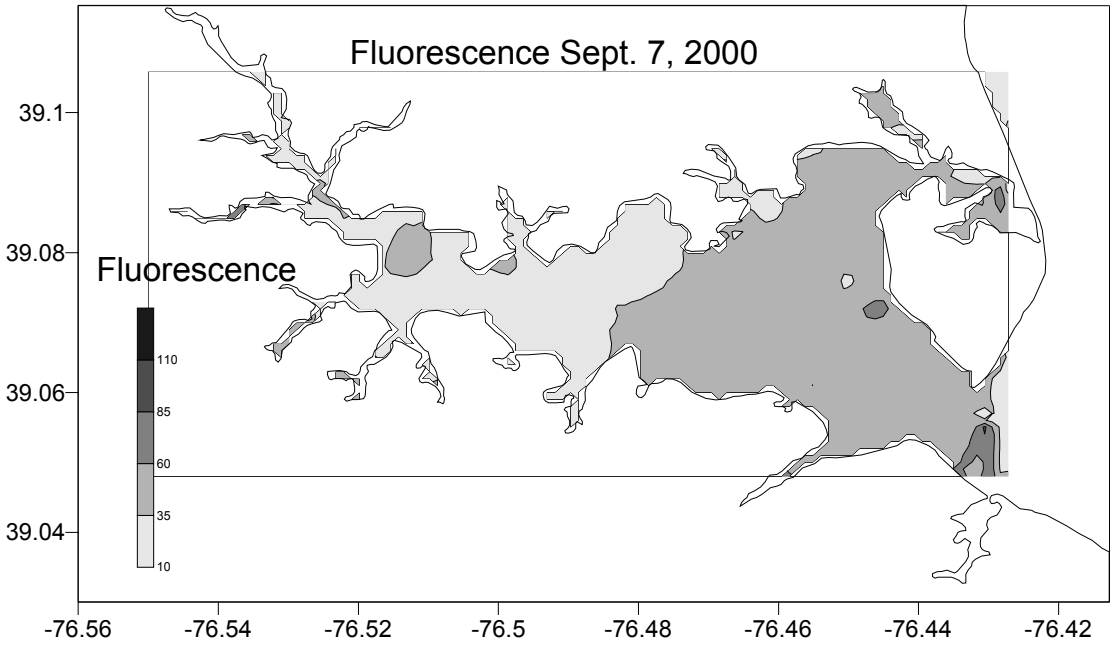

Figure 5-6. Contour map of fluorescence constructed from DATAFLOW data collected in the Magothy River on September 7, 2000.

5.4 Discussion

DATAFLOW technology provides a method to extend the spatial estimates of various water quality parameters beyond traditional channel monitoring into near-shore habitats and small tributary systems. This type of system excels at identifying spatial patterns and gradients and can be useful for assessing how well traditional channel monitoring represents near-shore conditions. However, as with any new system of data collection, substantial work is required to identify the most appropriate way to collect, use, and apply these data. Cruises in Tangier Sound during both 1999 and 2000 have measured substantial inshore-offshore gradients in water quality that would not have been identified with traditional channel based sampling. In contrast, strong inshore-offshore gradients were not typically found in the Magothy River during our sampling. Since the Magothy River is a much smaller system than Tangier Sound, it is not surprising to observe smaller gradients. Yet, mild gradients were found along the axis of the river probably resulting from the influence of Chesapeake Bay water on the river system, Results such as these have shed light on how to better monitor both large and small estuarine systems, and have generated additional questions regarding the use and application of data. For example, what is the potential influence of tidal state and how can it bias results when mapping near-shore habitats? In large systems such as Tangier Sound, how do we integrate data that take several days to collect, when short-term weather events (1 day and less) can have a substantial impact on shallow water conditions? Additional biweekly sampling is planned for 2001 on the Magothy and Severn Rivers and seasonal sampling is planned for Tangier Sound in 2001. Analysis of these additional data should help provide answers to these questions.

This type of data collection does have an important limitation that should be recognised. Some of the sensors used in DATAFLOW (transmissometer and fluorescence) record data in units (voltage, fluorescence) that are not readily translatable into standard units such as secchi depth, Kd or chlorophyll-*a*. This translation requires a calibration curve be generated from data collected at selected calibration stations during each cruise. The fit between field and DATAFLOW parameters has been variable and is dependent on the presence of an adequate gradient in water quality during each cruise. During 2000, correlation coefficients typically ranged from less than 0.50 to greater than 0.90. Occasionally, values were even lower and thus not very useful. To date, sufficient data have not been collected and analyzed to determine if these conversions can be improved, or if data from multiple cruises can be pooled to obtain a better result. At this stage of development, these translations provide a first order estimate of these parameters in near-shore waters. The huge increase in spatial extent and resolution is an improvement over the extrapolation of single fixed point monitoring of these habitats. The use of this type of data for assessment of habitat compliance is at this time limited by the accuracy of the correlation between standard ecological parameters (secchi, Kd, *etc.*) and the units measured by the instrument. As we gain confidence in the best way to collect and apply these data collected with this type of system we will be able to design specific mapping strategies to answer a variety of monitoring questions.

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6. RESEARCH PAPER SUBMITTED TO FOR PUBLICATION PHYTOPLANKTON DEPOSITION TO CHESAPEAKE BAY SEDIMENTS DURING WINTER-SPRING

James D. Hagy, Walter R. Boynton and David A. Jasinski

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Abstract

The often rapid deposition of phytoplankton to sediments at the conclusion of the spring phytoplankton bloom has been identified as an important component of benthic-pelagic coupling in temperate and high latitude estuaries and other aquatic systems. However, quantifying the flux is difficult, particularly in large and spatially heterogeneous environments. Surficial sediment chlorophyll-*a* (chl-*a*), which can be measured quickly at many locations, has been used effectively by previous studies as a biomarker indicating deposition of phytoplankton to estuarine sediments. In this study, surficial sediment chlorophyll-*a* was mapped in late spring at 20-50 locations throughout Chesapeake Bay during 8 years (1993-2000). A model was developed to estimate chlorophyll-*a* and carbon deposition using these measurements, while correcting for chlorophyll-*a* degradation during the time between deposition and sampling.

Bay-wide, the springtime accumulation of chlorophyll-*a* on sediments by late spring averaged 171 mg m^{-2}, from which the chlorophyll-*a* and carbon sinking fluxes, respectively, were estimated to be 353 mg m^{-2} and 26.5 g C m^{-2}. These deposition estimates were ~50% of estimates based on a sediment trap study in the mid-Bay. During 1993-2000, the highest average chlorophyll-*a* flux was in the mid-Bay (248 mg m^{-2}), while the lowest was in the lower-Bay (191 mg m^{-2}). Winter-spring average river flow was positively correlated with increased phytoplankton biomass in the lower Bay water column, increased chlorophyll-*a* deposition to sediments and down-Bay translation of chlorophyll-*a* deposition. In the 8 years of observation, estimates in several years diverged strongly from the overall pattern. A comparison of the carbon flux associated with the deposition of the spring bloom with annual benthic carbon

budgets indicated that the spring bloom did not contribute a disproportionately large fraction of annual carbon inputs to sediments. Regional patterns in chlorophyll-*a* deposition did not correspond with the strong regional patterns that have been found for net plankton metabolism during spring.

6.1 Introduction

The spring increase in phytoplankton production and biomass is a well-known feature of the phytoplankton dynamics of Chesapeake Bay and other temperate and high latitude aquatic ecosystems (*i.e.* lakes, estuaries, coastal zones and open ocean). In Chesapeake Bay, the spring increase in phytoplankton biomass typically begins in March. A decline in biomass begins some time in April and is concluded by the end of May (Figure 6-1). Termination of spring phytoplankton blooms in Chesapeake Bay has been attributed to nutrient limitation by phosphorus and dissolved silica (Conley and Malone, 1992, Malone *et al.*, 1996). This promotes sedimentation of diatoms (Conley and Malone, 1992), which are a major component of the winter-spring phytoplankton assemblage in Chesapeake Bay (Marshall and Nesius, 1996).

Excluding picoplankton, diatoms in winter-spring accounted for ~80% of phytoplankton cells in the lower Bay, 67% of cells in the mid-Bay (above pycnocline), and 56% of cells in the upper Bay (Chesapeake Bay Monitoring Program, *unpublished data*). *Note:* The **Upper Bay** in this study is the area from the Susquehanna River mouth to Annapolis, **Mid Bay** is the area from Annapolis to Potomac River mouth and the **Lower Bay** is the area from the Potomac River mouth to Chesapeake Bay entrance [Figure 6-2]). Diatoms accounted for similar proportions of phytoplankton carbon (R. Lacouture, *pers. comm.*, Table 6-1). Physiological responses to bloom senescence, such as formation of large aggregates, also enhance sedimentation and are an important aspect of the life cycle of diatoms (Smetacek, 1985). Consequently, sinking is a quantitatively important fate of diatom blooms. In a mesocosm experiment simulating a spring bloom in Narragansett Bay, Keller and Riebesell (1989) estimated that sedimentation accounted for 14-65% of gross production.

Rapid sedimentation of intact phytoplankton to sediments is an important pulsed input of organic matter to benthic communities in some marine systems. The importance arises not only from the quantity of the input, but from the high nutritional quality of the input, which has been shown to rapidly stimulate macrobenthic production (Graf *et al*., 1982; Marsh and Tenore, 1990), microbial processes, and nutrient regeneration (Jensen *et al*., 1990). Townsend and Cammen (1988) suggested that the large spring flux of organic matter to sediments could play a role in recruitment success of juvenile demersal fishes. Spring bloom phytoplankton deposition has been identified as a key annual event in Chesapeake Bay, linking ecosystem processes in the winter-spring period to subsequent summer conditions, including summer phytoplankton blooms and hypoxia (Malone, 1992).

