# **UMCES**

UNIVERSITY OF MARYLAND CENTER for ENVIRONMENTAL SCIENCE

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

# LEVEL ONE REPORT #16 (INTERPRETIVE)

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MARYLAND DEPARTMENT OF NATURAL RESOURCES

# MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

# **ECOSYSTEM PROCESSES COMPONENT (EPC)**

# **LEVEL ONE REPORT NO. 16**

# **INTERPRETIVE REPORT**

(July 1984 - December 1998)

#### PREPARED FOR:

Maryland Department of Natural Resources Resource Assessment Administration **Tidal Water Ecosystems Assessment Division** Tawes State Office Building, D2 580 Taylor Avenue Annapolis, MD 20401

### June 1999

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# **Ecosystems Processes**

### Interpretive Report Level 1 No. 16: June 1999 Executive Summary

The Ecosystems Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program during 1998 was composed of several distinct but complementary study elements. These elements included: measurement and characterization of sediment-water nutrient and oxygen exchanges (MINI-SONE and High Resolution Mapping) on the Patuxent River, an evaluation of near-shore habitat conditions relevant to submerged aquatic vegetation (SAV), measurement and assessment of high frequency dissolved oxygen conditions, and super high-resolution mapping of surface water conditions.

#### Sediment-water Oxygen and Nutrient Exchanges:

#### Patuxent River Long-term stations, MINI-SONE and High-Resolution Mapping

Sediment-water oxygen and nutrient exchange measurements were made monthly at 10 stations on the Patuxent River during June through September of 1998 using the MINI-SONE measurement technique. In order to extend the spatial resolution of these estimates on the Patuxent River, measurements of bottom water nutrient concentrations, bottom water physical parameters, and sediment chlorophyll-a concentrations were made at 27 additional stations. These measurements were used as inputs to statistical flux models to estimate sediment water fluxes at these additional stations.

#### Long-term trends:

At four of the 10 MINI-SONE stations, (Buena Vista [BUVA], Marsh Point [MRPT], Broomes Island [BRIS] and St. Leonard Creek [STLC]) long-term data permits the calculation of status

and trends at these locations which help establish linkages between management strategies and ecosystem response.

- No significant trends were found at any of the long-term monitoring stations for either improving or degrading conditions.
- High ammonium fluxes at the two upriver stations Buena Vista (BUVA) and Marsh Point (MRPT) were considered poor because of the well established linkage between ammonium availability and excessive phytoplankton biomass accumulation.
- High phosphorus fluxes at the two upriver stations Buena Vista (BUVA) and Marsh Point (MRPT) were considered poor because of the well established linkage between phosphorus availability and excessive phytoplankton biomass accumulation.



#### **Results MINI-SONE:**

The 10 MINI-SONE stations located between the most upriver station (Buena Vista ) and the most downriver station (St. Leonard Creek) provided data from a wide range of conditions found on the lower Patuxent River.

- The monthly pattern of Patuxent River flow was different in 1998 compared to 1997.
- These differences are reflected in differences in sediment-water exchanges. For the summer season, both ammonium (NH<sub>4</sub>) and phosphate (PO<sub>4</sub>) mean fluxes were statistically greater (p < 0.05) in 1998 compared to 1997 as shown below.</li>





#### **Management Recommendations:**

• The well-established linkage between nutrient loading and the sediment-water flux has shown that estuarine systems respond to nutrient loading on annual time scales or less. Thus inter-annual variation in loading resulting from wet versus dry years increases the difficulty of detecting long-term changes in estuarine responses as a result of long-term nutrient load reductions. Thus, a prudent course of action would be to continue monitoring sedimentwater fluxes to track ecosystem responses to help guide further management decisions. • In 1998, bottom water dissolved oxygen conditions were evaluated with an increased spatially intensive technique in order to estimate the total extent of bottom waters affected by low dissolved oxygen concentrations. A comparison of estimates constructed from 37 stations versus the 4 long-term stations indicated a four-fold over-estimation of area affected by low bottom-water dissolved conditions when only the long-term stations were used in the calculation. Thus, we recommend that future evaluations be conducted with as many locations as possible to more accurately evaluate subtle changes in bottom water conditions that may only be observed with a more spatially inclusive effort.

#### **Statistical Regression Models**

It is well known that the regeneration and transformation of nutrients in estuarine sediments is linked chemically and physiologically to a suite of bottom-water and sediment parameters. The goal of this analysis was to further develop statistically significant regression relationships between a few easily measured sediment and water quality parameters, and certain sedimentwater exchanges (fluxes). These regression relationships were used to estimate sediment-water fluxes at locations where direct measurements were not possible.

- With three years of MINI-SONE data, (1996, 1997 and 1998) the regression equation for ammonium explains 87% of the observed variation in summer mean sediment-water flux and indicates a very robust relationship between these parameters and sediment-water ammonium flux. This is important because ammonium flux is the largest internal source of nitrogen to the water column during the summer months and is the preferred form of nitrogen for biological utilization.
- For sediment-water phosphate flux bottom water phosphate concentrations remained as the most important predictor variable in all three years. This result illustrates how bottom water nutrient concentrations can influence diffusion gradients and sedimentwater fluxes. With the reformulated model, 77% of the variation in summer mean phosphate flux (PO<sub>4</sub><sup>-3</sup>) is explained.





#### Submerged Aquatic Vegetation (SAV) Habitat Evaluation

Submerged Aquatic Vegetation (SAV) is an integral part of near-shore bay ecology because it serves a variety of important roles. Some of these include providing habitat for juvenile finfish and shellfish, stabilizing near-shore sediments, and serving as a food source for waterfowl and other organisms. Declines in the abundance of SAV throughout Chesapeake Bay and other temperate regions over the past several decades have been the focus of much study. In 1998, the SAV habitat evaluation was composed of two discrete but complimentary study elements: the near-shore water quality evaluation and the epiphyte growth study.

#### **Near-shore Water Quality:**

In 1998, six mesohaline and one tidal fresh station were monitored on the Patuxent River. Of these stations, five were also monitored in 1997. Only stations SVBA (Buena Vista), and SVJB (Jug Bay) were new to the 1998 monitoring program. Six near-shore stations were selected in the mesohaline portion of Patuxent River Estuary and tributaries to reflect a variety of nutrient, salinity and wave exposure regimes.

- For water column light attenuation a strong spatial gradient was found along the axis of the river. The highest mean light attenuation of 3.38 m<sup>-1</sup> was found at the northernmost station SVJB (Jug Bay) while the lowest 1.20 m<sup>-1</sup>, was found at the most downriver station SV09 (CBL). This spatial trend was also seen at those stations sampled in 1997.
- For water column dissolved inorganic nitrogen (DIN) no spatial trend was found.



• For water column dissolved inorganic phosphorus (DIP) only a weak spatial trend was found.



#### **Epiphyte Growth Study:**

In order to assess the light attenuation potential of epiphytic growth on the leaves of submerged aquatic vegetation (SAV), artificial substrata in the form of thin strips of Mylar<sup>®</sup> polyester plastic were deployed at each of the seven near-shore stations for periods of 7 - 10 days of *in-situ* exposure.

• Spatially, epiphyte light attenuation increased in the down-river direction with the maximum mean light attenuation of 75% at station SV09 (CBL) and a minimum mean light attenuation of 37% at station SVJB (Jug Bay). On a seasonal basis, all stations except SVJB (Jug Bay) had mean light attenuation of 50% or greater after only one week of *in-situ* exposure.



• A strong relationship was found between epiphyte chlorophyll-a biomass and light attenuation indicating very low ammounts of epiphyte material can attenuate large amounts of available light.

Light Attenuation vs Epiphyte Total Chlorophyll-a Patuxent River



Epiphyte Total Chlorophyll-a ( $\mu$ g Chla cm<sup>-2</sup>)

• Epihyte chlorophyll-a accumulation was highly correlated ( $r^2 = 0.97$ ) with light availability suggesting that along the mesohaline portion of the Patuxent River SAV epiphytes are light limited not nutrient limited.



• *Management Recommendations:* The 1997 and 1998 monitoring provided valuable baseline information about near-shore habitats important to the growth and survival of SAV. However, we recommend that additional monitoring be conducted to evaluate inter-annual variability with regard to these habitats. In addition, we recommend further investigation into the possible effects of epiphyte light attenuation on the growth and survival of SAV in the Patuxent River.

#### **Patuxent River High Frequency Monitoring:**

Water temperature, salinity, and dissolved oxygen were measured 1 m below the water surface of Patuxent River at Benedict at 15 minute intervals from June through August 1998 using an automatic water quality monitoring device. These data were used to (1) evaluate the compliance of water at this location with dissolved oxygen habitat criteria and (2) estimate metabolic parameters that describe the production and respiration of the ecosystem. The 1998 metabolism estimates were compared with data from the 1960s and several other years in the 1990s.

- Dissolved oxygen (DO) at Benedict Bridge satisfied the dissolved oxygen criteria for most, but not all of the time. Periods in which DO in these above pycnocline waters was less than 5 mg l<sup>-1</sup> amounted to 20% of the record, or 494 hours. Although there were no DO excursions below 3 mg l<sup>-1</sup> that lasted more than 12 hours, shorter events recurred with less than a 48-hour intervening time interval.
- Estimates of plankton metabolism, which in 1997 appeared to be slowly tracking back toward 1960s levels, did not improve further in 1998. Average nighttime respiration (Rn) edged upward to 2.7 g  $O_2 \text{ m}^{-2} \text{ night}^{-1}$ , and maximum daytime apparent production (Pa\*) edged upward to 3.00 g  $O_2 \text{ m}^{-2} \text{ day}^{-1}$ . While this estimate of Rn is only 4% higher than estimates for 1964, Pa\* was still nearly two times the 1964 level. This condition is an improvement relative to 1992, when Rn and Pa\* were 1.6 and 3.0 times 1964 levels, respectively.

• *Management Recommendations:* These measurements were extremely useful because of the comparison to measurements collected several decades earlier when the Patuxent River was much less eutrophic compared to the present. However, as with other ecosystem measurements inter-annual variability tends to obscure long-term trends, and thus we do not feel the need to make these measurements on an annual basis. Perhaps, collecting this type of data on a bi-annual or less frequent schedule would provide the necessary information to evaluate ecosystem performance and response to nutrient reduction strategies that may take many years to implement.

#### Super High Resolution Mapping on Patuxent River:

The distribution of water temperature, salinity, dissolved oxygen, turbidity, and chlorophyll-a were mapped in the lower Patuxent estuary at high spatial resolution using a high speed surface water quality mapping instrument called DATAFLOW. The objective was to characterize the nature of spatial variability in water quality, including longitudinal variations, horizontal variations, and patchiness.

Two contrasting phytoplankton patches illustrate how production to respiration (P:R) ratios can vary. In an upstream patch, phytoplankton biomass and turbidity were substrantially elevated, but dissolved oxygen was not increased, suggesting low P:R. In two downstream patches, apparently with higher P:R, dissolved oxygen was elevated as much as 10 mg l<sup>-1</sup> relative to nearby areas with lower phytoplankton biomass.



• Correlation length scales, or patch sizes, for chlorophyll-a were 1-4 km. Similar patch sizes for dissolved oxygen were smaller, about 1-2 km. These results indicate the need for spatially resolved information for accurately characterizing water quality and especially for understanding ecosystem processes affecting water quality.

#### **1. INTRODUCTION**

During the past decade much has been learned about the effects of both natural and anthropogenic nutrient inputs (*e.g.*, nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and oxygen conditions in deep waters (Nixon, 1981, 1988; Boynton *et al.*, 1982; Kemp *et al.*, 1983; D'Elia *et al.*, 1983; Garber *et al.*, 1989; Malone, 1992; and Kemp and Boynton, 1992). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production and algal blooms are sustained through summer and fall periods by benthic recycling of essential nutrients (3) deposition of organic matter from surface to deep waters links these processes of production and consumption, and (4) submerged aquatic vegetation (SAV) communities are responsive to water quality conditions, especially light availability.

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

Nutrients and organic matter enter the bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on bay waters. Dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. A portion of this newly produced organic matter sinks to the bottom, decomposes and thereby contributes to the development of anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative and large nutrient storage capacities of estuarine sediments ensure a large return flux of nutrients from sediments to the water column that can sustain continued high rates of phytoplanktonic growth and biomass accumulation. Continued growth and accumulation supports high rates of deposition of organics to deep waters, creating and sustaining hypoxic and anoxic conditions typically associated with eutrophication of estuarine systems. To a considerable extent, it is the magnitude of these processes, which determines water quality conditions in many zones of the bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings decrease, changes in the magnitude of the processes monitored in this program are expected and will serve as a guide in determining the effectiveness of strategies aimed at improving bay water quality and habitat conditions. The schematic diagram in Figure 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.

Within the context of this model a monitoring study of sediment processes, water column metabolism and SAV habitat conditions has been developed. The Ecosystem Processes Component (EPC) has been gathering information since 1985, the earliest program was the Sediment-Water Oxygen and Nutrient Exchanges (SONE) program (1985-1997), while recently others were added, the MINI-SONE program (1996), the high frequency monitoring program (1996), and the SAV habitat evaluation (1997). At present all activities of the EPC are focused on the Patuxent River estuary as a representative system to examine how nutrient reductions can and do impact the system. The working hypothesis is that if nutrient and organic matter loading to this targeted estuary decrease then the cycle of deposition to sediments, sediment oxygen demand, release of sediment nutrients and continued high algal production will also decrease and the potential for SAV recolonization will increase.

#### **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), investigated techniques to increase the spatial coverage of measurements based on sediment chlorophyll-a and other bottom water quality distributions, evaluated habitat conditions relative to SAV reintroduction, conducted high frequency (daily) measurements of community metabolism and dissolved oxygen conditions during 1998. The Patuxent River estuary, where EPC efforts are concentrated, is an area of particular interest because substantial reductions in nutrient loading rates have been achieved in this system.

The EPC has been modified since its inception in 1984 while maintaining the overall objectives that are consistent with those of other Monitoring Program Components:

- 1. Characterize the present state (status) of the Patuxent estuary (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and sediment oxygen consumption rates.
- 2. Determine the current status and long-term trends that develop in sediment-water exchanges and sediment oxygen consumption rates in response to pollution control programs.
- 3. Develop statistical techniques for estimating the performance of estuarine sediments that allow greater spatial resolution than is possible with current approaches.
- 4. Evaluate near-shore water quality conditions relative to SAV habitat across a range of spatial and temporal scales in the Patuxent River estuary. This includes an investigation of the potential for light attenuation due to epiphytic fouling of SAV leaves.



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

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- 5. Continue high frequency measurements of community metabolism and dissolved oxygen characteristics at one site in the Patuxent estuary and relate these rates to nutrient load conditions and dissolved oxygen criteria, respectively.
- 6. Integrate the information collected in this program with other elements of the monitoring program to gain a better understanding of the processes affecting Chesapeake Bay water quality and its impact on living resources.

# **1.3 Status of the EPC of the Maryland Chesapeake Bay Water Quality Monitoring Program**

The Chesapeake Bay Water Quality Monitoring Program was initiated to provide guidelines for restoration, protection and future use of the mainstem estuary and its tributaries and to provide evaluations of implemented management actions directed towards alleviating some critical pollution problems. A description of the complete monitoring program is provided in Magnien *et al.* (1987). In addition to the EPC program portion, the monitoring program also has components that measure:

- 1. nutrient and pollution 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).

The first phase of the study was undertaken over a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the bay, including spatial and seasonal variation, which were keys in the identification of problem areas. The EPC measured sediment-water oxygen and nutrient exchange rates and determined the rates at which organic and inorganic particulate materials reached deep waters and the sediment surface. Sediment-water exchanges and depositional processes are major features of estuarine nutrient cycles and play an important role in determining water quality and habitat conditions. The results of EPC monitoring have been summarized in a series of interpretive reports (Boynton *et al.*, 1985, 1986, 1987, 1988, 1989, 1990, 1991, 1992, 1993, 1994, 1995, 1996, 1997 and 1998). The results of this characterization effort have largely confirmed the importance of deposition and sediment processes in determining water quality and habitat conditions.

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

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay was reevaluated. In this phase of the process, the monitoring program was used to assess the appropriateness of targeted nutrient load reductions as well as provide indications of water quality patterns 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 are dominant followed by forest and urban sources; the "controllable" fraction of nutrient loads is about 47% for nitrogen and 70% for phosphorus; point source reductions are ahead of schedule and diffuse source reductions are close to projected reductions; further efforts are needed to reduce diffuse sources; significant reductions in phosphorus concentrations and slight increases in nitrogen concentrations have been observed in some areas of the bay; areas of low dissolved oxygen have been quantified and living resource water quality goals established; simulation model projections indicate significant reductions in low dissolved oxygen conditions associated with a 40% reduction of controllable nutrient loads. During the latter part of 1997 the Chesapeake Bay Program entered another phase of re-evaluation. Since the last evaluation, programs have collected and analyzed additional information, nutrient reduction strategies have been implemented and, in some areas, habitat improvements have been accomplished. The overall goal of the 1997 re-evaluation was the assessment of the progress of the program and the implementation of necessary modifications where needed to the difficult process of restoring water quality, habitats and living resources in Chesapeake Bay.

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## 2. SEDIMENT-WATER OXYGEN AND NUTRIENT EXCHANGES: (MINI-SONE and High Resolution Mapping)

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#### 2.1 Introduction and Background

More than a decade of study 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 exchanges have significant potential to negatively affect water quality and living resources. However, the utilization and regeneration of nutrients within an estuary is governed by processes that are both spatially and temporally variable. Therefore, in order to evaluate an estuary's response to changes (especially reductions) in external nutrient loading, it is important to collect data on appropriate spatial and temporal scales. While previous studies have shown that the highest nutrient releases by sediments occur during the summer months (Garber *et al.*, 1989), less work has been done to evaluate the importance of spatial variability. Traditionally, sediment-water oxygen and nutrient exchange (SONE) measurements were made at a few fixed-location stations thereby providing only an indication of spatial gradients and variability. Yet, we know that observed spatial variability does not remain fixed in time, and we are uncertain whether sediment-water exchanges at these fixed stations respond to changes in external nutrient loading in a linear or non-linear fashion.

In recent years, the EPC has begun efforts to answer some of these questions by adopting new techniques that increase the spatial resolution of measurements in the Patuxent River. In 1996, six additional sediment-water exchange stations were added to four long-term stations (Table 2-1) 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 and net fluxes calculated. 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 help provide a more accurate assessment of sediment-water exchanges across the estuary as a whole, and thus more easily evaluate the river's response to nutrient management strategies.

In 1998, traditional SONE measurements (with replication) at the four long-term monitoring stations, BUVA (Buena Vista), MRPT (Marsh Point), BRIS (Broomes Island), and STLC (St. Leonard Creek) were not made 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. The other six MINI-SONE stations were monitored as usual in 1998.

While the addition of MINI-SONE measurements to the monitoring program significantly increased the ability to examine the full range of sediment-water fluxes on the Patuxent River, the development of statistical regression models provided a cost effective way to more fully examine the spatial variability across an estuary. Based upon easily measured water and sediment parameters, these models can provide estimates of sediment-water fluxes at high spatial resolutions. These data can be used to provide a comparison to the long-term fixed monitoring stations as well as to evaluate whole estuary responses to changes in nutrient loading. With this in mind, high-resolution mapping of surficial sediment chlorophyll-a began in 1996 at 37 stations

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(including the ten MINI-SONE stations) across the mesohaline portion of the Patuxent River. In 1998, high-resolution spatial mapping was expanded to include bottom water nutrient concentrations, bottom water physical parameters, and sediment chlorophyll-a concentrations at the same 37 stations across the estuary. Comparisons between data collected at the four long-term monitoring stations and the high-resolution mapping stations allow us to evaluate how well the long-term stations represent the overall range of conditions found in the Patuxent River.

#### 2.2 Methods

#### 2.2.1 Station Locations

#### 2.2.1.1 MINI-SONE and Long-term Patuxent River Station Locations

Ten MINI-SONE stations were chosen to represent the fullest possible range of sediment-water flux conditions found on the Patuxent River (Figure 2-1). Four of these stations, St. Leonard Creek (STLC), Broomes Island (BRIS), Marsh Point (MRPT) and Buena Vista (BUV) were previously monitored using the full suite of measurements referred to as Sediment-water Oxygen and Nutrient Exchanges (SONE) and are now referred to as the long-term monitoring stations. Initially MINI-SONE stations were selected from among 37 surficial sediment chlorophyll-a mapping stations on the Patuxent River based on a suite of water quality and surficial sediment parameters measured at each station during March, April, and May of 1996. These parameters included bottom water temperature, salinity, dissolved oxygen conditions as well as sediment chlorophyll-a concentrations. The remaining six MINI-SONE stations were PX07, PX15, PX21, PX23, PX25 and PX33. Station PX33 was substituted for PX32 in 1997 after a full review of the data indicated that station PX33 would better represent the full range of conditions found in the Patuxent River. These stations were initially chosen in 1996 from among 37 surficial sediment chlorophyll-a mapping stations (Boynton *et al.*, 1997).

#### 2.2.1.2 High Resolution Sediment and Bottom Water Mapping Locations

In the Patuxent River, 37 stations were sampled between the most upriver SONE station BUVA (Buena Vista) and the most down river station STLC (St. Leonard Creek, Figure 2-2). These stations were chosen to represent both a salinity and depth range found within this portion of the estuary.



**Figure 2-1.** Location of ten MINI-SONE Stations sampled in the Patuxent River, Chesapeake Bay. Relative locations of stations are shown in the Patuxent River and do not reflect exact geographic locations.



Figure 2-2. Location of 37 stations in the Patuxent River used in the High Resolution Sediment and Bottom Water Mapping.

Latitude and longitude are in decimal degrees. Relative locations of stations are shown in the Patuxent River and do not reflect exact geographic locations.

STATION CODE	LATITUDE (DGPS)	LONGITUDE (DGPS)	STATION DEPTH	MDE STATION	BAY SEGMENT
	, , ,	``´´	( <b>m</b> )		
Patuxent River					
BUVA	38° 31.050'	76° 39.738'	5.0	XDE9401	RET1
MRPT	38° 26.767'	76° 37.900'	7.0	XDE5339	LE1
BRIS	38° 23.600'	76° 33.067'	15.5	XDE2792	LE1
STLC	38° 22.817'	76° 30.067'	7.0	XDE2792	LE1
PX07	38° 29.352'	76° 39.375'	2.0		
PX15	38 ° 25.983'	76° 37.167'	10.0		
PX21	38° 25.500'	76° 35.017'	3.0		
PX23	38 ° 24.283'	76° 34.367'	11.0		
PX25	38° 25.183'	76 ° 34.483'	3.5		
PX33	38°22.531'	76° 30.640'	18.5		

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

#### Table 2-2. High Resolution Sediment and Bottom Water Mapping Station Locations and Salinity.

M = Mesohaline 5.0 - 18.0 p	эt
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Station Names (where available)	Station Code	Average Depth (m)	Latitude (DGPS)	Longitude (DGPS)	Median Salinity (ppt)
Teagues Point	PX01	3.0	38° 31 190'	76° 40 225'	(Code)
	PX02	5.0	38° 31.150'	76° 39 930'	7.6 (M)
		5.0	20.0 21.050	76 39.930	7.0 (141)
Buena Vista	BUVA	5.0	38° 31.050'	76° 39.738'	7.7 (M)
	PX03	2.0	38° 31.080'	76° 39.800'	7.4 (M)
Billiard Point	PX04	3.0	38° 29.256'	76° 40.045'	8.1 (M)
	PX05	5.0	38° 29.290'	76° 39.787'	8.6 (M)
	PX06	8.5	38° 29.304'	76° 39.686'	9.0 (M)
Buzzard Island	PX07	2.0	38° 29.352'	76° 39.375'	7.3 (M)
Sheridan Point	PX08	8.0	38° 28.338'	76° 39.090'	9.3 (M)
Marsh Point	PX09	3.5	38° 26.776'	76 ° 38.339'	8.3 (M)
Marsh Point	MRPT	7.0	38° 26.767'	76 ° 37.900'	9.7 (M)
	PX10	10.0	38° 26.787'	76° 37.836'	12.0 (M)
	PX11	6.0	38° 26.937'	76° 37.642'	9.3 (M)
Kitts Point	PX12	3.5	38° 27.165'	76° 37.231'	7.9 (M)
Prison Point	PX13	5.5	38° 26.275'	76° 36.853'	9.3 (M)
	PX14	7.0	38° 26.136'	76 ° 37.029'	11.1 (M)
	PX15	10.0	38° 25.983'	76° 37.167'	12.1 (M)
	PX16	2.5	38° 25.673'	76° 37.528'	8.0 (M)
Rolin Creek	PX17	6.0	38° 24.630'	76° 35.642'	9.4 (M)
	PX18	6.5	38° 24.787'	76° 35.574'	10.8 (M)
	PX19	12.5	38° 24.983'	76° 35.363'	12.0 (M)
	PX20	6.0	38° 25.291'	76° 35.190'	10.3 (M)
	PX21	3.0	38° 25.500'	76° 35.017'	8.6 (M)
Cole Creek	PX22	7.0	38° 24.050'	76° 34.586'	10.5 (M)
	PX23	11.0	38° 24.283'	76° 34.367'	12.5 (M)
	PX24	6.0	38° 24.625'	76° 33.861'	10.1 (M)
## Table 2-2. High Resolution Sediment and Bottom Water Mapping Station Locations and Salinity (Continued).

