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MARYLAND DEPARTMENT OF THE ENVIRONMENT

MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT NO. 8

PART 1: INTERPRETIVE REPORT

(January 1990 - December 1990)

PREPARED FOR:

Maryland Department of the Environment 2500 Broening Highway Baltimore, MD 21224

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PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in Contract 20-C-MDE-91 between the Maryland Department of the Environment (MDE), Chesapeake Bay and Special Projects Program and the University of Maryland, Center for Environmental and Estuarine Studies (CEES).

This report contains a brief description of sampling procedures used by the Ecosystems Processes Component (EPC) of Maryland's Chesapeake Bay Water Quality Monitoring Program to collect data. The major portion of the text documents various processes detected and the significance of interactions between the three most important nutrients: carbon, nitrogen and phosphorus. The hard copy listing of data collected by the EPC during 1991 is incorporated in Data Volumes III and IV (Boynton *et al.*, 1992¹ [UMCEES]CBL Ref. No. 92-042) of the four reference data volumes. Data collected during SONE cruise No. 24 through 28 is found in Appendix B (Continued), Volume III, and tables of VFX data in Appendix C (Continued), Volume IV. An additional section, Appendix D, Volume IV, contains data collected in association with a larger investigation of physical, chemical and biological characteristics of the deep channel region (deep trough) of the bay immediately south of the Bay Bridge at Annapolis.

SONE and VFX data for all previous years, August 1984 through December 1989, were submitted in two volumes with the Level 1, No 7 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 90-062 (Boynton *et. al.*, 1990). Change pages, with correction bars in the right margin indicating corrected data values, will be issued with future reports for insertion into data volumes as errors are encountered. One such set of update sets has been inserted into the data volumes I and II Boynton, Rohland and Matteson, 1992)².

Variable names, used in data tables, together with a description of the units presently used in these programs, and the matching variable used in the public information data base of the Chesapeake Bay Program called CHESSEE are listed in Appendix A Volume I (Boynton *et. al.*, 1990), and in the EPC Data Dictionary (Boynton and Rohland, 1990). Entries are arranged alphabetically using the MDE/EPC table names. A copy of the Ecosystem Processes Component Data Dictionary is available on request from Dr. R. Eskin (Maryland Department of the Environment) or from Dr. F.M. Rohland (Chesapeake Biological Laboratory). Any specific questions concerning changes in file or variable names should be directed to: Dr. F.M. Rohland: Tel. (410) 326-7215.

¹ Boynton, W.R., W.M. Kemp, J.M. Barnes, L.L. Matteson, J.L. Watts, S. Stammerjohn, D.A. Jasinski and F.M. Rohland. 1992. Ecosystem Processes Component Level 1 Interpretive Report No 9. Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. [UMCEES]CBL Ref. No. 92-042.

This reference is correct. It was finalized between the time this report appeared in draft form and in final format.

² Boynton, W.R., F.M. Rohland and L.L. Matteson. 1992. Update Pages (Volumes I and II). Chesapeake Biological Laboratory (CBL), University of Maryland System, Solomons, MD 20688-0038. [UMCEES]CBL Ref. No. 92-105.

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APPENDIX B

(Volume III: Boynton et al., 1992: [UMCEES]CBL Ref. No. 90-062)

1990:

SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) **DATA SET:**

DATA FILES FOR SONE PROGRAM: CRUISES 24 - 28 (January - December 1990)

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Vertical profiles of temperature, salinity, dissolved oxygen FILENAME: H2OPRFxx

1990

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SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) DATA SET:

DATA FILES FOR SONE PROGRAM: CRUISES 24 - 28 (January - December 1990)

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Vertical profiles of percentage H₂O particulates and pore water nutrients at SONE stations FILENAME: CORPRFxx

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SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) DATA SET:

DATA FILES FOR SONE PROGRAM: CRUISES 24 - 28

B-6. SEDIMENT-WATER FLUX:

Net sediment-water exchange rates of dissolved oxygen $[gO_2/(m^{2*}day)]$ and nutrients $[\mu M N, P, Si and S/(m^{2*}hr)]$B6-1 FILENAME: SWFLUXxx

(January - December 1990)

1990

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SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) DATA SET: DEEP TROUGH SITE: (Volume IV: Boynton et al., 1992: [UMCEES]CBL Ref. No. 92-042)

(July - August 1990)

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SEDIMENT OXYGEN AND NUTRIENT EXCHANGES (SONE) DATA SET: (Continued) DEEP TROUGH SITE: (Volume IV: Boynton et al., 1992: [UMCEES]CBL Ref. No. 92-042)

(July - August 1990)

D-4. CORE DATA:

1990 D-4.1. July and August 1990

D-5. SEDIMENT-WATER FLUX:

Net sediment-water exchange rates of
dissolved oxygen $[gO_2/(m^{2*}day)]$ and nutrients
$[\mu M N, P, Si and S/(m^{2*}hr)]$
FILENAME: DTSFLXxx

1990

D-5.1. July and August 1990......D5-1

ABSTRACT

The objectives of the Ecosystem Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program are to: (1) characterize the present state of the bay relative to sediment-water nutrient and oxygen exchanges and the deposition rate of particulate materials to deep waters, (2) determine the long-term trends that develop in sediment-water exchanges and deposition rates in response to pollution control programs, and (3) integrate the information collected in this program with other elements of the monitoring program. Measurements of sediment-water nutrient and oxygen exchanges are made five times per year between May and October at a total of eight mainstem bay and tributary river stations. Deposition rates are monitored almost continuously during spring, summer and fall periods at one mainstem Bay location. This program was initiated in July 1984, and the basic data collected during 1990 but emphasizes examinations of trends and relationships among variables collected during the entire monitoring period.

Sediment trap data collected during 1990 indicated a well-developed spring deposition period which began in early March, reached a peak in early May and then declined sharply. The single highest rate of total chlorophyll-a deposition yet observed was recorded in 1990 (36.6 mg m⁻² d⁻¹). Summer deposition rates were uniformly low (2.5-6.0 mg m⁻² d⁻¹) and there was an indication of a fall deposition event in early October (15 mg m⁻² d⁻¹). The seasonal pattern of deposition was similar to other years, except 1989, when the spring deposition period was very limited. Average deposition rates of total chlorophyll-a following the spring bloom were higher in 1990 than in any year since 1985 and exceeded 1989 deposition rates by a factor of two.

Sediment-water fluxes of oxygen were similar to previous years except in the Patuxent and Choptank Rivers where fluxes were somewhat larger; NH_4^+ fluxes were also similar to those observed earlier except in the upper Patuxent River where rates were slightly elevated; fluxes of $NO_2^- + NO_3^-$ from sediments to water continued to be the dominant pattern only at lower tributary sites not exposed to hypoxic conditions. Fluxes were more negative in the upper Patuxent River during 1990; inorganic phosphate (PO_4^-) fluxes were similar to those observed in previous years; silicate fluxes (Si) were often higher than in previous years, particularly in the upper Patuxent and lower Choptank Rivers. Fluxes of ammonium and dissolved inorganic phosphorus measured in the deep trough area of the bay south of the bay bridge at Annapolis were high but comparable to rates measured in other enriched zones of the bay.

Efforts to detect relationships between nutrient loading rates and selected environmental variables were expanded and the following preliminary conclusions emerged: (1) all sediment fluxes except Si were found to be correlated with N-loading but not with P-loading rates, (2) sediment fluxes were also well correlated with sediment concentrations of PN but less so with sediment PC or total chlorophyll-a concentrations and not at all with sediment PP concentrations, (3) spring deposition rates measured at one location in the mainstem bay, particularly an estimate that was corrected for resuspension effects, were correlated with nutrient loading rates. Other indices of deposition also indicated positive trends relative to nutrient loading rates but were not as strong, (4) examination of several small data sets containing high frequency measurements of sediment fluxes indicated a strong linkage between the magnitude of fluxes and deposition. Furthermore, lag times between deposition and sediment flux responses were small, ranging from days in summer to several weeks in early spring, (5) rates of oxygen decline in deep waters of the mainstem bay were also well correlated with spring deposition rates but not with measures of particulate material in the water column.

2. INTRODUCTION

During the past decade much has been learned about the effects of both natural and anthropogenic nutrient inputs (e.g., nitrogen, phosphorus, silica) on such important estuarine features as phytoplankton production, algal biomass, seagrass abundance and oxygen conditions in deep waters (Nixon, 1981; Kemp et al., 1983; D'Elia et al., 1983). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality issues. Of particular importance here, it has been determined that (1) algal primary production and biomass levels in many estuaries (including Chesapeake Bay) are responsive to nutrient loading rates, (2) high rates of algal production are sustained through summer and fall periods by benthic recycling of essential nutrients and (3) deposition of organic matter from surface to deep waters links these processes of production and consumption (Boynton et al., 1982a; Wassmann, 1984 and Christensen and Kanneworff, 1986).

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

Research conducted in Chesapeake Bay and other estuaries indicates that estuarine sediments can act as both important storages and sources of nutrients as well as sites of intense organic matter and oxygen consumption (Kemp and Boynton, 1984). For example, during summer periods in the Choptank and Patuxent estuaries, 40-70% of the total oxygen utilization was associated with sediments and 25-70% of algal nitrogen demand was supplied from estuarine sediments (Boynton *et al.*, 1982b). Processes of this magnitude have a pronounced effect on estuarine water quality and habitat conditions. Sediments in much of Chesapeake Bay, especially the upper Bay and tributary rivers, contain significant amounts of carbon, nitrogen, phosphorus and other compounds (Boynton *et al.*, 1991a). A large percentage of this material appears to reach sediments following the termination of the spring bloom and again after the fall bloom. A portion of this material is available to regenerative processes and once transformed into inorganic nutrients becomes available for algal utilization. Nutrients and other materials deposited or buried in sediments represent the potential "water quality memory" of the Bay.

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

Nutrients and organic matter enter the Bay from a variety of sources, including sewage treatment plant effluents, fluvial inputs, local non-point drainage and direct rainfall on Bay waters. These dissolved nutrients are rapidly incorporated into particulate matter via biological, chemical and physical mechanisms. Much of this particulate material then sinks to the bottom and is potentially available for remineralization. Essential nutrients released during the decomposition of organic matter may then again be utilized by algal communities. A portion of this newly produced organic matter sinks to the bottom, contributing to the development of anoxic conditions and the loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative capacities and the potentially large nutrient storages in bottom sediments insures a large return flux of nutrients from sediments to the water column and thus sustains continued phytoplankton growth. Continued growth supports deposition of organics to deep waters, creating anoxic conditions typically associated with eutrophication of estuarine systems.

To a considerable extent, it is the magnitude of these processes which determines nutrient and oxygen water quality conditions in many zones of the Bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are implemented and loadings decrease, changes in the magnitude of the processes monitored in this program will serve as a guide in determining the effectiveness of strategies aimed at improving Bay water quality and habitat conditions.

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

2.3 Objectives of the Water Quality Monitoring Program

The objectives of the Ecosystem Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program are to:

1) Characterize the present state of the bay (including spatial and seasonal variation) relative to sediment-water nutrient exchanges and oxygen consumption and the rate at which organic and inorganic particulate materials reach deep waters and the sediment surface.

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

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

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

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

The first phase of the study was undertaken over a period of four years (1984 through 1987) and had as its goal the characterization of the existing state of the Bay, including spatial and seasonal variation, and better identification of problem areas. The EPC determined sediment-water nutrient and oxygen exchange rates and rates at which organic and inorganic particulate materials reached deep waters and the sediment surface. Sediment-water

exchanges and deposition 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 reports (Boynton *et al.*, 1985a, 1986, 1987, 1989, 1990). The results of the 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, scheduled for completion during 1988-1991, was the identification of 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, 1991; Boynton *et al.*, 1991a).

In 1991 the program entered its third phase. During this phase the long-term 40% nutrient reduction strategy for the bay is to be re-evaluated. Basin-specific nutrient reduction guidelines will be developed together with additional guidelines addressing nutrient load reduction in tributary rivers. In this phase of the process, monitoring program data are to be used, in conjunction with results from the Chesapeake Bay water quality model, to assess the appropriateness of targeted nutrient load reductions as well as provide indications of water quality patterns which will most likely result from such management actions.

In this report EPC program data collected between 1985-1990 have been examined with particular emphasis placed on detection of trends in sediment-water exchanges and deposition rates in response to inter-annual changes in nutrient loading rates. In addition, a comparative approach was adopted for some analyses to determine the magnitude of sediment-water exchange rates under reduced nutrient loading regimes.

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3. PROJECT DESCRIPTION

Measurements of sediment-water nutrient and oxygen exchanges are made on a quarterly basis (five times per year beginning in 1989) at locations in the mainstem Bay and in each of three major tributary rivers (Patuxent, Choptank, and Potomac). These same parameters were monitored during the summer of 1990 (July and August) at two Deep Trough stations in the proposed deep water dredge disposal areas south of the Bay Bridge at Annapolis, MD. Deposition rates are monitored at one mainstem Bay location, in the central anoxic region. Deposition measurements are made almost continuously during the spring, summer and fall periods, but less frequently during the winter. Activities in this program have been coordinated with other components of the Maryland Chesapeake Bay Water Quality Monitoring Program in terms of station locations, sampling frequency, methodologies, data storage and transmission, reporting schedules and data synthesis. This program was initiated in July 1984 and the basic data collection scheme has been followed through December 1990.

Figure 3-1 shows the sampling locations for both the sediment oxygen and nutrient exchange (SONE) and the vertical flux monitoring (VFX) programs. A comprehensive listing of all SONE, Deep Trough and VFX stations, providing the station code names, associated latitude and longitude, basin and station location description and references to the nearest MDE station are outlined in Tables 3-1.1., 3-1.2. and 3-1.3. and in the Ecosystem Processes Component (EPC) Data Dictionary (Tables B-5.1., B-5.2. and B-5.3.). In 1990, two of the eight stations sampled as part of the SONE study are located in the mainstem Bay adjacent to Point No Point (north of the mouth of the Potomac River) and Buoy R-64 (south of the Choptank River mouth) and one each in the lower mesohaline regions of the Choptank and Potomac Rivers. Four stations are located in the Patuxent River estuary and one each in the lower mesohaline regions of the Choptank and Potomac Rivers. The two Deep Trough stations are located in the mainstem of the Bay Bridge at Annapolis, MD (Figure 3-2). The VFX station is located in the mainstem of the Bay in the central anoxic region (Figure 3-1). The salinity characteristics of each station and the four salinity codes are listed in Table 3-2 (also in EPC Data Dictionary Table B-7.).

3.1 Justification of Station Locations

3.1.1 SONE Stations

Locations of SONE stations (Figure 3-1 and Tables 3-1.1., 3-1.2. and 3-1.3; EPC Data Dictionary Figure B-6 and Tables B-5.2 and B-5.3.) were selected based on prior knowledge of the general patterns of sediment-water nutrient and oxygen exchanges in Chesapeake Bay. Several earlier studies (Boynton *et al.*, 1980, 1985b and Boynton and Kemp, 1985) reported the following:

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

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

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

In a few instances (Patuxent stations and Choptank station at Horn Point) SONE stations are not located exactly at the same site as other Maryland Chesapeake Bay Water Quality Monitoring Program stations, although they are close (< 10 km). The prime reason for including these stations was the considerable amount of benthic flux data available from the SONE sites selected in the Patuxent and Choptank that could be used by the monitoring program. In all cases our stations and the MDE stations are in the same estuarine zone. Benthic fluxes are reasonably similar over small spatial scales (10-20 km) within estuarine zones of similar salinity, sediment type and depth; therefore, this program retains a high degree of comparability with other program components (Boynton *et al.*, 1982b).