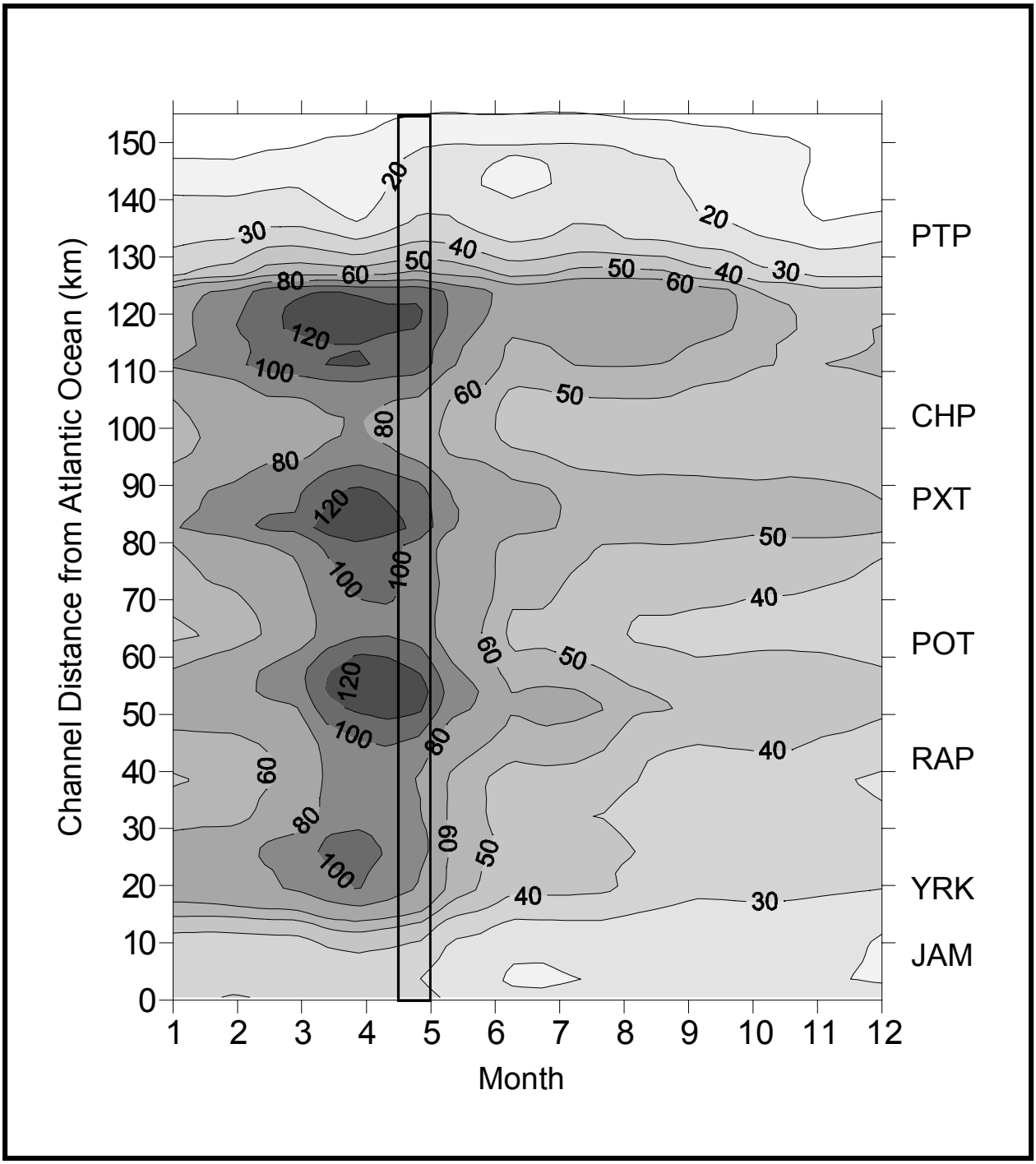

Figure 6-1. Average seasonal distribution of water column integrated chlorophyll-a (mg m-2) in Chesapeake Bay (1984-1999). Three letter codes refer to the major tributary rivers and are as follows: JAM=James River, YRK=York River, RAP=Rappahannock River, POT=Potomac River, PXT=Patuxent River, CHP= Choptank River, PTP=Patapsco River. The rectangle indicates the time period during which surficial sediment sampling was usually conducted. Exact dates are in Table 1. Data from the Chesapeake Bay Water Quality Monitoring Program (available from EPA Chesapeake Bay Program web site)

Table 6-1. The most abundant phytoplankton taxa (excluding picoplankton) in three regions of Chesapeake Bay during spring and the average fraction of total phytoplankton carbon contributed by diatoms. Phytoplankton species counts from unpublished Chesapeake Bay water quality monitoring program data (available from USEPA Chesapeake Bay Program web site). Unpublished carbon composition data provided by R. Lacouture (*pers. comm.*).

Upper Bay: Susquehanna River mouth to Annapolis
Mid Bay: Annapolis to Potomac River mouth
Lower Bay: Potomac River mouth to Chesapeake Bay entrance

Region	Most Abundant Phytoplankton Taxa (excluding picoplankton) during Jan-Apr. (% of cells)	% of Total Phytoplankton Counts (by diatoms)	% of Total Phytoplankton Carbon (by diatoms)
Upper Bay	unclassified centric diatoms[1] (23%), *Katodinium rotundatum*[2](12%), *Skeletonema costatum*[1](12%), *Crytomonas* spp.[3](12%), *Cyclotella* spp.[1](8%), *Skeletonema potamos*[1](7%).	56%	59%
Mid Bay	unclassified centric diatoms[1](17%), *Katodinium rotundatum*[2](15%), *Crytomonas* spp.[3](15%), *Cyclotella* spp.[1](12%), *Cerataulina pelagica*[1](9%), *Skeletonema costatum*[1](9%), *Chaetoceros* spp.[1](5%)	67% (above pycnocline)	69% (above pycnocline)
Lower Bay	*Skeletonema costatum*[1](20%), unclassified centric diatoms[1](18%), *Cerataulina pelagica*[1](9%), *Crytomonas* spp.[3](9%), unclassified pennate diatoms[4](9%), *Nitzschia pungens*[4](8%), *Rhizosolenia fragilissima*[4](4%), *Rhizosolenia delicatula*[4](3%).	83% (above pycnocline), 84% (below pycnocline)	Carbon conversion data not available

[1]centric diatoms, [2]dinoflagellates, [3]crytomonads, [4]pennate diatoms,

Because of the potential importance of spring bloom deposition to ecosystem processes, quantifying the flux is of particular interest. Unfortunately, this is technically challenging, a fact reflected in the paucity of flux estimates. Sediment traps have been used to quantify vertical fluxes of particles in various aquatic systems (*e.g.*, Smetacek *et. al.*, 1978), including in Chesapeake Bay (Boynton *et al.*, 1993). Although effective and useful, there are significant complications associated with the design and use of sediment traps (Blomqvist and Håkanson, 1981; Knauer *et al.*, 1984; Butman, 1986; Butman *et al.*, 1986; Asper, 1987). Among other problems, the effort and expense required to deploy and maintain sediment traps severely limits the number of traps that can be deployed. In spatially heterogeneous environments such as estuaries, this means that the small number of sediment traps likely to be employed may not adequately characterize the vertical particle flux. For example, if phytoplankton production is localized outside the vicinity of the trap, the measurement will underestimate the flux. Alternatively, an overestimate could result from phytoplankton being localized in the area surrounding the sediment trap. Therefore, an approach that can estimate the flux at many locations is preferable.

Previous studies have demonstrated that chlorophyll-*a* and other phytoplankton pigments are effective biomarkers for fresh phytoplankton inputs to sediments, and that biomarkers correlate with benthic biomass and production (Sun *et al.*, 1991; Josefson and Conley, 1997). This study used sediment chlorophyll-*a* measured in late spring as a biomarker for deposition to sediments of phytoplankton originating from the spring bloom. Since spring bloom sedimentation appears to occur rapidly and in relatively cold water, degradation rates are likely to be small relative to sedimentation rates. This suggests that chlorophyll-*a* accumulation in late spring, with an appropriate correction for degradation, could be used to estimate recent deposition of phytoplankton to sediments. To obtain adequate spatial resolution, sediment chlorophyll-*a* was mapped on a regular grid throughout the estuary. Recognizing the significant interannual variability, particularly in association with freshwater input rates (Boynton and Kemp, 2000), sediment chlorophyll-*a* was mapped annually for 8 consecutive years. Interpretation was supported by comparison with contemporaneous estimates of phytoplankton biomass in the water column, sedimentation estimates from a sediment trap study, estimated phytoplankton sinking rates, and by comparison with net plankton community production estimates.

6.2 Methods

6.2.1 Study Site

Chesapeake Bay is a large, partially stratified estuary that extends 300 km from the mouth of the Susquehanna River in Maryland to the Atlantic Ocean between Cape Henry and Cape Charles, VA. The oligohaline upper Bay has a mean depth of 5.1 m with a deeper (~10 m) channel near the eastern margin. The mesohaline mid-Bay has a deep central channel, 20-50 m, flanked by shallower shoal areas to the east and west, giving it a deeper mean depth of 11.9 m. The polyhaline lower Bay is broader with a wide central channel region averaging ~15 m depth as well as broad shoal areas on the flanks of the channel. The mean depth is 6.6 m.

The physical transport regime throughout most of the estuary is best characterized by 2-layer gravitational circulation in which net landward advection occurs below the pycnocline and net seaward advection occurs in the surface layer (Pritchard, 1952). In the upper Bay, the circulation begins seaward at all depths and at some point down-estuary makes a transition to the two-layer circulation.

Sediment-types vary throughout the estuary, possibly influencing vertical distributions of chlorophyll-*a* in sediments. North of Patuxent River and in the western half of the Bay south of Patuxent River (Figure 6-2), sediments are >80% silt-clay except in shallow waters. In these shallow waters, and in deeper areas of the eastern half of the south Bay, more porous sandy sediments (>80% sand) predominate (Kerhin *et al*., 1983; Chesapeake Bay Benthic Monitoring Program, unpublished data).

6.2.2 Field Methods

Sediment cores were obtained throughout the Bay during mid to late April in each year during 1993-2000 (Figure 6-3, Table 6-2). Sampling cruises were conducted aboard the R/V Cape Henlopen and were part of a multi-disciplinary research project (Chesapeake Bay Land Margin Ecosystem Research Program).