M = Mesohaline 5.0 - 18.0 ppt

Station	Station	Average	Latitude	Longitude	Median
	Code	Depth (m)	(DGPS)	(DGPS)	Salinity (ppt)
					(Code)
	PX25	3.5	38° 25.183'	76° 34.483'	8.8 (M)
	PX26	2.5	38°23.497'	76° 33.437'	8.8 (M)
Broomes Island	BRIS	15.5	38° 23.600'	76° 33.067'	10.2 (M)
Broomes Island	PX27	4.5	38° 23.998'	76° 32.868'	9.5 (M)
Island Neck	PX28	4.0	38° 24.188'	76° 32.568'	9.4 (M)
	PX29	5.5	38° 24.124'	76° 31.730'	10.0 (M)
	PX30	8.5	38° 23.548'	76° 31.650'	10.9 (M)
Sotterly Point	PX31	11.0	38° 23.291'	76° 31.611'	12.3 (M)
Greenwell State Park	PX32	8.0	38° 22.350'	76° 31.033'	11.2 (M)
	PX33	18.5	38° 22.531'	76° 30.640'	10.5 (M)
St. Leonard Creek	STLC	7.0	38° 22.817'	76° 30.067'	9.2 (M)

#### 2.2.2 Sampling Frequency

#### 2.2.2.1 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). These studies indicated four distinct periods during an annual cycle including:

- 1. A period characterized by the presence of a macrofaunal community, high concentrations of nitrate in surface waters and the development and deposition of the spring phytoplankton bloom (April June). Characteristics of sediment-water nutrient and oxygen exchanges typically include the following: relatively high sediment oxygen consumption (SOC) rates, nitrate uptake by sediments and low exchange rates of other nutrients.
- 2. A period during which macrofaunal biomass is low but water temperature and water column metabolic activity high with hypoxia or anoxia prevalent in deeper waters (July - September). Characteristics of sediment-water nutrient and oxygen exchanges typically include the following: low sediment oxygen consumption (SOC) and nitrate fluxes, high releases of ammonium  $(NH_4^+)$ , phosphate (PO<sub>4</sub><sup>-3</sup>) and silicate (Si(OH)<sub>4</sub>).
- 3. A period in the fall when anoxia is not present and macrofaunal community abundance is low but re-establishing (October November). Characteristics of sediment-water nutrient and oxygen exchanges typically include the following: increased sediment oxygen consumption (SOC) rates, intermediate release rates of ammonium ( $NH_4^+$ ), phosphate ( $PO_4^{-3}$ ) and silicate (Si(OH)<sub>4</sub>) and occasional nitrate release.
- 4. A winter period (December March) when fluxes are very low due primarily to low temperature. No samples were collected during the period November through April.

Previous studies also indicate that short-term temporal (day-month) variation in these exchanges is small; however, considerable differences in the magnitude and characteristics of fluxes appear among distinctively different estuarine zones (*i.e.*, tidal fresh *vs.* mesohaline regions). In light of these results, the monitoring design adopted for MINI-SONE studies involved four monthly measurements made between June and September, 1998. Sampling dates for these cruises together with alpha-numeric cruise identification codes can be found in Table 2-3.

CRUISE	DATE	<b>BEGIN DATE</b>	END DATE	RESEARCH VESSEL
MINI-SONE 1	JUN 1996	17 JUN	17 JUN	Orion
MINI-SONE 2	JUL 1996	25 JUL	25 JUL	Orion
MINI-SONE 3	AUG 1996	11 AUG	22 AUG	Orion
MINI-SONE 4	SEP 1996	13 SEP	13 SEP	Orion
MINI-SONE 5	JUN 1997	18 JUN	19 JUN	Aquarius
MINI-SONE 6	JUL 1997	21 JUL	21 JUL	Orion
MINI-SONE 7	AUG 1997	18 AUG	19 AUG	Orion
MINI-SONE 8	SEP 1997	9 SEP	10 SEP	Orion
MINI-SONE 9	JUN 1998	8 JUN	12 JUN	Orion
MINI-SONE 10	JUL 1998	20 JUL	22 JUL	Orion
MINI-SONE 11	AUG 1998	17 AUG	19 AUG	Orion
MINI-SONE 12	SEP 1998	14 SEP	17 SEP	Orion

#### Table 2-3. MINI-SONE Cruise Identifier

#### 2.2.2.2 Sampling Frequency for High Resolution Sediment and Bottom Water Mapping

The high resolution mapping stations were sampled monthly during May through September 1998. These months were chosen as optimum times to document the spatial distribution and magnitude of labile organic material deposited to sediments during and following spring and summer algal bloom. Bottom water nutrient concentrations, dissolved oxygen, and temperature, along with sediment redox potential (Eh) were also measured at these stations during June through September 1998

#### 2.2.3 Field Methods

#### 2.2.3.1 Field Methods for MINI-SONE

#### 2.2.3.1.1 Water Column Profiles

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

#### 2.2.3.1.2 Water Column Nutrients

Near-bottom (approximately 1/2 meter) water samples were collected using a high volume submersible pump system. Samples were filtered, where appropriate, using 0.7  $\mu$ m GF/F filter pads, and immediately frozen. Samples were analyzed by Nutrient Analytical Services Laboratory (NASL) for the following dissolved nutrients: ammonium (NH<sub>4</sub><sup>+</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), nitrite plus nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) and dissolved inorganic phosphorus corrected for salinity (DIP or PO<sub>4</sub><sup>-3</sup>).

#### **2.2.3.1.3** Sediment Profiles

At each MINI-SONE station an intact sediment sub-core was used to measure the redox potential, (Eh, in units of mV) of sediments. Measurements were taken at one centimeter above the sediment surface, at the sediment surface and at 1.0, and 2.0 cm sediment depth. Thereafter, measurements were taken every 2.0 cm, to approximately 10.0 cm of sediment depth. Additionally, surficial sediments were sampled for total and active sediment chlorophyll-a to a depth of 1 cm. Particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), were also sampled to a depth of 1 cm.

#### 2.2.3.1.4 Sediment Cores

The MINI-SONE protocols used an abbreviated set of measurements compared to the standard SONE techniques. MINI-SONE stations used a single sediment core with no blank core. Intact sediment cores constitute a benthic microcosm where changes in oxygen, nutrient and other compound concentrations are determined and from which fluxes can be determined.

A 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 such as large macrofauna or cracks in the sediment surface. If the sample is satisfactory, the core is fitted with an O-ring sealed top containing various sampling ports, and a gasket sealed bottom (Figure 2-3). The core is then placed in a darkened, temperature controlled holding tank where overlying water in the core is slowly replaced by fresh bottom water to ensure that water quality conditions in the core closely approximate *in-situ* conditions.

During the period in which the flux measurements are taken, the cores are placed in a darkened temperature controlled bath to maintain ambient temperature conditions. The overlying water in a core is gently circulated with no induction of sediment resuspension via stirring devices attached to the oxygen probes. Oxygen concentrations are recorded and overlying water samples (35 ml) are extracted from each core every 60 minutes during the incubation period. Standard SONE stations were 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<sub>4</sub><sup>-3</sup>). Oxygen and nutrient fluxes are estimated by calculating the mean rate of change in concentration during the incubation period and converting the volumetric rate to a flux using the volume: area ratio of each core.



Figure 2-3. Schematic Diagram of the Incubation Chamber

#### 2.2.3.2 High Resolution Sediment and Bottom Water Mapping

#### 2.2.3.2.1 Surficial Sediment Chlorophyll-a Measurements

At each of 37 stations in the Patuxent River an intact sediment core is acquired using a modified Bouma box corer. The sediment sample is subcored to a depth of one centimeter. This subcore is placed in a 50 ml centrifuge tube, frozen on shipboard, and analyzed back at the laboratory for both total and active chlorophyll-a concentrations. Bottom water quality parameters (temperature, conductivity, salinity and dissolved oxygen) are recorded. In addition, secchi disk measurements are taken.

#### 2.2.3.2.2 Bottom Water Physical Parameters

Near bottom water (approximately <sup>1</sup>/<sub>2</sub> meter from bottom) temperature, dissolved oxygen concentrations, conductivity and salinity were measured at each station with either a Yellow Springs International (YSI) Model 6920 or 600 multi-parameter water quality instrumentation.

#### 2.2.3.2.3 Bottom Water Dissolved Nutrients

Water samples were collected from near bottom (approximately  $\frac{1}{2}$  meter from bottom) with a submersible pump system. Whole water was then filtered with 0.7  $\mu$ m GF/F filters, and the dissolved component immediately frozen shipboard for later analysis.

#### 2.2.3.2.4 Sediment Redox (Eh) Potential

At each high resolution mapping station an intact sediment sub-core was used to measure the redox potential, (Eh, in units of mV) of sediments. Measurements were taken at one centimeter above the sediment surface, at the sediment surface, and at 1.0 cm sediment depth.

#### 2.2.4 Chemical Analyses used in MINI-SONE and High Resolution Mapping

Methods for the determinations of dissolved and particulate nutrients are as follows: ammonium  $(NH_4^+)$ , nitrite  $(NO_2^-)$ , nitrite plus nitrate  $(NO_2^- + NO_3^-)$ , and dissolved inorganic phosphorus (DIP or PO<sub>4</sub><sup>-</sup>) are measured using the automated method of EPA (1979); particulate carbon (PC) and particulate nitrogen (PN) samples are analyzed using a model 240B Perkin-Elmer Elemental Analyzer; particulate phosphorus (PP) concentration is obtained by acid digestion of muffled-dry samples (Aspila *et al.*, 1976); methods of Strickland and Parsons (1972) and Parsons *et al.* (1984) are followed for chlorophyll-a analysis.

#### 2.2.5. Data Contouring and Integrated Estimates

Contour maps and integrated estimates of various parameters were made with *Surfer*<sup>®</sup> contouring software using data collected from stations on the Patuxent River located between Benedict MD (just north of the Rt. 231 bridge crossing) and the mouth of St. Leonard Creek. To produce these estimates, actual data were interpolated to a uniform grid of 0.002 degrees latitude and longitude using a Kreiging interpolation method (grid squares represent areas of approximately 0.05 km<sup>2</sup>). Contour maps and integrated estimates were then created from this uniform grid. The accuracy of these estimates depends on the number and spacing of actual data points used. The addition of 37 mapping stations to the standard EPC monitoring (SONE and MINI-SONE) provided the opportunity to compare results using various subsets of this data. For example, in section 2.3.2.3 of this report, we can compare estimates of total bottom area exposed to hypoxic conditions using the four long-term SONE stations, ten MINI-SONE stations, or 37 mapping stations. In addition, area weighted integrated totals can also be calculated to provide estimates of sediment-water exchanges across the whole estuary.

#### 2.3 Results

Since estuarine ecosystems are both temporally and spatially variable, an accurate evaluation of ecosystem status and its response to nutrient loading require data on the appropriate spatial and temporal scales. Since 1996, the EPC has increased the spatial coverage of it's monitoring of the Patuxent River to include ten MINI-SONE stations, and 37 high resolution sediment and bottom water mapping stations. With this increased spatial coverage we can now calculate estuary-wide estimates of certain parameters and compare differences in these estimates using various subsets of the data. The assumption is that integrated estuary-wide estimates would be more accurate at evaluating an estuary's health because these estimates take into account spatial variability. In this way, we can begin to evaluate how well the four long-term monitoring stations (BUVA, MRPT, BRIS and STLC) actually reflect the estuary as a whole. While at this time these comparisons can only be made in a limited way, they can still be quite instructive and will become more valuable as the data base increases over the years.

#### 2.3.1 River Flow

River flow is an important external forcing function on estuarine processes influencing both temperature and salinity patterns as well as nutrient loading rtaes. In the Patuxent River, and in other estuaries, river flow has been shown as a good estimate of point source nutrient loading. However, not only is the magnitude of river flow important to understanding patterns, but also the timing of flow events that affect nutrient uptake and utilization. Therefore, an examination of inter-annual and monthly flow patterns help explain variation in estuarine processes such as sediment-water exchanges. Annual average Patuxent river flow was 437 cfs in 1998, 412 cfs in 1997 and 704 in 1996 and all were higher than the long-term average of 383 cfs (Figure 2-4). While average annual river flow in the last three years was higher than the long-term (21-year) average, the patterns of monthly average river flow differed significantly among the years. In





1998 and 1997 peak monthly river flow occurred in March (1131 and 875 cfs respectively), while in 1996, peak flow occurred in December (1357 cfs, Figure 2-4). 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 1997 or 1996. This resulted in significantly higher sediment-water fluxes at many locations within the river in 1998 compared to 1997, yet average annual flow was not very different between the years (437 cfs and 412 cfs respectively). 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, *in press*). This may also affect the deposition of labile material to the sediment surface, which in turn affects sediment-water exchanges. If sediment chlorophyll-a distributions continue to be measured during wet and dry years, quantifying the degree to which this transport actually occurs may be possible.

#### 2.3.2 Bottom Water and Sediment Conditions in the Patuxent River in 1998

#### 2.3.2.1 Temperature

Bottom water temperature conditions at all stations in the Patuxent River ranged from 19.8 °C at PX09 in June to 28.4 °C at PX02 in August. Bottom water temperature conditions at four SONE and six MINI-SONE stations ranged from 20.0 °C at PX33 in June to 28.4 °C at BUVA in August.

#### 2.3.2.2 Salinity

Bottom water salinity conditions at all stations in the Patuxent River ranged from 5.4 ppt at PX01 in June to 16.1 ppt at PX33 in September. Bottom water salinity conditions at four SONE and six MINI-SONE stations ranged from 6.5 ppt at PX07 in June to 16.1 ppt at PX33 in September.

#### 2.3.2.3 Dissolved Oxygen Concentration

Adequate dissolved oxygen concentrations in bottom waters are critical to the health and survival of an estuary's living resources. While species differ in their ability to tolerate low dissolved oxygen conditions, concentrations less than 2.0 mg l<sup>-1</sup> (hypoxia) are often used as a benchmark for determining stress to benthic habitats. Since bottom water conditions fluctuate naturally on various time scales, the duration of low dissolved oxygen concentrations is also an important consideration when evaluating habitat criteria. However, estimations of the extent of bottom area exposed to low dissolved oxygen concentrations may also be useful for evaluating how well an estuary responds to changes in nutrient loading.

Bottom water dissolved oxygen conditions were measured monthly at 37 mapping stations on the Patuxent River from May through September 1998. Contour maps of bottom water dissolved oxygen concentrations were created for each month using  $Surfer^{(B)}$  contouring software to help

visualize the temporal and spatial distribution of this important parameter (Figure 2-5). Based upon estimates derived using all 37 high-resolution mapping stations, low dissolved oxygen conditions (< 2.0 mg l-1) began to show up in June 1998, and were well developed by July. However, by August of 1998, bottom water dissolved oxygen concentrations began to increase.

While Figure 2-8 illustrates the frequency distribution of DO concentrations found at the four (4) long-term stations and the 37 high-resolution mapping stations during each month, in order to obtain better estimates of the total area affected by low dissolved oxygen conditions, integrated estimates were calculated for each month using *Surfer* <sup>®</sup> contouring software. This was done for various subsets of the data from the four long-term stations, through all 37 mapping stations (Figure 2-6). Comparisons of these estimates using various subsets of the data show that by increasing the number of stations used in the calculation, an accurate assessment of dissolved oxygen conditions is found at approximately 28 mapping stations (Figure 2-7). No significant changes in this estimate were found when the number of stations was increased from 28 to 37. While this result may suggest fewer stations are needed to accurately assess bottom water dissolved oxygen conditions, the number of stations necessary to characterize other important parameters may differ if spatial variability differs as well.







# Figure 2-6. Estimates of bottom water hypoxic area (DO concentration $< 2.0 \text{ mg I}^{-1}$ ) in the Patuxent River July 1998 calculated from (a) 37 mapping stations (b) 22 mapping stations (c) ten MINI-SONE stations and (d) four SONE stations.



Figure 2-7. Estimated bottom water hypoxic area in the Patuxent River July 1998 versus number of stations sampled.



Figure 2-8. Frequency histograms of dissolved oxygen measurements on the Patuxent River during (a) June (b) July (c) August and (d) September of 1998. Thirty seven stations were sampled in each month. Long term Patuxent River stations are indicated.

#### 2.3.2.4 Dissolved Nutrient Concentrations

Ammonium  $(NH_4^+)$  concentrations at all stations in the Patuxent River ranged from 0.3  $\mu$ M N at PX25 in August to 22.1  $\mu$ M N at PX33 in June. This was also the range of ammonium concentrations at the four long term Patuxent River stations and six MINI-SONE stations. Figure 2-9 illustrates how ammonium concentrations at the four long term Patuxent River stations are distributed monthly among all 37 high-resolution mapping stations.

Nitrite (NO<sub>2</sub><sup>-</sup>) concentrations at all stations in the Patuxent River ranged from 0.04  $\mu$ M N at many stations (BUVA, PX10, 13, 14, 24, 25, 30 and 31) in July to 10.92  $\mu$ M N at PX15 in September. Nitrite concentrations at the four SONE and six MINI-SONE stations ranged from 0.04  $\mu$ M N at BUVA and PX25 in July to 10.92  $\mu$ M N at PX15 in September.

Nitrite plus nitrate (NO<sub>2</sub><sup>-</sup>+NO<sub>3</sub><sup>-</sup>) concentrations at all stations in the Patuxent River ranged from 0.07  $\mu$ M N at PX28 in August to 13.4  $\mu$ M N at PX15 in September. Nitrite plus nitrate concentrations at the four SONE and six MINI-SONE stations ranged from 0.10  $\mu$ M N at PX15 in July to 13.4  $\mu$ M N at PX15 in September. Figure 2-10 illustrates how nitrite plus nitrate concentrations at the four long-term SONE stations are distributed monthly among all 37 high-resolution mapping stations.

Dissolved inorganic phosphorus (DIP) concentrations at all stations in the Patuxent River ranged from 0.07  $\mu$ M P at PX28 in June to 2.95  $\mu$ M P at PX01 in August. DIP concentrations at the four SONE and six MINI-SONE stations ranged from 0.11  $\mu$ M P at PX21 and PX25 in June to 2.69  $\mu$ M P at BUVA in August. Figure 2-11 illustrates how phosphate concentrations at the four long-term SONE stations are distributed monthly among all 37 high-resolution mapping stations.



Figure 2-9. Frequency histograms of bottom water ammonium concentrations on the Patuxent River during (a) June (b) July (c) August and (d) September of 1998. Thirty seven stations were sampled in each month.



Figure 2-10. Frequency histograms of bottom water nitrite plus nitrate concentrations on the Patuxent River during (a) June (b) July (c) August and (d) September of 1998. Thirty seven stations were sampled in each month.



Figure 2-11. Frequency histograms of bottom water dissolved inorganic phosphorus concentrations on the Patuxent River during (a) June (b) July (c) August and (d) September of 1998. Thirty seven stations were sampled in each month.

#### 2.3.2.5 Surficial Sediment Chlorophyll-a

A number of studies have shown that sediment-water nutrient and oxygen exchanges (fluxes) are responsive to the amount of labile material deposited to the sediment surface (*e.g.* Boynton *et al.*, 1992; Garber *et al.*, 1989). The use of surficial sediment chlorophyll-a as an index of labile organic material has proven useful for predicting certain sediment-water exchanges (*e.g.* Cowan and Boynton, 1996; Cowan *et al.*, 1996; Boynton *et al.*, 1998). In fact, an analysis of Patuxent River MINI-SONE flux data from 1996 through 1998 has shown that surficial sediment chlorophyll-a concentrations measured approximately one month prior to sediment-water fluxes are highly correlated with several sediment-water exchanges. In addition, significant monthly variation in the standing stock of chlorophyll-a on the sediment surface indicates that deposition of organic matter is a continuing process, and that increases in standing stock can occur throughout the summer when deposition exceeds decomposition (Boynton *et al.*, 1998). For example, in 1997 the highest mean sediment chlorophyll-a concentrations were found in September (Figure 2-12).

#### 2.3.2.5.1 Temporal Variation

In 1998, total sediment chlorophyll-a concentrations (from the top one centimeter of sediment) at all stations (including MINI-SONE stations) in the Patuxent River ranged from a maximum of 386.5 mg m<sup>-2</sup> at PX23 in May to a minimum of 11.80 mg m<sup>-2</sup> at PX21 in July. The pattern of monthly variation in sediment chlorophyll-a concentrations followed typical estuarine depositional models with maximum concentrations highest in the spring and lowest in the summer. Differences in mean monthly sediment chlorophyll-a concentrations were evaluated with analysis of covariance (ANCOVA), with station depth as a significant covariate. The mean sediment chlorophyll-a concentration was significantly higher in May 1998 (159.4 mg m<sup>-2</sup>) compared to all other summer months (P < 0.01, Figure 2.12). This is in contrast to 1997 in which the maximum mean concentration was highest in September. Minimum average concentrations were found in July 1998 (67.3 mg m<sup>-2</sup>), and were significantly lower than all other months measured (P < 0.01).

#### 2.3.2.5.2 Spatial Variation

In addition to seasonal and yearly variation in sediment chlorophyll-a concentrations in the Patuxent River, spatial variation was also an important feature. While station depth explains some of this variation (Boynton *et al.*, 1998), the distribution of sediment chlorophyll-a does not appear to be consistent on a yearly basis. This is illustrated by sediment chlorophyll-a contour maps constructed for May of 1996, 1997 and 1998 (Figures 2-13 to 2-15). While a visual representation of spatial variation is instructive, we can address the question of whether ten MINI-SONE stations adequately represent the estuary as a whole, or whether 37 mapping stations are necessary for an accurate assessment. An area-weighted estuary-wide estimate of sediment chlorophyll-a was calculated for these two subsets of data. *Surfer*® contouring software was used to interpolate data from actual stations (ten MINI-SONE or 37 mapping stations) to produce a uniform grid of 0.002 degrees latitude and longitude. From this uniform spatial grid, an area-weighted mean was calculated for each year (1996, 1997 and 1998) and



Figure 2-12. Mean, monthly total sediment chlorophyll-a concentration (collected to 1 cm depth) from 37 mapping stations on the Patuxent River during 1997 and 1998.



Figure 2-13. Sediment total chlorophyll-a concentrations contoured within the study area based on samples collected from the Patuxent River in May 1996 and area weighted mean sediment total chlorophyll-a based upon (a) ten MINI-SONE stations and (b) 37 high-resolution mapping stations.









each subset of the data. A 3-year mean was then calculated for each subset of data. Although a limited amount of data was available, no significant difference (P > 0.05) was found in area-weighted sediment chlorophyll-a concentration when calculated with either ten MINI-SONE stations or 37 mapping stations (Figure 2-16).

Particulate carbon (PC) (from the top one centimeter of sediment) at the four SONE and six MINI-SONE stations ranged from 0.12 % dry weight at PX21 in July to 3.88 % dry weight at PX33 in June.

Particulate nitrogen (PN) (from the top one centimeter of sediment) at the four SONE and six MINI-SONE stations ranged from 0.00 % dry weight at PX07 and PX21 in September to 0.54 % dry weight at PX33 in June.

Particulate phosphorus (PP) (from the top one centimeter of sediment) at the four SONE and six MINI-SONE stations ranged from 0.12 % dry weight at PX21and PX25 in June to 0.16 % dry weight at MRPT in September.

### 2.3.3 Characteristics of SONE and MINI-SONE Sediment-Water Oxygen and

#### Nutrient Fluxes: 1998 Patuxent River Study

#### 2.3.3.1. Long-term Patuxent River Stations

Monthly average sediment-water fluxes derived from the complete sediment-water oxygen and nutrient exchanges (SONE) data set are summarized using box and whisker plots (Figures 2-17.1 through 2-17.4) for four 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 are used to construct these plots. Two stations, Buena Vista (BUVA) and St Leonard Creek (STLC) were sampled over a period of thirteen calendar years (1985 through 1997) while the remaining two stations, Marsh Point (MRPT) and Broomes Island (BRIS), were sampled over a shorter period of nine years (1989 through 1997). Superimposed on these graphs are the single MINI-SONE flux measurements made at these four stations during 1998.

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.

Data collected at the four original SONE stations during the MINI-SONE program in 1998 are shown as bold dots superimposed on the box (Figures 2-17.1 through 2-17.4). The order of the



Figure 2-16. Mean area weighted sediment chlorophyll-a concentration for 1996, 1997 and 1998 calculated from ten MINI-SONE stations and 37 mapping stations.



Figure 2-17.1. 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 1998. 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  $I^{-1}$  dissolved oxygen in bottom waters.



Figure 2-17.2. Box and whisker plots for ammonium (NH₄<sup>+</sup>) 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 1998. 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  $I^{-1}$  dissolved oxygen in bottom waters.



Figure 2-17.3. 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 1998. 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  $I^{-1}$  dissolved oxygen in bottom waters.



Figure 2-17.4. Box and whisker plots for phosphorus (PO<sub>4</sub><sup>-3</sup> 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 1998. 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  $I^{-1}$  dissolved oxygen in bottom waters.

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 mouth (Marsh Point [MRPT] and Broomes Island [BRIS]) to the estuary mouth (St. Leonard Creek [STLC]).

#### **2.3.3.1.1** Sediment Oxygen Consumption (SOC)

Sediment oxygen consumption (SOC) rates for MINI-SONE stations in 1998 ranged from -0.64 g  $O_2 m^2 day^1$  at Marsh Point (MRPT) to -2.86 g  $O_2 m^2 day^1$  at Buena Vista (BUVA) in June, 1998; from -0.32 g  $O_2 m^2 day^1$  at Broomes Island (BRIS) to -2.25 g  $O_2 m^2 day^1$  at Buena Vista (BUVA) in July 1998; from -1.27 g  $O_2 m^2 day^1$  at Marsh Point (MRPT) to -2.65 g  $O_2 m^2 day^1$  at Buena Vista (BUVA) in August, 1998 and from -1.02 g  $O_2 m^2 day^1$  at Broomes Island (BRIS) to -2.73 g  $O_2 m^2 day^1$  at Buena Vista (BUVA) in September, 1998 (Figure 2-17.1; Tables D-5.9. - D-5.12.)

The magnitude of 1998 SOC observations was similar to those observed in previous years. There were no new record high or low values observed. At stations where bottom water dissolved oxygen concentrations tend to be depressed during summer months, SOC rates were also depressed, as expected due to the influence of low dissolved oxygen concentrations (< 2.0 mg l<sup>-1</sup>) on SOC rates. For example, SOC rates were low in July at MRPT and BRIS and both stations also exhibited low dissolved oxygen concentrations in bottom waters (< 1.0 mg l<sup>-1</sup>). Rates of SOC remained low at MRPT in August and September, 1998 despite the fact that dissolved oxygen concentrations had increased to levels not generally associated with depressed SOC rates continued to be higher at BUVA than at the other Patuxent River stations and this is thought to be the result of well oxygenated bottom waters (the water column at this site is well mixed) which promotes the potential for enhanced SOC rates and a well developed benthic macroinvertebrate community which contributes to SOC.

In general, sediment oxygen consumption (SOC) rates at these stations in the Patuxent River tend to be higher (more negative) in low flow years which, in turn, tend to be years in which bottom water dissolved oxygen concentrations remain elevated. The chain of coupled processes leading to this result probably include the following. In low flow years diffuse source nutrient loads are reduced because of lower run off. This leads to smaller algal blooms and reduced deposition of organic matter to bottom sediments. In addition, lower river flow leads to less developed vertical stratification and hence the opportunity for more mixing of oxygen-rich surface waters with deeper waters. The combination of reaeration from surface waters and modest supplies of organic matter to support respiratory processes results in dissolved oxygen concentrations being maintained at levels (> 1 mg l<sup>-1</sup> at which SOC can continue to occur).