Beginning July 1989 the number and location of SONE sampling stations was revised. Prior to July 1989, four of the ten stations sampled were located along the salinity gradient in the mainstem Bay between Point No Point (north of the mouth of the Potomac River) and Still Pond Neck (20 km south of the Susquehanna River mouth). Two stations were located in each of three tributary rivers (Patuxent River: Buena Vista and St. Leonard Creek, Choptank River: Windy Hill and Horn Point and Potomac River: Maryland Point and Ragged Point), one in the turbidity maximum or salinity transition zone and one in the lower mesohaline region. After July 1, 1989 sampling at all of the upper tributaries (except in the Patuxent River) and sampling at the two upper mainstem stations was discontinued and two stations (Marsh Point [MRPT] and Broomes Island[BRIS]) were added in the Patuxent River (Figure 3-1). These modifications were made in response to budget constraints, but also to improve spatial resolution in the Patuxent River which is a focal point of management activities.

3.1.2 Deep Trough Stations

This section of the program was initiated in August, 1989 and funding for four stations (DT-1, DT-4, DT-7 and DT-10) during that year was provided as a private consulting contract from VERSAR, Inc. This location (Figure 3-2 and Tables 3-1.1., 3-1.2. and 3-1.3; EPC Data Dictionary Figure B-6 and Tables B-5.2 and B-5.3.) in the deep channel area was being considered as a potential, additional site to accommodate disposal of dredge spoil resulting from continued maintenance dredging and proposed deepening of the approach channels to Baltimore Harbor. Over the years dredging of approach and inner harbor channels has been essential in order to maintain sufficient depths for the passage of commercial shipping vessels. During 1990 measurements were taken twice during the summer (July and August) at two additional stations (Figure 3-2), one south (DT-S1) and one north (DT-N1) of the original four stations. Funding for this portion of the project was made available by Maryland Department of the Environment.

3.1.3 VFX Stations

The use of sediment trap methodology to determine the net vertical flux of particulate material is restricted to the deeper portions of the Bay. In shallower areas local resuspension of bottom sediments is sufficiently large to mask the downward flux of "new" material. Hence, sediment traps are not a useful tool in the upper reaches of the mainstem

bay and in many tributary areas. The sediment trap array is positioned near the center of the region experiencing seasonal anoxia (Figure 3-1) to monitor the vertical flux of particulate organics reaching deeper waters. This location is close to MDE station 4.3.C. Since sediment traps are moored pieces of gear and exposed to damage or loss by commercial boat traffic, the location was selected to be out of main traffic lanes, but still close to the MDE station.



Figure 3-1. Location of current and previous SONE and VFX Monitoring Stations in the Maryland Portion of Chesapeake Bay



Figure 3-2. Location of stations sampled during the Deep Trough sediment-water flux survey

REGION	STATION NAME	STATION CODE NAME	SAMPLING ORDER ³ A B
Patuxent River	St. Leonard Creek	STLC	1 1
	Broomes Island	BRIS	2
	Marsh Point	MRPT	3
	Buena Vista	BUVA	2 4
Choptank River	Horn Point	HNPT	3 5
	Windy Hill	WDHL	4
Potomac River	Ragged Point	RGPT	56
	Maryland Point	MDPT	6
Chesapeake Mainstream	Point No Point	PNPT	7 7
	Buoy R-64 ¹	R-64	8 8
	Dares Beach	DRBH	x
	Thomas Point	TMPT	*
	Buoy R-78 ²	R-78	9
	Still Pond	SLPD	10
Chesapeake Mainstream - Deep Trough		DT-1	#
		DT-4	#
		DT-7	#
		DT-10	#
		DT-S1 ⁴	9
		DT-N1 ⁴	10

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

NOTES:

Stations sampled in SONE 1 - 21, August 1984 - June 1989. Numerical ranking indicates the order in which A = they appear in the data tables.

B = Stations sampled beginning with SONE 22 and future samples. Numerical ranking indicates the order in which they appear in the data tables.

* = Thomas Point was sampled July - August 1984. Thomas Point was replaced by station R-78. x = Dares Beach was a VFX station sampled from 11 July 1985 to 14 November 1986

= Four deep trough stations sampled during SONE 22 in August 1989. Funding for these measurements provided as a private consulting contract from VERSAR. This is the only current VFX station.

1 =

2 = This was also a VFX station which was sampled from 17 September 1984 to 27 June 1985.

3 = Prior to July 1, 1989, measurements at SONE stations were made four times per year (April or May, June, August and October or November). After this date, measurements were made five times per year (May, June, July, August and October).

4 = Two additional deep trough stations sampled during SONES 26 and 27, July and August 1990.

STATION CODE NAME	LATITUDE DEG MIN	LONGITUDE DEG MIN	STATION DEPTH	MDE STATION	BAY SEGMENT
Patuxent River					
STLC	38° 22.88'	76° 30.06'	7.0	XDE2792	LE1
BRIS	38° 23.64'	76° 33.17'	15.0	XDE2792	LE1
MRPT	38° 26.81'	76° 30.06'	5.2	XDE5339	LE1
BUVA	38° 31.12'	76° 39.82'	5.8	XDE9401	RET1
Choptank River					
HNPT	38° 37.18'	76° 08.09'	8.2	MET5.2	ET5
WDHL	38° 41.45'	77° 11.49'	3.8	NONE	ET5
Potomac River					
RGPT	38° 09.86'	76° 15.13'	16.5	XBE9541	LE2
MDPT	38° 21.37'	76° 26.63'	10.2	XDA1177	LE2
Chesapeake Mainstream			,		
PNPT	38° 07.99'	76° 15.13'	14.2	MCB5.2	CB5
R-64	38° 33.59'	76° 26.63'	16.8	MCB4.3C	CB4
DRBH	38° 33.50'	76° 29.30'	10.7	MCB4.3C	CB4
TMPT	38° 54.08'	76° 24,46'	52.0	MCB4.1W	CB4
R-78	38° 57.81'	76° 23.62'	15.8	MCB3.3C	CB4
SLPD	39° 20.87'	76° 10.87'	10.4	MCB2.2	CB2
Deep Trough					
DT-1	38° 53.86'	76° 23.60'	25.2	MCB4.0C	CB4
DT-4	38 [°] 54.96'	76° 23.47'	41.0	MCB4.0C	CB4
DT-7	38° 56.31'	76° 23.93'	20.5	MCB4.0C	CB4
DT-10	38° 56.75'	76° 23.64'	30.0	MCB4.0C	CB4
DT-S1	38° 52.76'	76° 23.81'	26.0	MCB4.1C	CB4
DT-N1	38° 58.72'	76° 22.23'	25.0	MCB3.3C	CB4

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

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Table 3-1.3. Station Code and Description

STATION CODE NAME	DESCRIPTION		
Patuxent River			
STLC	7.5 nautical miles upstream of Patuxent River mouth. ($R km^1 = 12.1$)		
BRIS	10 nautical miles upstream of Patuxent River mouth. (R km ¹ = 16.1)		
MRPT	14.5 nautical miles upstream of Patuxent River mouth. ($R km^1 = 23.4$)		
BUVA	0.75 nautical miles north of Route 231 Bridge at Benedict, MD. ($R km^1 = 31.5$)		
Choptank River			
HNPT	4.0 nautical miles downstream of Route 50 Bridge at Cambridge, MD. (R km ¹ = 18.6)		
WDHL	10.0 nautical miles upstream from Route 50 Bridge at Cambridge, MD. ($R \text{ km}^1 = 39.5$)		
Potomac River			
RGPT	1.5 nautical miles WNW of Buoy 51-B. ($R km^1 = 29.8$)		
MDPT	1250 yards SE of Buoy R-18. ($R \text{ km}^1 = 71.0$)		
Chesapeake Mainst	ream		
PNPT	3.2 nautical miles east of Point No Point. (R km ¹ = 129.0)		
R-64	300 yards north east of channel Buoy R-64.* ($R \text{ km}^1 = 177.4$)		
DRBH	West of channel Buoy R-64.* ($R \text{ km}^1 = 177.4$)		
TMPT	4.03 nautical miles south of channel Buoy R-78.* (R km ¹ = 219.3)		
R-78	200 yards NNW of channel Buoy R-78.* ($R \text{ km}^1 = 225.8$)		
SLPD	700 yards west of channel marker 41.* ($R km^1 = 258.1$)		
Chesapeake Mainst	Chesapeake Mainstream - Deep Trough		
DT-1	5.55 nautical miles south of Annapolis Bay Bridge, MD. ($R \text{ km}^1 = 113.2$)		
DT-4	4.5 nautical miles south of Annapolis Bay Bridge, MD. ($R km^1 = 115.2$)		
DT-7	3.25 nautical miles south of Annapolis Bay Bridge, MD. ($R km^1 = 117.5$)		
DT-10	2.6 nautical miles south of Annapolis Bay Bridge, MD. ($R \text{ km}^1 = 118.7$)		
DT-S1	6.4 nautical miles south of Annapolis Bay Bridge, MD. (R km ¹ = 111.7)		
DT-N1	0.65 nautical miles south of Annapolis Bay Bridge, MD. ($R km^1 = 122.3$)		

NOTES:

* Marked buoy numbers correspond to numbering system prior to USCG renumbering.

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

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Table 3-2. Station Salinity

STATION CODE	SALINITY CODE
Patuxent River	
STLC	M
BRIS	M
MRPT	M
BUVA	0
Choptank River	
HNPT	Μ
WDHL	0
Potomac River	
RGPT	<u>M</u>
MDPT	0
Chesapeake Mainstream	
PNPT	M
R-64 ·	•M
TMPT	M
R-78	M
SLPD	0
Chesapeake Mainstream - Deep Trough	
DT-1	_M
DT-4	M
DT-7	M
DT-10	M
DT-S1	M
DT-N1	M

The Salinity Zone layer codes are as follows:

SALINITY CODE	DESCRIPTION
F	Freshwater
0	Oligohaline 0.5 - 5.0 ppt
Μ	Mesohaline 5.0 - 18.0 ppt
P	Polyhaline 18.0 - 32.0 ppt

3.2 Sampling Frequency

3.2.1 SONE Stations

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

1) A period characterized by the presence of a large macrofaunal community, high concentrations of nitrite in surface waters and the development and deposition of the spring phytoplankton bloom (April - June).

2) A period during which macrofaunal biomass is low but water temperature and water column metabolic activity high with anoxia prevalent in deeper waters (July - September).

3) A period in the fall when anoxia is not present and macrofaunal community abundance is low but re-establishing (October - November).

4) A winter period when fluxes are very low and vary only slightly, during which the data collected would not add appreciably to our understanding of water quality conditions. No samples are collected during this period (December - March).

Previous studies also indicate that short-term temporal (day-month) variation in these exchanges is small; however, considerable differences in the magnitude and characteristics of fluxes appear among distinctively different estuarine zones (*i.e.*, tidal fresh vs. mesohaline regions). In light of these results, the monitoring design adopted for the SONE study involves quarterly measurements (five measurements per year since 1989: May, June, July, August and October). Review of data collected in concurrent sediment-water flux programs indicate that a better estimate of annual flux magnitude could be obtained by addition of another sampling period. A complete listing giving the sampling dates of all SONE cruises together with alpha-numeric cruise identification codes can be found in Table 3-3.1.

3.2.2 Deep Trough Stations

The original four stations (DT-1, DT-4, DT-7 and DT-10) were sampled only once during August 1989. Previous studies of sediment-water exchanges indicate that fluxes are largest during the warm seasons of the year when temperatures are in excess of 15 C (Boynton *et al.*, 1989). Additionally, phosphorus fluxes (PO_4^-) are largest during periods of hypoxia or anoxia which coincide with the summer season.

Two additional stations, DT-S1 and DT-N1, were sampled during July (SONE cruise 26) and August 1990. The purpose of making measurements at these sites was to establish baseline conditions prior to dredging operations and subsequently at yearly intervals to assess the impact of the operation should the site be selected. Sampling dates and alphanumeric cruise identification codes can be found in Table 3-3.5.

3.2.3 VFX Stations

The selection of sampling frequency for the VFX (organic deposition) monitoring program is governed by different constraints, although compatible with SONE sampling frequencies. Net deposition rates appear largest during the warm seasons of the year (April - October) and are lower during winter periods (November - March). Deposition of sediments and organics in one tributary of the Bay (Patuxent) followed a similar pattern (Boynton et al., 1982b; Kemp and Boynton, 1984). However, some variability occurs in warm season deposition rates, probably due to algal blooms of short duration (days - week), variation in zooplankton grazing rates (week - month) and other less well described features of the Bay. Given the importance of obtaining inter-annual estimates of organic matter deposition rates to deep waters of the Bay, sampling is almost continuous from spring to fall (March -November) and only occasional during the winter (December - February). Direct measurements of organic deposition to Bay sediments were monitored 19 to 31 times per year. To coordinate vertical deposition rate measurements with SONE measurements, sediment-water exchanges are monitored at the end of each intensive VFX deployment VFX measurements also coincide with other monitoring program sampling period. activities. The sampling schedule for this component of the monitoring program 1984-1986 is shown in Figure 3-3.1., for 1987-1989 in Figure 3-3.2. and for 1990 in Figure 3-3.3.(also EPC Data Dictionary Figures B-3, B-4 and B-5). Tables 3-3.1., 3-3.2., 3-3.3. and 3-3.4. (also EPC Data Dictionary Tables B-2.1., B-2.2., B-2.3. and B-2.4.) provide detailed cruise information including date, cruise number and research vessel.

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Figure 3-3.1. SONE and VFX Sampling Schedule for 1984-1986

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Figure 3-3.2. SONE and VFX Sampling Schedule for 1987 - 1989



Figure 3-3.3. SONE and VFX Sampling Schedule for 1990

CRUISE	DATE	BEGIN DATE	END DATE	RESEARCH VESSEL
SONE 01	AUG 1984	27 AUG	30 AUG	Aquarius
SONE 02	OCT 1984	15 OCT	18 OCT	Aquarius
SONE 03	MAY 1985	06 MAY	09 MAY	Aquarius
SONE 04	JUN 1985	24 JUN	27 JUN	Aquarius
SONE 05	AUG 1985	19 AUG	22 AUG	Aquarius
SONE 06	OCT 1985	14 OCT	17 OCT	Aquarius
SONE 07	MAY 1986	03 MAY	08 MAY	Aquarius
SONE 08	JUN 1986	23 JUN	26 JUN	Aquarius
SONE 09	AUG 1986	18 AUG	22 AUG	Orion
SONE 10	NOV 1986	10 NOV	<u>13 NOV</u>	Aquarius
SONE 11	APR 1987	20 APR	<u>23 APR</u>	Aquarius
SONE 12	JUN 1987	10 JUN	<u>15 JUN</u>	Aquarius
SONE 13	AUG 1987	17 AUG	20 AUG	Aquarius
SONE 14	NOV 1987	09 NOV	<u> 16 NOV</u>	Aquarius
SONE 15	APR 1988	17 APR	22 APR	Aquarius
SONE 16	JUN 1988	01 J <u>UN</u>	07 JUN	Aquarius
SONE 17	AUG 1988	15 AUG	21 AUG	Aquarius
SONE 18	NOV 1988	01 NOV	09 NOV	Aquarius
SONE 19	APR 1989	04 APR	10 APR	Aquarius
SONE 20	JUN 1989	12 JUN	16 JUN	Aquarius
SONE 21	JUL 1989	12 JUL	14 JUL_	Aquarius
SONE 22	AUG 1989	14 AUG	16 AUG	Aquarius
SONE 23	OCT 1989	16 OCT	18 OCT_	Aquarius
SONE 24	MAY 1990	1 MAY	3 MAY	Orion
		8 MAY	8 MAY	Aquarius
SONE 25	JUN 1990	11 JUN	14 JUN	Aquarius
SONE 26	JUL 1990	16 JUL	19 JUL	Aquarius
SONE 27	AUG 1990	17 AUG	22 AUG	Aquarius
SONE 28	OCT 1990	15 OCT	18 OCT	Aquarius

Table 3-3.1. SONE Cruise Identifier

Table 3-3.2 VFX Cruise Dates (23rd July 1984 to 30th August 1984) for Station Thomas Point(TMPT)

DATE	CRUISE NO.	RESEARCH VESSEL
23 JUL 1984	1042	Orion
30 JUL 1984	1046	Orion
07 AUG 1984	Note 1	Osprey
14 AUG 1984	Note 1	Osprey
22 AUG 1984	Note 1	Osprey
30 AUG 1984	766	Aquarius

NOTE 1: Divers Serviced Traps.