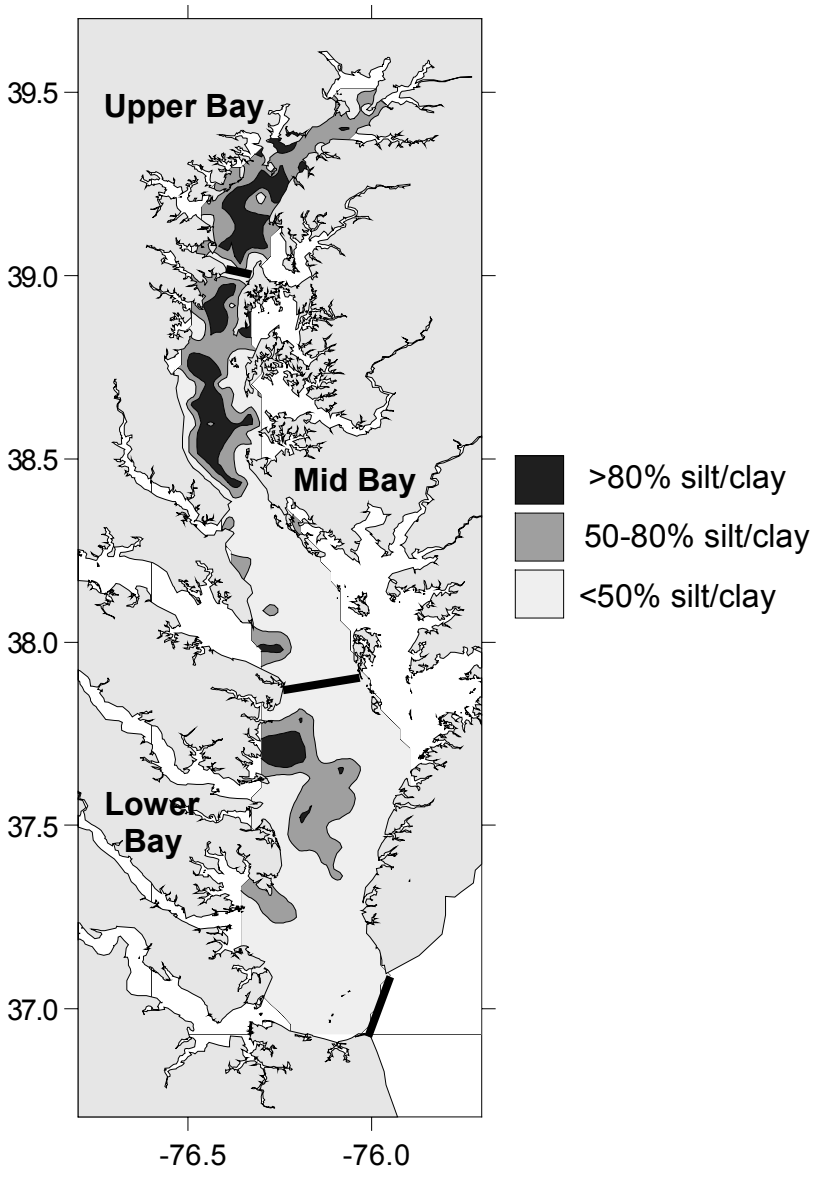

Figure 6-2. A map of Chesapeake Bay indicating regional boundaries and the distribution of sediment types as computed from the Chesapeake Bay Monitoring Program Benthic Data (data available from US EPA Chesapeake Bay Program Web Site). Distribution of sediment types is comparable to Kerhin *et al.* (1983).

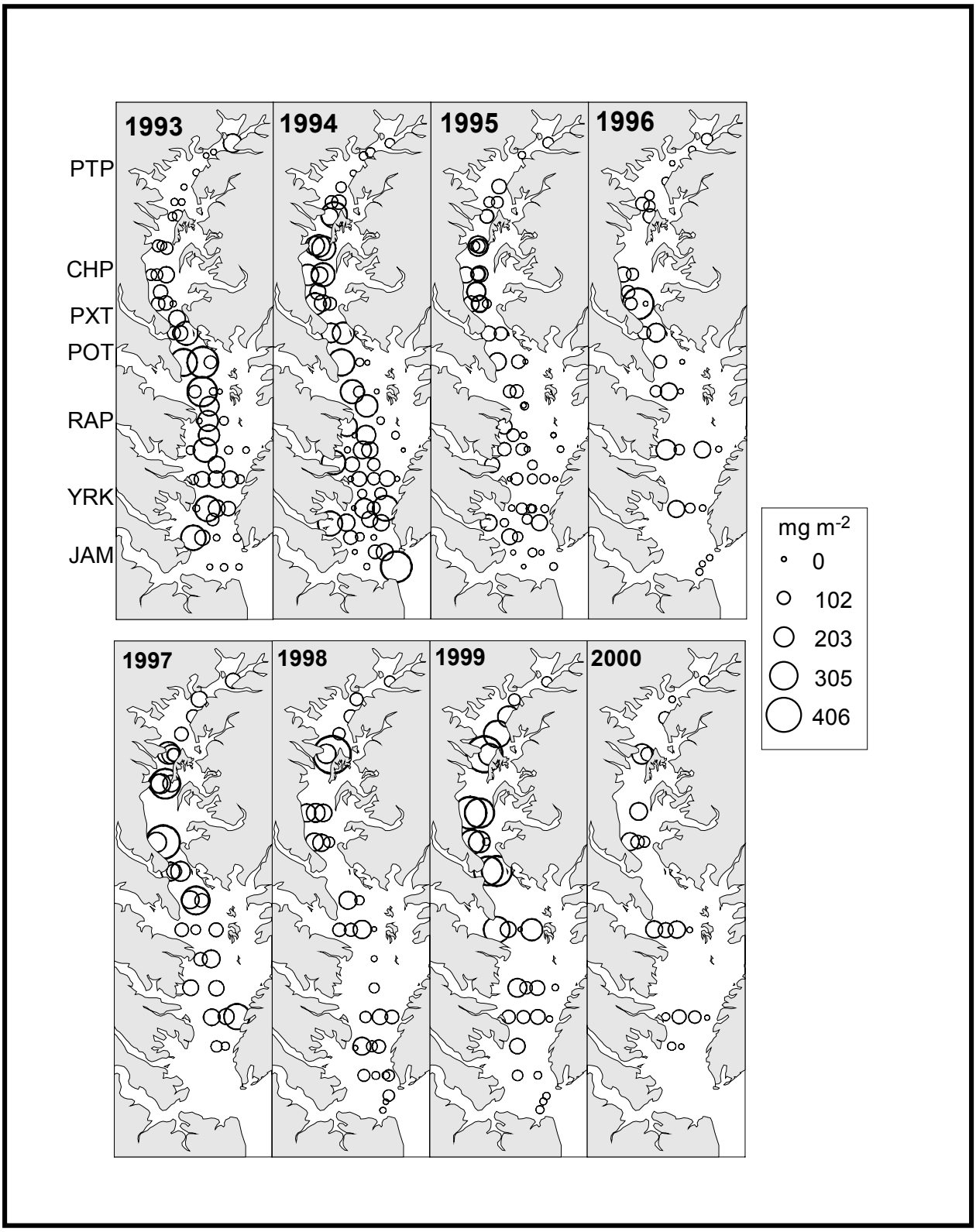

Figure 6-3. The distribution of total chlorophyll-*a* in the top 1 cm of Chesapeake Bay sediments during late spring in 1993-2000. The values for 1993 are estimated from total chlorophyll-*a* in the top 2 mm. The three letter codes adjacent to the 1993 map identify the major tributaries referenced in Figure 6-1.

Table 6-2. Cruise dates for sediment chlorophyll-*a* mapping.

Year	Begin	End
1993	5/8/93	5/12/93
1994 May		
1995	4/28/95	5/3/95
1996	4/27/96	5/7/96
1997	4/20/97	4/24/97
1998	4/11/98	4/15/98
1999	4/19/99	4/23/99
2000	4/29/00	5/2/00

Cores with an undisturbed sediment-water interface were obtained using a 0.25 m^2 Smith-Macintyre coring device at 20-50 locations usually located along horizontal transects spaced ~20 km apart. In 1993-1995, when the highest numbers of stations were sampled, additional stations were occupied between transects. Cores were obtained in waters from the deepest portions of the Bay to as shallow as 8 m. Shallower depths were not sampled due to draft limitations of the research vessel.

Once onboard, a sub-core was obtained using a modified 60 cc plastic syringe. This provided a sample of precise cross-sectional area and 1 cm depth, which was frozen immediately in a plastic centrifuge tube. In 1993, the top 2 mm from 2 sub-cores was combined in a single centrifuge tube, rather than 1 cm from a single sub-core. In 1994-1995, two samples were obtained at each station. One sample included the top 1 cm from a single sub-core, while the other included the top 2 mm from 2 sub-cores, as in 1993. This provided a means for comparing the two types of samples. The reasons for these changes in field methods were unrelated to this study, but provided a limited means to examine the vertical distribution of chlorophyll-*a* in Chesapeake Bay sediments.

6.2.3 Pigment Analysis

The Nutrient Analytical Services Laboratory at Chesapeake Biological Laboratory, Solomons, MD, quantified sediment chlorophyll-*a* and phaeopigment concentration using the method described below. Frozen sediment samples were briefly thawed at room temperature, then 40 ml of 90% acetone was added. Samples were extracted for 12 hours in a dark refrigerator, shaking 2-3 times during the course of the extraction, then centrifuged at ~1760 rpm for 5 minutes before decanting into a cuvette. Total chlorophyll-*a*, active chlorophyll-*a* and phaeopigment concentrations in the acetone extracts were determined fluorometrically using the acidification method described in Strickland and Parsons (1972) and Parsons *et al.* (1984). Only the total chlorophyll-*a* and phaeopigment data were examined in this study. The laboratory utilized a Turner Designs Model TD700 fluorometer calibrated against a spectrophotometer using pure chlorophyll-*a* from spinach (Sigma Chemical Company, C 5753), or liquid standards from Turner Designs, #10-850.

The extraction method that was used differed from that used by some published studies (*e.g.* Sun *et al*., 1991). Specifically, sediments were not sonicated prior to extraction, and only a single extraction was used. Therefore, a method comparison study was undertaken to determine whether the results would have been changed significantly by use of sonication and/or an additional extraction. In this experiment, surficial sediments were obtained from box cores collected on Patuxent River, then processed in the field as described above. In the laboratory, the samples were thawed, then homogenized. Fifteen equal size aliquots from the continuously stirred mud-slurry were extracted as described above after one of three sonication treatments. The treatments were: (1) no sonication (control); (2) microsonication for 3 minutes; and (3) sonication in a sonicator bath. The extracted pigments were decanted and analyzed as above. A second extraction of each sample was also analyzed as above, with the sum of the first and second extractions being recorded as the value for double-extraction. No sonication was performed prior to the second extractions. Although this design resulted in 30 values describing each of 6 treatment combinations, there were only 15 independent observations. Therefore, statistical significance was evaluated using repeated measures ANOVA. A comparison of single vs. double extraction (without any sonication) was also done on 7 non-homogenized samples from different locations in Patuxent River.

6.3 Results and Discussion

6.3.1 Pigment Analysis Method Comparison

The results of a method comparison experiment showed that sonication and multiple extraction of sediment samples (*e.g.*, Sun *et al.*, 1991) could be expected to give sediment chlorophyll-*a* measurements 15.6% higher that those obtained using the method used in this study (Table 6-3). The difference was found to be a nearly constant proportion of chlorophyll-*a* as measured using a single extraction and without sonication, allowing a correction to be applied. Compared to the control (no sonication, single extraction), 3% more chlorophyll-*a* was extracted after use of a sonicator bath and 4.6% more chlorophyll-*a* was extracted after microsonication ($p<0.01$, Table 6-3). The second extraction removed 9.9-11.3% additional chlorophyll-*a* ($p<0.01$), depending on the sonication treatment ($p<0.01$). A larger amount was extracted on the second extraction if microsonication was used prior to the first extraction. Sediment chlorophyll-*a* measured in 7 non-homogenized sediment samples from Patuxent River using a single extraction and no sonication varied between 77 and 148 mg chlorophyll-*a* m^{-2}. A second extraction obtained 11.0±0.5% (mean±std error) additional chlorophyll-*a*, a proportion comparable to that obtained for the corresponding treatments using homogenized samples (Table 6-3). This indicated that a proportional (15.6%) correction could be applied to the 1993-2000 Chesapeake Bay samples with a high degree of confidence. Although this correction is not large compared to other possible sources of uncertainty, it was applied in the interest of beginning the analysis with the most accurate measurements that could practicably be obtained.