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

Monthly ammonium  $(NH_4^+)$  MINI-SONE fluxes in the Patuxent River during 1998 ranged from 167.8  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at Marsh Point (MRPT) to 313.1 at Buena Vista (BUVA) in June 1998; from

216.3  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at Broomes Island (BRIS) to 723.5  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) in July, 1998; from 289.4  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) to 586.7  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at Marsh Point (MRPT) in August, 1998 and from 165.0  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) to 280.4  $\mu$ MN m<sup>-2</sup> hr<sup>-1</sup> at Broomes Island (BRIS) in September 1998 (Figure 2-17.2; Tables D-5.9. - D-5.12.).

With one exception, ammonium fluxes recorded in 1998 followed temporal trends exhibited in previous years. Fluxes tended to peak in July (early summer) and decline during the latter portion of the summer. Very large ammonium fluxes were recorded in July at BUVA and in July and August at MRPT. Ammonium flux at BRIS peaked in August rather than July during 1998.

The general magnitude of ammonium fluxes during 1998 tended to be above the long-term mean at all Patuxent stations. Of the 16 fluxes measured at these sites during 1998 (*i.e.*, four sites x four monthly measurements), only four were below long-term mean values. Fluxes were especially large at BUVA and MRPT, the two stations most proximal to the fall line nutrient sources, but ammonium fluxes were also high at the more down river stations as well (BRIS and STLC). Increased ammonium fluxes suggests an increase in the organic matter supply rate to sediments which probably reflect higher than normal nutrient loading rates during the high flow winter and spring of 1998. In addition DO concentrations in deep waters were particularly low in July. Low DO promotes high NH<sub>4</sub><sup>+</sup> fluxes in part because nitrification is reduced or stopped under low DO conditions.

#### **2.3.3.1.3** Nitrite + Nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) Fluxes

Monthly nitrite plus nitrate  $(NO_2^- + NO_3^-)$  fluxes for 1998 ranged from -53.81 µMN m<sup>-2</sup> hr<sup>-1</sup> at Broomes Island (BUVA) to 0.00 µMN m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) and Buena Vista (BUVA) in June, 1998; from 0.00 µMN m<sup>-2</sup> hr<sup>-1</sup> at Marsh Point (MRPT) and Broomes Island (BRIS) to 12.61 µMN m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) in July, 1998; from 0.00 µMN m<sup>-2</sup> hr<sup>-1</sup> at Broomes Island (BRIS) to 16.37 µMN m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) in August, 1998 and from -45.98 µMN m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) to 0.00 µMN m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) in September, 1998 (Figure 2-17.3; Tables D-5.9. - D-5.12.).

In general, nitrate 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 do occur as was the case at three stations in June, 1997 (STLC, MRPT and the most up-river station in the Patuxent, BUVA). No large fluxes from sediment to water or water to sediments were observed during 1998. However, even small nitrate fluxes from sediments to overlying waters provide a useful indication of sediment conditions. Specifically, production and release of nitrate from sediments is a strong indication that sediment nitrification is occurring. This process requires at least low levels of dissolved oxygen and is hence an indication that surface sediments have been in contact with oxygenated waters. During 1997 (a low flow year), ten of 16 nitrite plus nitrate flux measurements were more positive than the long-term average, indicating good sediment quality conditions. During 1998 only 5 of 16 flux measurements exhibited fluxes indicative of sediment nitrification. To provide addition contrast, during 1996 (an exceptionally high flow year) the overwhelming pattern was nitrite plus nitrate flux (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) from water

to sediments which was to be expected during a wet year when water column nitrate concentrations were high. During 1995, a very low flow year, stations in the Patuxent River exhibited relatively high rates of sediment nitrate release or much lower rates of nitrogen uptake. In fact, at the St. Leonard Creek (STLC) station sediments released nitrate through the entire monitoring period, a pattern never before observed. These are the types of nitrate fluxes to be expected under reduced nutrient load conditions (this was the case in 1995) both because these conditions favor improved dissolved oxygen conditions in deep waters and sediments and lower concentrations of nitrate in overlying waters. The direction and magnitude of nitrite plus nitrate fluxes between sediments and overlying waters appears to serve quite well as an indicator of sediment quality.

#### 2.3.3.1.4 Dissolved Inorganic Phosphorus (PO<sub>4</sub><sup>-3</sup> or DIP) Fluxes

Monthly dissolved inorganic phosphorus (DIP) fluxes in the Patuxent River during 1998 ranged from 7.68  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) to 24.58  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) in June 1998; from 11.8  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) to 166.29 at Marsh Point (MRPT) in July, 1998; from -2.84  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at Buena Vista (BUVA) to 38.88  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at Marsh Point (MRPT) in August, 1998 and from 2.22  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at St. Leonard Creek (STLC) to 53.48  $\mu$ MP m<sup>-2</sup> hr<sup>-1</sup> at Marsh Point (MRPT) in September, 1998 (Figure 2-17.4; Tables D-5.9. - D-5.12.).

The spatial pattern of phosphorus fluxes in the Patuxent River in 1998 are consistent with those reported for ammonium  $(NH_4^+)$  fluxes and were generally higher at up-river sites in closer proximity to nutrient sources and at sites exposed to hypoxic bottom waters. During 1998 very high phosphate fluxes were observed during July at two stations having low dissolved oxygen concentrations in bottom waters (MRPT and BRIS) and at one station where there is a well developed benthic macroinvertebrate community (BUVA). In the former case, these high fluxes probably resulted from dissolution in sediments of solid phase phosphorus compounds were noticeably reduced, while in the latter case, dissolved phosphate was probably pumped from sediments to overlying waters through the action of benthic invertebrates, particularly the clam, *Macoma balthica* (Boynton *et al.*, 1997).

In contrast to the 1998 observations, dissolved inorganic phosphorus ( $PO_4^{-3}$ ) fluxes in 1997 were particularly low. Our conceptual model of factors governing sediment-water exchanges indicates that phosphorus ( $PO_4^{-3}$ ) fluxes should be low during low flow years because of both low phosphorus loading rates to sediments and more oxidized sediments conditions, reduced phosphorus inputs from sediments via sorbtion reactions. During 1997 fluxes at Patuxent River stations were noticeably reduced; rates at BRIS were half those of the long term mean and fluxes were even more reduced at MRPT. It may be premature to conclude that reduced phosphorus inputs from point and diffuse sources is the cause of the pattern observed in the Patuxent River but the pattern observed during 1997 (and 1995, another low flow year) is consistent with this line of reasoning.

#### 2.3.3.2 Sediment-Water Exchanges (MINI-SONE Stations)

As expected, significant differences in sediment-water fluxes were found among the MINI-SONE stations in the Patuxent River (Figure 2-18). For example, on a seasonal basis, the highest mean ammonium flux in 1998 was 586.3  $\mu$ M N m<sup>-2</sup> hr<sup>-1</sup> at station PX33 (deepest station), while the lowest mean flux was below detection limits at station PX25 (Figure 2-18.b). At all but one station, mean ammonium flux was higher in 1998 compared to 1997. In fact, in 1998, mean ammonium flux values at four stations (BUVA, MRPT, PX23, and PX33) were higher than the maximum value of 404.9  $\mu$ M N m<sup>-2</sup> hr<sup>-1</sup> observed at BUVA in 1997 (Figure 2-18.b). While the absolute ranking of ammonium flux among stations was not consistent between 1997 and 1998, those stations with very low ammonium fluxes in 1997 were also low in 1998. This result is consistent with higher than normal spring river flow in 1998 compared to 1997 (Figure 2-4). High river flows in winter and spring (and associated nutrient loads) promote high releases of ammonium from sediments.

Sediment oxygen consumption (SOC) also varied considerably among stations in 1998. The maximum mean SOC value of  $-2.62 \text{ mg O}_2 \text{ m}^{-2} \text{ day}^{-1}$  was found at station BUVA while the minimum value of  $-0.82 \text{ mg O}_2 \text{ m}^{-2} \text{ day}^{-1}$  was found at station MRPT (Figure 2-18.a). With the exception of two stations (PX25 and STLC) SOC rates were higher (more negative) in 1998 compared to 1997. This indicates that sediments were more active metabolically in 1998 than in 1997. In general, the relative ranking of SOC rates among stations was similar in 1998 compared to 1997 indicating that similar processes were active in both years.

Combined nitrite plus nitrate  $(NO_2^- + NO_3^-)$  mean flux among MINI-SONE stations varied considerably in 1998 with some stations releasing nitrite plus nitrate to the water column, while other stations taking it up. Summer mean values ranged from a maximum of 32.0  $\mu$ M N m<sup>-2</sup> hr<sup>-1</sup> out of the sediment at station PX07 to a minimum of -45.24  $\mu$ M N m<sup>-2</sup> hr<sup>-1</sup> into the sediment at PX33 (Figure 2-18c). Although the magnitude of sediment-water flux at these stations differed between years, the direction of sediment-water fluxes at most stations remained the same.

In general, phosphate (PO<sub>4</sub><sup>-3</sup>) flux at most stations was considerably higher in 1998 compared to 1997. The maximum mean phosphate (PO<sub>4</sub><sup>-3</sup>) flux was 93.27  $\mu$ M P m<sup>-2</sup> hr<sup>-1</sup> at station PX23, while the minimum mean flux was 0.43  $\mu$ M P m<sup>-2</sup> hr<sup>-1</sup> at station PX21 (Figure 2-18.d.). The ranking of phosphate flux among stations was not consistent between 1997 and 1998. For example, phosphate flux at station PX23 was 4.33  $\mu$ M P m<sup>-2</sup> hr<sup>-1</sup> in 1997 and was among the lowest values recorded. However, phosphate flux at this station was 93.27  $\mu$ M P m<sup>-2</sup> hr<sup>-1</sup> in 1998 and was the highest value recorded (Figure 2-18.d.).



Figure 2-18. Comparison of Patuxent River MINI-SONE mean flux values calculated from monthly measurements from June through September 1997 and 1998 for:

- (a) sediment oxygen consumption (SOC) and
- (b) ammonium  $(NH_4^+)$  flux.

*NOTE:* All  $NH_4^+$  fluxes at station PX25 in 1998 were zero.





- c. nitrite plus nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) and
- d. phosphate (PO<sub>4</sub><sup>-3</sup>) flux.

NOTE: All  $PO_4^{-3}$  fluxes at station PX25 in 1998 were zero.
## 2.3.4. Statistical Analysis of MINI-SONE Data

## 2.3.4.1 Background

It is well known that the regeneration and transformation of nutrients in estuarine sediments is linked chemically and physiologically to a suite of bottom-water and sediment parameters. Previous studies have shown that factors such as water temperature, salinity and bottom water dissolved oxygen concentrations correlate well with certain sediment-water fluxes, (e.g. Boynton et al., 1980; Cowan and Boynton, 1996; Cowan et al., 1996; Boynton et al., 1998). For example, bottom water nutrient concentrations influence diffusion gradients and sediment-water exchanges (e.g. Boynton and Kemp, 1985; Sundby et al., 1992). In addition, certain sediment properties such as sediment chlorophyll-a concentrations and sediment oxidation-reduction potential (Eh) have been well correlated with several sediment-water fluxes (e.g. Boynton et al., 1998). In particular, sediment chlorophyll-a concentration is a good indicator of labile organic material available for recycling or regeneration and often explains much of the variation observed in sediment-water ammonium fluxes (Boynton et al., 1998). The goal of this analysis was to further develop statistically significant regression relationships between a few easily measured sediment and water quality parameters, and certain sediment-water exchanges (fluxes). These regression relationships could be then be used to estimate sediment-water fluxes at locations where direct measurement is not possible and to further increase the spatial resolution of sediment-water exchanges across an estuary.

In 1996 and 1997 MINI-SONE data was used to construct regression relationships for several important sediment-water fluxes. Data from those years was analyzed both as individual station observations and as summer season means (4 month average). A stepwise regression procedure (SAS statistical software version 6.10) was used to sort through various combinations of variables to construct the most parsimonious model using a combination of water quality and sediment parameters. In general the relationships developed for summer seasonal means were stronger and had higher predictive power than those for individual station observations (Boynton *et al.*, 1998). For that reason, in 1998, regression equations were only developed using the fourmonth summer season mean values.

#### 2.3.4.2 Data Sources

The statistical models presented here were constructed from sediment-water flux, water quality and surficial sediment data collected from six MINI-SONE, and four long-term SONE stations on the Patuxent River from 1996 through 1998. In 1998, sediment-water flux measurements at the four long-term monitoring stations were collected with the abbreviated MINI-SONE technique. Previously, data from these long-term stations were collected using the traditional SONE technique in which three replicate cores were measured to estimate sediment-water exchanges, instead of a single core used in the MINI-SONE technique. Despite this small difference, data from all three years was treated similarly in this analysis. Sediment-water flux and water quality data were collected monthly from June through September of each year, while surficial sediment chlorophyll-a was collected from May through September. The techniques

used to measure sediment-water flux, and sediment chlorophyll-a are outlined in section 2.2.3.1 of this report.

## 2.3.4.3 Results and Conclusions

The model fitting procedure used in 1998 was essentially the same as that used in previous years, in which the most parsimonious model was selected for each sediment-water flux based upon relevant biogeochemical properties, not just the best statistical fit. With three full years of data (1996,1997, and 1998) inter-annual differences in many parameters have necessitated changes in the regression equations that were originally developed with the first two years (1996, 1997) of data. These changes were made to improve the applicability of these models despite inter-annual differences in nutrient loading rates, temperature and salinity conditions. For some sedimentwater fluxes such as ammonium  $(NH_4^+)$ , only minor changes in the parameter coefficients were required to maintain highly predictive models when all three years of data are merged into a single data set. For example, with all three years of data, the regression equation for ammonium flux explained 87% of the observed variation in summer mean sediment-water flux ( $r^2 = 0.87$ , Figure 2-19), using sediment chlorophyll-a lagged one month (TCHL1M), and sediment redox potential (Eh) at 1 centimeter depth (SEDEHM1). These parameters were also selected as the most important predictor variables when the 1996 and 1997 data sets were analyzed separately (Boynton et.al., 1998). This result indicates a very robust relationship between these parameters and sediment-water ammonium flux. This is important because ammonium flux is the largest internal source of nitrogen to the water column during the summer months and is the preferred form of nitrogen for biological utilization (e.g. Boynton et al., 1998; Valiela, 1995). Thus the use of these relationships may prove very useful for estimating estuary wide summer time nitrogen release to the water column.

For sediment-water phosphate (PO<sub>4</sub><sup>-3</sup>) flux, some changes in input variables were made to the regression equations when the 1998 data was included in the full data set. In the reformulated 1998 model, sediment chlorophyll-a concentration lagged one month (TCHL1M) was substituted for sediment redox potential (SEDEHM1), and bottom water dissolved oxygen concentration (DO) to improve the generality of the relationship (Figure 2-20). However, bottom water phosphate concentrations remained as the most important predictor variable in all three years. This result illustrates how bottom water nutrient concentrations can influence diffusion gradients and sediment-water fluxes. With the reformulated model, 77% of the variation in summer mean phosphate flux (PO<sub>4</sub><sup>-3</sup>) is explained ( $r^2 = 0.77$ , Figure 2-20). When this same regression equation is applied to the 1996 and 1997 combined data, 78% of the variation is explained. Although this relationship does not predict phosphate flux as accurately as the model generated from the 1996 or 1997 data alone ( $r^2 = 0.87$ , Boynton *et al.*, 1998), the current reformulation is much more generally applicable.

For other sediment-water fluxes such as nitrite plus nitrate  $(NO_2^- + NO_3^-)$ , a combined data set with all three years substantially degraded the predictive power of the relationship. With all three years of data merged into a single data set, only 59% of the variation in sediment-water flux was explained using the parameters chosen for the combined 1996, 1997 and 1998 data set. It appears that inter-annual variation in the input variables substantially alters the relationship between bottom water and sediment conditions and sediment-water flux. In fact, inter-annual differences in sediment-water fluxes at certain stations were substantial, while at other stations the values were comparable. For example, stations PX25 and STLC had relative high positive mean fluxes in 1997 (64 and 54  $\mu$ M N m<sup>2</sup> day<sup>-1</sup> respectively), but very low positive fluxes in 1998 (8.8 and 4.4  $\mu$ M N m<sup>2</sup> day<sup>-1</sup> respectively), while at other stations, flux values were similar (Figure 2-18.c). The reason for this lack of agreement between regression equations generated from different years is unknown at this time. Perhaps the linear models that work so well for ammonium and phosphate fluxes are not adequate to explain nitrite and nitrate flux and more sophisticated non-linear models are required. Despite this lack of generality, the data indicate that within a specific year, sediment-water fluxes can be well estimated when calibrated with actual flux measurements. For example, using 1997 data alone a regression equation was constructed that explained 96% of the variation in summer mean nitrite plus nitrate flux (r<sup>2</sup> = 0.96, Boynton *et al.*, 1998). Using actual data collected within a specific year or season, estimates of nitrite plus nitrate flux can be made at many more locations than could be possible with direct measurements to increase the spatial resolution within an estuary.

While regression equations generated for sediment oxygen consumption (SOC) using combined 1996 and 1997 data were highly predictive ( $r^2 = 0.89$ , Boynton *et al.*, 1998) using bottom water temperature (TEMP) and sediment chlorophyll-a concentration lagged one month (TCHL1M), the preferred model also used sediment redox (Eh) as an important predictor variable. However, in 1998 a procedural change in the way sediment redox potential (Eh) was measured affected the calibration of these SOC regression models. While this change slightly affected the calibration of Eh values and did not affect all of the regression models, this procedural change will be revoked in further studies to be consistent with past studies. Because of this change in Eh calibration in 1998, and inter-annual differences in a variety of water and sediment parameters, the regression equation generated from the full three year data set for SOC could not explain as much of the variation as in past years ( $r^2 = 0.51$ ). However, a regression equation generated from 1998 data alone explains 88% of summer mean SOC ( $r^2 = 0.88$ ) using water temperature (TEMP) and concurrent sediment chlorophyll-a concentration (TCHL). Like the relationships generated for nitrite plus nitrate flux, when based upon current year actual measurements, estimates of SOC can be made to increase the spatial resolution within an estuary to obtain better estimates of whole system response to changes in nutrient loading.

All of the regression equations discussed above use sediment chlorophyll-a concentration as an important input variable and further illustrate the importance of the deposition of labile organic material to the sediment surface to sediment-water exchanges. Because sediment chlorophyll-a concentrations are spatially variable (Figure 2-15), we can assume that sediment-water fluxes are spatially variable as well. With direct sediment –water exchanges only being measured at a few fixed locations, this variability may not be taken into account. The use of statistically generated regression equations to estimate sediment-water exchanges at locations where direct flux measurements are not possible may help include this spatial variation in estuary wide responses to changes in nutrient loading. Using the relationship generated for ammonium flux (Figure 2-19), contour maps and integrated estimates of ammonium flux were generated using *Surfer*® contouring software for various subset of the data to evaluate how spatial variation may affect estimates of whole estuary ammonium flux. Contour maps and integrated estimates were generated by interpolating the various subsets of actual data (four SONE, ten MINI-SONE, and

27 MAPPING and ten MINI-SONE stations) to a uniform spatial grid of 0.002 degrees latitude and longitude within the studied portion of the Patuxent River (Figure 2-21). This procedure was similar to that used for mapping sediment chlorophyll-a (Section 2.3.2.5.2 of this report). This comparison shows that the highest total estuary ammonium exchange (8,260 Kg NH<sub>4</sub> day<sup>-1</sup>) was found using the fewest stations. This result suggests that a more sensitive analysis of system response to changes in nutrient loading could be done with actual measured fluxes in combination with estimates from regression models.



Figure 2-19. Predicted, sediment-water ammonium flux (NH4+) at MINI-SONE stations versus observed ammonium flux at these stations. Regression equation developed from four-month summer means collected from 1996 through 1998 on the Patuxent River. Data from the Buena Vista (BUVA) station was not included in the analysis.

The regression equation is:

Predicted ammonium flux = 2.120(TCHLA) - 0.585(SEDEHM1) + 92.447

Where TCHLA = mean total sediment chlorophyll-a (from May – August) to 1cm

depth,

SEDEHM1 = mean sediment Eh at 1 cm depth (from June – September).

Dashed lines indicate 95% confidence intervals for individual observations.



Figure 2-20. Predicted, sediment-water phosphate flux (PO<sub>4</sub><sup>-3</sup>) at MINI-SONE stations versus observed phosphate flux at these stations. Regression equation developed from four-month summer means collected from 1996 through 1998 on the Patuxent River.

The regression equation is:

Predicted phosphate flux = 37.658(BWPO4) + 0.315(TCHLA) - 40.186

Where BWPO4 = mean bottom water phosphate concentration

TCHL1M = mean total sediment chlorophyll-a (from May – August) to 1cm depth.

Dashed lines indicate 95% confidence intervals for individual observations.





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# **3. SEDIMENT-WATER FLUX STATUS AND TRENDS:**

# **1998 PATUXENT RIVER STUDY**

#### W.R. Boynton and F.M. Rohland

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The development of management actions to implement the 40% nutrient load reduction strategy has been a major thrust of the Chesapeake Bay Program during its third phase beginning in 1991. Prior to this, the Chesapeake Bay Water Quality Monitoring Program developed a data base containing information related to water quality conditions throughout the bay system. These data were used to describe conditions in the bay system and identify areas of poor water quality. The Ecosystem Processes Component (EPC) Program has been a part of this effort since 1984.

A part of the Ecosystem Processes Component (EPC) Program was also designed to examine the sediment flux data in order to define current status of these processes and identify long-term trends in sediment-water nutrient and oxygen exchanges. In previous Interpretive Reports (Boynton *et al.*, 1993, 1994,) results of statistical testing for trends were presented and discussed. As an addition to this, a time series of important environmental variables (river flow, bottom water dissolved oxygen concentrations and key sediment-water fluxes) were presented in graphical format in Interpretive Report #12 (Boynton *et al.*, 1995). These figures included monthly average data covering the first ten years of the monitoring program (1985 - 1994) collected at six sediment oxygen and nutrient exchanges (SONE) stations. The purpose of these

analyzes was to explore the data to determine temporal trends and to provide a basis for relating important environmental conditions to the characteristics of sediment fluxes.

More recently (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 comprise 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 dataset.

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

- 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 squareroot 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 mean of this 0-1 data is computed as and indicator of status in the current three year period. The median of n observations taken from a uniform distribution follows a Beta distribution with parameters (m,m) where m = (n+1)/2.
- 4. Based on the Beta density, the distribution of 3-year medians from the benchmark data is divided into thirds. If the median of the current three year period is in the upper third (where upper is chosen as the end of the distribution that is ecologically desirable) then the status rating is good, a median in the middle third is rated fair, and a median in the lower third is rated 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. Every flux measurement made at all four Patuxent River stations was used to develop the benchmark for each parameter. This 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.

# 3.1.1.2 Notes on the Current Status for the Patuxent River

A median value for the years 1996, 1996 and 1998 is calculated. The use of the last three years of data provides an "indicator" value of the status of the parameter relative to all other years during which measurements was taken. The median value of the last three years data has the effect of reducing the influence of extreme climatic conditions (*i.e.* very wet or very dry years) since such extremes do not usually occur several years in succession. Since river flow and nutrient loading rates are important variables which either directly or indirectly influence sediment-water exchanges, it is important to note that 1996 was a very wet year; in contrast, 1997 was a dry year and 1998 was intermediate in flow between these two years.

# 3.1.2 Evaluation of the Current Status for the Patuxent River

# i. Sediment Oxygen Consumption (SOC)

The current status (median of 1996, 1997 and 1998 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 poor range, and two were in the good range. The pattern of SOC fluxes in the Patuxent River provides substantiation that the benchmark is appropriate. SOC fluxes progress from good down-river to poor at the head of the deep water channel at station



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

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

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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.

#### ii. Ammonium (NH<sub>4</sub><sup>+</sup>)

The current status (median of 1996, 1997 and 1998 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. Among the four SONE stations in the Patuxent River two had ammonium fluxes in the fair range, and two were in the poor range. It should be noted here that high river flow years have a particularly strong influence on ammonium fluxes (fluxes increase). One of the three years considered was an exceptionally high flow year and ammonium fluxes at two down river sites were in the fair category (St. Leonard Creek [STLC] and Broomes Island [BRIS]). These sites behaved as expected moving towards the good category when river flows returned to normal levels in 1997. The other two sites had values in the poor range.

# iii. Nitrite (NO<sub>2</sub><sup>-</sup>)

The current status (median of 1996, 1997 and 1998 data) of nitrite fluxes 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, two had nitrite fluxes in the fair range and the other two were in the good range although one was a borderline case between fair and good. Stations are expected to move from poor to fair or fair to good when dissolved oxygen (DO) conditions in bottom waters improves, even if only enough to allow some nitrification activity to occur.

# vi. Nitrite plus Nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>)

The current status (median of 1996, 1997 and 1998 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, St. Leonard Creek (STLC). Buena Vista (BUVA), Broomes Island (BRIS) and Marsh Point (MRPT) were found to be poor.



# 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 3-1.c. 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<sub>4</sub><sup>-3</sup> or DIP)

The current status (median of 1996, 1997 and 1998 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, one station had phosphorus fluxes in the fair range (Broomes Island [BRIS]) and two stations, those farthest upstream (Buena Vista [BUVA] and Marsh Point [MRPT]), were in the poor range. St. Leonard Creek (STLC), the station furthest down stream, was in the good range. 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, 1996, was an exceptionally high flow year.

#### 3.2 Sediment-Water Oxygen and Nutrient Exchanges (SONE) Trends:

#### **1998 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 corrected for river flow, as is the case for testing other variables for trends within the monitoring program. This correction 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 - 1997 Data from the Patuxent River

Trend analysis is one method which can be use 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 Stations

Flux data were collected over a period of fourteen years (1985 - 1998) during seven months (April through November) at 4 stations in the Patuxent River (Buena Vista [BUVA], Broomes Island [BRIS], Marsh Point [MRPT] and St. Leonard Creek [STLC]). Flux data typically exhibit strong seasonality which may increase the variance of the data. In order to characterize the data initially, manual QA/QC checks were completed. Extreme outliers were examined and in certain

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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.

# 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, sediment oxygen consumption (SOC), ammonium  $(NH_4^+)$ , inorganic phosphorus, nitrite  $(NO_2^-)$  and nitrite plus nitrate  $(NO_2^- + NO_3^-)$ , 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 sediment oxygen consumption (SOC) fluxes indicated a 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 both ammonium (NH<sub>4</sub><sup>+</sup>) and nitrite (NO<sub>2</sub><sup>-</sup>) in the Patuxent River estuary for several stations (Buena Vista [BUVA)] and Marsh Point [MRPT]) and, in the case of these nutrients, is considered to be a degrading trend.