Table 3-3.3. VFX Cruise Dates (17th September 1984 to 27th June 1985) for Station R-78

DATE	CRUISE NO.	RESEARCH VESSEL
17 SEP 1984	774	Aquarius
24 SEP 1984	777	Aquarius
04 OCT 1984	784	Aquarius
<u>16 OCT 1984</u>	790	Aquarius
<u>30 NOV 1984</u>	802	Aquarius
<u>17 DEC 1984</u>	1082	Orion
<u>19 FEB 1985</u>	809	Aquarius
05 MAR 1985	1090	Orion
01 APR 1985	815	Aquarius
15 APR 1985	1097	Orion
<u>27 MAY 1985</u>	1109	Orion
05 JUN 1985	829	Aquarius
18 JUN 1985	1113	Orion
27 JUN 1985	833	Aquarius

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DATE	CRUISE NO.	RESEARCH VESSEL	DATE	CRUISE NO.	RESEARCH VESSEL
23 JUL 1984	1042	Orion	28 MAY 1986	1197	Orion
30 JUN 1984	1046	Orion	03 JUN 1986	1198	Orion
07 AUG 1984	Note 2	Osprey	12 JUN 1986	1201	Orion
14 AUG 1984	Note 2	Osprey	16 JUN 1986	906	Aquarius
22 AUG 1984	Note 2	Osprey	24 JUN 1986	910	Aquarius
30 AUG 1984	766	Aquarius	01 JUL 1986	912	Aquarius
17 SEP 1984	774	Aquarius	11 JUL 1986	915	Aquarius
24 SEP 1984	777	Aquarius	23 JUL 1986	1208	Orion
04 OCT 1984	784	Aquarius	30 JUL 1986	1212	Orion
16 OCT 1984	790	Aquarius	07 AUG 1986	1215	Orion
30 NOV 1984	802	Aquarius	14 AUG 1986	921	Aquarius
17 DEC 1984	1082	Orion	22 AUG 1986	1220	Orion
19 FEB 1985	809	Aquarius	14 OCT 1986	1231	Orion
05 MAR 1985	1090	Orion	23 OCT 1986	936	Aquarius
01 APR 1985	815	Aquarius	30 OCT 1986	1235	Orion
15 APR 1985	1097	Orion	06 NOV 1986	1237	Orion
30 APR 1985	1101	Orion	14 NOV 1986	941	Aquarius
08 MAY 1985	825	Aquarius	26 FEB 1987	1247	Orion
27 MAY 1985	1109	Orion	11 MAR 1987	1251	Orion
05 JUN 1985	829	Aquarius	25 MAR 1987	951	Aquarius
18 JUN 1985	1113	Orion	08 APR 1987	1256	Orion
25 JUN 1985	833	Aquarius	21 APR 1987	956	Aquarius
11 JUL 1985	1119	Orion	07 MAY 1987	959	Aguarius
24 JUL 1985	1123	Orion	12 MAY 1987	1272	Orion
30 JUL 1985	1125	Orion	19 MAY 1987	1276	Orion
05 AUG 1985	1128	Orion	26 MAY 1987	1279	Orion
13 AUG 1985	1130	Orion	02 JUN 1987	1283	Orion
21 AUG 1985	844	Aquarius	12 JUN 1987	968	Aquarius
17 SEP 1985	1141	Orion	17 JUN 1987	969	Aguarius
25 SEP 1985	851	Aquarius	23 JUN 1987	1288	Orion
01 OCT 1985	1146	Orion	01 JUL 1987	1292	Orion
16 OCT 1985	858	Aquarius	08 JUL 1987	1294	Orion
06 JAN 1986	1165	Orion	15 JUL 1987	1297	Orion
17 JAN 1986	872	Aquarius	23 JUL 1987	976	Aquarius
27 FEB 1986	884	Aquarius	28 JUL 1987	1301	Orion
12 MAR 1986	1170	Orion	05 AUG 1987	1304	Orion
28 MAR 1986	888	Aquarius	11 AUG 1987	1306	Orion
14 APR 1986	1178	Orion	18 AUG 1987	983	Aquarius
29 APR 1986	1185	Orion	14 OCT 1987	1323	Orion
05 MAY 1986	898	Aquarius	22 OCT 1987	998	Aquarius
14 MAY 1986	899	Aquarius	30 OCT 1987	1000	Aquarius
19 MAY 1986	1194	Orion	04 NOV 1987	1329	Orion

Table 3-3.4. VFX Cruise Dates (23rd July 1984 to 31st October 1990) for Station R-64 and DaresBeach (11th July 1985 to 14th November 1986).1

DATE	CRUISE NO.	RESEARCH VESSEL	DATE	CRUISE NO.	RESEARCH VESSEL
16 NOV 1987	1003	Aquarius	09 MAY 1989	1098	Aquarius
01 DEC 1987	1005	Aquarius	16 MAY 1989	1429	Orion
18 DEC 1987	1335	Orion	23 MAY 1989	1104	Aquarius
09 FEB 1988	1341	Orion	31 MAY 1989	1432	Orion
25 FEB 1988	1346	Orion	07 JUN 1989	1435	Orion
10 MAR 1988	1352	Orion	12 JUN 1989	1110	Aquarius
23 MAR 1988	1355	Orion	21 JUN 1989	1441	Orion
06 APR 1988	1015	Aquarius	27 JUN 1989	1112	Aquarius
22 APR 1988	1017	Aquarius	05 JUL 1989	1114	Aquarius
02 MAY 1988	1366	Orion	12 JUL 1989	1118	Aquarius
09 MAY 1988	1368	Orion	19 JUL 1989	1120	Aquarius
16 MAY 1988	1370	Orion	26 JUL 1989	1122	Aquarius
23 MAY 1988	1372	Orion	02 AUG 1989	1450	Orion
01 JUN 1988	1027*	Aquarius	09 <u>AUG 1989</u>	1128	Aquarius
08 JUN 1988	1027*	Aquarius	14 AUG 1989	1129	Aquarius
17 JUN 1988	1376	Orion	24 AUG 1989	1131	Aquarius
22 JUN 1988	1378	Orion	06 SEP 1989	1455	Orion
28 JUN 1988	1034	Aquarius	14 SEP 1989	1457	Orion
05 JUL 1988	1380	Orion	20 SEP 1989	1458	Orion
13 JUL 1988	1038	Aquarius	03 OCT 1989	1141	Aquarius
19 JUL 1988	1039	Aquarius	12 OCT 1989	1464	Orion
27 JUL <u>1988</u>	1385	Orion	17 OCT 1989	1146	Aquarius
04 AUG 1988	1043	Aquarius	02 NOV 1989	1469	Orion
11 AUG 1988	1389	Orion	08 NOV 1989	1470	Orion
17 AUG 1988	1047	Aquarius	15 NOV 1989	1155	Aquarius
06 SEP 1988	1392	Orion	30 NOV 1989	_1156	Aquarius
13 SEP 1988	1050	Aquarius	09 FEB 1990	_1483	Orion
19 SEP 1988	1395	Orion	21 FEB 1990	1487	Orion
12 OCT 1988	1401	Orion	08 MAR 1990	1489	Orion
17 OCT 1988	1404	Orion	22 MAR 1990	1492	Orion
24 OCT 1988	1066	Aquarius	06 APR 1990	1173	Aquarius
01 NOV 1988	1067*	Aquarius	19 APR 1990	1176	Aquarius
09 NOV 1988	1067*	Aquarius	01 MAY 1990	1499	Orion
17 NOV 1988	1070	Aquarius	08 MAY 1990	1180	Aquarius
23 NOV 1988	1408	Orion	15 MAY 1990	1181	Aquarius
08 FEB 1989	1082	Aquarius	01 JUN 1990	1505	Orion
27 FEB 1989	1084	Aquarius	08 JUN 1990	1186	Aquarius
10 MAR 1989	1087	Aquarius	13 JUN 1990	1187	Aquarius
22 MAR 1989	1089	Aquarius	21 JUN 1990	1189	Aquarius
05 APR 1989	1091	Aquarius	28 JUN 1990	1191	Aquarius
20 APR 1989	1093	Aquarius	05 JUL 1990	1193	Aquarius
02 MAY 1989	1426	Orion	10 JUL 1990	1509	Orion

Table 3-3.4. VFX Cruise Dates (23rd July 1984 to 31st October 1990) for Station R-64 and DaresBeach (11th July 1985 to 14th November 1986).1 - Continued

Table 3-3.4.	VFX Cruise	Dates (23rd	July 1984 to	31st October	1990) for	Station R-6	4 and Dares
Beac	h (11th July 1	1985 to 14th	November 19)86). ¹ - Contin	ued		

DATE	CRUISE NO.	RESEARCH VESSEL
16 JUL 1990	1195	Aquarius
26 JUL 1990	1515	Orion
01 AUG 1990	1198	Aquarius
08 AUG 1990	1522	Orion
17 AUG 1990	1203	Aquarius
21 AUG 1990	1203	Aquarius
05 SEP 1990	1525	Orion x

DATE	CRUISE NO.	RESEARCH VESSEL
06 SEP 1990	1526	Orion #
13 SEP 1990	1208	Aquarius
19 SEP 1990	1529	Orion
03 OCT 1990	1213	Aquarius
10 OCT 1990	1536	Orion
17 OCT 1990	1216	Aquarius

NOTES:

- 1. Dares Beach was sampled on the same VFX cruises as R-64 from 11 July 1985 to 14 November 1986.
- 2. Divers Serviced Traps.
- * Traps serviced at beginning and end of same SONE cruise.
- x Traps gone.
- # Traps reset.

Table 3-3.5. Deep Trough Cruise Dates (17th August 1989 to 8th August, 1990).

DATE	CRUISE NO.	RESEARCH VESSEL
17 AUG 1989	1130	Aquarius
18 AUG 1989		
16 JUL 1990	1195	Aquarius
17 JUL 1990	(SONE 26)	
08 AUG 1990	1522 (VFX Cruise)	Orion

4. DATA COLLECTION

4.1 Field Methods

Details concerning methodologies are described in the EPC Study Plan (Garber *et al.*, 1987) and fully documented in the EPC Data Dictionary (Boynton and Rohland, 1990). The following section provides an overview of field activities.

4.1.1 SONE Study

4.1.1.1 Water Column Profiles

At each of the ten SONE stations (eight stations since July 1989), vertical water column profiles of temperature, salinity and dissolved oxygen are obtained at 2 meter intervals from the surface to the bottom immediately prior to obtaining intact sediment cores for incubation. The turbidity of the water is measured using a Secchi disc.

4.1.1.2 Water Column Nutrients

Near-surface (approximately 0.5m) and near-bottom (approximately 1m) water samples are also collected using a high volume submersible pump system. Samples are filtered, where appropriate, using 0.7 μ m GF/F filter pads, and immediately frozen. Samples are analyzed for the following dissolved nutrients and particulate materials: ammonium (NH₄⁺), nitrite (NO₂⁻), nitrite plus nitrate (NO₂⁻ + NO₃⁻) dissolved inorganic phosphorus corrected for salinity (PO₄⁻ or DIP), silicious acid (Si(OH)₄), particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations and seston content.

Measurements of total dissolved nitrogen (TDN: $NH_4^+ + NO_2^- + NO_3^- + DON$), and total dissolved phosphorus (TDP: DIP + DOP) were discontinued at the end of the 1987 calendar year.

4.1.1.3 Sediment Profiles

At each SONE station an intact sediment core is used to measure Eh of sediments at 1 cm intervals to about 10 cm. Additionally, surficial sediments are sampled to a depth of 1cm (2mm since 9 August 1989) for particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), and total and active chlorophyll-a concentrations.

4.1.1.4 Sediment Cores

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

Three intact cores are used to estimate net exchanges of oxygen and dissolved nutrients between sediments and overlying waters (Figure 4-1). Prior to beginning flux measurements, the overlying water in the core is replaced by fresh bottom water to insure that water quality conditions in the core closely approximate in situ conditions. Gentle circulation of water, with no induction of sediment resuspension, is maintained in the cores during the measurement period via the stirring devices attached to the O_2 probes. The cores are placed in a darkened water bath to maintain ambient temperature. Oxygen concentrations are recorded and overlying water samples (35 ml) are extracted from each core every 30 or 60 minutes (depending on the rate of oxygen uptake) over a 2-5 hour incubation period. During the incubation period, five overlying water samples are extracted from each core. As a nutrient sample is extracted from a core, an equal amount of ambient bottom water is added. An opaque Plexiglass liner filled with bottom water, incubated and sampled as described above serves as a blank. Overlying water samples are filtered and immediately frozen for later analysis for ammonium (NH_4^+) , nitrite (NO_2^-) , nitrite plus nitrate $(NO_2^- + NO_3^-)$, dissolved inorganic phosphorous $(PO_4^- \text{ or DIP})$ and silicious acid $(Si(OH)_4)$ concentrations. Oxygen and nutrient fluxes are estimated by calculating the mean rate of change in concentration over the incubation period and then converting the volumetric rate to a flux volume: area ratio of each core. In general, changes in oxygen and nutrient concentrations over time in the cores are very linear (greater than 95%). Five samples were also found to provide a descriptionn on concentration change which was almost always highly statistically significant.

It should be noted that at low oxygen concentrations (< 2 mg Γ^1) SOC rates become proportional to oxygen concentrations as we noted in our previous report (Boynton *et al.*, 1987). Prior to 1989, between five and seven of the SONE stations rarely if ever experienced low bottom water DO concentrations. Since 1989, SONE stations have been modified and only three of eight stations rarely experience low oxygen concentrations. Hypoxic conditions are common at the remaining stations and influence SOC rates. This represents a methodological limitation which is more serious given our current configuration of stations. We are trying to develop a method for measuring total sediment metabolism (dissolved inorganic carbon flux or SO₄ depletion rates) which is independent of oxygen conditions.

4.1.2 Deep Trough Study

Sampling at the two deep trough stations followed the same overall procedure as that initiated at SONE stations and included the general characterization of both the water column (see Section 4.1.1.1) and sediment profile (see Section 4.1.1.3), measurement of dissolved water column nutrients and particulates (see Section 4.1.1.2) and sediment-water exchanges of oxygen (DO) and dissolved nutrients (see Section 4.1.1.4): ammonium (NH₄⁺), nitrite (NO₂⁻), nitrite plus nitrate (NO₂⁻ + NO₃⁻), dissolved inorganic phosphorous (PO₄⁻ or DIP) and silicious acid (Si(OH)₄) concentrations.





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4.1.3 VFX Study

At the VFX station, a water column profile of temperature, salinity and dissolved oxygen is obtained at 2 meters intervals from 0.5 meters to 1 meter off of the bottom to characterize the general physical features of the water column. Turbidity of the water is measured using a Secchi disc.

Water samples are also collected at three depths using a submersible pump system. Routinely, a sample is taken from near-bottom and near-surface waters and at the depth of the top of the middle sediment trap. Water samples are analyzed for particulate materials including particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations, biogenic silica and seston content. These data provide descriptions of the particulate matter in the field at the time of sampling and are useful in evaluating results obtained from sediment trap collections.

4.1.3.1 Sediment Sampling

During previous VFX monitoring cruises a surficial sediment sample (surface 1cm; 2mm since 9 August, 1989) was obtained using either a Van Veen grab or the Bouma box corer. During this reporting period the Bouma corer was used exclusively because it obtains a better surficial sediment sample. Sediment samples are later analyzed to determine particulate carbon (PC), particulate nitrogen (PN) and particulate phosphorous (PP), total and active chlorophyll-a concentrations.

4.1.3.2 VFX Sampling

The sampling device used to develop estimates of the vertical flux of particulate materials has a surface buoy connected to a lead or concrete anchor-weight (200 kg) by a series of stainless steel cables (0.8 cm diameter, Figure 4-2). The array is maintained in a vertical position through the water column by two sub-surface buoys (45 cm diameter, 40 kg positive buoyancy and 33 cm diameter, 16 kg positive buoyancy). Collecting frames with cups are attached at about 5 meters and 9 meters beneath the water surface to obtain estimates of vertical flux of particulates from the surface euphotic zone to the pycnocline and flux across the pycnocline to deep waters.