Table 6-3. Results of a method comparison experiment used to evaluate the effect of three sonication treatments and single vs. double extraction on the amount (mean±se, % change from control) of chl-*a* (µg/g) extracted from 15 aliquots of homogenized Chesapeake Bay sediments. Each sonication treatment was replicated 5 times. All effects (sonication,extraction and interaction effect) were statistically significant (Repeated-measures ANOVA, p<0.01).

	Single Extraction, µg/g	Double Extraction, µg/g
No Sonication	9.35 (0.02, 0%)*	10.32 (0.02, +10.4%)*
Microsonication	9.78 (0.05, +4.6%)	10.84 (0.06, +15.9%)
Sonicator Bath	9.63 (0.03, +3.0%)	10.56 (0.04, +12.9%)

* these treatments were also compared using 7 non-homogenized samples. The mean different in those samples was 11.0±0.5%

6.3.2. Computing Sediment Total Chlorophyll-*a* Inventories

Due to vertical mixing of sediments on short time scales (days to weeks), the total inventory (*i.e.*, vertically integrated concentration) of recently deposited chlorophyll-*a* may not have been accurately represented by the inventory within the top 0-10 mm of sediments. This leads to an underestimate of chlorophyll-*a* deposition, and, to the extent that sediment mixing could differ regionally, could affect comparisons among regions. The simultaneous collection of 0-2 mm and 0-10 mm sediment samples during 1994-1995 provided an opportunity to examine this issue and compute the sediment chlorophyll-*a* inventory. Bay-wide, the ratio of the 0-10 mm to 0-2 mm chlorophyll-a inventories was estimated to be 2.75. Being substantially <5, this indicates a decline in chlorophyll-*a* concentration with depth in the sediments. The ratio differed significantly among regions of the Bay (Kruskal-Wallis Test; p<0.05), whereas the respective median ratios for the upper-, mid- and lower-Bay regions were 2.7, 2.3, and 3.1. Using more detailed vertical profiling of sediment chlorophyll-*a* in the top 10 cm of Long Island Sound sediments, Sun *et al.* (1994) observed an exponential decrease in chlorophyll-*a* with depth below the sediment-water interface. This model has been assumed to apply to Chesapeake Bay as well. Accordingly, the chlorophyll-*a* inventory (C_{int}) integrated to a depth *h*, is

$$C_{\text{int}} = C_{\max} \int_{z=0}^{z=h} e^{-kz} = C_{\max} \frac{1}{k}\left(1 - e^{-kh}\right) \qquad (1)$$

where C_{max} is the maximum (surface) concentration and *k* is the rate of decrease with depth. Using this expression, the ratio, *R*, between the 0-10 mm concentration and the 0-2 mm concentration is $R = \frac{1-e^{-10k}}{1-e^{-2k}}$, which gives *k*=0.19, 0.25, and 0.14 for the upper-, mid- and lower-Bay. Using these estimates of *k*, the top 10 mm was estimated to include (in same order) 85%, 92% and 76% of the total chlorophyll-*a* inventory (≈ 0-10 cm integrated chlorophyll-*a*). These factors were used to compute the chlorophyll-*a* inventory from the measured concentrations.

The regional differences in vertical chlorophyll-*a* distribution (*i.e.*, in *k*) may reflect differences in sediment properties and/or mixing processes. The mid-Bay is characterized by fine, silty sediments (Figure 6-2), deep and seasonally anoxic water, and lower physical energy (*i.e.* waves and currents) than other areas of the Bay. This would be expected to minimize physical and biological mixing of sediments. In contrast, the lower Bay is shallower and has an increased prevalence of sandy sediments. During winter-spring, the penetration depth of ^{7}Be (half-life = 53 d) in the lower Bay was 3-5 cm, with physical mixing due to tidal current and wave action being dominant (Dellapenna *et al.*, 1998). This may explain the deeper mixing of deposited chlorophyll-*a* in the lower Bay, although no comparable data are available for the mid Bay or upper Bay. An April minimum sediment mixing minimum in the lower Bay, prior to a summer increase associated with bioturbation (Dellapenna *et al.*, 1998), suggests that macrobenthic activity was suppressed by low water temperature (5-15 °C) up until the time of surficial sediment chlorophyll-*a* mapping. This is most likely important to the overall approach of this study because losses of chlorophyll-*a* due to macrobenthic activity would be difficult to quantify.

6.3.3 Phaeopigments

Phaeopigments are a product of the early diagenesis of chlorophyll-*a*. As such, they are also a biomarker indicating deposition of phytoplankton. Macrobenthic biomass has been found to be positively associated with phaeopigments (Josefson and Conley, 1997); however, this may be due to the presence of phaeopigments in feces of plankton and macrobenthos and the slow degradation rate of phaeopigments as compared to chlorophyll-*a* (Furlong and Carpenter, 1988). With this in mind, a high ratio of chlorophyll-*a* to chlorophyll-*a*+phaeopigments suggests that substantial deposition of chlorophyll-*a* occurred recently. For the 84 measurements Bay-wide in 1996-2000 in which sediment phaeopigment concentration was measured, chlorophyll-*a* accounted for an average of 47% (range=38-58%) of chlorophyll-*a*+phaeopigments. This may be regarded as a high ratio (Josefson and Conley, 1997), suggesting that a significant amount of phytoplankton was deposited to Chesapeake Bay sediments each spring.

6.3.4 Distributions of Sediment Total Chlorophyll-*a*

The computed sediment total chlorophyll-*a* inventory averaged 175 mg m^{-2} over 272 observations Bay-wide during 1993-2000. The median value was 164 mg m^{-2} (interquartile range= 88-234 mg m^{-2}). Regional and overall mean chlorophyll-*a* was calculated for each year from interpolated distributions to account for the non-random distribution of observations. Computed in this way, the long-term overall mean was 171 mg m^{-2}, very close to the unweighted average of all observations. However, regional means, particularly the upper Bay mean, were slightly more sensitive to the averaging procedure. Therefore, the interpolated fields were used to compute means rather than the raw data. The highest average chlorophyll-*a* inventory, 195 mg m^{-2}, was found in the mid-Bay. Lower chlorophyll-*a* was found in the lower Bay (148 mg m^{-2}) and the upper Bay (172 mg m^{-2}, Table 6-4). Interannually, the highest Bay-wide mean chlorophyll-*a* inventory was 244 mg m^{-2} in 1999, while the lowest was 117 mg m^{-2} in 1995, a

>2-fold range (Table 6-4). The distribution of raw observations illustrates the patterns and magnitude of spatial and interannual variability in sediment chlorophyll-*a* (Figure 6-3).

Table 6-4. Regional/annual mean sediment total chlorophyll-*a* inventories. These were computed from 0-1 cm chlorophyll-*a* inventories by adjusting for mixing to below 1 cm on short time scales (i.e. days-weeks). Calculation of the overall mean accounts for differences in the area of the respective regions and is therefore not the mean of the regional means.

Year	Upper Bay	Mid Bay	Lower Bay	Overall	Jan-Apr Flow ($m^3 s^{-1}$)
1993	84	182	161	155	2989
1994	147	217	187	191	2624
1995	139	130	98	117	1206
1996	107	132	146	134	2383
1997	223	243	231	235	1403
1998	195	169	122	153	2471
1999	315	323	150	244	1392
2000	162	162	92	137	1739
Average	172	195	148	171	2026

Both the regional distribution of chlorophyll-*a* within the Bay and the Bay-wide average sediment chlorophyll-*a* concentration were related to the magnitude of winter-spring (Jan-Apr) discharge of freshwater into Chesapeake Bay (Figure 6-4). Over the past 15-years this was highly correlated (r^2=0.91) with the January through April discharge from the Susquehanna River, the largest tributary of the Bay (Hagy, 2001). Bay-wide, the average sediment chlorophyll-*a* increased with spring river flow, a pattern also observed for the lower Bay and less obviously for the mid-Bay. This positive association likely reflects a nutrient enrichment mechanism operating at a seasonal/whole-estuary scale. Since nutrient loading is positively and strongly correlated with river flow (Boynton and Kemp, 2000), increased river flow can be expected to increase phytoplankton biomass and production when nutrient limitation is important. Since nutrient limitation, principally by phosphorus and silicate (for diatoms), is well known near the end of spring in the mid- and lower-Bay (Conley and Malone, 1992; Fisher *et al*., 1992; Fisher *et al*., 1999), it is not surprising that a strong positive correlation between river flow and spring average water column chlorophyll-*a* was observed for the lower Bay (Figure 6-5). This increased phytoplankton biomass apparently contributed to increased chlorophyll-*a* export to sediments (Figure 6-6). Physical transport processes associated with high flow may enhance nutrient enrichment in the lower Bay by decreasing water residence times in the upper Bay (Hagy *et al.*, 2000), thereby increasing down-Bay nutrient transport. Whether by a river flow-dependent mechanism (this study) or in association with a flow-independent long-term nutrient loading rate increase (Harding and Perry, 1997), the effects of increased nutrient loading on primary production appear most dramatic in the lower Bay.

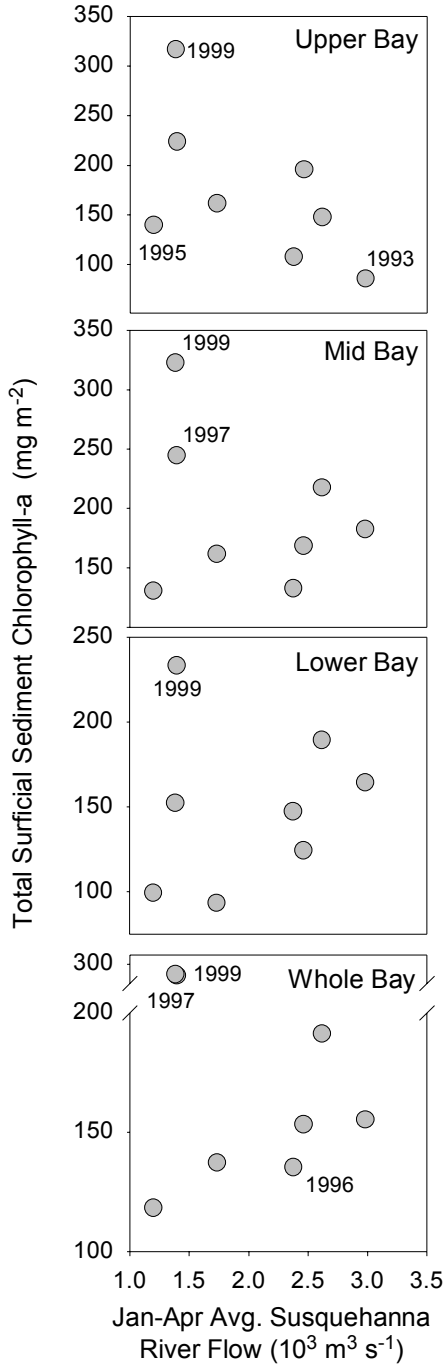

Figure 6-4. Regional and overall mean sediment total chlorophyll-*a* inventories in late spring related to winter-spring (January-April) average Susquehanna River flow. Sediment inventories were computed from 0-1 cm cores. The whole Bay mean reflects differences in the size of the respective regions. Note the y-axis scales, which vary to emphasize within-region pattern rather than among region differences.