There were no significant annual trends for dissolved inorganic phosphorus or nitrite plus nitrate fluxes in the Patuxent River estuary. During the last 14 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 a few consecutive years.

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

Observed data indicates that no river flow adjustments were applied to the raw data. Significance: \* p = 0.05, \*\* p = 0.01; \*\*\* p = 0.001NOTE: 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	ОСТ	NOV	
a. Sediment Oxygen Consumption (SOC; $g O_2 m^{-2} day^{-1} yr^{-1}$ )									
BUVA					* 🔺				*** 🔺
b. Amm	onium (NH	$H_4^+$ ; $\mu$ M N n	$h^{-2} hr^{-1} yr^{-1}$						
BUVA				*	* 🔻				*▼
MRPT		*▼							
c. Nitrite	$e(NO_2; \mu M)$	$1 \text{ N m}^{-2} \text{ hr}^{-1}$	yr <sup>-1</sup> )						
BUVA		*							* 🕈
d. Nitrite plus Nitrate (NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> ; $\mu$ M N m <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> ) No significant trends e. Dissolved Phosphorus (PO <sub>4</sub> <sup>-3</sup> ; $\mu$ M Pm <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup> ) 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	$\mathbf{NH_4}^+$	NO <sub>2</sub>	$NO_2 + NO_3$	$PO_4^{-3}$				
St. Leonard Creek (STLC)									
Sign	-38	40	22	14	6				
p value	0.22	0.21	0.35	0.67	0.87				
Slope	-0.036	1.886	0.498	0.375	0.018				
Marsh Point (M	RPT)								
Sign	-6	30	17	24	30				
p value	0.82	0.18	0.43	0.28	0.18				
Slope	-0.004	13.513	0.006	0.889	1.243				
Broomes Island	(BRIS)								
Sign	-30	-16	1	26	-4				
p value	0.18	0.49	1.00	0.23	0.89				
Slope	-0.041	-4.860	0.000	0.553	-0.022				
Buena Vista (BU	JVA)								
Sign	-106	74	47	-24	5				
p value	0.001***	0.02*	0.04*	0.44	0.89				
Slope	-0.088	9.880	0.858	-0.345	0.030				

# 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)

A significant negative yet improving trend was indicated for sediment oxygen consumption (SOC) fluxes at p < 0.05 at Buena Vista (BUVA) for August (Table 3-3.a).

#### ii. Ammonium (NH<sub>4</sub><sup>+</sup>)

Significant trends were indicated for ammonium  $(NH_4^+)$  fluxes at p < 0.05 in July and August at Buena Vista (BUVA; degrading trend) and May at Marsh Point (MRPT; degrading trend; Table 3-3.b).

#### iii. Nitrite (NO<sub>2</sub><sup>-</sup>)

A positive (improving) significant trend was indicated for nitrite (NO<sub>2</sub><sup>-</sup>) fluxes at p < 0.05 in the Patuxent River at Buena Vista (BUVA) in May (Table 3-3.c).

#### iv. Nitrite plus Nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>)

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

# v. Dissolved Inorganic Phosphorus (PO<sub>4</sub><sup>-3</sup> or DIP)

No significant trends were found for phosphorus  $(PO_4^{-3})$  fluxes (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	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): 1	985 - 1998							
Sign	-3	-10	-23	-21	-41	-2	-9	-3	
p value		0.28	0.23	0.07	0.03*	0.90	0.24		
n	3	8	14	10	14	8	7	3	
Marsh Point (	(MRPT): 19	989 - 1998							
Sign		-3	13	-7	-12	6	-3		
p value		0.72	0.26	0.60	0.38	0.55	1.00		
n		6	9	10	10	8	6		
Broomes Isla	nd (BRIS):	1989 - 199	8	-					
Sign		5	6	-3	-21	-6	-11		
p value		0.47	0.61	0.86	0.07	0.54	0.06		
n		6	9	10	10	8	6		
St. Leonards	Creek (STI	LC): 1985 -	1998	1	1	1	1		
Sign	-3	-10	17	-12	-18	-10	-5	-3	
p value		0.28	0.38	0.38	0.30	0.55	0.56		
n	3	8	14	10	13	8	7	3	
b. Ammonium $(NH_4^+; \mu M N m^{-2} hr^{-1} yr^{-1})$									
b. Ammoniu	m (NH <sub>4</sub> <sup>+</sup> ; $\mu$	$\frac{M N m^{-2} hr}{M \Delta Y}$	<sup>-1</sup> yr <sup>-1</sup> )	TTT.	AUG	SEP	ОСТ	NOV	
b. Ammoniu STATION	m (NH <sub>4</sub> <sup>+</sup> ; $\mu$ APR RIVER	$\frac{M N m^{-2} hr}{MAY}$	<sup>-1</sup> yr <sup>-1</sup> ) JUN	JUL	AUG	SEP	ОСТ	NOV	
b. Ammoniu <b>STATION</b> PATUXENT Buena Vista (	m (NH <sub>4</sub> <sup>+</sup> ; $\mu$ APR RIVER: (BUVA): 1	M N m <sup>-2</sup> hr MAY 985 - 1998	<sup>-1</sup> yr <sup>-1</sup> ) JUN	JUL	AUG	SEP	OCT	NOV	
b. Ammoniu <b>STATION</b> PATUXENT Buena Vista ( Sign	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3	M N m <sup>-2</sup> hr MAY 985 - 1998 10	<sup>-1</sup> yr <sup>-1</sup> ) JUN	<b>JUL</b> 25	<b>AUG</b>	<b>SEP</b>	<b>OCT</b>	<b>NOV</b>	
b. Ammoniu <b>STATION</b> PATUXENT Buena Vista ( Sign p value	m (NH <sub>4</sub> <sup>+</sup> ; μ APR RIVER: (BUVA): 1 <sup>4</sup> -3	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74	JUL 25 0.03*	AUG 45 0.02*	-8 0.40	<b>OCT</b> -3 0.77	<b>NOV</b>	
b. Ammoniu <b>STATION</b> PATUXENT Buena Vista ( Sign p value n	m (NH <sub>4</sub> <sup>+</sup> ; μ <b>APR</b> RIVER: (BUVA): 1 <sup>t</sup> -3 3	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14	JUL           25           0.03*           10	AUG 45 0.02* 14	-8 0.40 8	-3 0.77 7	NOV 1 3	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point (	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14	JUL 25 0.03* 10	AUG 45 0.02* 14	-8 0.40 8	<b>OCT</b> -3 0.77 7	NOV 1 . 3	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10	<b>JUL</b> 25 0.03* 10 11	<b>AUG</b> 45 0.02* 14 17	-8 0.40 8 -10	-3 0.77 7 9	NOV 1 . 3	
b. Ammonius STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value	m (NH <sub>4</sub> <sup>+</sup> ; μ APR RIVER: (BUVA): 1 -3 3 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02*	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36	JUL           25           0.03*           10           11           0.38	45         0.02*         14         17         0.16	-8 0.40 8 -10 0.28	-3           0.77           7           9           0.14	NOV 1 . 3	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9	JUL           25           0.03*           10           11           0.38           10	AUG 45 0.02* 14 17 0.16 10	-8         0.40           8         -10           0.28         8	-3         0.77           7         9           0.14         6	NOV 1 . 3	
b. Ammonius STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8	JUL           25           0.03*           10           11           0.38           10	45         0.02*         14         17         0.16         10	-8         0.40           8         -10           0.28         8	-3         0.77           7         9           0.14         6	NOV 1 . 3	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4	JUL       25       0.03*       10       11       0.38       10       1	AUG 45 0.02* 14 17 0.16 10 -13	-8         0.40         8           -10         0.28         8           2         2         2	-3         0.77           7         9           0.14         6           1         1	NOV	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3 0.72	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4 0.76	JUL       25       0.03*       10       11       0.38       10       1       1.00	AUG 45 0.02* 14 17 0.16 10 -13 0.29	SEP           -8           0.40           8           -10           0.28           8           2           0.90	OCT           -3           0.77           7           9           0.14           6           1           1.00	NOV	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 nd (BRIS):	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3 0.72 6	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4 0.76 9	JUL       25       0.03*       10       11       0.38       10       1       1.00       10	AUG 45 0.02* 14 17 0.16 10 -13 0.29 10	SEP           -8           0.40           8           -10           0.28           8           2           0.90           8	OCT           -3           0.77           7           9           0.14           6           1           1.00           6	NOV	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n Sig	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 (MRPT): 19 (MRPT): 19 (MRPT): 19 (MRPT): 19 (MRPT): 19	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3 0.72 6 	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4 0.76 9 1998	JUL       25       0.03*       10       11       0.38       10       1       1.00       10	AUG         45         0.02*         14         17         0.16         10         -13         0.29         10	SEP           -8           0.40           8           -10           0.28           8           2           0.90           8	-3         0.77           0.77         7           9         0.14           6         1           1.00         6	NOV           1           .           3	
b. Ammoniu STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n St. Leonards Sign	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 nd (BRIS): Creek (STI 1	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3 0.72 6 -2 C): 1985 - -4	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4 0.76 9 1998 6	JUL       25       0.03*       10       11       0.38       10       1       1.00       10       1       1.00       10	AUG         45         0.02*         14         17         0.16         10         -13         0.29         10         35	SEP           -8           0.40           8           -10           0.28           8           2           0.90           8	OCT           -3           0.77           7           9           0.14           6           1           1.00           6           5	NOV	
b. Ammonius STATION PATUXENT Buena Vista ( Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n St. Leonards Sign p value	m (NH <sub>4</sub> <sup>+</sup> ; µ APR RIVER: (BUVA): 1 <sup>4</sup> -3 3 (MRPT): 19 nd (BRIS): Creek (STI 1	M N m <sup>-2</sup> hr MAY 985 - 1998 10 0.28 8 989 - 1998 13 0.02* 6 1989 - 199 -3 0.72 6 .C): 1985 - -4 0.72	<sup>-1</sup> yr <sup>-1</sup> ) JUN 7 0.74 14 -10 0.36 9 8 -4 0.76 9 1998 6 0.78	JUL       25       0.03*       10       11       0.38       10       1       1.00       1       1.00	AUG         45         0.02*         14         17         0.16         10         -13         0.29         10         35         0.06	SEP           -8           0.40           8           -10           0.28           8           2           0.90           8           -4           1.00	-3         0.77           7         7           9         0.14           6         1           1.00         6           5         0.56	NOV	

#### 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	$(NO_2^-;$	$\mu M N$	$m^{-2}h$	r <sup>-1</sup> yr <sup>-1</sup> )	
----	---------	------------	-----------	-----------	------------------------------------	--

STATION	APR	MAY	JUN	JUL	AUG	SEP	ОСТ	NOV		
PATUXENT	RIVER:									
Buena Vista	(BUVA): 19	985 - 1998								
Sign	0	13	-2	21	9	0	6	0		
p value		0.02*	1.00	0.07	0.53	1.00	0.23			
n	1	6	10	10	11	8	5	1		
					1					
Marsh Point	(MRPT): 19	989 - 1998								
Sign		3	-2	4	7	-6	11			
p value		0.72	0.92	0.76	0.60	0.55	0.06			
n		6	9	9	10	8	6			
Broomes Isla	nd (BDIS).	1080 100	0							
Broomes Isla		1909 - 199		-		L .	Γ.			
Sign		-3	5	-8	-1	4	4			
p value		0.72	0.76	0.60	1.00	0.72	1.00			
n		6	9	9	10	8	6			
St. Leonards	Creek (STI	.C): 1985 -	1998							
Sign	0	1	-15	17	11	5	3	0		
p value		1.00	0.22	0.12	0.44	0.72	0.72			
n	1	6	10	9	11	8	6	1		
					•					
d. Nitrite plu	s Nitrate (N	$NO_2^- + NO_3$	$; \mu M N m^{-2}$	$hr^{-1} yr^{-1}$ )						
STATION	APR	MAY	JUN	JUL	AUG	SEP	ОСТ	NOV		
PATUXENT	RIVER:									
Buena Vista	(BUVA): 1	Buena Vista (BUVA): 1985 - 1998								
<i>a</i> :										
Sign	-3	-10	-2	7	-4	-4	-8	0		
Sign p value	-3	-10 0.28	-2 0.96	7 0.60	-4 0.85	-4 0.72	-8 0.38	0		
Sign p value n	-3 3	-10 0.28 8	-2 0.96 14	7 0.60 10	-4 0.85 13	-4 0.72 8	-8 0.38 7	0		
Sign p value n	-3 3	-10 0.28 8	-2 0.96 14	7 0.60 10	-4 0.85 13	-4 0.72 8	-8 0.38 7	0 3		
Sign p value n Marsh Point	-3 3 (MRPT): 19	-10 0.28 8 989 - 1998	-2 0.96 14	7 0.60 10	-4 0.85 13	-4 0.72 8	-8 0.38 7	0		
Sign p value n Marsh Point ( Sign	-3 3 (MRPT): 19	-10 0.28 8 989 - 1998 -5	-2 0.96 14	7 0.60 10 3	-4 0.85 13	-4 0.72 8	-8 0.38 7	0		
Sign p value n Marsh Point of Sign p value	-3 3 (MRPT): 19	-10 0.28 8 -5 0.47	-2 0.96 14 10 0.36	7 0.60 10 3 0.86	-4 0.85 13 11 0.38	-4 0.72 8 2 0.90	-8 0.38 7 3 0.72	0		
Sign p value n Marsh Point ( Sign p value n	-3 3 (MRPT): 19	-10 0.28 8 989 - 1998 -5 0.47 6	-2 0.96 14 10 0.36 9	7 0.60 10 3 0.86 10	-4 0.85 13 11 0.38 10	-4 0.72 8 2 0.90 8	-8 0.38 7 3 0.72 6	0 . 3		
Sign p value n Marsh Point ( Sign p value n Broomes Isla	-3 3 (MRPT): 19	-10 0.28 8 -5 0.47 6	-2 0.96 14 10 0.36 9	7 0.60 10 3 0.86 10	-4 0.85 13 11 0.38 10	-4 0.72 8 2 0.90 8	-8         0.38         7         3         0.72         6	0 . 3		
Sign p value n Marsh Point ( Sign p value n Broomes Isla	-3 3 (MRPT): 19 nd (BRIS):	-10 0.28 8 -5 0.47 6 1989 - 199	-2 0.96 14 10 0.36 9 8	7 0.60 10 3 0.86 10	-4 0.85 13 11 0.38 10	-4 0.72 8 2 0.90 8	-8 0.38 7 3 0.72 6	0 . 3		
Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign	-3 3 (MRPT): 19 nd (BRIS):	-10 0.28 8 -5 0.47 6 1989 - 199 -3	-2 0.96 14 10 0.36 9 8 10	7 0.60 10 3 0.86 10 8	-4 0.85 13 11 0.38 10	-4 0.72 8 2 0.90 8 6	-8 0.38 7 3 0.72 6	0		
Sign p value n Marsh Point of Sign p value n Broomes Isla Sign p value	-3 3 (MRPT): 19 nd (BRIS):	-10 0.28 8 -5 0.47 6 1989 - 199 -3 0.72	-2 0.96 14 10 0.36 9 8 10 0.36	7 0.60 10 3 0.86 10 8 0.60	-4 0.85 13 11 0.38 10 4 0.86	-4 0.72 8 2 0.90 8 6 0.55	-8         0.38         7         3         0.72         6         1         1.00	0		
Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n	-3 3 (MRPT): 19 nd (BRIS):	-10 0.28 8 989 - 1998 -5 0.47 6 1989 - 199 -3 0.72 6	-2         0.96         14         10         0.36         9         8         10         0.36         9	7 0.60 10 3 0.86 10 8 0.60 10	-4 0.85 13 11 0.38 10 4 0.86 10	-4 0.72 8 2 0.90 8 6 0.55 8	-8         0.38         7         3         0.72         6         1         1.00         6	0		
Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n St. Leonards	-3 3 (MRPT): 19 nd (BRIS):	-10 0.28 8 -5 0.47 6 -3 0.72 6 -C): 1985 -	-2 0.96 14 10 0.36 9 8 10 0.36 9 1998	7 0.60 10 3 0.86 10 8 0.60 10	-4         0.85         13         11         0.38         10         4         0.86         10	-4         0.72         8         2         0.90         8         6         0.55         8	-8         0.38         7         3         0.72         6         1         1.00         6	0		
Sign p value n Marsh Point ( Sign p value n Broomes Isla Sign p value n St. Leonards Sign	-3 3 (MRPT): 19 nd (BRIS): Creek (STI -3	-10 0.28 8 -5 0.47 6 1989 - 199 -3 0.72 6 -C): 1985 - 2	-2 0.96 14 10 0.36 9 8 10 0.36 9 1998 -14	7 0.60 10 3 0.86 10 8 0.60 10 18	-4 0.85 13 11 0.38 10 4 0.86 10 -11	-4 0.72 8 2 0.90 8 6 0.55 8	-8         0.38         7         3         0.72         6         1         1.00         6         7	0		
Sign p value n Marsh Point of Sign p value n Broomes Isla Sign p value n St. Leonards Sign p value	-3 3 (MRPT): 19 nd (BRIS): Creek (STI -3	-10 0.28 8 -1998 -3 0.72 6 -3 0.72 6 -3 0.72 -3 0.72 -3 0.72 -3 0.72 -5 0.47 -3 0.72 -5 0.47 -5 0.72 -5 0.72 -5 0.98 -5 0.72 -5 0.99 -5 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.72 -5 0.99 -3 0.99 -3 0.72 -5 0.99 -3 -3 -3 -3 -3 -3 -3 -3 -3 -3	-2         0.96         14         10         0.36         9         8         10         0.36         9         1998         -14         0.47	7 0.60 10 3 0.86 10 8 0.60 10 18 0.08	-4 0.85 13 11 0.38 10 4 0.86 10 -11 0.58	-4 0.72 8 2 0.90 8 6 0.55 8 16 0.06	-8         0.38         7         3         0.72         6         1         1.00         6         7         0.38	0 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 <sub>4</sub> <sup>-3</sup> ; $\mu$ M Pm <sup>-2</sup> hr <sup>-1</sup> yr <sup>-1</sup>	<sup>-1</sup> )
---	-----------------

STATION	APR	MAY	JUN	JUL	AUG	SEP	ОСТ	NOV		
PATUXENT RIVER:										
Buena Vista (BUVA): 1985 - 1998										
Sign	-3	2	-8	5	15	2	-9	1		
p value		0.90	0.67	0.73	0.44	1.00	0.24	•		
n	3	8	13	10	14	8	7	3		
Marsh Point (	Marsh Point (MRPT): 1989 - 1998									
Sign		1	18	5	-3	-2	11			
p value		1.00	0.08	0.73	0.86	0.90	0.06			
n		6	9	10	10	8	6			
Broomes Isla	nd (BRIS):	1989 - 199	8							
Sign		3	-4	1	-11	4	3			
p value		0.72	0.76	1.00	0.38	0.72	1.00			
n		6	9	10	10	8	6			
St. Leonards Creek (STLC): 1985 - 1998										
Sign	-2	4	19	5	-12	-10	1	1		
p value		0.72	0.32	0.73	0.55	0.28	1.00			
n	3	8	14	10	14	8	7	3		

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# 4. SUBMERGED AQUATIC VEGETATION (SAV) HABITAT EVALUATION

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

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#### 4.1 Introduction

Submerged Aquatic Vegetation (SAV) is an integral part of near-shore bay ecology because it serves a variety of important roles. Some of these include providing habitat for juvenile finfish and shellfish, stabilizing near-shore sediments, and serving as a food source for waterfowl and other organisms. Declines in the abundance of SAV throughout Chesapeake Bay and other temperate regions over the past several decades have been well documented, (*e.g.* Stevenson and Confer, 1978; Orth and Moore, 1983). While many studies have linked water quality deterioration and decreased light availability to SAV decline (*e.g.* Sand-Jenson, 1977; Twilley *et al.* 1985; Kemp *et al.* 1983; Orth and Moore 1983, 1984; Moore 1997), an understanding of the patterns and processes that regulate SAV survival are not yet complete. While water quality is certainly one of the most important forcing functions regulating SAV growth and survival, ecosystem response can often be modified through second order interactions such as grazer density, (*e.g.* Neckles *et al.*, 1993; Williams and Ruckelshaus, 1993), tidal influences (*e.g.* Koch, 1996), and temporal interactions with turbidity pulses (*e.g.* Moore *et al.*, 1997).

While nutrient loading to many of Chesapeake Bay tributaries has decreased in recent years resulting in improved water quality conditions (e.g. Boynton *et al.*, 1995), many tributaries historically populated with SAV beds, including the oligohaline/mesohaline reaches of Patuxent River, have not shown significant recovery. Therefore, in 1997 the EPC began an ambitious and diversified study of the near-shore water quality conditions important to SAV growth and survival on the Patuxent River. Major elements of this study included: the evaluation of near-shore water quality conditions for compliance with minimum habitat requirements (Batuik *et al.*, 1992), an evaluation of SAV propagule availability as a possible factor limiting SAV recovery, and an assessment of epiphyte growth and resultant light attenuation on SAV leaves. With information gathered during the first year of investigation, this study was refined and improved for the 1998 investigation. Several study elements were discontinued while others were added, and substantial modifications in sampling technique and frequency were made. In 1998, 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 health and survival of SAV in near-shore habitats depends on a variety of interacting parameters that control or regulate the availability of necessary resources. These include but are not limited to water column dissolved nutrient concentrations, water column light attenuation, epiphyte loading, wave exposure, tidal amplitude, and sediment composition and chemical characteristics (*e.g.*, presence or absence of hydrogen sulfide). In 1992, the Chesapeake Bay Program established a set of habitat criteria for five water quality parameters thought to be most important for SAV growth and survival (Batuik *et al.*, 1992). These habitat criteria were based upon correlation analyses from a variety of studies linking these water quality parameters found at existing SAV beds. These include water column dissolved inorganic nitrogen (DIN), water column dissolved inorganic phosphorus (DIP), light attenuation (Kd), total suspended solids (TSS), and chlorophyll-a

(Tchl-a). Light attenuation (Kd) is a direct measure of light availability, and is thought to be the most basic and often limiting resource for SAV survival. Dissolved nutrients are important because they affect light attenuation secondarily through the stimulation of phytoplankton, and epiphytic growth. Data collected from several near-shore locations on the Patuxent River were evaluated relative to these established habitat criteria. While a second revision and evaluation of these habitat requirements is currently being developed by the Chesapeake Bay Program, we shall refer in this report to the habitat criteria specified in the 1992 synthesis.

Routine water quality monitoring is typically done at river channel locations often distant from actual SAV habitats. These data, although very useful, may not reflect near-shore conditions due to a variety of localized conditions such as: resuspension of sediments, point source discharges, or existing algal communities. A review of studies comparing near-shore water quality conditions to conditions measured within river channels, show that spatial and temporal considerations are important and generalizations cannot be made across all estuaries (e.g. Parham, 1996; Karrh in press). Thus an accurate assessment of local near-shore conditions using data from river channel locations may be site specific. Data collected throughout the SAV growing season (April through October) at six stations distributed along the axis of the Patuxent River provides information on the spatial gradation of important parameters as well as their temporal variability. 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). The secondary goal of this study was to provide corresponding water quality data to be used in the evaluation of the epiphyte growth study.

# 4.1.2 Epiphyte Growth Study

Many studies have suggested that eutrophication of coastal systems and the subsequent reduction in water column light availability are responsible for the decline in the abundance of submerged aquatic vegetation (SAV) in many temperate estuaries (e.g. Sand-Jenson, 1977; Twilley et al. 1985; Orth and Moore 1984; Moore 1997). However nutrient enrichment may also lead to increased rates of epiphyte accumulation that further limit the amount of light reaching the blades of SAV (e.g. Kemp et al. 1983; Burt et al. 1995. While a number of field and mesocosm studies have found correlation's between epiphyte biomass accumulate rates and nutrient availability (Lin et al., 1995; Short and Burdick, 1995), others have shown that second order interactions such as grazer density can mediate the affects of nutrient enrichment (Neckles et al., 1993). Fewer studies however, have quantified the effects of epiphytes on light attenuation to SAV blades (e.g. Borum and Wium-Anderson, 1980; Twilley et al., 1985; Burt et al., 1995). In some studies, epiphyte material was removed from live SAV blades and resuspended in order to measure light attenuation (Borum and Wium-Anderson, 1980; Twilley et al., 1985). This technique destroys the algal matrix and redistributes embedded inorganic particles potentially changing the optical properties of the epiphyte layer. In addition, the process of collecting epiphtyes from live plants may require time consuming preparation and manipulation of delicate SAV blades (Dauby and Poulicek, 1995; Pinckney and Micheli, 1998). In other studies, artificial substrates have been used for this purpose and have the advantage of retaining an intact algal matrix thus preserving the optical properties of the accumulated biomass (*e.g.* Burt *et al.*, 1995; Boynton *et al.*, 1998). 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). However, comparing the results from various studies is confounded by 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.*, 1998). In addition, artificial substrates can be standardized between sites, and can provide a quick assessment of epiphyte growth potential at SAV restoration sites.

The epiphyte growth study was designed with several goals in mind. The first was to develop a simple technique using artificial substrates to evaluate epiphyte accumulation rates at locations where SAV currently do not exist. The second goal was to compare epiphyte accumulation rates to water quality data at various locations along the axis of the Patuxent River. The third goal was to provide field data for calibration of models predicting epiphyte biomass based upon simple, water quality data.

Based upon preliminary results from the 1997 season, several changes in sampling frequency and protocol were made for 1998. The most important change was the standardization of in-situ deployment intervals (6-8 days during the summer) to allow for a better comparison of results throughout the season. In addition, the deployment method for the artificial substrates (Mylar<sup>®</sup> strips) was changed in 1998 to better reflect actual conditions experienced by live SAV. A detailed description of the deployment method is found in section 3.2. Finally, a separate study (Grass/strip epiphyte comparison) was conducted to compare epiphytic growth rates on transplanted live SAV to the artificial substrates.

# 4.2 Methods

# 4.2.1 Near-shore Water Quality Evaluation

# 4.2.1.1 SAV Water Quality Station Locations

In 1998, one tidal fresh and six near-shore mesohaline stations reflecting a variety of nutrient, salinity and wave exposure regimes were monitored in the Patuxent River Figure 3-1, Table 3-1). Five of these stations were also monitored in 1997 while two stations SVBA (Buena Vista), and SVJB (Jug Bay) were new to the 1998 monitoring program. Stations SV1A, SV03, SV04, SV08 and SV10 were discontinued. Consideration was also given to locating stations in, or adjacent to, existing SAV beds as well as in areas where SAV are not currently present. A station at Jug Bay Wetlands Sanctuary in the tidal fresh portion of Patuxent River was added for comparison with the mesohaline sites.