The sediment trap string is routinely deployed and retrieved using CEES research vessels with normal sampling periods lasting one to two weeks. At the end of a sampling period, collecting cups are retrieved by hoisting the entire array to shipboard. Cups are not capped prior to retrieval. After fouling organisms are removed from the frames, new cups are attached and the array lowered back into the water.

The contents of a collecting cup are removed and aliquots taken for determination of particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations and seston content. Until the end of the 1987 calendar year, an additional 10 ml sample was preserved using a modified Lugol's solution and later examined to determine characteristics of collected particulate material (*e.g.*, algal speciation, zooplankton fecal pellets, *etc.*).

Particulate material concentrations in sampling cups are converted to units of vertical flux, at the depth of the collecting cup, using the cross-sectional area of the collecting cup, deployment time, sample and subsample volumes. Further details concerning this



FIGURE 4-2. Schematic Diagram of the Sediment Trap used in VFX Monitoring * Measurements are only made using surface and mid cups. Bottom array has not been deployed or retrieved since July 8, 1987.

monitoring program are provided in Boynton *et al.* (1985b), Garber *et al.* (1987) and Boynton and Rohland (1990).

4.1.4 Chemical Analyses

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

4.2 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.

- ICES inorganic nutrient round-robin communication. This will result in an international inter-comparison report to be issued in the near future.

- Dissolved nutrients in comparison with Horn Point Environmental Laboratory, Bigelow Laboratory, the University of Delaware and the University of New Hampshire.

- Cross calibration exercises with Virginia Institute of Marine Science (VIMS) and Old Dominion University (ODU). The most recent inter-comparison (March 1990) 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 Bureau of Standards and National Research Board of Canada reference materials, primarily estuarine sediment, as a check for their particulate and sediment carbon, nitrogen and phosphorus methods.

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

Specific EPC procedures include inorganic nutrients (ammonium $[NH_4^+]$, nitrite $[NO_2^-]$, nitrite plus nitrate $[NO_2^- + NO_3^-]$, dissolved inorganic phosphorus $[PO_4^- \text{ or DIP}]$ and silicious acid $[Si(OH)_4]$ for which a standard curve, usually comprising five concentrations encompassing the expected range for that particular sample set, is 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. The 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).

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5. DATA MANAGEMENT

Hard copy data table listings of every variable measured during SONE and VFX monitoring programs for all previous years, August 1984 through December 1989, were submitted in two volumes with the Level 1, No 7 Interpretive Report Part II: Data Tables [UMCEES]CBL Ref. No. 90-062 (Boynton *et al.*, 1990). Part II: Data Tables of this interpretive report includes tabular listings of SONE, VFX and Deep Trough data for 1990. Data files are given unique names which are a combination of an alpha code reflecting the type of data set and a numeric descriptor which indicates the number of the SONE cruise or sampling year in the case of Deep Trough and VFX files (EPC Data Dictionary: Boynton and Rohland, 1990).

5.1 SONE Study

The data collected at each SONE station are organized into six data sets:

WATER COLUMN PROFILES (Filename: H2OPRFxx, Table B-1) contain temperature, salinity and dissolved oxygen data measured at two meter intervals.

WATER COLUMN NUTRIENTS (Filename: H2ONUTxx, Table B-2) report surface and bottom water dissolved nutrient concentrations.

SEDIMENT PROFILES (Filename: SEDPRFxx, Table B-3) include redox potential and selected sediment measurements of particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations.

CORE PROFILES (Filename: **CORPRFxx**, Table B-4) lists percentage water, particulates and pore water nutrient measurements at SONE stations. Data is available only for SONES 2, 6 and 10.

CORE DATA (Filename: **CORDATxx**, Table B-5) lists dissolved oxygen and nutrient measurements in SONE sediment-water flux chambers.

SEDIMENT-WATER FLUX (Filename: SWFLUXxx, Table B-6) is a summary table providing oxygen and nutrient flux data.

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5.2 Deep Trough Study

Deep Trough data collected at two stations, DT-S1 and DT-N1 in the summer of 1990, are organized into five data sets:

WATER COLUMN PROFILES (Filename: DTHPRFxx, Table D-1) contain temperature, salinity and dissolved oxygen data measured at two meter intervals.

WATER COLUMN NUTRIENTS (Filename: DTHNUTxx, Table D-2) report surface and bottom water dissolved nutrient concentrations.

SEDIMENT PROFILES (Filename: DTSPRFxx, Table D-3) include redox potential and selected sediment measurements of particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations.

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

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

5.3 VFX Study

VFX data, currently collected only at one station, R-64, are organized into three data sets:

WATER COLUMN PROFILES (Filename: VFXPssxx, Table C-1) contain temperature, salinity and dissolved oxygen data measured at two meter intervals.

SURFICIAL SEDIMENT PARTICULATES (Filename: VFXSssxx, Table C-2) lists particulate material concentration data including particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), total and active chlorophyll-a concentrations.

VERTICAL FLUX OF PARTICULATES (Filename: **VFXDssxx**, Table C-3) which includes rate of deposition of particulate materials to collection cup depth for particulate carbon (PC), particulate nitrogen (PN), particulate phosphorus (PP), active and total chlorophyll-a concentrations, and a biogenic silica and seston measurement.

5.4 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 SONE and VFX program have been added.

5.5 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 NSAL are returned to us in written format. Data are keyed into Lotus using the standard format developed during the continuing effort begun in August 1989 to standardize all EPC data files. Hard copies of the files are manually checked for errors. Data files are corrected, a second printout produced which then is re-verified by a different staff member.

5.6 Statistical Analysis System (SAS) Files

The schedule of deliverables, an attachment to contract 20-C-MDE91, states that after verification data are to be submitted as Statistical Analysis System (SAS) files, readable on the VAX 8600, with labels and file structure documentation, to the EPA Chesapeake Bay Liaison Office (EPA/CBLO). Lotus files, which are only acceptable as an interim submission to EPA, are stripped of headings and converted into ASCII files. Final editing is completed using a word processing program. SAS data files are compiled containing detailed variable information which is used to prepare the necessary tape. A letter requesting the formal sign off of the data completes the process of data submission. It is hoped that submission of all data sets will be completed during 1992.

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Table 5-1. Analysis Problem Codes

ANALYSIS PROBLEM CODE	DESCRIPTION
Ā	Laboratory accident
В	Interference
С	Mechanical/materials failure
D	Insufficient sample
N	Sample lost
 P	Lost results
R	Sample contaminated
S	Sample container broken during analysis
v	Sample results rejected due to QA/QC criteria
W	Duplicate results for all parameters
X	Sample not preserved properly
AA	Sample thawed when received
BB	Torn filter paper
CC	Pad unfolded in foil pouch
EE	Foil pouch very wet when received from field, therefore poor replication be-
	tween pads, mean reported.
FF	Poor replication between pads; mean reported
HH	Sample not taken
JJ	Amount filtered not recorded (calculation could not be done)
LL	Mislabeled
NI	Data for this variable are considered to be non-interpretable
NN	Particulates found in filtered sample
PP	Assumed sample volume (pouch volume differs from data sheet volume; pouch volume used)
QQ	Although value exceeds a theoretically equivalent or greater value (e.g., PO4F>TDP), the excess is within precision of analytical techniques and there- fore not statistically significant
RR	No sample received
SS	Sample contaminated in field
TF	Dissolved oxygen probe failure
TS	Dissolved oxygen probe not stabilized
TT	Instrument failure on board research vessel
UU	Analysis discontinued
ww	Station was not sampled due to bad weather conditions, research vessel mechanical failure, VFX array lost or failure of state highway bridges to open or close
XX	Sampling for this variable was not included in the monitoring program at this time or was not monitored during a specific cruise
YY	Data not recorded.

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6. RESULTS AND DISCUSSION

6.1 Inter-annual Patterns of River Flow and Nutrient Loading

6.1.1 Overview

One of the primary objectives of the 1991 EPC Interpretive Report is to explore monitoring program data, as well as other data sources, for relationships between nutrient loading (e.g., point, non-point and atmospheric sources) and responses of sediment and deposition processes. Particulate material deposition, sediment oxygen consumption and nutrient release rates have been shown to have strong influences on water quality conditions (Boynton *et al.*, 1990) and are believed ultimately to be regulated by rates of external nutrient supplies. Thus, in this year when the Chesapeake Bay nutrient reduction strategy is to be re-evaluated, it is particularly appropriate to document relationships between nutrient loading, deposition rates and sediment oxygen and nutrient fluxes. As river flow rates and nutrient loading rates will be used throughout this report, a summary of these are provided here. Detailed treatment of these variables is given in Summers (1989).

6.1.2 Average Annual River Flows

Annual average river flows for the period 1978-1989 are show in Figure 6-1.1. Additionally, average flows for the period 1978-1989 to each system are indicated by horizontal lines on this figure (James et al., 1990). Considerably longer periods of flow records also exist for these systems (18-55 year records). Compared to these longer-term averages, the twelve year average flows shown in Figure 6-1.1 for the Susquehanna, Potomac, Patuxent and Choptank Rivers were 12% lower, 6% higher, 7% lower and 2% higher, respectively, than the long term average. Despite the fact that these basins are distinctly different, and separated in space by large distances in some cases, there are strong similarities in interannual flows among systems. For example, flows in all systems were above average in 1978 and 1979, below average from 1980 to 1982, higher during 1983 and 1984, generally lower from 1985 through 1988 and above average in 1989 in all systems except the Potomac River. Data for full calendar year periods beginning in 1985 are available for the EPC portion of the monitoring program. During the period, 1985 through 1989, flows from the Susquehanna and Potomac Rivers were near or slightly below average while in the Choptank River flows were well below average except in 1989. Flows in the Patuxent River have steadily increased between 1985 and 1989 but were above average only in 1989. In general, river flows have been average to below average during the EPC monitoring period. As a result of this, water column stratification might be expected to be less intense than usual and diffuse source nutrient loads to be lower than normal.

6.1.3 Average Annual Total Nitrogen and Phosphorus Loading Rates

Average annual estimates of total nitrogen (TN) and phosphorus (TP) loading rates are shown in Figures 6-1.2 and 6-1.3 for the period 1978-1989. Estimates of TN and TP loads include point, non-point and atmospheric sources from both above and below the fall-line (Summers, 1989). Both TN and TP include organic particulate and dissolved organic and inorganic forms of nitrogen and phosphorus. Several features of these loading rates should



Figure 6-1.1 Bar graphs of average annual river flow from the Susquehanna, Potomac, Patuxent and Choptank Rivers for the period 1978 through 1989. Flow data for 1990 are not available. Flows were measured at Conowingo, MD; Washington, D.C.; Bowie, MD and Greensboro, MD for the four systems, respectively.



Figure 6-1.2 Bar graphs of average annual total nitrogen (TN) loading to four estuarine portions of Chesapeake Bay for the period 1978 through 1989. TN includes both particulate and dissolved forms of nitrogen. Loadings include point, diffuse and atmospheric sources from both above and below the fall-line.



Figure 6-1.3 Bar graphs of average annual total phosphorus (TP) loading to four estuarine portions of Chesapeake Bay for the period 1978 through 1989. TP includes both particulate and dissolved forms of phosphorus. Loadings include point, diffuse and atmospheric sources from both above and below the fall-line.

be noted. First, there is a strong correspondence between loading rates and river flows in all systems indicating the importance of diffuse sources of both TN and TP. Secondly, in the case of TN loadings, there were few obvious trends apparent other than increasing loads in the Patuxent River which corresponded to increased river flows during the period 1985 through 1989. With few exceptions (*e.g.*, 1989 in all systems but the Potomac River), TN loads have been below the 12 year average during the EPC program monitoring period. Loading rates of TP also tended to be below the 12 year average loading rate but there were some important differences between TN and TP loading rates. In the Patuxent River, TP loads decreased steadily from 1983 through 1988 despite increased river flows. This trend was reversed, but only slightly, in 1989, in response to higher than average river flows. Except in years of high flow, it appears that point source control of TP discharges has effectively decreased loading rates to the Patuxent River. Total phosphorus loads to the Choptank River in 1989 were considerably larger than in previous years, probably resulting from increased runoff during 1989.

6.1.4 Average Annual Areal Loading Rates for 1985-1989

While it is useful to review absolute loading rates for each of these systems, it is not possible to compare loading rates among systems because of substantial differences in the size of drainage basins and hence the absolute magnitude of the loads. As a first step towards making such comparisons possible, TN and TP loads to each of these systems were divided by the surface area of the system, thereby providing an areal weighted loading rate (Figures 6-1.4 and 6-1.5). Areal loading rates were calculated for several different periods of the year and, for the Susquehanna and Choptank River systems, using two modifications of TN and TP loads and estuarine surface areas.

In earlier work, we used calender year as the time interval for calculating loading rates and have also used this here. However, recent analyses (Boynton *et al.*, 1991a) suggested that such features as primary production in the mainstem bay and sediment-water nutrient exchanges were particularly responsive to nutrient additions which occurred during the cool portions of the year. For this reason two additional nutrient loading rates were developed, both of which included nutrient additions which occur during the fall of the year as well as those associated with the spring freshet. In one of these we included nutrient loading cycle. In the other, all portions of the annual cycle were included but loads were calculated from October through September following the procedure used by the USGS for calculating water years. In general, the October through June loading rates were highest, which was expected, because most of the annual nutrient load is associated with higher than normal flows which occur during this portion of the year.

Areal TN loads varied among systems by almost an order of magnitude. During the period 1985-1989 areal loads were highest in the Potomac River(25-47 gN m⁻² yr⁻¹) followed by the Maryland mainstem (17-28 gN m⁻² yr⁻¹), Patuxent River (13-19 gN m⁻² yr⁻¹) and Choptank River(5-10 gN m⁻² yr⁻¹) systems. In the case of phosphorus, loading rates among systems varied even more widely, with maximum differences approaching a factor of twenty. Areal loading rates for phosphorus for the period 1985 through 1989 were highest in the Potomac River (1.3-5.1 gP m⁻² yr⁻¹), similar in the Maryland mainstem bay (0.7-1.3 gP m⁻² yr⁻¹) and Patuxent River (0.8-1.5 gP m⁻² yr⁻¹), and lowest in the Choptank River(0.3-0.6 gP m⁻² yr⁻¹).

Areal loading rates can also serve as an index of the degree to which these sub-systems of the bay are being impacted by nutrient additions. Viewed in this light, these sub-systems

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Figure 6-1.4 Bar graphs showing areal total nitrogen (TN) loading rates to four regions in the Maryland portion of Chesapeake Bay for the period 1985 through 1989. Specific areas include the Maryland Mainstem (Susquehanna River, A and B), Potomac River (C), Patuxent River (D) and Choptank (E and F) River discharges.

Estuarine surface area estimates were taken from Cronin and Pritchard (1975). Loading rate data were from Summers (1989). The forms of nitrogen and nitrogen sources are as indicated in Figure 6-1.2. Temporal schemes used to calculate annual loading rates included the following: monthly loads between 1 October of the preceding year were combined with loads through 30 September of the current year and averaged; monthly loads from 1 October of the preceding year were combined with monthly loads through 30 June of the current year and an average rate calculated for the cooler portion of the year; monthly loading rates for the current calendar year were averaged to obtain an average annual rate.

Two separate areal loading calculations were done for the Susquehanna and Choptank systems:

Susquehanna:

The first estimate included total nitrogen (TN) loads only from the Susquehanna River and these loads were prorated over the surface area of the mainstem bay (tributary areas not included) north of the mouth of the Potomac River. The second estimate (B) includes below fall-line nutrient loads as well as those from the Susquehanna River and the combined loads were prorated over the surface area of the mainstem (north of the mouth of the Potomac River) plus the surface areas of tributary rivers.