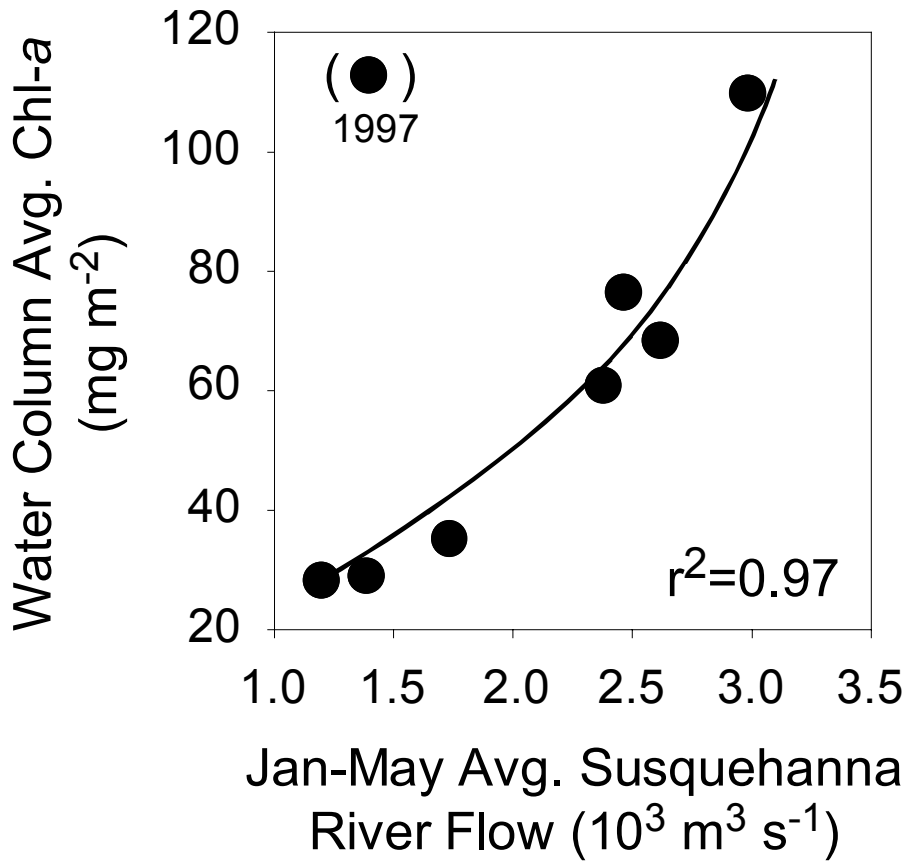

Figure 6-5. January-April average water column integrated chlorophyll-*a* in the lower Chesapeake Bay during 1993-2000 related to January-April average Susquehanna River flow. A second-order polynomial explains 97% of the variation, excluding the 1997 observation.

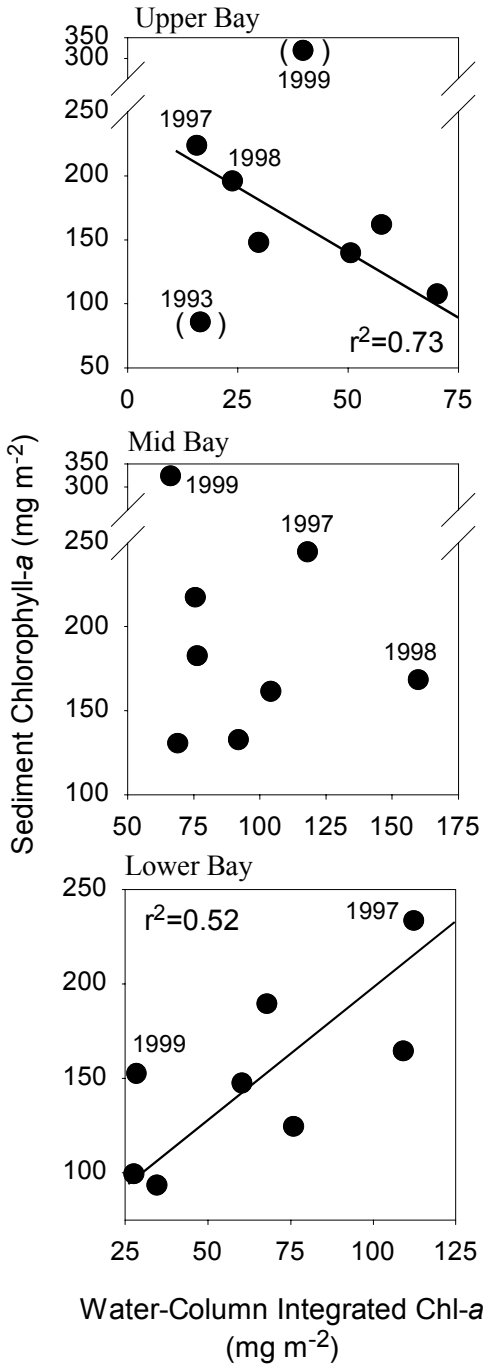

Figure 6-6. The relationship between January-April average water column integrated chlorophyll-*a* and sediment chlorophyll-*a* in each of three regions of Chesapeake Bay. There is a significant correlation in the lower Bay; the indicated line is the model II regression line. For the upper Bay, the trend line indicates the model II regression line excluding the 1993 and 1999 observations.

In contrast to the mid and lower Bay, sediment chlorophyll-*a* in the upper Bay tended to decrease with increasing river flow (Figure 6-4). One possible explanation is that high river flow decreased water residence time and increased turbidity. This would be expected to translate phytoplankton biomass and primary production down-estuary, precluding deposition to sediments in the upper Bay region. If this were a sufficient explanation for decreased sediment chlorophyll-*a* in high flow years, then one would expect to make two observations: (1) water column chlorophyll-*a* and river flow would be strongly and negatively correlated and (2) water column chlorophyll-a would be positively correlated with sediment chlorophyll-*a*. The first expectation did not hold very well. Although a broad negative association was present between water column chlorophyll-*a* and river flow, the correlation was not strong. In fact, the negative correlation between river flow and sediment chlorophyll-*a* (Figure 6-4) was stronger. The second expectation did not hold at all. Instead, in 6 of 8 years, sediment chlorophyll-*a* was lower when water column chlorophyll-*a* in the upper Bay was higher (Figure 6-6). A speculative explanation for this relationship is that high phytoplankton deposition to sediments may cause low phytoplankton biomass in the water column due to low primary production and negative net plankton production (Smith and Kemp, 1995). Conversely, in the presence of low rates of primary production, high phytoplankton biomass can generally only occur in the absence of high deposition rates. Of course, as originally hypothesized, simultaneously low phytoplankton deposition to sediments and low phytoplankton biomass in the water column could result from very high flushing rates. This "wash-out" could have occurred during the record floods of spring 1993, explaining the low sediment chlorophyll-*a* that year (Figure 6-6, upper panel). On the other hand, sediment chlorophyll-*a* in the upper Bay in 1999 was consistent with expectation based on low river flow in that year (Figure 6-4), but water column chlorophyll-*a* remained high. This made 1999 an outlier in the water column vs. sediment chlorophyll-*a* relationship (Figure 6-6).

In an effort to explain more of the variability that was observed in sediment chlorophyll-a during 1993-2000, we examined the species composition of the winter-spring phytoplankton assemblage in those years (Chesapeake Bay Monitoring Program, unpublished data). It was hypothesized that higher sedimentation in some years was due in part to a greater relative abundance of diatoms, whose tendency toward sinking has been noted (Smetacek, 1978). Some suggestive results were obtained. In the lower Bay, diatom counts largely paralleled average chlorophyll-*a* due to the dominance of diatoms in the winter-spring phytoplankton community in the lower Bay. However, diatom counts did not predict sediment chlorophyll-*a* as well as water column chlorophyll-*a*, probably due to the larger variance associated with less frequent sampling of diatom counts. Sediment chlorophyll-*a* in the upper Bay appeared to increase with average diatom counts, apparently contradicting the results based on chlorophyll-*a*. However, there were two substantial outliers and a weak relationship among the remaining observations, suggesting that the appearance of any relationship was due to chance. Thus, the analysis of phytoplankton species data neither contradicted nor supported the hypothesis, in significant part because the temporal resolution of these labor-intensive data collections was too low to adequately characterize the highly variable phytoplankton community during the winter-spring period.

As the above discussion illustrates, a variety of ecosystem processes can affect relationships among river flow, water column chlorophyll-*a* and sediment chlorophyll-*a*. These clearly have

the potential to cause dramatic departures from relationships expressed by empirical models. However, the predictable ecosystem responses that were observed among many observations indicates that, on a region-specific basis, certain mechanisms appear to maintain first-order importance and drive large (2-3 fold) responses. In some cases, outliers illustrate that an implicit assumption of the model was not met. For example, the conceptual basis for Figures 6-4 through 6-6 implicitly assumes a January-April time domain for forcing and response. The 1997 outlier, in which water column chlorophyll-*a* in the mid- and lower-Bay was much higher than expected, may reflect the unseasonably high flow that occurred during fall 1996. This river flow substantially increased January nutrient concentrations (N, P, Si) in surface waters at a station in the lower Bay from their long-term (1984-1999) averages. Total N increased from 27 to 41 µM, total P from 0.88 to 1.16 µM and dissolved Si from 5.5 to 11.6 µM (Chesapeake Bay Monitoring Program, unpublished data). These high January nutrient concentrations reduced the importance of a normal spring freshet for supplying the 1997 spring phytoplankton community with nutrients.