## 4.2.1.2 SAV Water Quality Sampling Frequency

Sampling was conducted aproximately bi-monthly from April through May 1998 and weekly from June through October 1998. A total of 23 SAV sampling cruises were completed.

#### 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 Thirsty-mate<sup>®</sup> hand operated boat pump, and a portion immediately syringe filtered with a 25 mm, 0.7  $\mu$ m (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<sub>4</sub><sup>+</sup>), nitrate (NO<sub>2</sub><sup>-</sup>), nitrite plus nitrate (NO<sub>2</sub><sup>-</sup> + NO<sub>3</sub><sup>-</sup>) and phosphate (PO<sub>4</sub><sup>-3</sup>). Whole water portions were filtered in the laboratory using 47 mm 0.7  $\mu$ m (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.



# Figure 4-1. Map of Submerged Aquatic Vegetation (SAV) stations and DNR monitoring stations on the Patuxent River 1998.

Latitude and longitude are in decimal degrees. Relative locations of stations are shown in the Patuxent River and do not reflect exact geographic locations.

#### Table 4-1. Submerged Aquatic Vegetation (SAV) Station Abbreviations and Locations.

Latitude and Longitude were based on Differential Global Positioning System (DGPS) instrumentation.

Geographic Location of Station	Station Abbreviation	Latitude (DGPS)	Longitude (DGPS)
Buena Vista	SVBA	38° 31.050'	76° 39.783'
Jack Bay	SV02	38° 28.086'	76° 35.934'
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'
Jug Bay Wetland Sanctuary (at end of pier)	SVJB	38° 46.000'	76° 41.000'

# 4.2.1.4 Chemical Analysis Methodology

Methods of analysis for water column nutrients appear in section 2.xx.

# 4.2.2 Epiphyte Growth Survey

# 4.2.2.1 Epiphyte Sampling Locations and Frequency of Sampling

The epiphyte growth survey was completed concurrently with the SAV water quality element at all seven sites (see section 3.2.1, Figure 3-1, Table 3-1)

# 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<sup>®</sup> polyester plastic were deployed at each of the seven near-shore stations for periods of one to two weeks depending on season. During each cruise throughout the sampling season, replicate strips exposed to natural fouling were retrieved and new strips deployed. The use of transparent Mylar<sup>®</sup> 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**

The design of the epiphyte collector array was changed for the 1998 field season to better reflect the actual hydrodynamics experienced by live SAV. In 1998, each collector array consisted of a square PVC frame filled with steel rebar to help it remain flush with the sediment surface. A vertically oriented PVC shaft in the center of the square (Figure 3.2.) was used as an attachment point for a floatation marker. Each Mylar<sup>®</sup> strip (2.5 cm x 51 cm x 0.7 mil) was attached at one end along the perimeter of the square frame. Small foam floats (~3.5 x 3.3 cm) were attached to the top of each strip to help maintain a vertical position in the water column yet still allow the Mylar<sup>®</sup> strips to move freely with water currents. Each collector array held up to eight strips per deployment. This configuration, used in 1998 was different from that used to collect data in 1997 in which the Mylar<sup>®</sup> strips were fixed to a sub-surface float and allowed to hang freely in the water column just above the sediment surface. Thus, the end of the Mylar<sup>®</sup> strip closest to the sediment surface was allowed to move freely in the water column.

# 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. On each sampling date typically 3 replicate strips (exposed for the minimum time interval of 1-2 weeks) were removed for light attenuation measurements, and placed in individual PVC transport tubes. These



Figure 4-2 Diagram of SAV Epiphyte Collector Array: (a) Epiphyte Collector Array and (b) Mylar<sup>®</sup> strips.

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 concentration analysis. This strip was cut into small sections and placed directly into a 60 ml centrifuge tube. The tube was then placed in a cooler for transport back to the laboratory. The samples were immediately frozen upon arrival at the laboratory and transferred to NASL for analysis.

An additional strip was removed for analysis of total volatile solids (TVS). This strip was placed in 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 Measuring Epiphyte Light Attenuation

Measurements of light attenuation due to epiphytic growth and fouling on the Mylar<sup>®</sup> strips were accomplished with the use of the "LAMA" or Light Attenuation Measurement Apparatus (Figure 3-3). The LAMA consists of a fixed light source, a *Li-Cor* Li-192SA underwater quantum sensor, and a strip support track. This configuration is similar to that used by Burt *et al.* (1995). All light flux measurements were made in 0.2 µm filtered seawater. The Li-192SA quantum photo sensor measures photosynthetically active radiation (PAR). The LAMA has been configured such that light flux reaching the sensor through a blank (clean) strip is in the range of 90-105 µmol m<sup>-2</sup> sec<sup>-1</sup>.

Each fouled strip was carefully removed from the transport tube and gently placed on the support track where it was held in place with small pins. Each strip was then placed in the water bath between the light sensor and the light source. Light flux measurements taken through the epiphyte layer were made within three pre-marked regions of each strip (top, middle, and bottom). Light flux measured through a blank (clean) strip was used as a control. Light flux measurements through the clean, control strips were made after every few fouled strips to control for the possible effects of contamination by resuspended epiphyte material in the filtered water bath. The difference between the light flux recorded through the blank and that recorded through the fouled strips was the light attenuation.

# 4.2.2.6 Processing Inorganic Epiphyte Material

Mylar<sup>®</sup> 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 are 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  $\mu$ m (GF/F) glass fiber filter. Once filtered, the pads were immediately frozen and delivered to NASL for analysis.



Figure 4-3. Light Attenuation Measurement Apparatus (LAMA) used in the laboratory to measure photosynthetically active radiation (PAR) passing through Mylar® strips: (a) Side View (b) Top View and (c) Cross Section.
# 4.2.3 SAV Grass/strip Epiphyte Comparison

# 4.2.3.1 Location of Stations for Epiphyte Comparison

The comparison of epiphyte accumulation between live seagrass blades and artificial substrates (Mylar<sup>®</sup> strips) was conducted at 2 SAV monitoring stations on Patuxent River. At station SVJB (Jug Bay) in the tidal fresh portion of the river, a comparison of epiphyte accumulation was made between wild celery (*Vallisineria americana*) and Mylar<sup>®</sup> strips. A similar study was conducted at station SV09 (CBL) using live eelgrass (*Zostera marina*).

# 4.2.3.2 Sampling Frequency of SAV (Grass/strip) Epiphyte Comparison

Each study was conducted once during June and August 1998.

# 4.2.3.3 Field Procedures and Data Collection

At each location multiple Mylar<sup>®</sup> strips and live seagrass were deployed for each study. At station SV09 (CBL) live eelgrass (*Zostera marina*) plants were initially cleaned of existing epiphytes by gently scraping the blades with the edge of a flexible plastic ruler. The terminal shoot of each plant was marked to identify existing leaf area from new growth by piercing the blades with a small pin. The resulting hole or scar remains on the blade as an identifying mark. The live plants were then planted in bundles of three approximately 10 centimeters apart, in a half meter square plot. Mylar<sup>®</sup> strips were deployed adjacent to the live plants on epiphyte collector arrays similar to those used in the SAV habitat evaluation (see section 3.4.2.2 and 3.4.2.3; Figure 3-2). Water depth at these sites was approximately one meter, mean low tide. The preparation and deployment of live plants and artificial substrates at station SVJB (Jug Bay) was similar to that at station SV09 except that wild celery (*Vallisineria americana*) was used for the live plant comparison, and the plants were planted in a tray of sediment placed on the river bottom.

# 4.2.3.4 Sample Retrieval and Sample Intervals

Replicate Mylar<sup>®</sup> strips and whole plants were retrieved every few days for approximately 2 weeks in order to estimate the rate of epiphyte growth. Mylar<sup>®</sup> strips were placed in individual PVC tubes for transport back to the laboratory. The tubes were filled with either tap water for SVJB samples or 0.2 µm filtered seawater for CBL (SV09) samples. Whole SAV plants were removed from the sediment and placed in shallow plastic containers with no water. The sealed containers kept the plants moist until processing.

#### 4.2.3.5 Sample Processing

Three Mylar<sup>®</sup> strips retrieved during each census were used to estimate the light attenuation caused by epiphytic fouling. This method was also used for the routine monitoring of epiphyte fouling (see section 4.2.1). Each strip was then scraped with a flexible plastic ruler to collect the epiphyte material using a technique similar to Burkholder *et al.* (1990). This material was then diluted to a known volume (200-500ml) depending on the severity of fouling. The sample was then thoroughly mixed on a stir plate and small aliquots were filtered for analysis of chlorophyll-a and total volatile solids (TVS). The collection and processing of epiphyte material from the live plants was very similar. Individual blades were removed and only blade material that had been cleaned prior to transplanting was scraped. Old blade tissue was identified from recent growth by the small scar on each blade that resulted from piercing the blade with a small pin prior to transplantation. This epiphyte material was then processed in exactly the same manner as material removed from the Mylar<sup>®</sup> strips. The blade area was then measured to the nearest mm to standardize data to a unit area measurement.

A rough taxonomic enumeration was maded of the epiphytes on the Mylar strips from each station collected during a single deployment by Richard LaCouture. He found that the epiphyte community was composed primarily of pennate and centric diatoms with small contributions by a variety of other species. In addition, there was no obvious difference in species composition among samples collected at all the mesohaline stations. Only the sample collected from the tidal fresh station at Jug Bay (SVJB) was different from the others. He also examined samples collected from the live SAV blades and found no obvious difference in species composition. During 1998, it did not appear that encrusting organisms such as bryozoans and hydroids contributed significantly to the fouling of the Mylar strips. However, small protozoans were present within the algal/sediment matrix that composed the fouling material.

# 4.2.3.6 Laboratory Analysis

Filtered material was sent to NASL for processing. All protocols were the same as for the routine monitoring of MINI-SONE and SAV data (see section 2.2.4).

#### 4.3 Results

#### 4.3.1 Results of Water Quality Evaluation

#### 4.3.1.1 Dissolved Oxygen

Water column dissolved oxygen concentrations among all stations ranged from a minimum of 4.05 mg  $l^{-1}$  at station SV07 (Hungerford Creek) on 31 July 1998, to a maximum of 15.32 mg  $l^{-1}$  at station SV06 (St. Leonard Creek) on 4 May 1998 (Table 4-

2). Dissolved oxygen values were very similar in 1997 and ranged from a minimum of 4.61 mg  $\Gamma^1$  at station SV1A (Buzzard Island) to a maximum of 13.42 mg  $\Gamma^1$  at station SV06 (St. Leonard Creek).

# 4.3.1.2 Salinity

Small differences in inter-annual salinity in 1998 compared to 1997 were likely the result of a wetter than normal spring in 1998 compared to 1997. For example, among the mesohaline stations, minimum water column salinity was 2.79 ppt at station SVBA (Buena Vista) on 30 March 1998, compared to 3.70 ppt at station SV1A (Buzzard Island) in 1997. Lower than normal river flow during the 1998 summer period led to a maximum salinity of 17.06 ppt at station SV09 (CBL) on 10 October, compared to a maximum of 15.48 at station SV09 (CBL) in 1997. Station SVJB (Jug Bay) in the tidal fresh portion of the river ranged from a minimum of 0.11 ppt on 29 May 1998 to a maximum of 0.71 ppt on 21 September 1998 (Table 4-2).

# 4.3.1.3 Temperature

Water column temperature among all stations ranged from a minimum of 11.79 C at station SV5A (J. Patterson Park) on 10 April 1998, to a maximum of 29.42 C at station SV06 (St. Leonard Creek) on 23 July 1998 (Table 4-2). This compares to a minimum of 8.52 C at station SV5A and a maximum of 29.50 at station SV10 in 1997.

# 4.3.1.4 Dissolved Nitrogen Concentrations (DIN)

As expected, water column dissolved nutrient concentrations varied seasonally at most sampling stations. Among the mesohaline stations, DIN concentrations in general were highest in March and April but decreased substantially by the end of May after which they remained relatively low for the remainder of the season (Figure 4-4, Table 4-2). Within the meshaline region, the minimum observed DIN concentration was 0.31  $\mu$ M N at station SV09 (CBL), while the maximum of 53.3  $\mu$ M N was found at station SVBA (Buena Vista). Dissolved inorganic nitrogen concentrations at the tidal fresh station SVJB (Jack Bay) were substantially higher than the other mesohaline stations throughout the spring and early summer. A maximum concentration of 91.3  $\mu$ M N was measured on 4 July 1998 (Figure 4-4, Table 4-2). However, DIN concentrations dropped to very low levels during August and September (to a minimum of 1.09  $\mu$ M N) and then rebounded to concentrations above 60  $\mu$ M N for the remainder of the sampling season.

While a strong spatial trend was not as evident among the down-river stations, the highest mean values were found at the Jug Bay station (SVJB), the most upriver station, followed by station SVBA. Of those stations also sampled in 1997, mean DIN concentrations

		SVJB	SVBA	SV02	SV5A	SV06	SV07	SV09
Temperature	Max	28.85	28.86	28.93	29.24	29.42	28.62	28.22
(C)	Min	15.19	13.16	12.46	11.79	13.30	12.42	12.13
	Mean	23.59	23.54	23.05	23.18	24.14	23.24	22.97
Salinity	Max	0.71	12.79	15.09	15.74	15.61	16.46	17.06
(ppt)	Min	0.11	2.79	5.11	5.91	5.47	6.35	6.65
	Mean	0.24	7.61	9.96	10.40	10.00	11.11	11.53
Dissolved Oxygen	Max	14.25	9.22	12.99	15.21	15.32	15.01	14.48
$(\text{mg l}^{-1})$	Min	5.69	4.17	4.46	4.58	5.89	4.05	6.83
	Mean	8.43	6.43	7.45	8.11	8.94	8.28	8.88
Percent Oxygen	Max	185.20	103.00	132.60	153.00	173.80	158.40	162.70
Saturation	Min	65.70	55.50	62.50	60.20	80.50	54.30	85.30
(%)	Mean	101.49	77.68	90.98	98.80	111.51	103.06	109.53
Secchi Depth	Max	0.70	0.80	1.10	1.30	1.30	1.10	1.30
(meters)	Min	0.30	0.30	0.30	0.40	0.60	0.60	1.00
	Mean	0.46	0.58	0.68	0.81	1.07	0.89	1.13
Light Attenuation	Max	4.32	3.76	5.18	3.55	3.63	2.86	1.87
Coefficient	Min	1.71	1.39	1.13	0.88	0.52	0.75	0.79
$[Kd] (m^{-1})$	Mean	3.38	2.54	2.37	1.82	1.60	1.47	1.20
Total Suspended	Max	48.00	41.30	59.20	51.60	30.40	31.20	30.20
Solids	Min	14.70	9.50	8.30	7.90	6.70	5.90	5.80
(mg l-1)	Mean	28.98	24.18	26.64	21.63	14.65	17.03	15.42
Total Chlorophyll-a	Max	107.00	82.28	112.70	75.46	157.58	89.42	69.20
(µg l-1)	Min	8.64	5.65	5.87	5.22	7.85	8.01	8.79
	Mean	50.75	25.65	24.36	20.20	25.70	22.80	21.68
Dissolved	Max	91.30	53.30	23.20	21.50	7.77	18.92	42.20
Inorganic Nitrogen	Min	1.08	0.97	0.36	0.49	0.41	0.51	0.31
(µmol N)	Mean	44.51	9.35	2.84	3.57	1.42	5.59	8.98
Dissolved	Max	2.29	3.76	1.05	1.62	1.17	1.06	0.65
Inorganic	Min	0.29	0.20	0.05	0.08	0.06	0.05	0.04
Phosphorus								
(µmol P)	Mean	1.08	1.83	0.39	0.39	0.38	0.34	0.24

Table 4-2. Table of the maximum, minimum and mean values of all water column nutrient and physical water quality data recorded at the six mesohaline and one tidal freshwater (SVJB) SAV sites visited in the Patuxent River from late March through late October 1998.



Figure 4-4. Dissolved inorganic nitrogen (DIN) concentrations for (a) upriver stations (b) downriver stations and (c) seasonal means for the Patuxent River April through October 1998.

Dashed lines represent minimum Tier II mesohaline SAV habitat requirement as specified in the Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration targets: A technical synthesis (Batuik, et al., 1992).

followed a similar spatial pattern. Overall, 1997 seasonal mean values were higher than 1998. However, this was probably the result of higher spring season DIN concentrations in 1997 compared to 1998, coupled with an increased number of samples collected during the summer of 1998 compared to 1997. Seasonal mean values at all mesohaline stations were below the maximum DIN concentration (10.2  $\mu$ M N) established for Tier II SAV habitat requirements (Batuik et al., 1992).

## **4.3.1.5** Dissolved Phosphorus Concentrations (DIP)

Dissolved inorganic phosphorus (DIP) concentrations varied seasonally at all stations (Figure 4-5, Table 4-2). For most stations, DIP concentrations increased marginally throughout the summer. However, the northernmost mesohaline station (SVBA) at Buena Vista increased dramatically over this period reaching a maximum of  $3.76 \,\mu\text{M}$  P on 6 August 1998. SONE monitoring in this region of the river indicates large sediment releases of DIP during summer seasons as a possible source of this phosphorus.

On a seasonal basis, the highest mean DIP concentrations were found at station SVBA (2.29  $\mu$ M P), while the lowest were found at station SV09 (0.24  $\mu$ M P). Of the stations sampled in 1997, DIP concentrations appear somewhat lower in 1997 compared to 1998, however this may be a statistical artifact caused by increased number of samples collected during the summer period of 1998 compared to 1997. Seasonal mean values at most mesohaline stations were marginally above the maximum DIP concentration (0.32  $\mu$ M N) established for Tier II SAV habitat requirements (Batuik *et al.*, 1992). However, station SVBA (Buena Vista) had DIP concentrations much higher than recommended, and station SV09 (CBL) had DIP concentrations slightly lower than the recommended maximum (Batuik *et al.*, 1992).

# 4.3.1.6 Water Column Light Attenuation

Water column light attenuation (Kd) did not appear to show any strong seasonal trends during the time period sampled (April – October). However, a strong spatial gradient was found along the axis of the river (Figure 4-6, Table 4-2). Station SVJB (Jug Bay) had the highest mean light attenuation at  $3.38 \text{ m}^{-1}$ , while station SV09 (CBL) had the lowest at  $1.20 \text{ m}^{-1}$ . This spatial trend was also seen at those stations sampled in 1997. Of those stations sampled in both 1997 and 1998, water column light attenuation (Kd) did not differ substantially between years. Only stations SV07 (Hungerford Creek) and SV09 (CBL) had light attenuation coefficients (Kd) below the recommended maximum Kd of  $1.5 \text{ m}^{-1}$  for Tier II restoration targets in mesohaline waters (Batuik *et al.*, 1992).



Figure 4-5. Dissolved inorganic phosphorus (DIP) concentrations for (a) upriver stations (b) downriver stations and (c) seasonal means for the Patuxent River April through October 1998.

Dashed lines represent minimum Tier II mesohaline SAV habitat requirement as specified in the Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration targets: A technical synthesis (Batuik, et al., 1992).



Figure 4-6. Water column light attenuation (Kd) for (a) upriver stations (b) downriver stations and (c) seasonal means for the Patuxent River April through October 1998.

Dashed lines represent the upper limit for Tier II mesohaline SAV habitat requirements as specified in the Chesapeake Bay SAV Technical Synthesis (Batuik, et al., 1992).

#### 4.3.1.7 Water Column Total Suspended Solids

Water column total suspended solids (TSS) did not show any distinct seasonal trends (Figure 4-7, Table 4-2). However, aperiodic peaks in total suspended solids were likely the result of isolated weather events resuspending bottom sediments. On a seasonal mean basis, there was a strong spatial gradient along the axis of the river with a maximum value of 28.98 mg  $1^{-1}$  at station SVJB and a minimum of 15.42 mg  $1^{-1}$  at station SV09 (Figure 4-7). This was not surprising since water column light attenuation is positively correlated with total suspended solids ( $r^2 = 0.45$ ). Mean values for those stations sampled in 1997 were not significantly different from 1998. On a seasonal basis, only the three most downriver stations, SV06 (St. Leonards Creek), SV07 (Hungerford Creek) and SV09 (CBL) were close to the maximum TSS limit of 15 mg  $1^{-1}$  for mesohaline Tier II habitat requirements (Batuik *et al.*, 1992).

#### 4.3.1.8 Water Column Chlorophyll-a

Water column chlorophyll-a values did show a small but significant decline over the sampling season, with a very pronounced peak during the May 5 1998 cruise (Figure 4-8, Table 4-2). On a spatial basis, there was no significant down-river trend among the mesohaline stations with a minimum seasonal mean value of 5.65 g  $\Gamma^1$  at station SVBA and a maximum seasonal mean of 20.20 µg l-1 at station SV07 (Figure 4-8). However, station SVJB (Jug Bay), had the highest seasonal mean chlorophyll-a value (50.75 µg  $\Gamma^1$ ). Of the stations sampled in both years, mean water column chlorophyll-a values did not differ significantly between 1997 and 1998.

#### 4.3.2 Results of Epiphyte Growth Study

#### 4.3.2.1 Station Depth

Since water depth at each station affects the total light flux reaching the bottom, we attempted to place each station at approximately the same depth of water. However, logistical constraints limited the placement of stations, subsequently mean water depth differed slightly among stations. Station SVJB (Jug Bay) was the shallowest station (mean depth of 0.77 meters), while station SV06 (St. Leonard's Creek) was the deepest (mean depth of 1.60 meters). Mean water depth for all stations is shown in Figure 4-9. An analysis of median station depth found that of the mesohline stations, SVO6 (St. Leonard Creek) was significantly deeper than any other station (p < 0.05).



Figure 4-7. Water column total suspended solids (TSS) concentrations for (a) upriver stations (b) downriver stations and (c) seasonal means for the Patuxent River April through October 1998.

Dashed lines represent minimum Tier II mesohaline SAV habitat requirement as specified in the Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration targets: A technical synthesis (Batuik, et al., 1992).



Figure 4-8. Water column total chlorophyll-a (Tchl-a) concentrations for (a) upriver stations (b) downriver stations and (c) seasonal means for the Patuxent River April through October 1998.

Dashed lines represent minimum Tier II mesohaline SAV habitat requirement as specified in the Chesapeake Bay Submerged Aquatic Vegetation Requirements and Restoration targets: A technical synthesis (Batuik, et al., 1992).



**Figure 4-9. Mean station depth for SAV monitoring station on the Patuxent River 1998.** *Stations with similar letter designations were not significantly different from one another.* 

## 4.3.2.2 Epiphyte Light Attenuation

Early in the sampling season (April and May 1998), the Mylar<sup>®</sup> strips were deployed on approximately a bi-weekly basis because of low epiphyte growth rates. During this time, light attenuation through the Mylar<sup>®</sup> strips was typically quite low (0% to 18%) for deployments less than 14 days. However, from June through October 1998, fouling rates were significantly higher and *in-situ* deployments were typically limited to 6 to 8 days to prevent extreme fouling of the strips. This standardization of the *in-situ* deployment interval allowed a more accurate comparison of epiphytic growth rates and subsequent light attenuation across the entire sampling season. For this reason, figures throughout this report showing rate processes (*i.e.* chlorophyll-a accumulation rates) were constructed from data collected during 6 - 8 day deployments from June through October.

Several important spatial and temporal patterns were observed in epiphyte light attenuation. Significant week to week variation was seen at most stations and was likely the result of weekly variation in weather and water conditions (Figure 4-10a, b). By June 1998, light attenuation at several stations was as high as 100% of light exposure. Fouling rates remained high throughout most of the season and only began to drop substantially in October.

Spatially, epiphyte light attenuation increased in the down-river direction (Figure 4-10c) with the maximum mean light attenuation of 75% at station SV09 (CBL) and a minimum mean light attenuation of 37% at station SVJB (Jug Bay). On a seasonal basis, all stations except SVJB (Jug Bay) had mean light attenuation of 50% or greater after only one week of *in-situ* exposure.

# 4.3.2.3 Epiphyte Chlorophyll-a and Dry Weight Accumulation

Since epiphyte light attenuation is a result of both organic and inorganic material deposited to the Mylar surface it was not surprising to find similar temporal and spatial patterns for epiphyte chlorophyll-a and dry weight (Figures 4-11 and 4-12). Significant week to week variation in epiphyte total chlorophyll-a and epiphyte dry weight were also seen throughout the sampling season. A strong spatial gradient along the axis of the river was found for both epiphyte chlorophyll-a and epiphyte dry weight accumulation rates with increasing accumulation rates in the downriver direction. The maximum mean chlorophyll-a accumulation rate (0.483  $\mu$ g cm<sup>-2</sup> day<sup>-1</sup>) and maximum mean dry weight accumulation rate (0.525 mg cm<sup>-2</sup> day<sup>-1</sup>) were both found at station SV09 (CBL). The minimum mean chlorophyll-a accumulation rate (0.085  $\mu$ g cm<sup>-2</sup> day<sup>-1</sup>) was found at station SVBA (Buena Vista) and the minimum dry weight accumulation rate (0.057 mg cm<sup>-2</sup> day<sup>-1</sup>) was found at station SVJB (Jug Bay). Epiphyte chlorophyll-a accumulation rates at Jug Bay may have been elevated slightly compared to other stations because of a significantly shallower deployment depth and subsequent higher light flux levels.



Figure 4-10. Epiphyte light attenuation through Mylar<sup>®</sup> strips deployed along the Patuxent River for *in-situ* exposures of 6-8 days from June through October 1998: (a) upriver stations (b) downriver stations and (c) seasonal means.



Figure 4-11. Epiphyte total chlorophyll-a accumulation rates on Mylar<sup>®</sup> strips deployed along the Patuxent River for *in-situ* exposures of 6-8 days from June through October 1998:

(a) upriver stations (b) downriver stations and (c) seasonal means.





#### 4.3.2.4 Correlations and Relationships

Strong relationships were found between epiphyte light attenuation and epiphyte dry weight as well as between epiphyte light attenuation and epiphyte chlorophyll-a (Figure 4-13). These relationships provide good estimates of potential light attenuation to SAV leaves when epiphyte chlorophyll-a or dry weight can be measured. In addition, the data show that regardless of Mylar<sup>®</sup> strip deployment method, (1997 top down vs. 1998 bottom up; see section 4.2.4) the relationships between epiphyte light attenuation and epiphyte biomass are similar. These relationships also show that relatively small amounts of epiphytes can attenuate a very large percentage of the available light. For example, only 2 mg cm<sup>-2</sup> of epiphyte dry weight can attenuate almost 80% of available light. During most of the summer season, this amount of fouling can accumulate in as little as one week of *in-situ* exposure.