Choptank:

The first estimate (E) of areal loading in the Choptank River involved simple prorating of inputs over the surface area of the estuary while the second (F) involved increasing the annual loading rates of both TN and TP by the amount indicated to be imported into the Choptank River from the mainstem bay based on nutrient budget calculations (Boynton *et al.*, 1991b).

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Figure 6-1.4 Bar graphs showing areal total nitrogen (TN) loading rates to four regions in the Maryland portion of Chesapeake Bay for the period 1985 through 1989.

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Figure 6-1.5 Bar graphs showing areal total phosphorus (TP) loading rates to four regions in the Maryland portion of Chesapeake Bay for the period 1985 through 1989. Specific areas include the Maryland Mainstem (Susquehanna River, A and B), Potomac River (C), Patuxent River (D) and Choptank (E and F) River discharges.

Estuarine surface area estimates were taken from Cronin and Pritchard (1975). Loading rate data were from Summers (1989). The forms of phosphorus and phosphorus sources are as indicated in Figure 6-1.3. Temporal schemes used to calculate annual loading rates included the following: monthly loads between 1 October of the preceding year were combined with loads through 30 September of the current year and averaged; monthly loads from 1 October of the preceding year were combined with monthly loads through 30 June of the current year and an average rate calculated for the cooler portion of the year; monthly loading rates for the current calendar year were averaged to obtain an average annual rate.

Two separate areal loading calculations were done for the Susquehanna and Choptank systems:

Susquehanna:

The first estimate included total phosphorus (TP) loads only from the Susquehanna River and these loads were prorated over the surface area of the mainstem bay (tributary areas not included) north of the mouth of the Potomac River. The second estimate (B) includes below fall-line nutrient loads as well as those from the Susquehanna River and the combined loads were prorated over the surface area of the mainstem (north of the mouth of the Potomac River) plus the surface areas of tributary rivers.

Choptank:

The first estimate (E) of areal loading in the Choptank River involved simple prorating of inputs over the surface area of the estuary while the second (F) involved increasing the annual loading rates of both TN and TP by the amount indicated to be imported into the Choptank River from the mainstem bay based on nutrient budget calculations (Boynton *et al.*, 1991b).



Figure 6-1.5 Bar graphs showing areal total phosphorus (TP) loading rates to four regions in the Maryland portion of Chesapeake Bay for the period 1985 through 1989.

span a substantial range with the Potomac River being more heavily loaded than the mainstem followed by the Patuxent and Choptank Rivers. In a qualitative fashion these loading rates seem to parallel eutrophication patterns indicated by water quality indices developed by the Maryland Department of Environment (Haire *et al.*, 1991). With few exceptions, there have been relatively small inter-annual changes in total areal nutrient loading rates in any of these systems since the EPC program was initiated. Exceptions include phosphorus loads to the Patuxent River which decreased from 1985 through 1988 and nitrogen loads to the Patuxent and Choptank Rivers which generally increased during this period.

6.2 Intra-annual Characteristics of Sediment-Water Oxygen and Nutrient Exchanges

6.2.1. Overview

In this section monthly average sediment-water fluxes are summarized in the form of bar graphs for five variables: SOC, ammonium (NH₄+), nitrite plus nitrate (NO₂⁻ + NO₃⁻), phosphate (PO₄), and silicate (Si(OH)₄). In each of the five figures (Figures 6-2.1a to 6-2.1e) data collected over a period of six calendar years, 1985 through 1990, were utilized. Each bar represents the mean flux value for a particular month of this six year period, while the error bar indicates the standard deviation from this mean. In those cases where the standard error of a monthly mean is large, this indicated that there was considerable interannual difference in monthly fluxes rather than that the variability among replicates from any particular measurement was high. Data collected during 1990 (SONE cruises 24 though 28; mean flux value of three replicates) are shown as bold dots superimposed on the bars. The order of the eight stations reflects their spatial position in the Chesapeake Bay. The four stations on the left side of the figures are located in the Patuxent River from the lower estuary (St. Leonard Creek [STLC]) to the turbidity maximum zone (Buena Vista [BUVA]). The right half of the figure shows one station in the lower Choptank River (Horn Point [HNPT]), one in the lower Potomac River (Ragged Point [RGPT]) and two stations in the mainstem bay. Data has only recently been collected at two stations in the Patuxent River (Broomes Island [BRIS] and Marsh Point [MRPT]). Error bars are not indicated for those months for which only one year of data are available. For the most part in this section seasonal patterns of flux are simply described but in sections 6.3, 6.5 and 6.11 the factors responsible for these patterns are discussed.

6.2.2 Sediment Oxygen Consumption (SOC)

Mean monthly SOC fluxes ranged from almost zero (0.0) to about 2.3 g O₂ m⁻² d⁻¹ and were generally higher in the Patuxent and Choptank Rivers than at other sites (Figure 6-2.1a). In all cases a seasonal pattern was evident with peaks or increased rates of SOC in the springtime (May and June), depressed values in the summer (August) and increased rates in the fall (October). The largest fluxes were recorded in May and June, with a secondary peak recorded in October. The 1990 data followed the same pattern as previous years. However, fall fluxes in the Patuxent River were particularly high and fluxes at Horn Point (HNPT) were higher than the six year mean by a factor of almost two. Spring and fall SOC rates at most stations are of sufficient magnitude to constitute a substantial direct dissolved oxygen loss (Kemp, *unpublished data*). However, as indicated in an earlier report (Boynton *et al.*, 1990) SOC is not an adequate measure of sediment metabolism during summer



Figure 6-2.1a Monthly SOC rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay. Monthly means and standard deviations were calculated using all flux data available for a specific month at each station. In general there was one set of triplicate flux values available for each month for 1985 through 1990. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on 1989 and 1990 data. The bold dots indicate average monthly fluxes for 1990. Station locations are shown in Figure 3-1.

Figure 6-2.1b Monthly ammonium flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay. Monthly means and standard deviations were calculated using all flux data available for a specific month at each station. In general there was one set of triplicate flux values available for each month for 1985 to 1990. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on 1989-1990 data. The bold dots indicate average monthly fluxes for 1990. Station locations are shown in Figure 3-1.

Figure 6-2.1c Monthly nitrite plus nitrate $(NO_2^- + NO_3^-)$ flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay. Monthly means and standard deviations were calculated using all flux data available for a specific month at each station. In general there was one set of triplicate flux values available for each month for 1985 through 1990. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on 1989 and 1990 data. The bold dots indicate average monthly fluxes for 1990. Station locations are shown in Figure 3-1.

Figure 6-2.1d Monthly phosphorus (PO4⁻ or DIP) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay. Monthly means and standard deviations were calculated using all flux data available for a specific month at each station. In general there was one set of triplicate flux values available for each month for 1985 through 1990. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on 1989 and 1990 data. The bold dots indicate average monthly fluxes for 1990. Station locations are shown in Figure 3-1.

Figure 6-2.1e Monthly silicate (Si) flux rates (April to November) at eight SONE stations located in the Maryland portion of Chesapeake Bay. Monthly means and standard deviations were calculated using all flux data available for a specific month at each station. In general there was one set of triplicate flux values available for each month for 1985 through 1990. Monthly values at Broomes Island (BRIS) and Marsh Point (MRPT) are based on 1989 and 1990 data. The bold dots indicate average monthly fluxes for 1990. Station locations are shown in Figure 3-1.

periods of low oxygen conditions. The SOC rates reported here during periods of low oxygen concentrations grossly underestimate sediment metabolism and oxygen demand exerted by reduced sulphur compounds (Roden, 1990). The EPC program is attempting to add a routine measure of anaerobic sediment metabolism to better estimate total sediment oxygen demand.

6.2.3 Ammonium Fluxes

Average monthly ammonium fluxes ranged from about 1 μ MN m⁻² h⁻¹ at St. Leonard Creek (STLC) to 525 μ MN m⁻² hr⁻¹ in the lower Potomac River (Ragged Point [RGPT]). In most cases highest values were recorded in the summer months of July or August. Several interesting spatial patterns were also evident (Figure 6-2.1b). For example, NH₄⁺ fluxes tended to increase from the mouth to the turbidity maximum zone of the Patuxent River. This qualitative pattern reflects the expected trend of deposition rates of organic matter to the sediment surface. In fact, deposition rates measured at six sites along the longitudinal axis of the Patuxent River in the late 1970's indicated a deposition maximum in the area of Buena Vista (BUVA) (Boynton *et al.*, 1982b). Similarly, the exceptionally high rates of NH₄⁺ release from sediment at R-64 (Mainstem bay) are double those recorded at a site farther down the bay in an area where primary production, chlorophyll-a stocks and presumably deposition rates were considerably lower. The values recorded in 1990 generally followed the trends exhibited in previous years. However, NH₄⁺ fluxes were well above mean values for several months of 1990 at the two upper estuary stations in the Patuxent River and at the single station in the lower Potomac River.

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

Lower nitrite plus nitrate fluxes were found at the two mainstem bay stations, while larger flux values were generally found at tributary sites. Nitrite plus nitrate fluxes ranged between 49 and -163 μ MN m⁻² hr⁻¹ (Figure 6-2.1c). With few exceptions (e.g., BRIS in June), NO₂⁻ + NO₃⁻ fluxes in either direction (into or out of sediments) were small compared to NH₄⁺ fluxes. At most stations nitrite plus nitrate fluxes recorded during 1990 closely followed previous trends. As noted for other fluxes, NO₂⁻ + NO₃⁻ fluxes in the Patuxent River were substantially greater in some months, June and August, of 1990 than in previous years. It is suspected that 1990 nutrient loading and subsequent deposition of organic matter to the sediment surface is involved but nutrient loading data for this period are not yet available to either confirm or reject this suggestion.

6.2.5 Dissolved Inorganic Phosphorus (PO₄ or DIP) Fluxes

The overwhelming trend indicated a net flux of dissolved inorganic phosphorus (PO₄⁻) from sediments to the overlying waters. Values ranged from -2 to 98 μ MP m⁻² hr⁻¹. Flux values peaked during the summer (July or August), varying from 12 to 98 μ MP m⁻² hr⁻¹ during this period (Figure 6-2.1d). With the exception of the station in the upper Patuxent River (Buena Vista, BUVA), all large PO₄⁻ fluxes were associated with hypoxic or anoxic conditions in overlying waters. It has been suggested that the high PO₄⁻ fluxes observed at Buena Vista (BUVA) were caused, at least in part, by the burrowing and irrigation activities of the large benthic macrofaunal community present at this location rather than iron sulphur (Fe-S) reactions which are probably responsible for high fluxes elsewhere under low dissolved oxygen conditions. Recent data closely followed already well established trends, although in August, 1990 flux rates at six stations were considerably higher than previous

years, ranging from 30 to 86 μ MP m⁻² hr⁻¹. Fluxes at stations in the Patuxent River also exhibited increasing rates in an upstream direction.

6.2.6 Dissolved Silicate Fluxes

The magnitude of monthly mean silicate fluxes ranged between 100 and 800 μ MSi m⁻² hr⁻¹ (Figure 6-2.1e). There were no marked differences among sites for silicate fluxes as was the case for other nutrient and oxygen fluxes. In fact, the most striking aspect of these monthly data is the similarity among sites, especially in light of the very different TN and TP loading rates to which different sites are exposed. In addition, seasonal patterns were not well developed. For example, while such flux variables as NH₄⁺ and PO₄⁻ exhibited higher values during the summer, this was not consistently true for silicate even though at times values for the months of June or July were marginally higher than in adjacent months, May and August. The 1990 data were similar to the long-term average at some stations (Marsh Point [MRPT], Ragged Point [RGPT] and Point No Point [PNPT]) but higher during some months at several others (Buena Vista [BUVA] and Horn Point [HNPT]). River flow data for 1990 are not yet available but may indicate that during 1990 silica loading originating from diffuse sources was also high. This would provide a partial explanation of these trends.

6.3 Relationships of Sediment-water Fluxes to in situ Environmental Conditions

6.3.1 Overview and Approach

In this section the observed magnitude of sediment-water exchanges is examined for relationships to *in situ* environmental conditions existing at the time measurements were taken. In earlier reports (Boynton *et al.*, 1987) results of extensive correlation analyses performed were reported. While a number of significant correlations were found between specific sediment-water fluxes (*e.g.*, PO_4^- fluxes) and environmental variables (*e.g.*, bottom water dissolved oxygen levels, or sediment characteristics), the r² values were generally low indicating a lack of predictive power. Those evaluations were primarily designed as a survey tool to simply establish that suspected relationships were evident, although complicated by additional interactions.

In this report a visual approach, 3-dimensional graphics, is used to extend continuing analysis of interactions between sediment-water fluxes and environmental characteristics. The following environmental variables were included in these analyses; bottom water temperature (in every analysis), bottom water dissolved oxygen concentration, bottom water salinity, bottom water nitrate concentration, and surficial sediment concentrations of particulate phosphorus and nitrogen. Specific analyses considered the following; SOC flux versus bottom water dissolved oxygen concentrations and temperature, silicate flux versus bottom water salinity and temperature, ammonium and phosphorus fluxes versus bottom water dissolved oxygen concentration and temperature, and phosphorus fluxes versus sediment particulate nitrogen and phosphorus concentrations and nitrate fluxes (both into and out of sediments) versus bottom water nitrate concentrations and temperature.

Data from all eight current SONE stations collected from April 1986 through October 1990 were used in these analyses except in cases involving sediment particulate nutrient concentrations which included data collected from August 1989 through October, 1990 (during this period 2-3 mm thick surficial sediment samples were available). Flux values

shown in these diagrams represent the mean of triplicate measurements. Environmental variable values are exclusively based on a single observation. In those rare cases were more than one observation occurred at the same location in the diagram, the mean of the two (or more) sets of flux measurements were plotted.

6.3.2 Sediment Oxygen Consumption (SOC) versus Bottom Water Dissolved Oxygen Concentrations and Temperature

Sediment oxygen consumption (SOC) rates have been used throughout the monitoring period as a measure of the instantaneous rate of oxygen consumption by sediments and as an indirect measure of the fate of organic matter. In both cases it is only possible to make the measurement when there is appreciable (> 1 mg l^{-1}) oxygen overlying sediments. Hence, the relationship between SOC rates and dissolved oxygen concentration is of interest. Temperature was also included in this analysis because of the influence of this variable on metabolic rates and chemical reactions in general. The results of this analysis are shown in Figure 6-3.1a. As expected, SOC rates were always low (< 1.0 gO₂ m⁻² d⁻¹) when bottom water dissolved oxygen concentrations were less than about 2.5 mg 1-1, regardless of temperature conditions. This suggests that SOC rates become oxygen limited at low concentrations and further indicates, as we discussed at length in the previous interpretive report (Boynton et al., 1990), that the method is not a reasonable index of sediment metabolism under low oxygen concentrations. Additionally, substantial SOC rates $(>1.0 \text{ gO}_2 \text{ m}^{-2} \text{ d}^{-1})$ were not observed below 12 C even when oxygen concentrations were high. The majority of substantial fluxes were observed within an environmental surface bounded by low oxygen concentrations ($<2.5 \text{ mg } l^{-1}$) and low temperatures (<12 C). It is obvious that considerable variability still exists within these boundaries and this is most likely attributable to differing supply rates of labile organic matter to the sediment surface and the status of the benthic infaunal community at the time of measurement (Kemp and Boynton, 1991).