Another possible source of uncertainty in the observed relationships (Figure 6-4, Figure 6-6) is the variable timing of the ecosystem response, specifically the dates of maximum phytoplankton biomass accumulation and bloom collapse relative to the dates of sediment chlorophyll-a mapping (Figure 6-7). For example, peak water column chlorophyll-*a* in 1996 occurred on 5/14/96 in both the mid- and lower Bay, one week after sediment mapping was concluded. This may explain why Bay-wide average sediment chlorophyll-*a* in 1996 was lower than expected from the level of spring river flow. In contrast, peak water column biomass in the mid and lower Bay in 1997 occurred on 4/3, ~2 weeks prior to sediment mapping (Figure 6-7). This probably contributed to the high sediment chlorophyll-*a* observed in that year. Peak phytoplankton biomass also occurred very close to the sediment sampling dates in 1998 and 2000. In 1999, the highest sediment chlorophyll-*a* deposition was observed despite the lack of any large accumulation in the water column before or after sampling. Importantly, 1996, 1998 and 2000 were not substantial outliers in the analysis (Figure 6-4, Figure 6-6) as was 1997 in Figure 6-5. This suggests that deposition of chlorophyll-*a* to sediments occurred at least in part in a relatively steady-state process whereas some fraction of production was continuously deposited to sediments. Deposition could not be explained simply by a pattern of biomass accumulation in the water column followed by mass deposition to sediments.

6.3.5 Estimates of Chlorophyll-*a* Deposition

A simple diagenetic model was used to estimate the deposition of phytoplankton to sediments during spring in each year using the observed accumulation of sediment chlorophyll-*a*. A few simplifying assumptions were needed due to data limitations. It was assumed that the input to sediments occurred at a constant rate, I (mg m^{-2} d^{-1}) over a period of t days, during which time deposited chlorophyll-*a* decayed at a first-order decay rate, k (d^{-1}). The net accumulation rate of chlorophyll-*a* on the sediment surface can be described by $dC/dt = I - kC$. Solving under the boundary condition that when $t=0$, $C=C_0$ yields

$$C_t = \frac{I}{k} + \left(C_0 - \frac{I}{k}\right)e^{-kt} \qquad (2)$$

Solving for I gives

$$I = \frac{k\left(C_t - C_0 e^{-kt}\right)}{1 - e^{-kt}} \qquad (3)$$

Although not immediately obvious, it can be shown using L' Hôpital's rule that $\lim_{k \to 0} I = \frac{C_t - C_0}{t}$. Thus, if the degradation rate is very small, and minimal chlorophyll-*a* was present prior to the period of interest ($C_0 \approx 0$), total deposition equals the observed accumulation (C_t) and is insensitive to t. In contrast, the deposition rate depends inversely on t. As the degradation rate (k) increases relative to the deposition rate (I), a steady state model as suggested by Sun *et al.* (1991) may be more appropriate. In Chesapeake Bay, the time period, t, during which most spring bloom phytoplankton deposition occurs probably varies from year to year (Figure 6-7), but it was assumed that most deposition occurred between mid to late February and the time of mapping, a period of ~60 days. Based on Figure 6-7, a range of 30-75 days was considered possible. A few measurements of sediment chlorophyll-*a* in Chesapeake Bay in early January-February were available for a number of years during the 1980's (Garber *et al*., 1989). These values varied between 37-83 mg m^{-2} and averaged 58 mg m^{-2}, providing a base case and range of variability for C_0. Estimates for the first-order chlorophyll-*a* decay rate (k) were obtained by considering the work of Sun *et al.* (1993a) and other studies by Sun and colleagues (Sun *et al*., 1991, *Sun et al.*, 1993b, *Sun et al.*, 1994). These studies provide a good assessment of early chlorophyll-*a* diagenesis under a variety of conditions. The rates most applicable for this study appear to be those obtained for fresh, oxic sediments (Sun *et al.*, 1993a), although it is possible that sediments at 1 cm depth were completely anoxic in some places. Oxic degradation of chlorophyll-*a* is highly temperature-dependent, with the first-order decay constant for free chlorophyll-a (k_d) increasing 4-fold between 5 ˚C and 25˚C (Sun *et al.*, 1993a). The first-order rate for release of chlorophyll-*a* from a particle-bound state to a free state (k_r), which was required for most chlorophyll-*a* degradation, also increases more than 6-fold over the same temperature range (Sun *et al.*, 1993). Over 5-25 ˚C, k_r was 30-50 times greater than k_d; therefore, only the smaller rate is relevant here. During the period from mid-March through May 1, bottom water temperature increased from 4 to 15 ˚C in the upper and lower Bay and from 4 to 13 ˚C in the mid-Bay. The average in all regions during March-May was ~7-9 ˚C. In this temperature range, k_d was 0.028 d^{-1}. Thus, 0.028 d^{-1} was used as a base case estimate for k in eq. (1) and eq. (2), with values between 0.02 and 0.04 considered as a reasonable range of variability.

Estimates of chlorophyll-*a* deposition (±standard deviation) were computed for each region and year using Monte-Carlo simulations (Table 6-5, Table 6-6). In these simulations, the parameters C_0, t and k were chosen randomly from triangular distributions specified using the estimated min, max and mode, which is equal to the base case estimate for each parameter (Table 6-5). For each value of C_t (i.e. each region, year), many (10^4) estimates of the average deposition rate (I) and total deposition (It) were computed using eq. 3. Means and standard deviations were then computed (Table 6-6). The 1993-2000 average chlorophyll-*a* deposition rate was estimated to range from 5.08 mg m^{-2} d^{-1} in the lower Bay to 6.81 mg m^{-2} d^{-1} in the mid-Bay. Average

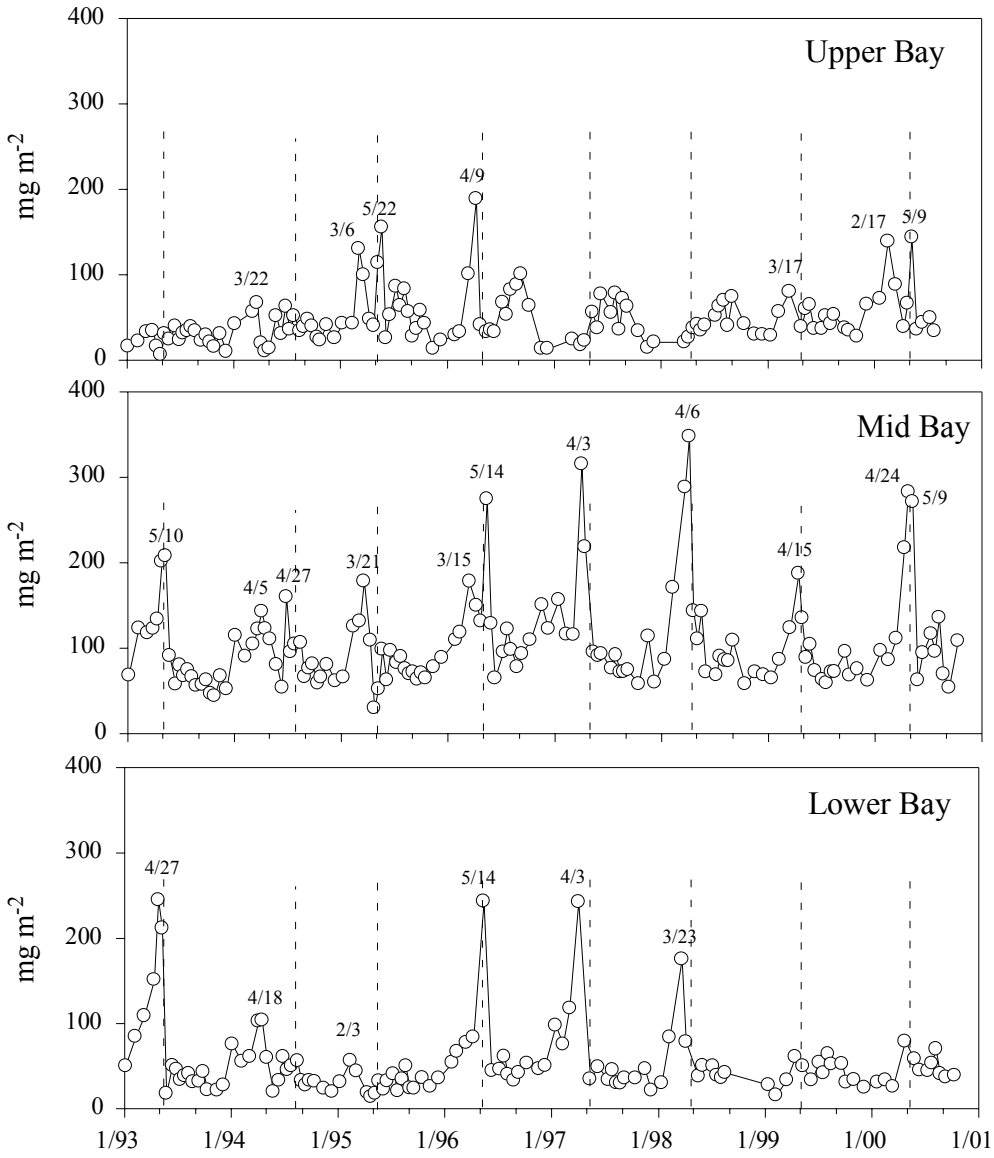

Figure 6-7. Water column integrated chlorophyll-*a* concentrations in Chesapeake Bay averaged by region. Vertical dotted lines indicate the dates of sediment chlorophyll-a mapping studies. Dates indicate the date of the adjacent water column chlorophyll-*a* observation which can be compared to the sediment chlorophyll-*a* mapping dates indicated in Table 6-2.

Table 6-5. Minimum, maximum and modal values used to specify triangular distributions for parameters in eq. 3. Parameter values were randomly drawn from these distributions and used in Monte Carlo simulations to estimate the mean and standard deviation of chlorophyll-*a* deposition in each region and year.

Parameter	Min	Mode	Max
Initial chl-a concentration, C_0, mg m^{-2}	30	58	80
First-order decay coefficient, k, d^{-1}	0.02	0.028	0.04
Period of Bloom deposition, t, days.	30	60	75

Table 6-6. Estimated average (±standard deviation) chlorophyll-*a* deposition rates (mg m^{-2} d^{-1}) and total winter-spring chl-a deposition (mg m^{-2}) for winter-spring in the upper, mid and lower Chesapeake Bay during 1993-2000.