For the most part, epiphyte coverage was quite uniform at most stations throughout the sampling season, although it did vary somewhat from week to week depending weather and water quality conditions. However, epiphyte coverage at station SV06 (St. Leonard Creek) tended to be a bit more patchily distributed than the other stations. The exact reason for this is unknown, however station SV06 was the most sheltered from wave energy of all the stations. It was also the only station located on a tributary creek and not directly on the Patuxent River.

While epiphyte standing stock or accumulated biomass may be affected by external factors such as grazer densities (*e.g.* Neckels *et al.*, 1993) or hydrodynamic shear (e.g. Strand and Weisner, 1996), in the absence of these factors epiphyte growth rates are ultimately regulated by dissolved nutrient availability, temperature, and light flux. However, at any given point in time, only one of these parameters can actually limit or constrain the growth of epiphytes. This data set provides a unique opportunity to examine epiphyte chlorophyll-a accumulation rates along the Patuxent River and compare them to light and nutrient availability. Since deployment intervals were standardized across the entire season, and temperatures remained fairly constant, summer mean values can be used to compare chlorophyll-a accumulation rates against light and nutrient availability.

A strong downriver trend in epiphyte chlorophyll-a accumulation rates (Figure 4-11) along with increasing water clarity (Figure 4-6) suggests that light availability was an important factor regulating epiphyte growth. However, light availability is a function of water column turbidity and depth, and since station depth varied among stations, it was necessary to calculate a standardized light intensity (I<sub>st</sub>) that would compensate for differences in station depth. This parameter, calculated from the Beers-Lambert equation for the exponential decay of light through water (I<sub>st</sub> = I<sub>0</sub> exp<sup>-Kd\* z</sup>), incorporates both water column turbidity (Kd) and station depth (z). Since these stations were geographically very close, and likely experienced similar surface light flux conditions, a single value for I<sub>0</sub> was used for all stations and arbitrarily set to 100 micro-einsteins for convenience. A regression of mean epiphyte chlorophyll-a accumulation rate versus



Figure 4-13. Epiphyte light attenuation from Mylar<sup>®</sup> strips deployed along the Patuxent River 1998 and 1997 versus:

(a) epiphyte chlorophyll-a , where LA = 77.36\*(1-exp(-2.082\*Epchla) and

(b) epiphyte dry weight , where LA = 84.638\*(1-exp(-0.963\*Epdw).

LA= epiphyte light attenuation, Epchla = epiphyte total chlorophyll-a cm<sup>-2</sup>, and Epdw = epiphyte dry weight cm<sup>-2</sup>.

standardized light intensity ( $I_{st}$ ) was highly significant (P < 0.001, r<sup>2</sup> = 0.97, Figure 4-14a). This suggests that along the mesohaline portion of the Patuxent River, virtually all of the variation in chlorophyll-a accumulation can be explained by light availability.

Mean summer dissolved inorganic phosphorus (DIP) concentrations at all of the mesohaline stations except SVBA (Buena Vista) were very similar to each other and only slightly above the established habitat criteria of 0.32  $\mu$ M P (Batuik *et al.*, 1992). Only station SVBA (Buena Vista) had a mean summer DIP concentration (2.09  $\mu$ M P) significantly greater than the other stations yet epiphyte accumulation rates at Buena Vista were among the lowest recorded. Not surprisingly, no relationship was seen in a plot of mean chlorophyll-a accumulation against mean summer dissolved inorganic phosphorus (DIP) concentrations (Figure 4-14b). In addition, the mean DIN/DIP ratio at all stations was less than 16 (Redfield ratio), suggesting that DIP concentrations are not limiting epiphyte growth along the Patuxent River.

Mean summer dissolved inorganic nitrogen (DIN) concentrations did vary significantly among the mesohaline stations. While a plot of epiphyte chlorophyll-a accumulation rates against DIN concentrations did show a positive trend (Figure 4-14c), station SVBA (Buena Vista) contradicted that trend with the highest recorded DIN concentration (5.6  $\mu$ M N), yet one of the lowest mean chlorophyll-a accumulation rates. These results suggest that while mean DIN concentrations were below established maximum allowable concentrations for mesohaline Tier II habitat restoration (Batuik *et al.*, 1992), epiphyte growth appears to be light limited, not nitrogen limited along the Patuxent River.

# 4.3.3 Results of Grass/Strip Comparison Study

#### **4.3.3.1** Station SV09 (CBL)

The comparison between epiphyte biomass accumulation rates on artificial substrates and live SAV blades suggest a close correspondence between artificial substrates and natural surfaces for short-term deployments of up to 10 days using this technique. Epiphyte biomass accumulation rates were greater during the June deployment compared to the August deployment (Figure 4-15). In June, after 10 days of *in-situ* exposure, mean accumulation of total chlorophyll-a biomass on live *Zostera marina* blades was 15.1 µg cm<sup>-2</sup> compared to 8.9 µg cm<sup>-2</sup> on Mylar ® strips. However, no statistically significant difference was detected (p > 0.05) due to the high variance among the samples. In August, after 10 days of exposure, mean accumulation of total chlorophyll-a on live *Zostera marina* blades was 7.3 µg cm<sup>-2</sup> compared to 8.2 µg cm<sup>-2</sup> on Mylar<sup>®</sup> strips. No statistically significant difference was detected in epiphyte chlorophyll-a accumulation of epiphytic growth on the Mylar<sup>®</sup> strips resulted in nearly 100% light attenuation after 10 days of *in-situ* exposure (Figure 4-16).



Figure 4-14. Seasonal mean epiphyte light attenuation versus (a) standardized light intensity (b) mean dissolved inorganic phosphorus (DIP) and (c) dissolved inorganic nitrogen (DIN) for mesohaline stations on the Patuxent River June through October 1998 for 6-8 day deployments.

The importance of these results is that the fouling rates were incredibly high in June and August, and that Mylar strips do provide a good first order ESTIMATE of fouling rates. It would be nieve to expect that plastic strips would exactly mimic real grass blades, but this technique can still provide very useful data about epiphyte loading rates should SAV be introduced to a barren area for restoration purposes.

#### 4.3.3.2 Station SVJB (Jug Bay)

In general, epiphyte accumulation rates at station SVJB (Jug Bay) were lower than station SV09 (Figure 4-15). Epiphyte accumulation rates on live *Vallisneria americana* blades and artificial substrates during both June and August were similar up to 6 to 8 days of *insitu* exposure, but diverged significantly by 10 days of exposure. In June, the accumulation of chlorophyll-a biomass on live *Vallisneria americana* blades reached an asymptote between 6 and 8 days of exposure, resulting in a maximum mean chlorophyll-a biomass of 2.20  $\mu$ g cm<sup>-2</sup>. However, chlorophyll-a biomass on Mylar<sup>®</sup> strips accumulated exponentially over the entire 10 days of *in-situ* exposure resulting in a maximum mean biomass of 4.79  $\mu$ g cm<sup>-2</sup> which was significantly higher (p < 0.05) compared to live SAV blades.

In August, epiphyte chlorophyll-a accumulation rates on both Mylar<sup>®</sup> strips and live SAV blades reached an asymptote before 10 days of *in-situ* exposure. However, at the end of 10 days, mean chlorophyll-a biomass remained higher on Mylar<sup>®</sup> strips (8.2  $\mu$ g  $cm^{-2}$ ) compared to the live SAV blades (7.3 µg cm<sup>-2</sup>), however, no statistically significant difference was found (p > 0.05). Differences in epiphyte chlorophyll-a biomass observed between stations and deployment date are reflected in similar differences in epiphyte light attenuation. Maximum mean light attenuation through Mylar<sup>®</sup> strips exposed at station SVJB (Jug Bay) was approximately 78% in June compared to nearly 100% at station SV09 (CBL). In August, by comparison, maximum mean light attenuation was less than 60% at station SVJB (Jug Bay), while it remained nearly 100% at station SV09 (CBL) after 10 days of exposure (Figure 4-16). Anytime an artificial system (such as a mesocosm) is set up to mimic a natural system, there are bound to be differences that become magnified over time as system trajectories diverge. Therefore, we can only speculate about why differences took place after 10 days. One possible reason could be that the Vallisneria blades were much shorter than the Mylar strips as well as the Zostera blades and may have experienced a very difference hydrodynamic regime.



Figure 4-15. Epiphyte total chlorophyll-a accumulation versus days *in-situ* for live SAV, Mylar® strip growth comparison in (a) June at station SVJB (Jug Bay) (b) August at station SVJB (Jug Bay) (c) June at station SV09 (CBL) and (d) August at station SV09 (CBL).



Figure 4-16. Epiphyte light attenuation on Mylar<sup>®</sup> strips versus days *in-situ* from (a) June 26 – July 2, 1998 and (b) August 3 – 14, 1998.

#### 4.4 Discussion and Conclusions

#### 4.4.1 Near-shore Water Quality Evaluation

Based upon two years of SAV growing season data (1997 and 1998) it does not appear that dissolved nutrient concentrations (DIN and DIP) at most of the mesohaline stations significantly exceed the recommendations for maximum habitat requirements established by the Chesapeake Bay Program (Batuik, et al., 1992). In fact, mean DIN concentrations at all mesohaline stations fell below established maximum criteria, while DIP concentrations at all but the northern-most mesohaline station (SVBA) were only slightly above recommended maximum concentrations. In contrast, mean water column light attenuation varied significantly with river location. Only the two most downriver stations (SV07 and SV09) met or exceeded the established water clarity requirements, while conditions just south of Broomes Island at station SV5A (Jefferson-Patterson Park) were only marginally above maximum habitat limits. However, temporal shifts in water quality conditions over the growing season also play an important role for the establishment of SAV species on the Patuxent River. In general, water column light attenuation and epiphytic fouling rates are much lower early in the growing season allowing certain species to take advantage of more suitable conditions. For example, in 1997, the early spring annual SAV Zannichellia palustris was seen at all but the northernmost station. This species typically completes it growth cycle before epiphytic fouling becomes extreme and water quality conditions deteriorate in the summer. Another indication that seasonal shifts in water quality conditions may be important for SAV survival was the observation that small patches of Zostera marina transplanted to station SV09 during the summer of 1998 survived the winter and were growing well in April of 1999. This is consistent with previous studies (Moore et al., 1996) that suggest the critical time period for Z. marina is spring and fall when growth is at a maximum, rather than the summer months. These small plots of transplanted eelgrass survived periods of extremely high epiphytic fouling rates during the summer of 1998, and were able to survive until conditions improved. This may have been possible due to large carbohydrate reserves stored prior to transplantation while growing in a more favorable Further monitoring of these transplants will provide valuable insight into habitat. possible long term, eelgrass survival in the lower Patuxent River. However, other species that cannot rely on stored carbohydrate reserves may be more susceptible to declining water quality conditions and epiphyte loading during summer months. For example, a healthy bed of *Potomogeton pectinatus* was observed at station SV07 during the spring and early summer of 1997 indicating adequate water quality conditions during this time. However, by August of 1997 the entire bed had died. Although the exact cause of this die-off is unknown, high epiphytic fouling rates were observed during this time and may have contributed to the total light attenuation at this site. Unfortunately, this bed of P. pectinatus did not return in 1998.

An evaluation of both 1997 and 1998 EPC SAV data, along with a review of the literature, lend support for the hypothesis that the failure of recolonization of eelgrass to recolonize the lower Patuxent may not be due to poor water quality alone. For example,

water quality conditions found at station SV09 (CBL) were similar to conditions found at several locations with healthy eelgrass populations (Table 4-3).

In a study by Moore *et al.* (1996), eelgrass transplanted in the York River survived well for several years at locations with water quality conditions similar to those found at station SV09 (CBL). A comparison of dissolved nutrient concentrations and water column light attenuation found in Maryland's coastal bays (Chris Lee, pers. comm.) is also similar to that found in lower Patuxent River. However, epiphyte loading in the coastal bays appears to be significantly less compared to the Patuxent River (personal observation). While no long-term establishment of SAV has been observed at these down-river locations it appears that adequate water quality conditions to support eelgrass survival, may exist for at least part of the SAV growing season. Alternative hypotheses such as propagule limitation or extreme epiphyte loading may also play a large role in limiting eelgrass recruitment. For example, during the 1997 survey of SAV propagules along the axis of the Patuxent River, not a single eelgrass propagule was found. While the relative importance of epiphytic growth on eelgrass blades and their attenuation of available light may be mitigated by the ability to store carbohydrate reserves during the spring and fall, epiphytic fouling during the summer months may be an important limitation for other SAV species.

# 4.4.2 Epiphyte Growth Study

Although a number of studies have contributed to our understanding of the complex interactions between epiphyte growth, nutrient dynamics and SAV survival, a full understanding of these processes is not yet complete. However, several important patterns and observations have emerged from this work that may provide some insight into SAV epiphyte growth and light attenuation.

The relationships between epiphyte biomass expressed as either chlorophyll-a or dry weight, versus percent light attenuation appear to be relatively robust and may be used to obtain first order estimates of light attenuation from epiphyte biomass (Figure 4-13). Despite differences in the deployment method of Mylar strips between 1997 and 1998 (see section 4.2.2.4), a fixed mass of epiphyte material expressed as either dry weight or chlorophyll-a biomass will attenuate the same amount of light regardless of the way in which the material was exposed to fouling. These relationships also compare favorably to those found by Burt *et al.* (1995) for artificial substrates exposed for 80 days off the western coast of Australia. In both studies, an epiphyte chlorophyll-a biomass as small as  $1 \,\mu g \, \text{cm}^{-2}$  predicts approximately a 60% reduction in the available light.

Table 4-3. Comparison of summer seasonal near-shore water quality conditions at Chesapeake Biological Lab Patuxent River 1998, Gloucester Point York River from 1986<sup>1</sup>, and Chincoteague Bay from 1998<sup>2</sup>.

<sup>1</sup> Moore *et al.*, 1996 ; <sup>2</sup> Chris Lea (*pers. comm.*)

Location	Light attenuation (Kd)	DIN (µMol)	DIP (µMol)	TSS (mg l <sup>-1</sup> )	Chlorophyll-a (µg l <sup>-1)</sup>
Chesapeake					
<b>Biological Lab</b>					
Patuxent River	1.2	4.5	0.28	17.0	20.8
Gloucester					
Point York	1.2	4	0.7	15	5.0
River					
Spence Cove					
Chincoteague	2.1	4	0.25	12	8
Bay					

While it is important to know how much light may be attenuated by a fixed mass of epiphytic material, an equally important measure is the rate of epiphyte accumulation. In general, fouling rates on the Patuxent River were quite low in April but increased substantially by mid May, and remained quite high for the rest of the growing season compared to most other studies reported in the literature. For comparison, the typical deployment intervals from other studies ranged from 60 - 100 days (Horner, 1987; Burt *et al.*, 1995; Pinckney and Micheli, 1998). For this reason, all attempts were made to standardize Mylar strip exposure to 6-8 days throughout summer growing season (June-October). Even with these relatively short *in-situ* exposure times, mean light attenuation by the epiphyte layer was substantial and ranged from 38% at station SVJB (Jug Bay) to 75% at station SV5A (Jefferson-Patterson Park). In 1997 and 1998 Mylar strips exposed for longer in-situ intervals accumulated significantly more epiphyte biomass. Thus it seems likely that SAV blade tissue older than 6-8 days would likely be fouled to an even greater degree and be subjected to a corresponding higher light attenuation.

Results of the grass/strip epiphyte comparison, suggest that over short exposure intervals of up to 10 days, there was no statistically significant difference in epiphyte accumulation on the artificial substrates compared to live eelgrass blades. This is in contrast to results found by Pinckney and Micheli (1998), in which live *Zostera marina* blades supported significantly more epiphyte biomass than the artificial substrates. However, very few details of sampling methods were given, and most environmental parameters were very different compared to that found on the Patuxent River. In general, studies comparing epiphyte accumulation rates on live SAV to artificial substrates differ greatly in sampling technique, species, and geographic range thus making direct comparisons almost impossible.

While the Mylar strips provide a good estimate of epiphyte accumulation rates and light attenuation, it is the interaction between epiphyte accumulation and the growth rate of the SAV blades that ultimately determines the overall impact of epiphyte accumulation on the SAV. For example, if the production of new blade tissue can outpace the accumulation of epiphytic growth then high biomass levels would be restricted to the oldest portions of the plant thus mitigating the effects of epiphyte growth. However, the timing of maximal SAV growth rates may be different from the timing of maximum fouling rates. For the SAV species Zostera marina, maximal growth takes place in the spring and in the fall, thus taking advantage of improved water quality conditions relative to the summer. However, each plant or plant system must still have enough carbohydrate reserves to sustain itself during the warm water and low light conditions of summer. Despite this typical growth pattern, Z. marina plants transplanted to station SV09 for the grass/strip comparison grew quite rapidly in June and August with more than 2 inches of new blade growth in 10 days. It is not uncommon for artificial systems to diverge from natural systems after a certain amount of time, as is the case for experimental mesocosms. After ten days of exposure the fouling had become so extreme that a three dimensional structure was developing due to hydroid and bryozoan growth. The accumulation ob the actual SAV blades was causing the blades to lie on the bottom or to break off while the Mylar remained intact.

While fouling rates were in general quite high during the summer months, the strong relationship between epiphyte chlorophyll-a accumulation and light availability suggests light, rather than nutrients, limit epiphyte growth along the Patuxent River. This is particularly relevant because mean concentrations of dissolved nutrients already fell below maximum habitat criteria established for SAV restoration (Batuik, *et al.*, 1992).

From this observation if follows that any improvement in water clarity at the more upriver stations, even without concurrent nutrient reduction, would be followed by increased rates of epiphyte loading which would reduce the benefits of improved water quality. Furthermore, it is also unknown how responsive epiphytes will be to reductions in nutrient concentration. Tomasko and LaPoint (1991) have suggested that dissolved nutrient concentrations may not be an accurate indicator of nutrient availability because of extremely rapid uptake by phytoplankton and epiphytes. Further monitoring of the Patuxent River and other Chesapeake Bay regions may help answer some of these questions. Results of the grass/strip epiphyte comparison indicate that this technique can be used effectively to evaluate and monitor potential SAV restoration sites with regard to epiphyte loading and light attenuation. Lastly, this data should be used to help calibrate the models that the Chesapeake Bay Program is currently developing to predict epiphyte light attenuation. Preliminary comparisons of actual field data to model predictions based upon water quality parameters suggest that epiphyte growth rates are more responsive to lower nutrient concentrations than the model would predict. In addition, the extreme growth rates observed on the Patuxent River also suggest that epiphyte light attenuation is also a function of exposure time. At present the Bay Program model doesn't take this potentially important parameter into consideration.

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

#### F.M. Rohland

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# 5.1 MINI-SONE Data Sets

Appendix D of this report contains data listings for variables measured during the MINI-SONE study conducted in June, July, August and September, 1998. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor which indicates the number of the MINI-SONE cruise (EPC Data Dictionary; Boynton and Rohland, 1990).

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

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

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

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

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

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

# 5.2 Patuxent River Submerged Aquatic Vegetation (SAV) Habitat Evaluation Data sets

Appendix F of this report contains data listings for variables measured during the SAV Evaluation conducted from March through October, 1998. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor indicating the month (mm) and the year (yy) of the SAV samples were collected.

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

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

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

**EPIPHYTE LIGHT ATTENUATION MEASUREMENTS** (Filename: Raw data file - **ELTRmmyy**, Table F-4; Mean data file - **ELTMmmyy**, Table F-5) includes 3 light transmission measurements, top, mid and bottom and data relating to strip type. Similar measurements were also taken with a clean strip that is used as a "blank" value to determine relative light attenuation. **EPIPHYTE NUTRIENT MEASUREMENTS** (Filename: Raw data file - **ENTRmmyy**, Table F-6; Mean data file - **ENTMmmyy**, Table F-7) contains epiphyte chlorophyll-a concentrations (total and active), total epiphyte dry weight and percent inorganic fraction measurements.

# 5.3 High Resolution Sediment and Bottom Water Data Sets

Appendix C of this report contains data listings for variables measured in the chlorophylla mapping cruises in May, June, July, August and September, 1998. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor which indicates the number of the mapping cruise (EPC Data Dictionary; Boynton and Rohland (1990).

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

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

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

**WATER COLUMN NUTRIENTS** (Filename: **HRHNUTxx**, Table C-3, added in 1998) report bottom water dissolved nutrient concentrations.

**SEDIMENT PROFILES** (Filename: **HRSPRFxx**, Table C-4, added in 1998) contains redox potential values.

# 5.4 Benedict Bridge High Frequency Monitoring Data Set

This report does not contain hardcopy data listings for variables measured during 1998 (5 June, 1998 through 25 September, 1998) at the Benedict Bridge during the High Frequency Monitoring Program. This is due to the large size of the data set. A summary of the variables sampled is included as Appendix E (Table E-1) and an electronic version is available on request from Dr Walter R. Boynton.

# 5.5 Incorporation of Error Codes in Data Tables

In order to eliminate blank spaces in the data tables a one or two letter alpha code (Table 5-1) is used to describe the problems associated with questionable parameter values. Valid entries from the Sediment Data Management Plan (EPA, 1989) are used and where necessary additional codes which are related to the EPC have been added.

ANALYSIS PROBLEM CODE CODE	DESCRIPTION
Α	Laboratory accident
В	Interference
С	Mechanical/materials failure
D	Insufficient sample
Ν	Sample Lost
Р	Lost results
R	Sample contaminated
S	Sample container broken during analysis
V	Sample results rejected due to QA/QC criteria
W	Duplicate results for all parameters
Χ	Sample thawed when received
BB	Torn filter paper
DA	Damaged epiphyte array
DS	Damaged epiphyte strip
EE	Foil pouch very wet when received from field, therefore poor
	replication
	between pads, mean reported
FF	Poor replication between pads; mean reported
HD	Particulate and chlorophyll-a samples only taken at -1.0 cm of the
	Eh profile
HH	Sample not taken
JJ	Amount filtered not recorded (Calculation could not be done)
LA	Lost epiphyte array
LL	Mislabeled
LS	Lost epiphyte strip
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
NR	No replicate analyzed for epiphyte strip chlorophyll-a
	concentration
PP	Assumed sample volume (pouch volume differs from data sheet
	volume; pouch volume used)
QQ	Although value exceeds a theoretically equivalent or greater value
	(e.g., PO4F>TDP), the excess is within precision of analytical
~~	techniques and therefore not statistically significant
SD	All sampling at station discontinued for one or more sampling
aa	periods
SS	Sample contaminated in field
SW TE	Snanow water, light flux measured at two points only
	Dissolved oxygen probe failure
	Instrument failure in research laboratory
TS	Dissolved oxygen probe not stabilized

## Table 5-1. Analysis Problem Codes

ANALYSIS PROBLEM CODE CODE	DESCRIPTION
TT	Instrument failure on board research vessel
UU	Analysis discontinued
VV	Station was not sampled due to bad weather conditions, research vessel mechanical failure, VFX array lost or failure of state highway bridges to open or close
WW	High 750 nm OD, actual value reported
XX	Sampling for this variable was not included in the monitoring program
	at this time or was not monitored during a specific cruise
YB	No blank measured for MINI-SONE fluxes
YY	Data not recorded

#### Table 5-1. Analysis Problem Codes (Continued)

## 5.6 Data Tables Quality Assurance/Quality Control (QA/QC)

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

# 5.6.1 Statistical Analysis System (SAS) Files

Lotus files are stripped of headings and converted to ASCII files. The data files are available on request from DNR or CBL. Additional information regarding the format of the data and details of variable labels, file structure and data and sampling anomalies are to be submitted as a meta-data file to fulfill the requirements of the EPA Chesapeake Bay Liaison Office (EPA/CBLO).

# 5.7 Quality Assurance/Quality Control (QA/QC) Checking

#### **5.7.1 Incorporation of Error Codes in Data Tables**

In order to eliminate blank spaces in the data tables a one or two letter alpha code (Table 5-1) is used to describe the problems associated with questionable parameter values. Valid entries from the Sediment Data Management Plan (EPA, 1989) are used and where

necessary additional codes which are related to the MINI-SONE program have been added.

# 5.7.2 Preparation of Data Tables for MINI-SONE

Data recorded by instruments in the field are entered directly onto specially prepared data sheets. Data from samples analyzed by Nutrient Analytical Services Laboratory (NASL) are returned in written format. Data are keyed into Lotus using the standard format developed during the continuing effort begun in August 1989 to standardize all EPC data files.

# 5.7.3 Preliminary Checking of Data Tables for MINI-SONE

Hard copies of the files are manually checked for errors. Data files are corrected, a second printout produced which is re-verified by a different staff member. The full data set is plotted and outlier values reevaluated. In the early years (1985 and 1986) some of the methods had not been perfected, so close scrutiny of outlier values was important. Values below detection limits are also indicated in the data tables.

# 5.7.4 Analytical Methods Quality Assurance/Quality Control (QA/QC)

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

- Particulate carbon and nitrogen cross calibration with Woods Hole Oceanographic Institution and Horn Point Environmental Laboratory.
- International Council for the Exploration of the Sea (ICES) inorganic nutrient round-robin communication. The fourth international intercomparison report was published in 1991 (Kirkwood, Aminot and Perttilä, 1991).
- Comparisons of dissolved nutrient analyses conducted at Horn Point Environmental Laboratory, Bigelow Laboratory, the University of Delaware and the University of New Hampshire.
- Quarterly cross calibration exercises with Virginia Institute of Marine Science (VIMS) and Old Dominion University (ODU). The most recent inter-comparison (November 1995) confirmed all parameters
routinely analyzed by these laboratories as part of the Chesapeake Bay Monitoring Program. Samples from various salinities and nutrient regimes were analyzed under this exercise.

- Environmental Protection Agency (EPA) unknown audits for various nutrients have been conducted.
- EPA audits of known nutrients were analyzed using samples in different salinity water while looking for possible matrix effects.

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

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

Specific EPC procedures include inorganic nitrogen (ammonium  $[NH_4^+]$ , nitrite  $[NO_2^-]$ , nitrite plus nitrate  $[NO_2^- + NO_3^-]$  and dissolved inorganic phosphorus [DIP or PO\_4^-3] for which a standard curve usually comprising five concentrations encompassing the expected range for that particular sample set, are analyzed at the beginning of each new run. A standard, which is treated as a sample, is analyzed at least every 20 samples. Baseline corrections are determined either manually or automatically, depending on the instrument providing the analysis. Data needed to calculate concentrations are recorded along with the sample concentration in laboratory notebooks, a carbon copy of which is provided to the EPC group. This procedure is also carried out for other parameters performed by the laboratory in support for the EPC effort. Precision and limits of detection for the variables measured by the EPC program are provided in the EPC Data Dictionary (Boynton and Rohland, 1990).