6.3.3 Silicate Flux versus Bottom Water Temperature and Salinity Conditions

Silicate fluxes have been found to be a most dependable measurement, most of the data was readily interpretable. The most important controlling factor for setting the upper boundary of the magnitude of flux seems to be the rate at which biogenic silica is delivered to the sediment surface. According to Yamada and D'Elia (1984), temperature and salinity also play a central role in determining dissolution rates and hence silicate flux rates from There was a fairly broad range of sediments to overlying waters (Figure 6-3.1b). temperature and salinity conditions under which large (>200 μ MSi m⁻² hr⁻¹) silicate fluxes have been observed. Relatively low fluxes uniformly occur at temperatures below about 14 C regardless of salinity conditions. Despite the effect of salinity in enhancing dissolution rates, highest silicate fluxes were not associated with highest salinity conditions. In fact, no high silicate fluxes were observed at salinities above 16 ppt but occasionally very high fluxes were recorded at salinities as low as 4.5 ppt. However, most of the large fluxes occurred at temperatures above 16 C and between salinities of 8-16 ppt. It seems most reasonable to assume that the remaining variability in silicate fluxes can be explained by variations in the rate of biogenic silica delivery to the sediment surface. The most striking aspect of silicate fluxes is the uniformity of rates. Similar rates occur in systems with very different TN and TP loads. However, silicate loads may be similar among systems because there is little if any anthropogenic additions to the load. If silica is effectively depleted each spring by the diatom bloom, about the same amount of biogenic silica would reach sediments and result in dissolved silicate fluxes of similar magnitudes later in the spring and summer. It may be possible to estimate the relative contribution of diatoms to the total amount of organic


Figure 6-3.1 Three dimensional bar graphs showing sediment oxygen consumption rates (SOC) versus bottom water temperature and dissolved oxygen conditions (a) and sediment silicate fluxes versus bottom water salinity and temperature conditions (b). Refer to sections 6.3.2 and 6.3.3 for details concerning data used in these plots.

matter reaching sediments by comparing ammonium fluxes to silicate fluxes. In those cases where external supplies of TN or TP are very large, a greater portion of sedimenting material would be non-diatomaceous (not containing biogenic silica but having N and P) and presumably would yield a high ratio of nitrogen to silicate fluxes.

6.3.4 Ammonium (NH₄⁺) and Phosphate (PO₄⁻) Fluxes versus Bottom Water Dissolved Oxygen and Temperature Conditions

Relationships of ammonium (NH_4^+) and phosphate (PO_4^-) fluxes to bottom water dissolved oxygen and temperature conditions are summarized in Figures 6-3.2a and 6-3.2b. In both cases temperature was included because of its influence on metabolic rates and chemical reactions. Oxygen conditions were included in the NH_4^+ flux analysis because at high oxygen levels, nitrification can result in lower NH_4^+ fluxes. Conversely, at low oxygen concentrations, nitrification is effectively blocked and most, if not all, of the nitrogen being remineralized is available for release from sediments. In the case of PO_4^- fluxes, oxygen was included as an indicator of a set of iron sulphur (Fe-S) reactions which can only occur under anoxic conditions and when completed result in the liberation of PO_4^- through the sedimentwater interface (Cornwell, *pers comm.*, Klump and Martens, 1981).

It appears that NH₄⁺ fluxes tend to be relatively small (< 150 μ MN m⁻² hr⁻¹) at temperatures less than 14 C and at oxygen concentrations greater than about 7 mg l⁻¹. There appears to be a considerably stronger response to temperature in the case of NH₄⁺ fluxes than to oxygen conditions. Most of the very high fluxes occurred at temperatures greater than 20 C and some of these occurred under conditions where bottom water oxygen conditions were close to saturation. Again, much of the remaining variability is probably associated with differing organic matter loading rates to the sediment surface.

Of all the sediment-water fluxes routinely measured, substantial PO_4^- fluxes occurred under the most restricted set of environmental conditions (Figure 6-3.2b). Large fluxes only occurred when dissolved oxygen concentrations were less than 1.5 mg l⁻¹ and the temperature was greater than 14 C and in most cases greater than 20 C. Under all other oxygen and temperature conditions PO_4^- fluxes were small and in the majority of cases did not represent a significant summer season source of nutrients to phytoplankton communities. Maintaining some oxygen (> 1.5 mg l⁻¹) in deep waters during summer periods appears to be very important because it effectively limits both N and P releases.

6.3.5 Ammonium (NH_4^+) and Phosphate (PO_4^-) Fluxes versus Sediment PP and PN Concentrations and Temperature Conditions

Relationships of ammonium (NH_4^+) and phosphate (PO_4^-) fluxes to sediment particulate phosphorus (PP) and particulate nitrogen (PN) concentrations are summarized in Figures 6-3.3a and 6-3.3b. Temperature was also included here because of its influence on metabolic rates and chemical reactions. The sediment stocks of PP and PN were examined because they can be considered an estimate of the amount of material potentially available for remineralization. Particulate phosphorus (PP) and particulate nitrogen (PN) are indirect indicators of flux potential and several problems exist relative to this approach. First, particulate matter concentrations are at least one step removed from the dissolved phase that actually crosses the interface. It is possible therefore to have relatively low PP or PN concentrations but high fluxes because nitrogen or phosphorus has been remineralized from the particulate to the dissolved phase.



Figure 6-3.2. Three dimensional bar graphs showing sediment ammonium ($NH4^+$) fluxes versus bottom water temperature and dissolved oxygen conditions (a) and sediment phosphorus (PO4⁻) fluxes versus bottom water temperature and dissolved oxygen conditions (b). Refer to sections 6.3.4 and 6.3.5 for details concerning data used in these plots.



Figure 6-3.3 Three dimensional bar graphs showing sediment PO4⁺ fluxes versus bottom water temperature and sediment PP conditions (a) and sediment NH4⁺ fluxes versus bottom water temperature and sediment PN conditions (b). Refer to section 6.3.5 for details concerning data used in these plots.

The opposite case is also possible. Secondly, we do not have much information concerning the nature of the PP and PN materials at the sediment surface. In some portions of the bay this material could be very labile while in others the material could be quite refractory. In the case of PO_4^- fluxes, relationships to sediment PP concentrations were not particularly striking. The highest fluxes did occur at high PP concentrations (> 0.15%) but substantial fluxes also occurred at much lower PP concentrations. All ecologically significant fluxes occurred at temperatures greater than 24 C probably reflecting low oxygen conditions in deep waters during summer periods (Figure 6-3.3a).

Despite the limitations referred to above, there was a strong relationship between NH_4^+ flux and sediment PN concentrations and temperature (Figure 6-3.3b). For the most part, large NH_4^+ fluxes occurred at elevated temperatures and high PN concentrations. While there are exceptions (primarily low fluxes in segments of the diagram where higher fluxes would be expected to occur) the pattern is quite striking and is indirect evidence linking the magnitude of organic matter deposition from the water column to the large amount of sediment NH_4^+ released.

6.3.6 Nitrite plus Nitrate ($NO_2^{-} + NO_3^{-}$) Flux versus Water Column Nitrite plus Nitrate ($NO_2^{-} + NO_3^{-}$) Concentrations and Temperature

Relationships between sediment nitrite plus nitrate flux and $NO_2^- + NO_3^-$ concentrations in bottom waters and temperature are shown in Figures 6-3.4a (flux from sediments to overlying waters) and 6-3.4b (flux from water to sediments). Temperature was also included here because of its influence on metabolic rates and chemical reactions. Nitrate has often been observed to move from water to sediments in proportion to the concentration in overlying waters. This flux from water to sediments seems to represent a real N loss from the system as much of this $NO_2^- + NO_3^-$ appears to be denitrified (Boynton *et al.*, 1980; Jenkins and Kemp, 1984). Fluxes of $NO_2^- + NO_3^-$ from sediments to water indicate that sediment nitrification is taking place and exceeds sediment capacity for denitrification.

In virtually all cases nitrite plus nitrate fluxes both from and to sediments were small compared to NH₄⁺ fluxes. However, some interesting patterns emerged. First, with only several exceptions, NO₂⁻ + NO₃⁻ fluxes from sediments to overlying waters occurred when NO₂⁻ + NO₃⁻ concentrations in overlying waters were low ($<5 \mu$ MN l⁻¹) and temperatures intermediate between spring lows and late summer highs. The spring and fall periods, which correspond to this temperature range, have been shown to be periods of active nitrification (Jenkins and Kemp, 1984; Kemp and Boynton, 1991) and this is the probable source of NO₂⁻ + NO₃⁻ coming from sediments. Secondly, NO₂⁻ + NO₃⁻ uptake by sediments occurred at substantial rates only at temperatures above 20 C and at NO₂⁻ + NO₃⁻ uptake was 2-3 times higher than NO₂⁻ + NO₃⁻ release rates from sediments, but both were generally much smaller than NH₄⁺ releases.

6.4 Inter-annual Trends in Nutrient and Oxygen Fluxes

6.4.1 Overview

One of the central purposes of the Maryland Chesapeake Bay Water Quality Monitoring Program is to detect water quality trends that develop in response to pollution control programs (see Section 2.2). The program has now completed six full years of monitoring



Figure 6-3.4. Three dimensional bar graphs showing sediment $NO_2^{-} + NO_3^{-}$ fluxes from sediments to overlying waters versus bottom water temperature and $NO_2^{-} + NO_3^{-}$ concentrations (a) and sediment $NO_2^{-} + NO_3^{-}$ fluxes from overlying waters to sediments versus bottom water temperature and $NO_2^{-} + NO_3^{-}$ concentrations (b). Flefer to section 6.3.6 for details concerning data used in these plots.

sediment-water exchanges. There are six SONE stations for which this record is complete and these are the focus of the following analysis. These include two Patuxent River stations (St Leonard Creek [STLC] and Buena Vista [BUVA]), one lower Choptank River station (Horn Point [HNPT]), one lower Potomac River station (Ragged Point [RGPT]) and two stations in the mesohaline portion of the mainstem bay (Point No Point [PNPT] and R-64). In the early phases of the monitoring program stations were also located in the oligohaline portions of the mainstem bay (Still Pond [SLPD]), Potomac (Maryland Point [MDPT]) and Choptank Rivers (Windy Hill [WDHL]). The record is shorter for these stations and they are not included in this analysis. Finally, two new stations (Broomes Island [BRIS] and Marsh Point [MRPT]) were added in the Patuxent River in mid 1989 and they are also excluded due to the limited record. The purpose of this section is to present an approach for calculating "annual" nutrient and oxygen fluxes for six key stations in the bay region and to conduct some rudimentary statistical analyses on those data to detect inter-annual differences or trends.

6.4.2 Approach and Methods

There are several points that need clarification prior to discussing "annual" sediment-water nutrient and oxygen exchange rates. First, the term "annual" is used here as a matter of convenience and for lack of a better term. The "annual" flux estimates reported here are average flux rates (μ M m⁻² hr⁻¹) based on data collected between 15 April and 15 November of each year. The mean of triplicate measurements made within a year (4-5 sampling cruises per year) were time-weighted to account for differing time intervals between cruises in different years. Time weighting was accomplished by multiplying flux measurements for each sampling period within a year by the total number of days represented by that sampling period. These values were summed and divided by the number of days within that year. In addition, time weighted average "annual" fluxes were also calculated using the upper and lower standard errors of the means derived from triplicate measurements. Thus, a mean estimate of flux and a high and low estimate is derived. The "annual" means reported here are higher than means would be based on a twelve-month year. Data collected during the BEST program included observations made during winter. Fluxes measured during the cold portions of the year were uniformly low (Garber et al., 1989) and are not considered in these calculations. Finally, the three estimates of "annual" flux were used in a simple t-test to provide a rudimentary estimate of differences in fluxes between years at the six long-term SONE stations. If we had chosen to test for differences among individual SONE cruises (*i.e.*, compare June SONE data among years at a specific station) a more formal and acceptable statistical approach could have been used. However, we are quite sure that the time at which maximum fluxes occurs differs among years and at this point we can not predict exactly when maximum rates occur. A simple comparison of specific months from different years would yield a large number of statistically significant differences which would have little if any ecological meaning. This being the case, it seems more useful to obtain an estimate of "annual" flux and expose these values to an examination for inter-annual differences. Fluxes which were examined included SOC, NH_4^+ , $NO_2^- + NO_3^-$, PO_4^- and Si. A graphic summary of inter-annual fluxes is provided in Figures 6-4.1a through 6-4.1e. A summary of t-test results is given in Table 6.4.1.

6.4.3 Annual Average Nutrient and Oxygen Exchanges

Annual estimates of SOC for the years 1985 through 1990 are shown in Figure 6-4.1a and inter-annual differences are summarized in Table 6.4.1. As indicated in section 6.1, annual SOC rates were also substantially higher at tributary sites not exposed to summer hypoxia or anoxia. This in itself is an interesting result. Both the tributary sites and sites exposed to low



Figure 6.4.1a Bar graphs showing estimates of "annual" SOC rates for six SONE stations for the years 1985 through 1990. The solid bars represent the mean estimate of annual flux while the lines indicate the range of high and low estimates of annual flux. Refer to section 6.4.2 for details of calculation of "annual" rates.



Figure 6.4.1b Bar graphs showing estimates of "annual" NH_4^+ fluxes for six SONE stations for the years 1985 through 1990. The solid bars represent the mean estimate of annual flux while the lines indicate the range of high and low estimates of annual flux. Refer to section 6.4.2 for details of calculation of "annual" rates.



Figure 6.4.1c Bar graphs showing estimates of "annual" $NO_2^- + NO_3^-$ fluxes for six SONE stations for the years 1985 through 1990. The solid bars represent the mean estimate of annual flux while the lines indicate the range of high and low estimates of annual flux. Refer to section 6.4.2 for details of calculation of "annual" rates.



Figure 6.4.1d Bar graphs showing estimates of "annual" PO_4 fluxes for six SONE stations for the years 1985 through 1990. The solid bars represent the mean estimate of annual flux while the lines indicate the range of high and low estimates of annual flux. Refer to section 6.4.2 for details of calculation of "annual" rates.



Figure 6.4.1e Bar graphs showing estimates of "annual" Si fluxes for six SONE stations for the years 1985 through 1990. The solid bars represent the mean estimate of annual flux while the lines indicate the range of high and low estimates of annual flux. Refer to section 6.4.2 for details of calculation of "annual" rates.

Table 6-4.1 Summary of results of simple t-tests in which mean annual sediment-water and oxygen fluxes at specific stations were examined for differences among years at each station. Significant differences at the 0.05% probability level are indicated by x's. In each t-test, n = 3.

STLC	SOC	NH4	NO3+ NO2	DIP	51	RGPT	soc	NH4	N03+N02	DIP	Si
1965-86	×		x		x	1960-86				x	
·	-					-67					
	•		· •								
-90						-00	~			-	
1986-87			•			1086-87	-			•	
-44								-			
-80								- -			
-90						-00	×	-			
1987-88					-	1987-88	-				
-89				×		-49					
-90						-40					
1988-89				x		1988-89					
-90						-90					
1989-90		*		x		1989-90					
BUVA	SOC	NH4	NO3+NO2	DIP	51	PNPT	SOC	NH4	N03+N02	DIP	Si
1985-86					x.	1985-86	x			x	x
-87					x	-87	x	x			×
-86				x	×	-86	x				×
-89			x		x	-89	x				x
-90	x	x	X .	x	x	-90	x				x
1986-87						1986-87	x				
-86						-06	×			x	
89	x		x			-69					
-90			x	x	¥	-90	×			x	
1987-88						1967-88					
-89			x			-69					
-90			x	x	x	-90					
1988-89						1986-89					
-90			x	x	x	-90					
1989-90	×	X	×	X	×	1989-90	×.				
HNPT	SOC	NH4	NO3+NO2	DIP	9	R-44	900	NH4	NO3+NO2	DIP	Si
1985-86	×		x			1965-86					
-87	x		x			-67		x			x
-86	x		×			-46					x
-89	x	x	x	x		-89		×			x
-90			x		x	-90					×
1986-87						1986-87			x	x	
-48						-86			×		
-59	x					-00				x	x
-90	x				x	-90			x	x	
196/-66						1967-88		x		x	
-59	-					-89			x		
-W-	×				, x	-90					
1900-09	_					1988-89		×	x		
1080.001				-	X	-90					
1969-90	I.			x	x	1969-90					

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oxygen conditions exhibited the same seasonal patterns, with higher rates in spring and fall and lower rates during summer. It is not clear why the hypoxic sites have relatively low SOC rates even when there appears to be adequate dissolved oxygen in overlying waters, as is the case in spring and fall. Annual SOC rates at the hypoxic stations (Ragged Point [RGPT], Point No Point [PNPT] and R-64) were uniformly low (~0.5 gO₂ m⁻² d⁻¹), similar among sites and did not differ significantly among years at specific sites with the exception of Point No Point (PNPT) in the lower portion of the Maryland mainstem bay. SOC rates at this site declined sharply between 1985 and 1990, with a small increase in 1989. In part this pattern is due to declining dissolved oxygen concentrations in deep waters at this site from 1987 through 1990. In 1985 and 1986 there was ample dissolved oxygen in deep waters to support SOC (>2.0 mg l-1) during the summer and high rates were observed. Our current inability to routinely measure sediment metabolism under hypoxic/anoxic conditions points to the need for developing a reliable measurement technique that captures this aspect of sediment-water interactions. In the Patuxent River there were some significant inter-annual differences in SOC rates but distinctive patterns are not evident. Annual estimates of SOC in the lower Patuxent River (St Leonard Creek [STLC]) tracked TP loading through 1989 but this pattern was not evident at the upper river station (BUVA) in the Patuxent. At the site in the lower Choptank River (HNPT), annual SOC rates declined sharply from 1985 through 1989 and then increased abruptly in 1990. The rates in the lower Choptank River paralleled those of river flow for this time period if a one year lag in the flow-flux relationship is allowed.