(a) Average deposition rate during winter-spring (mg m^{-2} d^{-1})

Year	Upper Bay	Mid Bay	Lower Bay
1993	2.69±0.34	6.34±0.73	5.56±0.64
1994	5.04±0.58	7.64±0.88	6.52±0.74
1995	4.74±0.55	4.40±0.52	3.21±0.39
1996	3.55±0.43	4.48±0.52	4.99±0.59
1997	7.86±0.90	8.61±0.98	8.16±0.94
1998	6.81±0.79	5.85±0.67	4.10±0.49
1999	11.29±1.28	11.57±1.33	5.14±0.59
2000	5.59±0.65	5.59±0.64	2.99±0.37
Average	5.95	6.81	5.08

(b) Winter-spring chlorophyll-*a* deposition (mg m^{-2})

Year	Upper	Bay	Mid
1993	148±28	345±54	304±49
1994	275±45	415±63	355±55
1995	258±42	241±41	175±32
1996	193±34	244±41	272±44
1997	429±65	470±70	444±67
1998	371±57	319±51	224±38
1999	613±90	631±92	280±45
2000	305±49	305±48	163±30
Average	324	371	277

cumulative winter-spring chlorophyll-*a* deposition varied from 277 mg m^{-2} in the lower Bay to 371 mg m^{-2} in the mid-Bay. Estimated coefficients of variation for chlorophyll-*a* deposition rate and cumulative deposition estimates averaged 12% and 16%, respectively. Chlorophyll-*a* deposition rate and cumulative deposition were not directly proportional to the late-spring chlorophyll-a inventory (C_t) because C_0 was not equal to zero (see eq. 3). However, because C_t was typically much greater than C_0, the ratios I/C_t and It/C_t were much less variable than C_t. For example, I/C_t ranged from 0.032 to 0.036 d^{-1}. The ratio It/C_t ranged from 1.76 to 1.95. In other words, the cumulative winter-spring deposition of chlorophyll-*a* was slightly less than two times the observed sediment chlorophyll-*a* inventory near the end of April. Therefore, regional and interannual patterns of chlorophyll-*a* deposition rates were comparable to corresponding patterns in late spring chlorophyll-*a* inventories (Table 6-4, Figures 6-4 and 6-6).

Boynton *et al*. (1993) estimated chlorophyll-*a* deposition in the mid-Bay during 1985-1992 using consecutive short-term (~1 week) deployments of sediment traps at one station. In most years, chlorophyll-*a* deposition measured just below the pycnocline was ~5-10 mg m^{-2} d^{-1} in late February, then increased to 10-20 mg m^{-2} d^{-1} in April. From the earliest trap deployments in early February until early May, integrated chlorophyll-*a* deposition as measured by the traps was 600 to 1200 mg m^{-2} with an average of 789 mg m^{-2}. The comparable mid-Bay estimate from this study is 371 mg m^{-2}, or about 50% of the sediment trap estimate. This study estimated the average chlorophyll-*a* deposition rate in the mid-Bay to be 6.81 mg m^{-2} d^{-1}, 71% of the 9.6 mg m^{-2} d^{-1} estimated using the sediment traps. Because of the limitations of sediment traps (Blomqvist and Håkanson, 1981; Knauer *et al.*, 1984; and Asper, 1987) one cannot assume that sediment traps provided a more accurate estimate. It is possible that the sediment traps retained particles more effectively than the sediment surface, leading to an overestimate of the flux to sediments. This "resuspension" effect clearly affected the deeper sediment traps for which the flux measurements were often several times larger than the mid-cup fluxes (Boynton *et al.*, 1993).

Another check on the chlorophyll-*a* deposition estimates can be made by using the estimated chlorophyll-*a* deposition rate and estimates of water column chlorophyll-*a* concentrations to estimate an effective sinking velocity for phytoplankton cells. This velocity can then be compared with measurements from the published literature. This approach requires that one assume a uniform vertical chlorophyll-*a* distribution in the water column, which may be appropriate in late winter and early spring in Chesapeake Bay. The effective sinking rate (v_z) can be estimated from the integrated water column chlorophyll-*a* concentration (C_{int}), the mean depth ($\bar{z}$) and the rate of chlorophyll-*a* deposition to sediments (F) using

$$v_z = \frac{F}{C_{wc}}, \text{ where } C_{wc} = \frac{C_{\text{int}}}{\bar{z}}$$

Given C_{int}= 50-100 mg m^{-2} (Figure 6-2), $\bar{z} \approx 8$ m, and F=6.0 mg m^{-2} d^{-1}, this gives v_z=0.5-1.0 m d^{-1}. Mean upwelling velocities in the range of 0.5 m d^{-1} would affect cells sinking through the

water column (Hagy, 2001). Thus, the actual sinking rate may be 1.0-1.5 m d^{-1}, approximately the same as the 1.1-1.5 m d^{-1} estimated for larger cells (8-53 µm) within a whole phytoplankton assemblage in an experimental enclosure (Bienfang, 1981). This estimate exceeds the minimum sinking rates estimated for *Skeletonema costatum*, the most abundant species in lower Chesapeake Bay in winter-spring (Table 6-1), but approximates the maximal sinking rates for the same species (Smayda, 1970). Thus, the observed deposition probably represents sinking of senescent and/or nutrient limited cells, consistent with observations of Smetacek (1985).

The analysis of average sinking rate noted above is intended to show only that the estimated chlorophyll-*a* deposition is consistent with reported sinking rates and observed chlorophyll-*a* concentrations in the water column. It is not known, however, if the deposition actually occurred at this average sinking velocity. Formation of large "flocs" can lead to settling rates of 10-100 m d^{-1} (Smetacek, 1978), sufficient to deposit an entire senescent phytoplankton bloom to Chesapeake Bay sediments within one day.

6.3.6 Carbon Flux to Sediments

Given an estimate of C:chlorophyll-*a*, the estimated spring chlorophyll-*a* flux to sediments described above can be used to estimate the carbon flux associated with spring bloom phytoplankton deposition. The long-term January-April average C:chlorophyll-*a* in mid-Bay and lower-Bay bottom water is ~100. In the upper-Bay, average C:chlorophyll-*a* during winter-spring was >250. These values are higher than those typical of phytoplankton, indicating a large non-phytoplankton (*i.e.* detritus) component within the POC. When chlorophyll-*a* increased quickly and substantially (*e.g.* Figure 6-7), C:chlorophyll-*a* decreased to an asymptotic value of ~50, with typical values between 50-100 when chlorophyll-*a*>20 µg l^{-1}. Following a bloom, C:chlorophyll-*a* was found to increase quickly as chlorophyll-*a* decreased. This suggests that the phytoplankton community had C:chlorophyll-*a* ≈50-100 and that particles lost at the termination of the bloom, possibly due to sinking, also had a C:chlorophyll-*a* in the range of 50-100. This was supported by sediment trap data (Boynton *et al*., 1993), which showed that the ratio of carbon to chlorophyll-*a* sinking flux in March-April was ~75 when the chlorophyll-*a* flux was >8 mg m^{-2} d^{-1}.

Using C:chlorophyll-*a*=75 and an average total chlorophyll-*a* deposition of 277-371 mg m^{-2} (Table 6-6) the carbon flux to sediments associated with spring bloom phytoplankton deposition is estimated to have been 21-28 gC m^{-2}. Similarly converted to C, the chlorophyll-*a* deposition rate was equivalent to 0.51 gC m^{-2} d^{-1}, 71% of the C flux computed from chlorophyll-*a* fluxes to sediment traps (also assuming C:Chlorophyll-a=75), but only 36% of the directly measured PC fluxes to the same sediment traps (Figure 6-8, Boynton *et al*., 1993). The larger disparity observed between directly measured PC fluxes and estimates from this study reflects periods in which the sediment traps received particles with C:chlorophyll-*a* higher than 75, potentially due to resuspension effects on the sediment traps.

These carbon flux estimates for the spring bloom in Chesapeake Bay are substantially higher than reported carbon fluxes associated with spring phytoplankton blooms in some other systems.

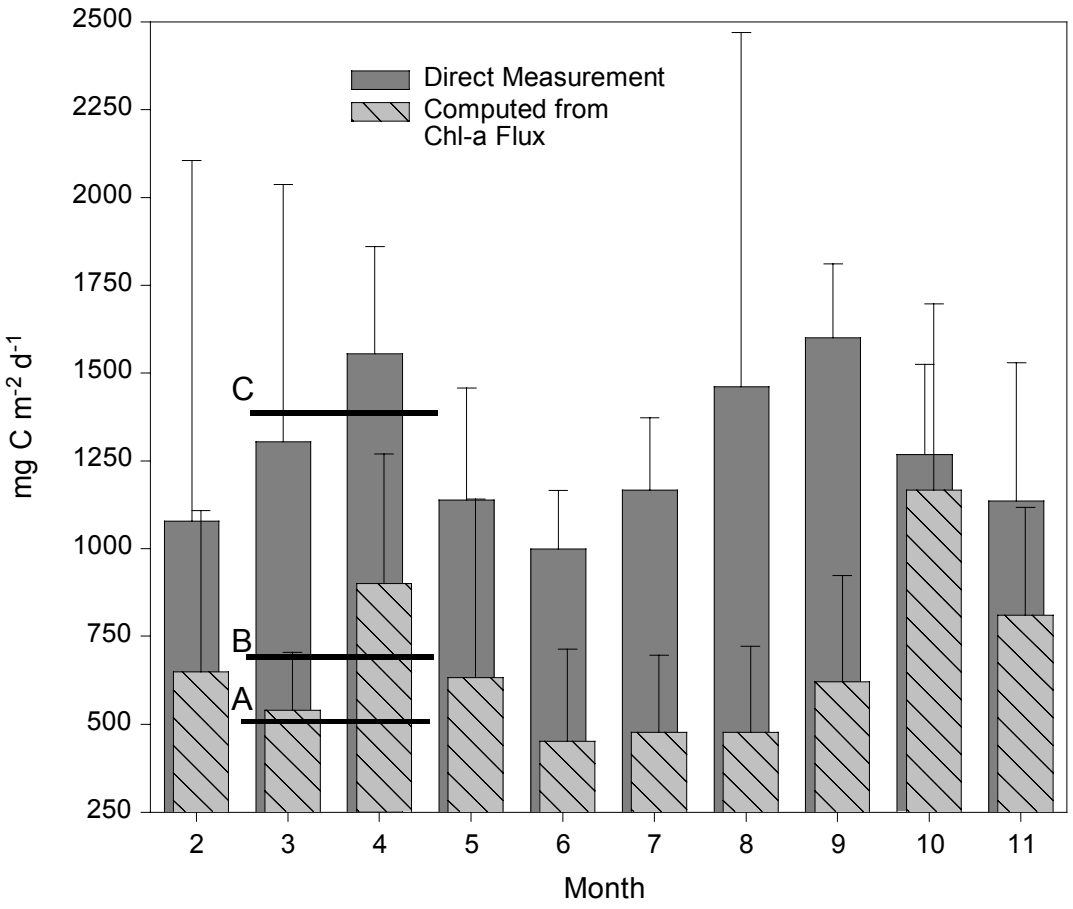

Figure 6-8. Monthly means and standard errors of particulate carbon (PC) sinking fluxes measured using sediment traps just below the pycnocline in the mid Chesapeake Bay (station R-64) during 1984-1992. Stippled bars indicate vertical PC fluxes computed from chl-*a* fluxes. Reference lines indicate: A=spring average PC deposition (510 mg C m^{-2} d^{-1}, this study); B=March-April average PC deposition computed from chl-*a* flux to sediment traps (720 mg C m^{-2} d^{-1}); C=March-April average deposition computed directly from PC flux to sediment traps (C:chl-*a*=75 in all cases).