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

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

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# 6. PATUXENT RIVER HIGH FREQUENCY MONITORING

J.D. Hagy III, W.R. Boynton, R.M. Stankelis and J.M. Frank

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

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

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

#### 6.1 Historical Eutrophication Evidence from the Patuxent River

The deterioration of water quality in the Patuxent River has been documented since 1936 (Mihursky and Boynton, 1978). Nutrient enrichment associated with increases in nutrient inputs from upstream point and diffuse sources has been associated with increases in phytoplankton biomass, decreases in dissolved oxygen in the bottom waters of the lower estuary, decreased water column transparency, and the resultant loss of submerged aquatic vegetation (SAV). The consequences of eutrophication in the Patuxent River were particularly evident in 1978 when persistently low dissolved oxygen concentrations were recorded (Domotor *et al.*, 1989). Intensive research and legislation in recent years (1982 - 1992), in particular the Patuxent Nutrient Reduction Strategy, has contributed to the recovery of the tributary through reduction of loading of nitrogen and phosphorus from point sources. Superimposed on that overall improvement has been a pattern of highly variable hydrologic conditions during the 1990's which has created some years in which much higher nutrient loading rates occur than in other years (*e.g.* 1996 and 1993 were years with higher than average river discharge and nutrient loading rates).

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

River during a period (1964 - 1969) when water quality conditions were better and nutrient loads to the system were lower than in recent decades.

With the availability of continuous data in the Patuxent River prior to recent water quality deterioration, a new study was initiated to similarly measure and quantitatively assess current water quality conditions and contrast current observations to earlier conditions. The procedure described by Odum and Hoskins (1958) for measurement of community metabolism with the diurnal curve method was adapted to analyze both the earlier data collected by Cory and contemporary measurements to represent current conditions for comparative analysis. Sampling at the same site (following the same protocol used by Cory during the 1960's) was repeated from April through October in 1992, and June through October 1996 and 1997, using a modern temperature, salinity and dissolved oxygen instruments. While this modern instrument was compact and had internal data storage, the basic sensors were the same as those used by Cory and the same rigorous schedule of cleaning and calibration was followed.

The Cory data set and the 1992 data set were analyzed by Sweeney (1995) and the 1996-97 data by the EPC Program (Boynton et al., 1997; Burger and Hagy, 1998). Average rates during 1992 were much larger than in the past. Rates of maximum daytime net community production (Pa\*) in 1992 exceeded those in 1964 by a factor of three (300%) while estimates of community respiration at night (Rn) in 1992 were greater than those in 1964 by a factor of two (200%). Analysis by Sweeney (1995) indicated a statistically significant trend towards higher values for both daytime net community production (Pa\*) and community respiration at night (Rn) between 1964 and 1969 and significant differences between the data collected in the 1960's and 1992. Furthermore, there were changes in the seasonal pattern of metabolism between the 1960's and 1992. In the 1960's, daytime net community production (Pa\*) exhibited very low values during late winter and then increased sharply at the beginning of May (week 17). With one exception this was the highest value of daytime net community production (Pa\*) recorded during the year and probably represents enhanced production associated with the spring algal bloom. By 1992 this was substantially changed. Daytime net community production increased to a summertime maximum which persisted through early September, generally following the temperature cycle (Sweeney 1995, Figure 6-1). This change in pattern was probably caused by a relief of summer time nutrient limitation. Rates of oxygen consumption (Rn) also increased and during 1992 exhibited a longer By 1992 this was substantially changed. Daytime net period of enhanced rates. community production increased to a summertime maximum which persisted through early September, generally following the temperature cycle (Sweeney 1995; Figure 6-1).

In 1996 and 1997, daytime production and nighttime respiration appeared to track back toward 1964 levels (Burger and Hagy, 1998), possibly in response to recent reductions in nutrient loading. In particular, average nighttime respiration in 1997 was actually slightly lower than respiration in 1964 (2.3 vs. 2.6 g  $O_2 \text{ m}^{-3} \text{ d}^{-1}$ ). While daytime apparent production averaged higher in 1997 (2.3) than 1964 (1.6), production was substantially lower than the 1992 high of 4.9 and appeared to continue a trend as both production and



Figure 6-1. Weekly mean maximum apparent daytime net production (Pa\*) at Benedict Bridge in 1964 and 1992.

Data from Sweeney (1965).

respiration declined in 1996 and 1997 relative to 1992, despite very high river flow in 1996 and more average hydrologic conditions in 1997.

Examination of the 1960's, 1992, 1996, and 1997 data sets demonstrated the utility of the diel oxygen technique for measuring community production and respiration as a powerful and cost effective complement to monitoring efforts in the Patuxent River estuary and possibly other sites as well. Preliminary results indicated a clear association of historical nutrient loading to community metabolism responses inferred from continuously measured water quality data. It appears the technique can quantify temporal changes in the community metabolism rates which are known to be strongly impacted by nutrient supply rates, and therefore provide a genuine and measurable dynamic linkage between the effectiveness of nutrient reduction in the watershed coupled to water quality in receiving waters. This chapter presents results from continued high frequency measurements during 1998. With 4 full years of data in the 1990's, plus a reference condition from the 1960's, the emphasis will be on a comparison among years rather than an analysis of mechanisms driving intra-annual variations. It is considered that 4 years of this type of data is in fact substantial and justifies a good comparison among years.

#### 6.2 High Frequency Monitoring during 1998

Submersible self-recording environmental monitoring instruments were deployed from June 6 through September 24, 1998 from the Maryland Route 231 bridge at Benedict. This is exactly the same location used for 1997 recordings. The same instruments were used in 1998 as in 1997, as were the same quality assurance measures. This included regular comparisons of oxygen measurements from the high frequency recording instruments and those made using Winkler titrations, the most precise method for measuring dissolved oxygen, but also very labor intensive.

The major objectives of this effort were:

1. To examine dissolved oxygen data to determine if dissolved oxygen habitat criteria were achieved in 1998 and how compliance in 1998 compared to 1996 and 1997.

2. To use temperature, salinity and dissolved oxygen data to calculate daily water column production and respiration for this zone of the estuary and

3. To compare this year's calculated metabolism rates to rates from the recent past and to rates from the 1960's.

#### 6.3 Examination of 1998 Data

#### 6.3.1 Database Compilation

All raw data was retained for permanent storage. Copies of raw data were formatted for later retrieval as a "meta-file", which includes synoptic measurements of water quality sensor data, corresponding results of water sample analyses and meteorological data. Continuous sampling from June through September yielded a total of 11,502 observations for each water quality variable (water temperature, conductivity, salinity, dissolved oxygen percentage saturation and dissolved oxygen concentration) at 15 minute intervals. The resulting continuous data set consists of uninterrupted time series, sufficient for estimating metabolic parameters (see below) for 92 days out of the total 110 days that sensors were deployed. Corresponding to the beginning and end of each sensor deployment, 15 dissolved oxygen measurements were made via Winkler titrations (Table 6-1).

#### 6.3.2 Data Evaluation

Before the high frequency data could be utilized for analysis, it was necessary to verify the accuracy of the observations. The first step in the time series analysis was to plot the observations against time. The plots of temperature, salinity and dissolved oxygen provide visual means of detecting basic features of the data such as trend and seasonality, as well as discontinuities and outliers which most likely indicate instrument error. These graphs are mainly used for diagnostic purposes and are less informative than other data presentations and are therefore not included.

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

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

Differences between dissolved oxygen measurements made with sensors calibrated in air and in-situ Winkler determinations were always less than 1.0 mg l<sup>-1</sup> at the time of sensor deployment (Table 6-1), indicating that air calibrations were effective and did not result in gross errors. However, there was a small, statistically significant (paired t-test, p=0.03) bias in these measurements. Winkler titrations measured 0.32 mg l<sup>-1</sup>, or about 5% more dissolved oxygen on average than the sensor. This difference is very close to the expected analytical precision of dissolved oxygen sensors of the type that were used.

Deployment	Initial	Winkler	Final Sensor Winkler		Retrieval
Date	Sensor				Correction <sup>3</sup>
	DO	DO	DO	DO	
	(mg l <sup>-1</sup> )				
5-Jun-98	4.91	5.84	4.96	6.10	1.14
12-Jun-98	TT	6.10	TT	6.87	NA
18-Jun-98	6.71	6.87	4.37	6.17	1.80
26-Jun-98	5.72	6.17	2.46	5.61	3.15
2-Jul-98	5.40	5.61	2.90	6.00	3.10
10-Jul-98	5.09	6.00	3.48	6.14	2.66
16-Jul-98	5.69	6.14	3.23	5.00	1.77
23-Jul-98	4.85	5.00	1.83	5.23 <sup>1</sup>	3.51
31-Jul-98	4.77	5.23 <sup>1</sup>	2.68	5.22	2.54
6-Aug-98	HH	5.22	3.22	5.34	2.12
13-Aug-98	5.60	5.34	3.57	5.04	1.47
20-Aug-98	4.64	5.04	3.91	5.21 <sup>2</sup>	1.30
27-Aug-98	5.37	5.21 <sup>2</sup>	1.82	5.25	3.43
3-Sep-98	TT	5.25	4.75	NA	NA
15-Sep-98	HH	HH	HH	HH	NA
21-Sep-98	5.40	5.35	4.45	5.51	1.06

 Table 6-1. Summary information for Benedict Bridge dissolved oxygen data and Winkler titrations.

#### NOTES:

- End point correction based upon YSI 600 corresponding values; Winkler values considered non-interpretable.
- <sup>2</sup> End point correction based upon the mean of August Winkler value; Winkler values on 8/20/1998 considered non-interpretable.
- 3 Retrieval Correction derived by subtracting the final sensor reading (column 4) from the Winkler value (Column 5).

#### **Error Codes:**

- HH Sample not taken
- NA Not applicable: value cannot be calculated
- TT Instrument failure

In contrast to the general agreement of Winkler titrations with sensor measurements at the beginning of deployments, comparisons at the end of each sensor deployment revealed that sensor readings declined by about 2.2 mg  $l^{-1}$  dissolved oxygen. As has been discussed in past EPC reports (Burger and Hagy, 1998) this decline, associated with biofouling, requires that data be adjusted to compensate for the drift in sensor readings.

#### 6.3.3 Data Compensation

The question of whether to accept, reject or compensate for a portion of the deployments that ended with sensor dissolved oxygen data more than 1.0 mg  $\Gamma^1$  lower than Winkler dissolved oxygen was based on the comparison of sensor readings with pre- and post-deployment Winkler determinations. A protocol was established to compensate data for sensor drift as needed using a linear interpolation correction for each dissolved oxygen value between accepted sensor end and beginning values (as done by YSI software) based on the following criteria:

- 1. All sensor data from deployments with both beginning and end point measurements within  $+1 \text{ mg } \Gamma^1$  of respective Winkler concentrations were retained unchanged. This did not occur for any deployments during 1998.
- 2. If end point sensor measurements were more than 1 mg  $l^{-1}$  less than the Winkler concentration, the difference was computed, then added to the end point concentration. All preceding measurements were similarly compensated by addition of a linearly decreasing value from end to beginning of that deployment, where correction was zero for the first dissolved oxygen measurement. Then, compensated percent oxygen saturation was computed from each temperature and salinity observation and compensated dissolved oxygen concentration. This was applied for each of the deployments in 1998.
- 3. Deployments with beginning point sensor measurements that exceeded the acceptable  $\pm 1 \text{ mg l}^{-1}$  range of respective end point sensor data and Winkler dissolved oxygen concentrations were also similarly compensated. No deployments were compensated in this manner in 1998.

Sensor drift is mainly a function of fouling. We can't be certain why there was more fouling in 1998 and than in 1997. One observation is that the area where the meters have been maintained every year was home to an enormous jellyfish population in 1998, possibly due to salinity effects. This could have led to more fouling because the planktivorous grazer population would have been wiped out. Explanations aside, sensor fouling leads to downward drift. This is why we have extablished the means for testing for correcting for drift and why we used it in 1998.

Both raw and compensated water quality sensors were then integrated with simultaneous meteorological data and archived in a (nearly) continuous time series format suitable for analysis.

## 6.4 Qualitative Description of 1998 High Frequency Data

Due to the extremely high number of observations, a continuous graph of each observation has not been included. As a more informative alternative, 24-hour means have been presented, illustrating the trends observed in raw water quality data over the year (Figure 6-2). For comparison, daily averages (24-hour mean value) from 1997 are also plotted, illustrating the differences.

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

# 6.4.1 Temperature

Water temperature during the period of record (Figure 6-2, middle) followed a typical seasonal pattern, from a low of about 20 °C at the beginning of June and increasing to a nearly constant maximum of around 28-30 °C during July-August. Shorter term temperature variations of approximately 5 °C reoccur on a fortnightly frequency that appears to correspond to lunar spring tides. During the initial 1998 spring deployment, a sharp decrease in water temperature was observed, similar to the type of pattern that was observed in 1997. These most likely reflect translation of the axial temperature gradient (warmer fresh water, colder salt water) as the effects of tidal mixing and river flow variations combine. This is most clearly illustrated by the increasing salinity and decreasing temperature during the initial 1998 deployment.

# 6.4.2 Salinity

Salinity showed a typical seasonal pattern for Patuxent River, increasing steadily over the period of record from a minimum of 5-6 ppt to 12 ppt in late September (Figure 6-2, upper). However, the 1998 salinity data revealed that salinity was lower through much of 1998 relative to 1997. This reflects the higher river flow that occurred during the spring of 1998. Even though river flow declined toward the middle of 1998, salinity in Chesapeake Bay, offshore from Patuxent River, probably continued to reflect the higher flow earlier in the year.



Figure 6-2. Daily average salinity, water temperature and percent dissolved oxygen saturation at the sampling site, Maryland Route 231 bridge on the Patuxent River during 1997 and 1998.

#### 6.4.3 Dissolved Oxygen

More than dissolved oxygen concentration measurements, percent dissolved oxygen saturation (DOSAT) measurements reflect the effects of biological activity on dissolved oxygen concentrations. Of course, in the absence of any biological activity, oxygen concentrations would equilibrate with the atmosphere, resulting in DOSAT near 100%. Throughout 1998, DOSAT was less than 100%, declined from early June to a minimum in late August, then increased slightly in the few September observations. The range of DOSAT was in the same range as in 1997, although the extreme variability that occurs in the parameter makes such visual determinations difficult. The average DOSAT was 75%, slightly less than the 80% average for the subset of the 1997 record that coincided with the 1998 record. This indicates that Patuxent River was slightly more heterotrophic in 1998 than in 1997.

## 6.4.4 Compliance with Dissolved Oxygen Habitat Criteria

Recognizing the need to manage the Chesapeake Bay as an integrated ecosystem, living resource and water quality goals were sought as a commitment to the 1987 Chesapeake Dissolved oxygen conditions deemed to provide viable habitat Bay Agreement. conditions for reproduction, growth and survival of fish, mollusc, crustacean, benthic and planktonic species indigenous to Chesapeake Bay were estimated from known tolerance levels of various species. Because of the natural fluctuations of dissolved oxygen in the water column and the varied ability of different species to tolerate low dissolved oxygen conditions (hypoxia), habitat requirements could not be expressed as a single critical concentration (Jordan et al., 1992). Rather, criteria were established to provide a systematic way to assess the degree to which dissolved oxygen conditions in Chesapeake Bay are sufficient to support growth and survival of important living resources. The conditions cited reflect recognition that detrimental levels of oxygen stress can be compounded by prolonged or repeated exposure to sub-lethal concentrations and ultimately, acute mortality following exposure to lethal concentrations (Table 6-3). Based on tolerances of certain species, the criteria demarcate acceptable dissolved oxygen means over specified time intervals between hypoxic excursions to address exposure of organisms to the inherent fluctuations above and below threshold dissolved oxvgen levels.

The 1998 high frequency data collected from the bridge at Benedict were evaluated to assess compliance with living resource habitat criteria for dissolved oxygen as defined in Table 6-2. Patuxent River tidal reaches (and all tidal reaches of tributaries in Chesapeake Bay) are designated anadromous fish spawning river and nursery areas (Funderburk *et al.*, 1991). The sample depth (1 meter) at Benedict effectively describes conditions for above pycnocline waters at the sample location. As such, water quality conditions in that tributary region and water column portion are evaluated following the more stringent criteria for dissolved oxygen.

#### Table 6-2. Dissolved Oxygen Habitat Criteria

- 1. The dissolved oxygen concentration should be at least 1.0 mg l<sup>-1</sup> at all times throughout Chesapeake Bay and its tributaries, including sub-pycnocline waters.
- 2. Dissolved oxygen concentrations between 1.0 and 3.0 mg l<sup>-1</sup> should not occur for longer than 12 hours and the interval between excursions of dissolved oxygen between 1.0 and 3.0 mg l<sup>-1</sup> should be at least 48 hours throughout Chesapeake Bay and its tidal tributaries, including subpycnocline waters.
- 3. Monthly mean dissolved oxygen concentrations should be at least 5.0 mg  $l^{-1}$  throughout the above-pycnocline waters of Chesapeake Bay and its tidal tributaries.
- 4. Dissolved oxygen concentrations should be at least 5.0 mg l<sup>-1</sup> at all times throughout the above pycnocline waters of anadramous fish spawning reaches, spawning rivers and nursery areas of Chesapeake Bay and its tidal tributaries as defined in Habitat Requirements for Chesapeake Bay Living Resources, 1991 revised edition (Funderburk *et al.*, 1991).
- 5. In addition, where dissolved oxygen conditions presently exceed the requirements, these conditions should be maintained.

Dissolved oxygen averaged over the period of record in 1998 about 5.8 mg  $l^{-1}$ , lower than the 6.2 mg  $l^{-1}$  average for 1997. Although mean monthly dissolved oxygen concentrations were all greater than the 5 mg  $l^{-1}$  minimum for the criteria, excursions below 5 mg  $l^{-1}$  amounted to 494 hours, of 20% of the period of record. This is approximately the same percentage of observations during the 1997 record, although a more complete record in 1997 observed 689 hours of dissolved oxygen readings below 5 mg  $l^{-1}$ .

Excursions below 3 mg  $l^{-1}$  totaled 8.5 hours in 1998 but these excursions were relatively short lived. None exceeded 48 hours. On eight occasions, dissolved oxygen declined below 3.0 mg  $l^{-1}$  less than 48 hours past the last excursion, mostly in successive days. For example, declines below 3.0 mg  $l^{-1}$  occurred in the nighttime hours on August 11, 12, and 13. There were no occasions in 1998 on which dissolved oxygen at this shallow depth declined to below 1 mg  $l^{-1}$ .

As in 1997, the 1998 dissolved oxygen data showed that during fully 20% of the time, this representative portion of Patuxent River exhibited oxygen conditions that were frequently not sufficient for anadromous fish spawning reaches and nursery areas (*i.e.* less than 5 mg  $\Gamma^1$ ). Although the dissolved oxygen excursions below 3 mg  $\Gamma^1$  were brief, infrequent and punctuated by daily dissolved oxygen fluctuations reaching saturation concentrations, the overall low monthly means do not adequately convey the persistently marginal conditions that many species are able to tolerate only over short term (Funderburk *et al.*, 1991). Accumulative stress on tolerances of organisms is likely during the large proportion of July and August when excursions below 5 mg  $\Gamma^1$  lasted from 12 to 15 hours on the majority of days.

Any sense that these data represent adequate habitat conditions should be tempered with the awareness that these observations were collected at 1 m below the water surface and are a "best case" for this portion of the estuary. Since the water was undersaturated with respect to dissolved oxygen for much of the time, surface waters have both the benefits of most primary production and most of the reaeration from the atmosphere. While the water column in this area is usually not strongly stratified, one can still expect a vertical gradient in dissolved oxygen, with the highest concentrations near the surface and the lowest concentrations near the sediment surface. Thus, waters near the bottom where many marine organisms live, may fail the dissolved oxygen criteria more frequently.



Figure 6-3. Frequency histogram of dissolved oxygen concentrations in 1997 and 1998 at the Maryland Route 231 bridge on the Patuxent River.

#### 6.5 An Introduction to Open Water Metabolism Measurements

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

#### 6.5.1 Background and Definitions

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

The high frequency time series of dissolved oxygen from the bridge over the Patuxent River at Benedict (Maryland Route 231) were used to generate daily estimates of surface water (top 1 m) metabolism for the period of record from late spring through early fall 1998. The open water technique used relies on the daily excursions in dissolved oxygen caused by the diel cycle of incident irradiance (sunlight). While certain assumptions (see section 5.5.2) are required, as with all other techniques, the open water technique is especially useful for characterizing ecosystems because it integrates across ecosystem components, time and space. Open water techniques are also particularly well-suited to metabolically active systems such as Patuxent River.

Surface water dissolved oxygen typically increases over the course of a sunny day as oxygen is produced by phytoplankton photosynthesis. The combination of phytoplankton respiration, oxygen-consuming processes by all marine organisms and other chemical reduction and oxidation processes throughout the water column lead to an overall dissolved oxygen decline during low sunlight conditions and at night. This results in a diel pattern in which oxygen reaches a daily maximum in late afternoon and declines overnight to a minimum shortly after dawn. The pattern is affected by oxygen exchange (diffusion) across the air-sea interface from air-to-sea when water is lower than 100% dissolved oxygen saturation (under-saturated), or in the opposite direction, from sea-to-air, when water is over-saturated. The exchange of oxygen is proportional to the degree of over- or under-saturation. Our metabolism estimates are based on this conceptual model. The parameters used for community metabolism estimates are defined in Table 6-3.

## 6.5.2 Estimation Algorithms

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

- 1. Times of sunset and sunrise were obtained from the US Naval Observatory for each day. Supplemental dissolved oxygen concentration (DO) and percent oxygen saturation (POSAT) were computed by interpolation for times when sunrise or sunset did not correspond to measured observations. Using times of sunrise and sunset, DAYPART labels were assigned to distinguish each observation measured during either daylight or nighttime.
- 2. Change in DO ( $\Delta$ DO), mean POSAT and time interval in hours ( $\Delta$ t) were computed between each observation and preceding observation.
- 3. Air-sea oxygen exchange (ASEXCH) during each interval was computed, assuming a constant exchange coefficient of 0.5 g O2 m-2 hr-1 at 100% saturation deficit (Kemp and Boynton, 1980). This equation is:

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

Resulting units are g  $O_2$  m<sup>-2</sup>.

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

#### Table 6-3. Parameter definitions for metabolic parameters.

Parameter	Definition
Rn	Night Respiration (g $O_2$ m <sup>-3</sup> day <sup>-1</sup> ): oxygen consumption
	between sunset and sunrise.
Rn/hr	Night Respiration Rate (g $O_2$ m <sup>-3</sup> hr <sup>-1</sup> ): mean hourly oxygen
	consumption rate between sunset and sunrise.
SRm	Metabolic Sunrise: time of dissolved oxygen minimum during
	daylight hours
SSm	Metabolic Sunset: time of dissolved oxygen maximum during
	daylight hours
Pa	Net oxygen production (g $O_2$ m <sup>-3</sup> day <sup>-1</sup> ) between sunrise and
	sunset.
Pa*	Net oxygen production during period of net autotrophy (g $O_2 m^{-3}$
	day <sup>-1</sup> ), which occurs between times of dissolved oxygen
	minimum (SRm) and maximum (SSm).
Pg	Gross oxygen production (g $O_2$ m <sup>-3</sup> day <sup>-1</sup> ) between sunrise and
	sunset, assuming daytime respiration rate is equal to nighttime
	respiration rate (Rn hr <sup>-1</sup> ) during subsequent night.
Pg*	Gross oxygen production during period of net autotrophy (g $O_2$
	m <sup>-3</sup> day <sup>-1</sup> ), assuming daytime respiration rate is equal to
	nighttime respiration rate (Rn hr <sup>-1</sup> ) during subsequent night.

Once the above operations were completed, daily metabolic parameter values were computed by summation of all values in each METPART group for that METDAY. The parameters  $Rn hr^{-1}$ , Pg and Pg\* were calculated using the formulas in Table 6-3. Once all of these parameters were calculated, any daily observations for which insufficient data were available were eliminated.

Several assumptions are required to utilize this method for calculating ecosystem metabolism. These include:

1. Diel changes in observed dissolved oxygen concentration result from either metabolic activities or exchanges of dissolved oxygen with the atmosphere. Thus, changes due to advection are assumed to be negligible.

2. Exchange of oxygen with the atmosphere is assumed to occur at a rate proportional to the percent oxygen saturation. This neglects changes in the proportion that occur as a result of wind-induced surface water turbulence.

3. Respiration during the day is assumed to occur at the same rate as respiration during the preceding night. This assumption only affects the estimation of gross production (Pg and Pg\*).

While it is known the all of these assumptions are not strictly met, we believe that they are adequately met. Violations of the assumptions appear to contribute an acceptable level of uncertainty.

#### 6.5.3 Results and Discussion of Metabolism Calculations

The following sections describe estimates of metabolic parameters in 1998 and compare them to similar estimates for 1964, 1992 (Sweeney, 1995) 1996 and 1997 (Burger and Hagy, 1998). These years encompass an increase in nutrient loading rates from the 1964 through 1979. Subsequently TP loading decreased, reaching levels comparable to 1960 by 1992. TN loading rates continued at elevated levels until implementation of biological N removal at sewage treatment plants in the Patuxent River watershed, beginning in 1991, led to decreasing N loading levels. While it would have been useful to compare metabolic rates in the mid-1980's to present levels and 1960's levels, no data are available for the 1980's. Thus, the following analysis considers whether changes may have occurred between 1992 and recent years, potentially in response to changes in nutrient loading rates.

## 6.5.3.1 Respiration (Rn)

Nighttime respiration averaged 2.70 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$  over the period of record (6/6/98 - 9/2/98), ranging from a maximum of 4.48 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$  to a minimum of 1.00 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$  (Table 6-4). The maximum rates of nighttime respiration increased from June

through July and remained at those levels throughout the summer (Figure 6-3). Respiration in 1998 was slightly higher than the average rates for the same dates in 1997 (2.62 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$ ), but lower than respiration in 1996 (3.44 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$ ; Table 6-4). The average nighttime respiration for 1992 was 4.1 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$ , (Burger and Hagy, 1998). While the period during 1992 corresponding to this mean was different than the period of record in 1998, it included periods in spring and fall when respiration is typically lower. Therefore, respiration during summer of 1992 was definitely higher than in 1998. Respiration rates in 1998 were slightly higher than the 1964 mean, which was 2.6 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$  (Burger and Hagy, 1998).