Annual estimates of ammonium flux for the years 1985 through 1990 are shown in Figure 6-4.1b and inter-annual differences are summarized in Table 6.4.1. There were few differences in annual NH₄+ fluxes among years at specific stations. However, as will be discussed in more detail later (Section 6.10), there were some substantial differences among sites. In general, fluxes were higher at sites exposed to high nutrient loads (*i.e.*, Ragged Point [RGPT], R-64 and Buena Vista [BUVA]) and lower at locations where nutrient loads were lower (*i.e.*, St. Leonard Creek [STLC], Point No Point [PNPT] and Horn Point [HNPT]). This type of linkage is consistent with the conceptual model guiding this monitoring effort. The load-flux relationship indicates that when nutrient loads to the bay decrease so too will the nutrient releases from sediments which are largely responsible for poor summer water quality conditions such as stimulation of algal blooms.

Annual estimates of nitrite plus nitrate fluxes for the years 1985 through 1990 are shown in Figure 6-4.1c and inter-annual differences are summarized in Table 6.4.1. There are some striking visual, as well as statistical, differences among years at SONE stations. First, in the Patuxent and Choptank Rivers, $NO_2^- + NO_3^-$ fluxes have decreased in magnitude over the six year period and, in the Patuxent River, the direction of the annual flux has actually changed from positive (*i.e.*, sediments to water column) to negative (*i.e.*, sediment uptake of $NO_2^- + NO_3^-$). This sort of pattern could conceivably be in response to higher concentrations of $NO_2^- + NO_3^-$ in overlying waters (Boynton *et al.*, 1980; Boynton and Kemp, 1985). Total nitrogen loads in both systems have been slowly increasing over the period of record (Section 6.1), consistent with this explanation.

A related, but slightly different, explanation is that sediment nitrification rates have been decreasing and hence there is less nitrate available for flux through the sediment-water interface. Decreased sediment nitrification rates would be expected under increased nutrient loading rates if oxygen levels at the sediment surface decreased. Annual fluxes of $NO_2^- + NO_3^-$ at stations that routinely experience some degree of hypoxia/anoxia (Ragged Point [RGPT], Point No Point [PNPT] and R-64) did not exhibit clear inter-annual trends. Fluxes which were mainly directed from water to sediments were small relative to fluxes of NH_4^+ and were rarely as large as the positive $NO_2^- + NO_3^-$ fluxes observed at Ragged Point (RGPT), Point No Point (PNPT) and R-64.

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Annual estimates of phosphorus flux for the years 1985 through 1990 are shown in Figure 6.4.1d and inter-annual differences are summarized in Table 6.4.1. There were some strong similarities between annual PO_4^- and NH_4^+ fluxes. In both cases stations with the highest loading rates had the highest annual fluxes. The most distinctive trend apparent for PO_4^- flux data was the generally consistent increase in fluxes at Buena Vista (BUVA) located in the upper Patuxent River. This pattern generally parallels the increase in TN loading rates experienced between 1985 and 1989 in the Patuxent. However, TP loading rates during this period did not vary much, exhibiting a small decrease from 1985 through 1988, followed by a small increase in 1989. It may be that infaunal communities at this site are playing a large role in regulating PO_4^- and other fluxes. Holland *et al.* (1989) have reported that large infaunal populations are present at this location.

Annual estimates of silicate flux for the years 1985 through 1990 are shown in Figure 6-4.1e and inter-annual differences are summarized in Table 6.4.1. One of the interesting features of annual silicate flux estimates is that they do not exhibit the same relationship to nutrient load as do fluxes of N and P. While there were some statistically significant inter-annual differences among years at some stations (e.g., Buena Vista [BUVA], R-64 and Point No Point [PNPT]), the general magnitude of silicate fluxes was the same at all locations. The monitoring program does not measure the flux of total biogenic silica into the bay so it is not possible to directly relate inter-annual changes in silicate sediment fluxes to loadings. Loadings of dissolved silica are monitored and it may be possible to use these data as an index of total load. Sediment silicate fluxes generally paralleled freshwater inputs, especially if river flows from the previous year were considered in some cases. This suggests that there is a fixed amount of silica that enters each system, that it is virtually all used via uptake by diatom assemblages and that it is recycled back to the water column from sediments. In other words, while there is in all probability differing amounts of organic matter reaching sediments in different regions of the bay (proportional to N or P loading rates), there is a more constant amount of silica available for algal uptake and eventual deposition to sediments. Organic matter deposition rates vary according to load, and so also do N and P sediment fluxes, but silicate fluxes are relatively constant because only a fixed amount of silica reaches the sediment surface and that is generally the same amount in all systems.

6.5 Relationships between Sediment-Water Fluxes and Nutrient Loading Rates

6.5.1 Conceptual Model

The conceptual model of a relationship between sediment flux and nutrient loads requires the following considerations and assumptions:

1. Nutrients from all sources enter the bay and are rapidly incorporated by phytoplankton communities. While much of the N, but little of the P, enters the bay in a reactive form (*e.g.*, $NO_2^- + NO_3^-$, NH_4^+ , PO_4^-), we have assumed that TN and TP adequately represent the nutrient load either immediately or eventually available into phytoplankton communities.

2. Phytoplankton biomass accumulates to annual maxima in spring, a large portion of which settles to the sediment surface. Deposition during the summer is generally of smaller magnitude and more sporadic in occurrence.

In some years there is also a fall phytoplankton bloom and a portion of this material also sinks to the sediment surface.

3. As temperatures begin to rise in the spring, metabolic activity at the sediment-water interface increases, resulting in releases of nutrients and oxygen consumption.

4. There are many factors besides organic matter loading rate that influence the characteristics and magnitude of sediment-water exchanges. The oxidation-reduction status of sediments and benthic infaunal community characteristics are but two of the more important ones.

5. Since we have a limited ability to include the influence of such factors in this analysis (which we have not attempted), it is only strong load-flux signals that we can detect. While this is a limitation, it is of less importance here because we have taken a comparative approach using data from four systems which have very different nutrient loading rates (Boynton *et al.*, 1991b) and sediment-water nutrient and oxygen exchange rates.

6.5.2 Approach and Methods

In section 6.4, data from 1985 through 1990 were examined for inter-annual trends in nutrient and oxygen fluxes. While this approach provided preliminary indications of where and when fluxes at a particular station were different, it did not provide any direct information concerning the possible causes of inter-annual differences in flux magnitude. In this section, annual flux data from several SONE sites were considered relative to nutrient loading rates.

Annual fluxes were calculated, as described in section 6.4.2, for stations in the lower Potomac, Patuxent (two stations in this tributary for 1990) and Choptank Rivers and for one location in the mainstem bay (R-64). In addition, "summer" fluxes were also calculated using June and August data (June, July and August data in 1989). Annual fluxes for the period 1985 through 1989 were included. Although sediment flux data are available for 1990, nutrient loading data for 1990 have yet to be released and hence 1990 flux data were excluded from this analysis.

Nutrient loading rates (TN and TP) were also organized for the years 1985 through 1989 for the Potomac, Patuxent and Choptank Rivers and for the mainstem bay. In each case loads included above and below fall-line inputs from point and diffuse sources as well as atmospheric deposition of TN and TP (wet-fall only) directly to estuarine surface waters (Summers, 1989). Nutrient loads were divided by the surface area of each system and expressed as areal loads. Earlier examinations of nutrient load-sediment flux relationships suggested that temporal scales of nutrient loading other than calendar year may yield improved insights as to the nature of the interaction (Boynton et al., 1991a). Accordingly, TN and TP loads were calculated for two additional temporal scales, in addition to the calendar year (Section 6.1). The first included loads for an annual period beginning in October of the year previous to the year being considered and ending in September. This load function is similar to the USGS water year which covers the same temporal period, beginning and ending during the low-flow fall period of the year. The last load function emphasized the fall-winter freshet, but excluded summer loads which are typically lower. In this case, loads were calculated for the period October-June period for each year that data were available.

6.5.3 Nutrient Load-Flux Relationships

The patterns from all combinations of load-flux variables were generally the same, although some were stronger than others. The results of regression analyses relating summer fluxes (average of June-August data) to TN loads averaged from October through June are given in Figure 6-5.1 as an example of the type of results often obtained.

Of particular importance, sediment-water fluxes were consistently better correlated with TN loading than with TP loading. Even sediment fluxes of PO_4^- exhibited a stronger relationship with TN loads than with TP loads. In part this may result from the fact that there is a considerably broader range in TN loads than TP loads (Section 6.1). It may not be possible to resolve TP influences on flux over this relatively narrow loading range. Alternatively, the poor correspondence may indicate that most of the phytoplankton debris that reach sediments, and eventually supports sediment-water fluxes, was produced more in response to N than P availability. In spite of the multiple factors that are known to influence the characteristics of sediment-water exchanges, flux responses to loads were quite strong for most flux variables (all significant at 0.05 probability level).

Summer SOC rates exhibited a reasonably strong negative relationship to TN loads, having an r² value of 0.68 (3 especially high values observed in the Patuxent and Choptank Rivers in 1985 and 1986 excluded; Figure 6-5.1). The basis of this relationship is not one in which sediment metabolism decreases under conditions of increased nutrient loading. The case is just the opposite. Under conditions of intense nutrient loading, systems often exhibit decreased oxygen concentrations in deep waters and, as a result, also exhibit lower rates of aerobic respiration as estimated by SOC measurements. In fact, total sediment metabolism is probably highest at the most heavily loaded sites, but mediated via sulfate reduction (Roden, 1990), the end products of which will eventually exert an oxygen demand. The particularly high values observed at St Leonard Creek (STLC) and Horn Point (HNPT) in 1985 and 1986 were associated with years of low river flow and consistently high oxygen conditions in bottom waters during summer sampling periods.

Both NH_4^+ and PO_4^- fluxes were positively correlated with TN loading rates and both exhibited high and significant r^2 values (Figure 6-5.1). Ammonium fluxes at the lower Choptank River station were elevated relative to that expected given the loading rates estimated for this site (circled data in Figure 6-5.1). Of any of the sites, estimates of nutrient loadings are most problematic in the Choptank River because only a small fraction of the drainage basin is located above the fall-line. The bulk of the diffuse source TN and TP load must be estimated from a land-use model, the accuracy of which is difficult to judge (Summers, 1989). In addition, there are some data that indicate that there may be significant nutrient inputs to the lower Choptank River from the mainstem bay via deep water intrusions (Sanford and Boicourt, 1990). Annual nutrient budgets for the Choptank River indicate that internal nutrient losses due to denitrification and burial in sediments exceed point, diffuse and atmospheric inputs, a result which adds support to the idea that nutrient loads to the Choptank are underestimated. The divergence in PO₄ fluxes in the Choptank were not so apparent which is not surprising since bottom waters are generally well oxygenated in this system and P is effectively retained under these conditions. However, low dissolved oxygen conditions were present in 1989 and PO_4^- fluxes were larger. There were also several low flux values observed in the lower Potomac in 1987 and 1988. We believe that these values are anomalously low because they were based only on two summer measurements (June and August). Beginning in 1989 flux measurements were also made in June, July and August and in both 1989 and 1990 peak rates occurred in July. There may be year-to-year shifts in the timing of maximum flux rates based on the timing of spring bloom deposition, water temperatures, oxygen conditions and the like. At this stage of our understanding, it seems prudent to make measurements as frequently as possible



Figure 6-5.1 Scatter plots relating various sediment nutrient and oxygen exchange rates (average summer period fluxes) to total nitrogen (TN) loading rates (average for October through June). Flux data are from SONE stations R-64, Ragged Point (RGPT), St Leonard Creek (STLC) and Horn Point (HNPT) for the years 1985 through 1989. Summer flux data for 1989 are also included for one additional station in the Patuxent River (Broomes Island [BRIS]). Points on the diagram that are either circled or identified by years and location were not included in the regression analyses.

during the summer season. When converted to the same units as those in which loads are expressed, NH_4^+ fluxes are nearly the same as external TN inputs and occur in a 7 month period. Finally, if Choptank River NH_4^+ fluxes are excluded, the N:P ratio of fluxes is 12.8, just slightly less than that expected based on Redfield concepts of plankton composition (Redfield, 1934). This suggests that there is not a strong differential sink for N via denitrification in sediments, a finding consistent with direct measures of denitrification in various areas of the bay (Jenkins and Kemp, 1984; Twilley and Kemp, 1987).

Fluxes of $NO_2^- + NO_3^-$ were negatively correlated with loading rate and were significant at the 0.05% probability level (Figure 6-5.1). However, $NO_2^- + NO_3^-$ fluxes were relatively small in either direction, seldom amounting to more than 10% of the NH_4^+ flux. It is interesting that at loading rates above 30 gN m⁻² yr⁻¹ annual fluxes were never positive while at lower loading rates annual fluxes were always positive. Positive fluxes of $NO_2^- + NO_3^$ are an indication of sediment nitrification occurring at rates in excess of that being denitrified in sediments. Evidence of nitrification *per se* is a sign that deep waters have been exposed to oxygenated waters in the recent past because nitrification requires oxygen. Based on this, there is an emerging trend where $NO_2^- + NO_3^-$ fluxes become more positive which is a sign of improving water quality conditions. The exceptionally high $NO_2^- + NO_3^$ fluxes observed at St Leonard Creek (STLC) and Horn Point (HNPT) in 1985 both occurred in low flow years in which bottom waters remained particularly well oxygenated.

Sediment fluxes of silicate were only weakly related to TN loading rates (Figure 6-5.1). Fluxes tended to decrease as loading rates increased. At first the poor relationship to loading seemed counterintuitive. It seemed that as organic matter supply to the sediments increased, as indexed by nutrient loading rates, so should the return supply of silicate, as was the case for NH_4^+ and PO_4^- fluxes. The answer is probably related to the fact that not all organic matter production, and subsequent deposition, is associated with diatoms. Some fraction of the organic matter reaching the bottom, possibly a very large fraction during the summer, is not carrying with it biogenic silica associated with diatoms. In fact, since dissolved silica is generally depleted each year at the end of the spring diatom bloom there may be roughly the same amount of silica reaching sediments in all of the study areas which, in turn, results in roughly equivalent sediment silicate fluxes in systems receiving differing amounts of N and P loading. The uncertainty concerning this explanation could be at least partially resolved if estimates of silicate loading rates were examined for these systems.

6.5.4 Management Implications

Establishing these types of relationships is of importance for management purposes. It has already been established that the spring phytoplankton bloom is in response to "new nutrient" inputs from land sources. However, summer and fall blooms, which act to maintain poor water quality conditions in deeper waters for much of the summer period, are supported by recycled nutrients, a substantial fraction of which comes from sediments. The load-flux relationships reported here establish that sediment fluxes are related to nutrient loading rates, via the model described earlier, and further indicate that summer water quality conditions should improve in response to decreased phytoplankton blooms which are supported, in part, by sediment nutrient releases. When loadings from the land decrease so too should sediment nutrient releases.