Sediment trap data from Boynton *et al.* (1993) and related unpublished data.

For example, a 34-day bloom in the Baltic Sea deposited 6.2 g C m^{-2} to sediments (Smetacek *et al.*, 1978, cited in Keller and Riebesell, 1989). A 25-day bloom in the Kiel Bight deposited 11.5 g C m^{-2} (Peinert *et al.*, 1982, cited in Keller and Riebesell, 1989). The estimated C flux rate for Chesapeake Bay is similar to that of the Kiel Bight bloom, but persisted for a longer period of time, leading to a larger cumulative C flux (Table 6-6). This seems reasonable given the eutrophic condition of Chesapeake Bay.

The estimated carbon flux associated with the spring bloom (21-28 g C m^{-2}) sediments accounts for 10-14% of annual benthic respiration (163 g C m^{-2} y^{-1}) plus carbon burial (39 g C m^{-2} y^{-1}, Kemp *et al.*, 1997), slightly less than proportional to the fraction of the year encompassed (60/365 days = 16%). That the spring bloom deposition did not support a larger fraction of annual metabolic C demand was surprising considering the clear seasonality of phytoplankton biomass (Figure 6-1) and net plankton metabolism (Kemp *et al.*, 1997), and the importance generally ascribed to this annual ecosystem event. Assuming that the spring bloom deposition was not larger than estimated, but that it was important to the macrobenthic community as has been suggested, one may conclude that the importance arises from food quality rather than quantity (*e.g.* Marsh and Tenore, 1990).

Another surprising result is that the spring phytoplankton deposition differed only slightly by Bay region and that the regional variation did not parallel regional differences in net plankton metabolism (NPM, Smith and Kemp, 1995), which increased strongly down-estuary. For the mid-Bay, the estimated carbon flux (0.51 g C m^{-2} d^{-1}) is slightly greater than NPM (=0.34 gC m^{-2} d^{-1}) estimated by Smith and Kemp (1995; converted from O_2 flux using g C=0.3125 g O_2). In contrast, the estimated winter-spring carbon deposition to sediments in the lower Bay (0.38 g C m^{-2} d^{-1}) was only 29% of the much higher estimate of NPM for the lower Bay (1.3 g C m^{-2} d^{-1}, Smith and Kemp, 1995). The fate of the apparent surplus production in the lower Bay is unknown, but may include export to the mid-Bay via the landward advection in the lower water column, or possibly export to the coastal ocean. The presence of significant chlorophyll-*a* fluxes to sediments in the upper Bay, despite negative NPM may indicate that allochthonous C inputs supported plankton respiration and reduced NPM, while autochthonous phytoplankton production supported vertical C fluxes to sediments.

6.4 Conclusions

Surficial sediment chlorophyll-*a* can be used effectively as a biomarker for spring bloom phytoplankton deposition to sediments. These deposition estimates obtained are the only known Bay-wide estimates for Chesapeake Bay. Deposition was 2-4 times greater than estimated spring bloom deposition from some other estuarine and coastal systems, illustrating the intense primary production associated with spring phytoplankton blooms in Chesapeake Bay. Deposition increased with river flow and was translated down-Bay in high flow years, suggesting the importance of both nutrient enrichment and physical transport processes in determining phytoplankton deposition to sediments during spring. The estimated deposition, although large,

did not account for a larger than proportional fraction of annual benthic metabolic requirements. A lack of regional correspondence between net plankton production and deposition to sediments leaves important questions about this important benthic-pelagic coupling mechanism.

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7. MANAGEMENT SUMMARY

Based on a review of previous Ecosystem Processes Component (EPC) Reports (Boynton *et al*., 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997, 1998 and 1999), and the analyses presented in this report, the following observations are provided that have relevance to water quality management in the Patuxent River estuary and Tangier Sound.

Nutrient loading rate estimates (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 1984-1999. A summary of that review is again included here because changes in these loads are of central interest in the Bay Program. 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, and 1998). Because of the severe drought during 1999, TP loads during 1999 were among the lowest on record. 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 kg day^{-1} $year^{-1}$. TN loads were also reduced during 1999, again because of the effects of the drought in reducing diffuse source run off of TN. This inspection of loads will be extended to include 2000 data when they become available. There is strong evidence that substantial nutrient load reductions at the fall line have occurred in recent years.

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.

Dissolved oxygen conditions in the Patuxent River were examined using monthly data collected at the four long-term sediment-water exchange (SONE) stations. In general dissolved oxygen conditions in deep water at the deeper sites (MRPT and BRIS) were poor to fair in 2000. For example, dissolved oxygen remained below 0.8 mg l^{-1} at station MRPT during July-September. During the drought year of 1999 DO never decreased below 2.7 mg l^{-1} at this site indicating the importance of flow and nutrient loads on DO conditions.

Sediment –Water Oxygen and Nutrient exchanges were similar to the long-term average at most stations and sampling periods. Rates during 2000 (a normal flow year) contrasted with those measured during 1999 (a drought year) and the contrast is consistent with the conceptual model of how sediment-water exchanges are regulated in estuarine systems. For example, SOC rates were larger at the two mid-river sites during most of the 1999 sampling period compared to 2000. These enhanced values very probably resulted because dissolved oxygen concentrations in deep water were higher during 1999 than in most previous years or during 2000. SOC rates become limited (reduced in magnitude)

when bottom waters are depleted in dissolved oxygen. A significant positive trend in SOC rates was detected at the most up-river station (BUVA) during 1999; no other significant trends were detected. The status of SOC was good at the most up-river site (BUVA), poor at the two mid-river sites (MRPT and BRIS) and fair at the most down-river site (STLC).

Ammonium (NH_4^+) fluxes were also larger during 2000 than during the 1999 drought. The relatively low fluxes observed during 1999 is very probably a response to reduced nutrient loads associated with drought conditions. The large reductions in ammonium flux between 1996 and 1998 (years of high nutrient load and very high river flow) and 1999 parallels patterns of spring flow and nutrient loading. This "same year" response by sediments to loading conditions 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 influence fluxes in subsequent years. In short, this is evidence for relatively limited nutrient memory and the potential for rapid (year rather than decade scale) responses to management actions. There were no trends in ammonium fluxes detected at SONE sites in the Patuxent River. Ammonium fluxes at the two up-river sites (BUVA and MRPT) were judged to be in the poor range and fluxes at the two down-river sites (BRIS and STLC) were in the fair range.

Positive sediment nitrate and nitrite fluxes (fluxes directed from sediments to the water column) are a definite sign of sediment nitrification activity, a microbial process converting ammonium to nitrite and then nitrate and one that requires that oxygen be present. Positive nitrate fluxes are a sign of good sediment quality. Positive fluxes were observed during 1999 at all stations for most of the sampling period. However, during 2000 fewer positive sediment nitrate and nitrite fluxes were observed, consistent with generally lower DO conditions and higher river flows. We continue to believe that the presence of positive nitrate flux is a good tool for monitoring the general biogeochemical health of sediments.

During 2000, inorganic phosphate fluxes *(PO_4^- or DIP)* were similar to the long-term averages and considerably higher than those observed during the 1999 drought year. During the drought year DIP fluxes were near or below the long-term average at all sites. At three of the sites (BUVA, MRPT and BRIS) phosphorus fluxes were far below average rates in July and August of 1999. Experimental studies involving phosphorus flux and dissolved oxygen (DO) conditions indicated a tight negative relationship between flux and DO status. When dissolved oxygen conditions improve, phosphorus flux decreases. In addition, these experimental studies indicated that the time needed for estuarine sediments to respond to decreased phosphorus loads 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 much beyond the annual time scale. There were no significant temporal trends in phosphorus fluxes at any station. Phosphorus flux status was poor at the up-river site (BUVA), fair at the two mid-river sites (MRPT and BRIS) and good at the down-river site (STLC).

During 2000 an ambitious and broad ***evaluation of littoral zone habitats*** was continued in the lower 35 km of the Patuxent River estuary (mesohaline zone) and extended to several locations in Tangier Sound focusing on the parameters important to submerged aquatic vegetation (SAV). The stimulus for this program was the observation that substantial nutrient load reductions recently achieved in the Patuxent have led to improving water quality conditions with little or no resurgence in SAV. In addition, this study was also designed to compare the habitats of the Patuxent where no persistent SAV exists to Tangier Sound where SAV has been continuously present. 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 these shallow water habitats. In both regions a full suite of water quality parameters was measured weekly for three consecutive weeks each in the spring, summer and fall seasons. Results of data collected along the Patuxent confirm both temporal and spatial variation along the longitudinal axis of the River. In general, water quality was not substantially better in Tangier Sound compared to many of the down-river stations in the Patuxent River. Only chlorophyll-*a* concentrations were significantly higher in the Patuxent compared to Tangier sound. This was especially true during the spring season. Differences were much less dramatic during the fall sampling season. Dissolved nutrient concentrations in both regions were also generally below the habitat limits established by the USEPA (2000) in both regions for much of the year. Given the limited sampling, epiphyte fouling rates in Tangier Sound were also very comparable to many locations on the Patuxent River. These findings suggest that factors other than water quality may be limiting SAV recovery in the Patuxent. The results of transplant experiments to the lower Patuxent suggest that both a source of new recruitment (propagules) and grazing by waterfowl may hinder and limit the expansion of SAV that may recruit to the area. The determination of minimum bed size that may be required for self-sustainability has not yet been made. Continued transplantation and monitoring of SAV to the lower Patuxent will help establish the conditions necessary for long-term SAV survival.

High resolution spatial water quality data was collected in Tangier Sound and the Magothy River using the DATAFLOW IV mapping system. The goal of this effort was to identify the spatial scales of water quality variability in these systems and to further develop this method of data collection for enhanced near-shore and tributary monitoring. Two cruises were made in each system in the spring and two cruises in the fall of 2000. In Tangier Sound large north-south gradients in water transparency were present in all cruises. Short-term weather events also were responsible for large areas of sediment resuspension in areas around South Marsh and Smith Island. The duration of these resuspension events could not be determined from the data available. In the Magothy River, substantial gradients in water transparency were found during some of the research cruises. However, in this system water quality was also found to be quite homogeneous indicating that both season, and weather events can have an impact on the spatial variability of water quality in this system. This data also will allow us to evaluate the adequacy of single (or multiple) station monitoring of small systems such as the Magothy. Collectively, this data will also provide the means to begin a detailed and thorough analysis of the error associated with this type of mapping and parameter

extrapolation that is inherent in this type of data collection. Further monitoring of these systems and others will provide the data necessary to fully evaluate the potential for high resolution DATAFLOW type monitoring for evaluation of shallow littoral zone habitats.

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