#### 6.5.3.2 Net Daytime Production (Pa and Pa\*)

Net daytime production (Pa) in 1998 average -0.18 g  $O_2$  m<sup>-3</sup> day<sup>-1</sup>, lower than for the same period in 1996 (0.27) and 1997 (0.11) (Table 6-4). The fact that net daytime production was less than zero is an interesting result: the ecosystem consumed more oxygen than it produced, even during the day. The appears to reflect a decrease in gross production, since respiration did not increase substantially. This may reflect an expected transition from net autotrophy to net heterotrophy as inorganic nutrient loads decline (Kemp and Boynton, 1998) relative to organic carbon loading. The highest Pa, up to 3.3g  $O_2$  m<sup>-3</sup> d<sup>-1</sup>, occurred during the earlier part of the year, probably due to higher river flow and more availability of nutrients relative to the later period (Figure 6-3). Maximum net daytime production (Pa\*) measures net production during the period of the day when gross production was sufficient to increase the oxygen concentration. Thus, a large Pa\* and a lower Pa, as was observed in 1998 (Table 6-4) indicates that just after sunrise and just before sunset, incident irradience was not sufficient to support net production in excess of respiration. This occurred to a greater extent in 1998 than in 1997, but less than 1996, mirroring the pattern in nighttime respiration.

#### 6.5.3.3 Gross Production (Pg)

Daytime gross production (Pg) averaged 3.78, an intermediate value relative to the same period in 1996 (5.07 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$ ) and 1997 (3.93 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$ ; Figure 6-3). Estimates of Pg ranged from a near zero to 9.54 g  $O_2 \text{ m}^{-3} \text{ day}^{-1}$  (Figure 6-3). While Pg is by definition a positive value, negative values can be observed because respiration and net production are not measured simultaneously and both are subject to measurement error.



Figure 6-3. Time series of daytime apparent production (Pa), nighttime respiration (Rn) and daytime gross production (Pg) in 1998.

Table 6-4. Average metabolic rates for 6/1 through 9/15 during 1996, 1997 and 1998. In addition, average metabolic rates for the period of record in 1992 and 1964 (Sweeney 1996) are shown for comparison.

Year	Pa	Pa*	Pg	Pg*	Rn	Rn hr <sup>-1</sup>
<b>1964</b> <sup>1</sup>		1.6			2.6	
1992 <sup>1</sup>		4.9			4.1	
1996	0.28	3.96	5.07	8.76	3.44	0.34
1997	0.12	2.81	3.93	6.62	2.62	0.27
1998	-0.18	3.00	3.78	6.97	2.70	0.28

Rates for these years are for the respective period of record, rather than the 6/1 to 9/15 period, however, the differences are expected to be minimal. Means of Pa, Pg, Pg\* and Rn hr<sup>-1</sup> were not available in Boynton *et al.* (1998), the source for the other 1964 and 1992 means.

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# 7. HIGH RESOLUTION MAPPING ON PATUXENT RIVER

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It has long been recognized that water quality and especially chlorophyll-a concentrations can be highly patchy in estuaries. However, to date, the vast majority of monitoring in estuaries has been done at discrete station locations. Patuxent River, which is one of the most intensely monitored estuaries in the world, has nine regular water quality monitoring stations in the lower portion of the estuary. While this kind of sampling can be expected to quantify vertical water column structure at the locations sampled, as well as broad regional patterns in water quality features, there are important limitations imposed by this discrete sampling. Even the most basic goals of monitoring programs are affected. Because the spatial resolution of regular discrete sampling may be less than the scales of variability inherent in the data, the possibility of "aliasing" is created. This introduces an apparently random component to the data which can lead to more confusing analysis later. For the purposes of interpreting water quality status and trends, a number of "aberrant" observations and "mixed results" may reflect aliasing of spatial patterns introduced by sampling as much as real stochasticity in water quality responses to nutrient loading. Another often-cited limitation of the discrete station sampling is a lack of sampling of lateral variations in water quality except at a few locations in the mainstem of Chesapeake Bay. For a few important variables, high frequency mapping addresses this data need. Finally, discrete sampling at a few points will most likely miss the extreme values that may be particularly important for investigating food webs in the ecosystem. The non-linearity often characteristic of feeding relations and other trophic interactions can mean that a few small areas with particularly high chlorophyll-a could account for a large fraction of population growth rates (e.g. menhaden). This possibility has been noted via the use of bioenergetics models for several species of fish. Given the increased emphasis on establishing linkages between water quality and living resources in Chesapeake Bay, it will be increasingly important to sample water quality at the temporal and spatial scales most relevant to food webs. Again, high resolution mapping addresses that data need.

#### 7.1 The DATAFLOW System

Mapping systems have long been employed on larger research vessels. Called SAIL systems, for Serial Analytical Instrument Loop, these systems generally receive surface water through a hull pump, pump the water through a series of instruments which monitor water quality, then continuously log the data on a computer system. Recent reductions in cost and other improvements in the satellite based global positioning system (GPS) technology have also made it possible for these systems to continuously log position and time along with the instrument readings.

The DATAFLOW system incorporates this basic design with several key improvements that improve the speed and portability of the system and improve its durability in the field. The most important improvement is the combined use of a "ram" and air bubble trapping device to facilitate sampling of water from just below the water surface as a small vessel moves at planing speeds. Water is obtained from below the hull's planing surface, decreasing and nearly eliminating disturbance of the water and inclusion of air bubbles. At speeds in excess of 10 knots, water flows freely and rapidly through the system. If air bubbles were to enter the system, the bubble trapping would quickly remove them and prevent them from passing through the instrumentation loop. That few bubbles are observed in this trapping device (unless intentionally introduced to demonstrate its effectiveness) also indicates the effectiveness of the ram for collecting undisturbed water samples at high speeds. Surprisingly, neither the ram nor the bubble trapping device appear to disturb the water to a great extent. To illustrate this point, zooplankton samples that were obtained from the discharge hose of the system at sampling speeds of over 20 knots have survived and reproduced in captivity.

The other key development of the DATAFLOW system is elimination of the need for a computer. Instead, a highly shock-resistant and water-resistant data logging device records the instrument readings and positioning data. Once the sampling trip has been concluded, these data can be readily downloaded into a computer.

The analytical instrumentation included in the DATAFLOW system includes a water temperature and conductivity sensor, dissolved oxygen probe, transmissometer and fluorometer. Ancillary information includes time, position, and water depth obtained via an acoustic transducer mounted on the transom of the vessel next to the ram.

#### 7.1.1 Water Temperature

The water temperature sensor, located within the dissolved oxygen sensing device is calibrated to within  $\pm 0.25$  °C. Water temperature readings are used to compensate the other sensors, including dissolved oxygen, requiring temperature compensation.

## 7.1.2 Conductivity

DATAFLOW has a Signet 2820 Series conductivity sensor. This instrument is calibrated using potassium chloride (KCl) standards prior to each deployment of the instrument

## 7.1.3 Dissolved Oxygen

The BC Electronics OD7685 model digital dissolved oxygen controller included in DATAFLOW is designed to withstand the rigors of continued high flow rates within a pipe. In addition, it has an acceptably high response rate for sampling surface waters. This sensor is air calibrated prior to and following each deployment of the instrument. Although this was not implemented during 1998, the current protocol suggests that several water samples during the course of the deployment be fixed for later dissolved oxygen determinations using Winkler titrations.

#### 7.1.4 Transmittance

The Wetlabs, Inc. C-Star transmissometer in DATAFLOW has a 10 cm path length. Prior to deployment, the optics of this instrument were thoroughly cleaned to ensure that the full range of sensitivity is obtainable during the deployment. However, we have not to date calibrated the transmissometer to any standard units such as nephelometric turbidity units (NTU). Instead, instrument output voltages are related to *in situ* properties such as Secchi depth. In general, very high correlation has been observed (*e.g.*  $r^2 > 0.95$ ) between output voltages and secchi depth, indicating the effectiveness of this approach for estimating these important *in situ* properties. Of course, as the need arises, other calibration procedures can be used, including calibration to NTUs via NTU standards.

#### 7.1.5 Fluorescence

The Wetlabs, Inc. Wetstar fluorometer in DATAFLOW has a nominal response range of 0-200  $\mu$ g l<sup>-1</sup>, making it suitable for measuring *in situ* fluorescence in estuaries. As with the transmissometer, the pre-deployment protocol includes a careful cleaning of the optics to ensure adequate response of the instrument. Calibration is accomplished by collecting water samples for later analysis via the EPA approved acetone extraction methods.

#### 7.1.6 Positioning and Depth Information

Positioning and depth information is obtained through the National Marine Electronics Association (NMEA) bus of a Garmin 12-satellite Global Positioning System (GPS)/sounder system. The accuracy of this device is nominally 100m, which is more than adequate for sampling Patuxent River at 20+ knots. Moreover, positioning errors are correlated in time due to the properties of selective-availability, indicating that the relative positions of successive data points are usually very accurate. While a differential beacon receiver was not installed in 1998, this has been installed during December 1998, improving positioning accuracy to 5m. This will be of greatest value for sampling near shore areas where position relative to the shoreline is important. The depth sounder integrated in this device records depth to  $\pm 0.1$  m.

#### 7.2 Vessel Operations, Cruise Track, and Instrument Calibration

Sampling operations on 8/13/98 were conducted on board the R/V Pisces, a 25 foot cuddy cabin research vessel equipped with an outboard motor. Although the R/V Pisces is capable of speeds up to nearly 30 knots, sampling with DATAFLOW was conducted at approximately 22 knots to conserve fuel, improve reliability of the depth sounder, and reduce strain on the sampling ram. Slower speeds were maintained in shallow water (1-2 m), although in familiar waters planing speeds are maintained. In addition, because the DATAFLOW system provides real-time display of water quality parameters, slower speeds were used and cruise tracks were occasionally elaborated in the vicinity of notable water quality features such as substantial fronts.

The cruise track on 8/13/98 followed a zig-zag pattern, crossing the channel and proceeding as far inshore as safe navigation permitted (Figure 7-1). Sampling began at 13:06 at Chesapeake Biological Laboratory, proceeded east beyond Drum Point, then began the zig-zag pattern up-river without interruption to Chalk Point. Subsequently, a down-estuary axial transect was followed, interrupted by 9 stations. Surface chlorophyll-a samples were collected at 7 stations, while secchi depth was measured at all 9 stations.

The calibration curves for the transmissometer and fluorometer are shown in Figure 7-2. The coefficients of determination  $(r^2)$  for the fluorometer calibrations were  $r^2=0.81$  for total chlorophyll-a and  $r^2 = 0.83$  for active chlorophyll-a. This values are in the same range as is generally obtained for calibrating *in situ* fluorescence against extracted chlorophyll-a concentrations. The response for the transmissometer response regression illustrates the good agreement between secchi depth and transmissometer readings. Note that to obtain a linear relationship, secchi depth was transformed to an estimate of the light attenuation coefficient, K<sub>d</sub>, using an approximation usually found to be accurate for estuarine waters such as Patuxent River (K<sub>d</sub> = 1.4/SD).

## 7.3 Water Quality Maps

Maps showing the distribution of dissolved oxygen, total chlorophyll-a and light attenuation in Patuxent River on 8/13/98 are shown in Figure 7-3. These distributions illustrate three main regions in which chlorophyll-a concentrations were substantially elevated - near Benedict, just up-estuary from Broomes Island, and offshore from Solomons Island. Maximum chlorophyll-a concentrations in these regions, in excess of



Figure 7-1. The cruise track followed by the R/V Pisces on 8/12/98 along with the locations at which secchi depth was measured and water samples were filtered for chlorophyll-a determinations.



Figure 7-2. The response curves for the flurometer (upper) and transmissomtere (lower). One of the extracted chlorophyll-a observations exceeded 800  $\mu$ g l<sup>-1</sup> and the flurometer reading was off scale. Consequently, this observation was omitted from the calibration.

Figure 7-3. Maps of dissolved oxygen, total chlorophyll-a and light attenuation in the lower Patuxent River on 8/13/98.

100  $\mu$ g l<sup>-1</sup> may be considered very high. In contrast, chlorophyll-a concentrations were much lower throughout most of the rest of the river. The highest concentrations in the patch just south of Broomes Island were concentrated on the western shore, while the main patch north of Broomes Island was in the main channel of the river.

The highest dissolved oxygen concentrations correspond spatially with the highest chlorophyll-a distributions in the middle reach of the estuary, indicating that not only was there high phytoplankton biomass, but net phytoplankton production was also very high. Interestingly, the area over which dissolved oxygen concentrations were elevated was greater than the corresponding area of increased phytoplankton biomass and included one area where chlorophyll-a concentrations were only slightly enhanced. In the patch near Benedict, dissolved oxygen was elevated to a lesser extent than in the Broomes Island patch, suggesting lower rates of net production, despite high phytoplankton biomass. These differences indicate that rates of net production per unit phytoplankton biomass An additional note regarding the dissolved oxygen varied among the patches. distributions is the very small area of increased dissolved oxygen concentration offshore of Solomons Island, corresponded with a similar patch in the chlorophyll-a distribution. Since this area was transited at a boat speed of approximately 20 knots, this correspondance would appear to discount concerns regarding the adequacy of the response time of the dissolved oxygen probe.

Light attenuation was somewhat correlated with chlorophyll-a; however, there was clearly much higher light attentuation in the Benedict area than in the patch near Broomes Island. This suggests that either suspended solids and/or dissolved organics were also attenuating light at the Benedict patch to a greater extent than at the Broomes Island patch. This may be the cause of the apparently higher dissolved oxygen production at the Broomes Island patch.

## 7.4 Spatial Scales of Variability

One of the important uses of very high resolution sampling is to identify the minimum spatial resolution needed to embody most of the information contained at the highest resolution. This type of information can be obtained from autocorrelograms (Figure 7-4). Autocorrelograms illustrate the rate of decline of correlation among observations as the distance between them increases. Such correlation is called "auto" correlation because the points are members of the same spatial series (*i.e.* the same cruise track). The autocorrelograms for total chlorophyll-a and dissolved oxygen indicate similar rates of decline in spatial autocorrelation for lags of up to approximately 1 km. Beyond 1 km, however, dissolved oxygen observations became essentially independent - i.e. lacking spatial autocorrelation. Thus, to describe the dissolved oxygen distribution would require sampling at a spatial resolution of less than 1 km. Practically, this can only be accomplished with a high resolution sampling device such as DATAFLOW. Chlorophyll-a concentrations remained somewhat correlated at slightly longer length scales, probably reflecting the presence of the larger phytoplankton patches.



Figure 7-4. Correlograms illustrating the length scales of spatial variability for chlorophylla and surface dissolved oxygen on 8/12/98. The scale of the x-axis is lag observation, which corresponds to approximately 100 meters per lag.

Nonetheless, the same conclusion applies for chlorophyll-a as for dissolved oxygen; high resolution sampling is required to characterize the phytoplankton distribution.

#### 7.5 Future Work

The results presented here describe one of a small number of mapping excursions conducted in Patuxent River since the DATAFLOW instrument was obtained. In addition, sampling was conducted in the middle Chesapeake Bay on 6 consecutive days as part of project supported by the National Science Foundation. Each of these distributions revealed interesting features upon mapping. Thus, there are two main needs suggested by this type of sampling. First, much more sampling is needed to describe the full range of water quality distribution that may be expected. Secondly, but of no lesser importance, is the need for analysis. An enormous quantity of data were collected with the result that an aggressive data analysis effort is required to obtain the most information possible from the data.


Figure 7-3. Maps of dissolved oxygen, total chlorophyll-a and light attenuation in the lower Patuxent River on 8/13/98.

## 8. 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 and 1998), and the analyzes presented in this report, the following observations are provided which have relevance to water quality management in the Patuxent River estuary.

Nutrient loading data (fall line load of TN and TP; above and below fall line point source loads of TN and TP) for the Patuxent River were reviewed for the period 1984-1996. A summary of that review is again included here because decreases 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). 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<sup>-1</sup> year<sup>-1</sup>. Both TN and TP loads during 1995 were, or were close to, the lowest on record since 1984. This inspection of loads will be extended to include 1998 data when they become available. Given the distinctive spring pulse in flow observed during 1998, diffuse source loads were probably moderate, at least compared to those observed during 1996 and some of the other high flow years observed during the late 1980s (1989) and 1990s (1993, 1994, 1996). It is also important to note that while loads increased in 1993 and 1994 (years of strong river flow) the increases were small, barely larger than loads associated with recent dry year loads, and much smaller than loads associated with wet years during the late 1980's. Thus, there is evidence that substantial nutrient load reductions have occurred in recent years.

**Dissolved oxygen conditions** in the Patuxent River were evaluated using an intensive spatial mapping approach for the first time during 1998. A total of 37 stations were sampled during June - September and the area of the bottom with dissolved oxygen conditions less than 2 mg l<sup>-1</sup> computed. There were small hypoxic zones (0.064 km<sup>2</sup>) during June, about 13 km<sup>2</sup> during July and none in August and September. Major hypoxic areas were located in deep waters in the vicinity of Broomes Island and St. Leonard Creek. The relatively brief period during which hypoxic conditions. While DO conditions in 1998 were not as high as those observed during 1995 which was a low flow (and nutrient load) year summer dissolved oxygen conditions were not depressed during August, 1998 as they were during August, 1997. The estimates of hypoxic areas developed from intensive mapping of bottom water DO conditions were compared with less intensive sampling at channel stations over estimated hypoxic areas almost by a

factor of four. Attention to spatial gradients related to depth and proximity to shorelines is needed and worth the effort.

Ammonium  $(NH_4^+)$  fluxes at long-term monitoring stations (BUVA, MRPT, BRIS and STLC) in the Patuxent River were generally higher than the long-term average and much above the long term average during July (at BUVA) and July and August at MRPT. The higher than average fluxes at these stations may well be a response to nutrient loads associated with a strong spring freshet. The large reductions in ammonium flux between 1996 (a year of high nutrient load and very high river flow) and 1997 and the increased fluxes in 1998 parallels patterns of spring flow and nutrient loading. This "same year" responses 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 support enhanced 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. The enhanced ammonium flux at the most up river station (BUVA) is part of a statistically significant trend at this site. The reasons for this are not definitely known but several possibilities exist. First, because of reductions in turbidity in the upper river chlorophyll-a stocks have increased. Enhanced ammonium fluxes could be the result of this material being deposited in the vicinity of BUVA. Second, enhanced fluxes could be the result of an expanding benthic invertebrate community; enhanced ammonium fluxes can result from the excretion of wastes from infauna and from the bioturbating activities of these animals.

Positive *sediment nitrate flux* (fluxes directed from sediments to the water column) is a definite sign of sediment nitrification activity which is a microbial process converting ammonium to nitrate and one that requires that oxygen be present. Positive nitrate fluxes are a sign of good sediment quality. Positive fluxes were observed during June, 1997 at three stations where bottom water oxygen concentrations were adequate (STLC, MRPT and BUVA). During 1998 there were also some positive fluxes although these were not large. We continue to believe that the presence of positive nitrate flux is a good tool for monitoring the biogeochemical health of sediments.

During 1997, *inorganic phosphate* ( $PO_4$  or DIP) *fluxes* were near or below the long-term average at all sites except during July when very high values were observed at three stations (BUVA, MRPT and BRIS). Experimental studies involving phosphorus (PO4-) flux and dissolved oxygen (DO) conditions indicated a tight coupling between flux and DO status and further indicated that the time needed for estuarine sediments to respond to decreased loading rates is probably quite short (weeks to months) despite large storages of particulate nutrients in sediments (Jasinski, 1995). It appears that sediment phosphorus fluxes have responded to reduced inputs of phosphorus and that sediments do not contain active phosphorus reserves that can sustain high sediment releases beyond the annual time scale.

An analysis of sediment oxygen and nutrient exchanges (SONE) data for *status and trends* was again completed for all Patuxent River stations. Indications of current status (average of fluxes during 1996, 1997 and 1998) were as expected; status was poor or fair

in areas exposed to high rates of loading, status was poor or fair in areas with low DO levels during summer months and status was poor or fair at locations proximal to nutrient sources. At other locations status was fair to good for most flux variables. The high load year of 1996 probably moved several status bars towards poorer conditions than would have been the case if recent river flows had been lower. There were few statistically significant trends evident at the Patuxent River stations with the strong exception of the most up river site (BUVA) where there are strong increases in SOC, ammonium and nitrite fluxes. We conclude that nutrient load reductions have not been large enough to allow for detection of interannual trends at other stations which is not surprising given the large interannual differences observed in river flows and loading rates.

Results of *sediment chlorophyll mapping* in the Patuxent River indicated substantial (> 2x) month to month variability in the mass of deposited chlorophyll from May through September, 1998. Sediment chlorophyll-a levels were highest following deposition of the spring phytoplankton in May and then were lower for the rest of the summer. During most of the monitoring period chlorophyll mass tended to be highest in deeper areas (possibly because of particulate material focusing) and in the saltier portion of the mesohaline reach. It is in this reach that water column monitoring data indicate that spring and summer algal blooms occur with regularity. Thus, there is an emerging understanding linking production and deposition of labile organic matter in this system. The mass of chlorophyll-a deposited to sediments was computed using both the most intensive spatial array of stations (37) and a less intensive array (10). There was not a statistically significant difference between these two approaches. However, there was more variability associated with the more intensive sampling approach probably reflecting the greater diversity of habitats measured. For the third year, a MINI-SONE set of measurements was completed at six stations in the Patuxent River (in addition to measurements made at the four long-term sites in the Patuxent River). MINI-SONE measurements are a simplification of SONE measurements (e.g. one sediment core per station) and have been added to the EPC program as a means of increasing the spatial extent of sediment process measurements and to assist in the development of predictive statistical models of sediment-water exchanges. MINI-SONE flux measurements made in 1998 were almost uniformly larger in magnitude than those observed during 1997. This is consistent with current understanding of the influence of loading on sediment-water exchanges (river flows and associated nutrient loads were higher in 1998 than in 1997). Using sediment chlorophyll mass as one of several key variables (others include sediment Eh and bottom water oxygen and nutrient concentrations), statistically significant *regression models* (linear single and multiple variable models) were developed for SOC, ammonium, phosphorus and nitrite plus nitrate fluxes. This analysis was repeated using 1997 data and repeated again using the combined 1996, 1997 and 1998 data sets. Results continued to indicate that this approach has great merit. We recommend that MINI-SONE and spatially intensive mapping of sediment chlorophyll-a and bottom water quality conditions be adopted for both traditional monitoring purposes and for verification of statistical sediment-water flux modeling. It is clear that spatial variability in these processes is an important feature and that this variability is understandable in the context of environmental conditions. Finally, spatially intensive measurements allows reasonable estimates to be made at larger scales such as the full estuary which are of direct interest to management.

The Benedict Bridge *high frequency sampling* effort generated a nearly continuous record of salinity, water temperature and dissolved oxygen from June through mid-September, 1998. The high frequency sampling is important because extreme values, often observed for only short periods of time, may have large ecological impacts due to the non-linear nature of many biological responses. These extreme values are not likely to be observed with conventional periodic sampling and, if measured, may be perceived as erroneous without the context of high frequency observations. An algorithm was developed during 1996 to estimate metabolic parameters such as net production and respiration using the high frequency dissolved oxygen observations and this algorithm was used again in 1998 with some improvements. Net daytime production was in the range of -2.5 to 3.5 g  $O_2$  m<sup>-3</sup> day<sup>-1</sup>, while nighttime respiration ranged from near zero to -4.5 g  $O_2$  m<sup>-3</sup> day<sup>-1</sup>. These observations indicated generally lower levels of metabolic activity than were observed in 1992 and 1996, but considerably greater than in 1964, 1965 and 1966 when nutrient loading rates to the estuary were lower. Data collected during 1996 were examined for relationships with possible controlling factors; analyzes indicated at about 60% of daily variability in metabolism could be accounted for by temperature and daily insolation. In addition, seasonal average metabolic rates were examined for relationships to nutrient loading rates; initial simple regression analysis did not indicate significant relationships but when seasonal or annual nutrient loads were scaled by water residence time for this sector of the estuary very significant, positive relationships emerged. Again, this indicates the importance of both loading rates and the particular characteristics (residence time in this case) of the estuary being monitored. These analyzes are part of a continuing effort to establish relationships between ecosystem performance and key management objectives (effects of nutrient load reductions in this case).

During 1998 an ambitious and broad evaluation of littoral zone habitats was continued in the lower 35 km of the Patuxent River estuary (mesohaline zone) concerning the suitability of this region for SAV growth and possible reintroduction. The stimulus for this program was the observation that substantial nutrient load reductions recently achieved in this system have led to improving water quality conditions with little or no resurgence in SAV. The goal of this program element was to accurately measure and characterize many of the complex and interacting parameters necessary for SAV growth and survival in this shallow water habitat. As part of the baseline assessment, a full suite of water quality parameters was measured along the salinity gradient of the estuary from April through October 1998. Results of near shore water quality sampling indicate substantial temporal and spatial variation along the longitudinal axis of much of the Patuxent River. In general, water quality conditions were much better during the spring months of April, May and June, but deteriorated rapidly through the summer months. Although down river locations appear to have slightly better water quality conditions compared to up-river locations, overall most locations experienced water quality conditions for at least brief periods of time that do not meet estimated minimum habitat requirements for SAV growth and survival. In addition, estimates of epiphytic light

attenuation during summer months suggested that after 20 days of exposure, epiphytic growth can potentially remove up to 80% of the available light reaching the leaves of SAV. Despite water quality conditions that overall were near or exceeded estimated limits for SAV growth and survival, certain early spring species of SAV were able to exist, and at some locations thrive, on the Patuxent River. These species complete their life cycle before water quality conditions become detrimental. Epiphytic fouling appears to be directly and very strongly correlated with light availability and because of this fouling rates were greatest in the clearer portions of the estuary. This finding suggests that nutrient concentrations (or probably more accurately the rate at which nutrients are delivered to SAV epiphytes) is still too high to be limiting to the growth of epiphyte communities. The 1997 and 1998 monitoring provided baseline information about these near shore habitats; we recommend that additional monitoring be conducted to evaluate inter-annual variability since the success and growth of SAV requires consistent water quality conditions from year to year. Finally, since light availability is a critical requirement for SAV survival, we recommend a more diversified study of SAV epiphyte light attenuation and development of a simple and useful monitoring tool for SAV habitat evaluation.

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