6.6 Deep Trough Sediment-Water Nutrient and Oxygen Exchanges

6.6.1 Overview

Dredging of the approach and inner harbor channels of the Port of Baltimore has been required to maintain sufficient depths to allow passage of commercial shipping vessels. Dredge spoil resulting from maintenance dredging operations have primarily been deposited at various subtidal sites in the Upper Chesapeake Bay and inside of the Hart-Miller Island dredge spoil disposal area. The Maryland Department of Transportation and the Baltimore Port Authority were considering other locations in the Chesapeake Bay as possible additional disposal sites to accommodate dredge spoil from continuing maintenance dredging and proposed deepening of the approach channels to Baltimore Harbor. One such site was the deep channel area of the bay south of the bay bridge at Annapolis, Maryland. The Deep Trough Monitoring Program, conducted during the summers of 1989 and 1990, was undertaken to characterize sediment-water nutrient and oxygen exchanges during July and August 1990 at two stations (DT-N1 and DT-S1, north and south of the four original deep trough stations) located in mesohaline, deep waters south of the Bay Bridge at Annapolis, MD (Figure 3.2). These data were collected to provide a set of baseline flux measurements prior to any dredge spoil disposal. The 1989 work was reported in Boynton and Garber (1989). The results of the 1990 work are reported here.

6.6.2 Sediment Oxygen Consumption (SOC) Rates

Very low sediment oxygen consumption rates were recorded for both stations during 1990, as expected, because of low dissolved oxygen concentrations in deep waters. Sediment oxygen consumption rates ranged from 0.0 to $-0.27 \text{ gO}_2 \text{ m}^{-2} \text{ d}^{-1}$ (Appendix D, Level I, Data Report No. 8, Data Tables). During the 1989 survey the net fluxes of oxygen were also found to be low (Boynton and Garber, 1989). The rates recorded in both sampling periods were too small to have any appreciable influence on dissolved oxygen concentration in the deep waters at the time of measurement. The SOC fluxes reported at station R-64 (located 50 km to the south) during July and August, 1990 were zero (0.0) and 0.01 gO₂ m⁻² d⁻¹, respectively.

Sediment oxygen consumption rates are not an adequate measure of sediment metabolism when oxygen conditions in overlying waters are low (*i.e.*, <1 mg l⁻¹) because SOC rates are limited by the lack of oxygen. Bacterial activity continues in anoxic waters and sediments, but is based on the oxidation of organic matter involving electron acceptors other than oxygen. In marine waters the predominant anaerobic metabolic process involves the reduction of SO₄⁻ to S. We are currently considering a technique for measuring anaerobic sediment metabolism and will apply this technique in environments such as the deep trough when the evaluation procedure is complete.

6.6.3 Ammonium and Nitrite plus Nitrate (NO₂⁻ + NO₃⁻) Fluxes

Ammonium fluxes recorded at the northern station (DT-N1) were lower (463 to 479 μ MN m⁻² hr⁻¹) than those measured at DT-S1 (527 to 798 μ MN m⁻² hr⁻¹), the magnitude of the difference being almost a factor of two (Figure 6-6.1a). Measurements made in July and August, 1989 at the original deep trough stations ranged from 291 to 764 μ MN m⁻² hr⁻¹ (Boynton and Garber, 1989). The values at DT-1 and DT-4 were of the same magnitude as



Figure 6.6.1 Net sediment water fluxes for three variables measured at two deep trough stations during July and August, 1990: (a) ammonium flux, (b) dissolved inorganic phosphorus (PO_4) flux and (c) dissolved silicate flux. The bars represent the mean values and the lines the standard deviations of measurements from triplicate sediment cores.

that reported for DT-S1 and were as high or slightly higher than any NH_4^+ fluxes observed in the mainstem Bay during the first four years of the monitoring program. The northern station followed the trend observed at DT-7 and DT-10 and, although they were high, were more comparable to those observed at other mainstem bay locations.

The magnitude of nitrite plus nitrate fluxes was close to zero (0.0) at both stations in 1990 as in the previous year. This is the expected pattern under summer conditions in hypoxic/anoxic zones of the bay. Under these conditions $NO_2^- + NO_3^-$ fluxes from sediments to water are not possible because sediment nitrification is blocked by low dissolved oxygen conditions. Nitrite plus nitrate fluxes from water to sediments are also low because deep water nitrate concentrations are also low at this time of year (Magnien *et al.*, 1990).

6.6.4 Dissolved Inorganic Phosphorus (PO₄⁻ or DIP) Fluxes

Dissolved inorganic phosphorus fluxes indicated sediment releases of PO_4^- following the same trend as ammonium fluxes. The values at the southern station (DT-S1) were between 62 and 110 μ MP m⁻² hr⁻¹, compared with values of 72 and 61 μ MP m⁻² hr⁻¹ at the northern station (DT-N1) (Figure 6-6.1b). Average fluxes reported at the original four deep trough stations in 1989 ranged from about 10 to 70 μ MP m⁻² hr⁻¹ (Boynton and Garber, 1989). Dissolved inorganic phosphorus flux values at these stations were among the highest yet observed in the mainstem bay and represent a major source of PO₄⁻ to overlying waters. Using algal composition ratios (C:N:P ratio of 100:16:1, for example) it is possible to estimate algal production rates which could be supported by such PO₄⁻ fluxes. A dissolved inorganic flux of 76 μ MP m⁻² hr⁻¹ (mean of the four observations) yields a potential algal production rate of about 2.2 gC m⁻² d⁻¹, which is very substantial. Average ammonium fluxes at this site were capable of supporting about half as much phytoplankton production as PO₄⁻ fluxes.

6.6.5 Dissolved Silicate Fluxes

The fluxes for silicate were positive indicating movement of silicious acid from sediments to the water column. At both stations, values were higher in August than in July, the value for the southern station (DT-S1) being 457 μ MSi m⁻² hr⁻¹ compared to 384 μ MSi m⁻² hr⁻¹ measured at DT-N1 (Figure 6-6.1c). Silicate fluxes were not measured at the four original deep trough stations during 1989. The magnitude of Si fluxes measured during the 1990 summer was very similar to those observed in other areas of the mainstem bay and tributary rivers (Section 6.2).

6.7 Long Term Patterns of Particle Deposition Rates at R-64

6.7.1 Overview

There are several ecological concepts that are central underpinnings of nutrient control programs applied to estuarine systems such as Chesapeake Bay. One of these is that algal biomass levels have upper bounds that are ultimately set by the degree of nutrient loading to which the system is exposed and that biomass levels will respond to loading rate changes. A second, and more recent concept, is that sediment processes in shallow systems play an important, and at times dominant, role in processing nutrients and organic matter. Some of the success experienced with the new Chesapeake Bay water quality model is apparently a

result of explicit incorporation of a sediment sub-model within the main modeling structure. In systems that are moderately stratified, as are portions of the bay, primary production (and algal biomass accumulation) and decomposition processes are separated in space, the former occurring primarily in the upper mixed layer while a large percentage of the latter occurs beneath the pycnocline and at the sediment-water interface. Deposition of particulate organic materials is one of the key mechanisms linking processes of production and decomposition.

From a management viewpoint, information concerning deposition rates is important because it is a measure of the amount of organic matter reaching deep waters which serves to support decomposition processes which, in some areas, cause oxygen depletion and habitat loss. Our conceptual model suggests that as nutrient loads decrease in response to management actions, so to will algal biomass levels, deposition rates and oxygen depletion of deep waters.

Particle deposition rates have been measured at one station, R-64, in the mesohaline reach of Chesapeake Bay since the summer of 1984. Data for six complete calendar years, beginning with 1985, are presented for both particulate carbon and total chlorophyll-a deposition rates measured in the upper mixed layer (surface collecting cups) and at depths in the vicinity of the pycnocline (mid-depth collecting cups). The purpose of this section is to describe patterns of deposition of particulate carbon and total chlorophyll-a for the period 1985 through 1990. Sections 6.8, 6.9 and 6.10 of this report address issues concerning the effects of resuspension on deposition rates, chemical composition of depositing material, inter-annual differences in deposition rates and relationships of deposition to nutrient loading rates and to sediment-water nutrient exchanges.

6.7.2 Particulate Carbon Deposition Rates

Particulate carbon data collected during the period 1985 through 1990 from surface collecting cups (deployed at a depth of 5 meters from the surface) are represented in six individual bar graphs. Particulate carbon values plotted in these graphs (Fig. 6-7.1a) have not been corrected for resuspension effects. The height of each bar indicates the amount of deposition and the width of each bar represents the period from the time of deployment to the time of retrieval. The length of deployment periods varied from four to fourteen days. During spring, the traps were deployed for longer periods than during summer-fall months because during summer and early fall fouling organisms (epiphytic plants and animals) fell into collecting cups and grew on the surface of cups, masking the collection rate of newly depositing particulates. Zero (0.0) values (or the absence of bars) indicate periods when traps were not set.

Deposition rates varied between 350 and 1005 mg m⁻² d⁻¹ in 1985; 280 and 1900 mg m⁻² d⁻¹ in 1986; 220 and 1205 mg m⁻² d⁻¹ in 1987; 200 and 1700 mg m⁻² d⁻¹ in 1988; 300 and 1200 mg m⁻² d⁻¹ in 1989 and 220 and 1000 mg m⁻² d⁻¹ in 1990. In most years, there was an increase in deposition rates during mid spring (circa day 100) which coincided with the spring phytoplankton bloom period. Additionally, in four of the six years (1986, 1987, 1988 and 1989) high rates of particulate carbon deposition (> 1000 mgC d⁻¹) were recorded during the summer, between the end of June and the middle of August. Finally, in 1985, 1987, 1989 and 1990 deposition rates increased sharply for a brief period in the fall, presumably in response to the deposition of the fall diatom bloom.

The seasonal pattern for particulate carbon deposition rate to a depth of 9 meters (middepth collecting cups), is much stronger than in surface collections, and values were generally greater than in surface collections, often by a factor of two or more (Fig. 6-7.1b).

PARTICULATE CARBON DEPOSITION RATES a. Surface Cup Collections, 1985 - 1990



Figure 6-7.1a/6-7.1b Bar graphs showing estimated particulate organic carbon deposition rates for the period 1985 through

1990 based on data collected at station R-64 in the mid Chesapeake Bay.

a. Data collected from surface water collecting cups (5 meter depth).

b. Data collected from deep water collecting cups (9 meter depth).

Values are uncorrected for resuspension. The height of each bar indicates the estimated rate of deposition of particulate organic carbon while bar widths represent the time interval the collecting cups were deployed.

In part these differences were due to the fact that mid-depth cups were closer to the sediment surface and hence more prone to collect resuspended material than were surface cups. Particulate carbon values from mid-depth traps were also not corrected for resuspension effects. However, mid-depth cups were also exposed to a larger water column from which to collect new material. Additionally, some portion of the spring bloom is concentrated in deeper waters and deposition of this material is more available to mid-depth cups. The magnitude of rates varied from 400 to 1800 mg m⁻² d⁻¹ in 1985, 450 to 1690 mg m⁻² d⁻¹ in 1986, 380 to 1500 mg m⁻² d⁻¹ in 1987, 405 to 1600 mg m⁻² d⁻¹ in 1988, 420 to 2417 mg m⁻² d⁻¹ in 1989 and 310 to 1510 mg m⁻² d⁻¹ in 1990. The spring bloom was clearly seen in all six years (Figure 6-7.1b). Values were not as large in 1985 than in other years but this could be an artifact of the less intense sampling regime employed that year. During three years (1987, 1989 and 1990) there was also a strong peak during the fall period. Values obtained during the summer months did not show any striking trends but there were brief periods when rates were substantial, indicating deposition of a summer bloom.

6.7.3 Total Chlorophyll-a Deposition Rates

Data collected during the period 1985 through 1990 for total chlorophyll-a from surface collecting cups (deployed at a depth of 5 meters from the surface) are represented in six individual bar graphs (Figure 6-7.1c). Total chlorophyll-a values have not been corrected for resuspension effects, but we believe corrections would be small because chlorophyll-a is labile and hence would not last long enough to be subjected to cycles of resuspension and redeposition (Section 6.9). The height of each bar indicates the rate of deposition while the width of each bar represents the period from the time of deployment to the time of retrieval. The length of deployment periods varied from four to fourteen days. During spring the traps were deployed for longer periods than during summer months because during summer (and early fall) fouling organisms (epiphytic plants and animals) were abundant and their inclusion in samples would mask the rate of collection of newly depositing particulates. Zero (0.0) values (or the absence of bars) indicate periods when traps were not set.

Total chlorophyll-a deposition rates may present a clearer picture of deposition rates of "new material" than uncorrected estimates based on particulate organic carbon, nitrogen or phosphorus because resuspension effects are probably minimal in the case of chlorophyll-a. The magnitude of total chlorophyll-a deposition rates in the surface layer varied from 1.5 to 25.5 mg m⁻² d⁻¹ during the monitoring period. If chlorophyll-a deposition rates are converted to carbon (using a carbon : chlorophyll-a ratio of 50), rates of 0.1-1.3 gC m⁻² d⁻¹ are obtained and are probably close to being unbiased by resuspension effects. These rates represent a substantial percentage (40-60%) of annual phytoplankton production in surface waters and indicate the strength of benthic-pelagic coupling in the central bay region. In most years there was a readily interpretable seasonal pattern of total chlorophyll-a deposition. Rates were high for a period in the spring (circa day 100), variable but generally lower during summer (days 150-275) and briefly elevated during early fall (circa day 300). Spring deposition is in response to the settling of the spring diatom bloom. Spikes in summer deposition rates are probably the result of settling of summer algal blooms. In most years, but not all, there is a brief fall diatom bloom (Magnien et al., 1990) and the settling of this bloom is reflected in increased deposition rates.

Estimates of total chlorophyll-a deposition based on mid-depth cup collections ranged from 2.4 to 36.6 mg m⁻² d⁻¹. More typical rates were in the range of 5-15 mg m⁻² d⁻¹. In carbon equivalents these rates range from 0.1 to 0.8 gC m⁻² d⁻¹ with maximum rates reaching 1.8 gC m⁻² d⁻¹. In general, mid-depth collection rates were only somewhat greater than surface collections. As noted above, this was not the case for particulate carbon deposition rates, where mid-depth collections were considerably greater, possibly because of resuspension





TOTAL CHLOROPHYLL-a DEPOSITION RATES d. Mid-depth Cup Collections, 1985 - 1990



Figure 6-7.1c/6-7.1d Bar graphs showing estimated total chlorophyll-a deposition rates for the period 1985 through 1990 based on data collected at station R-64 in the mid Chesapeake Bay.

c. Data collected from surface water collecting cups (5 meter depth).

d. Data collected from deep water collecting cups (9 meter depth).

Values are uncorrected for resuspension. The height of each bar indicates the estimated rate of deposition of total chlorophyll-a while bar widths represent the time interval the collecting cups were deployed.

effects. The seasonal pattern of chlorophyll-a deposition was very similar to that observed in surface waters but was more distinct at depth. Additionally, inter-annual differences were also more apparent from mid-depth collections. For example, there was but a small indication of a spring bloom in 1989, as noted in other portions of the monitoring program (Magnien *et al.*, 1990; Sellner, 1989) but well developed bloom signals in other years.

We have found strong and repeatable patterns of deposition which appear to be related to inter-annual variations in nutrient loading and plankton dynamics. Additionally, a substantial fraction of primary production from overlying waters is deposited in deeper waters.

6.8 Particulate Organic Matter (POM) Deposition Rates versus Suspended Concentrations

Although peak rates of phytoplankton production occurred in mid-to late summer in 1985 and 1986, maximum densities of chlorophyll (integrated over the euphotic zone) were consistently observed in early April (Figure 6-8.1). For both years, variations in winterspring chlorophyll stocks were generally coherent with changes in chlorophyll deposition, and both chlorophyll stocks and deposition also exhibited small summer maxima. In fact, by combining data from the two years, we observed significant correlations between chlorophyll stocks and deposition rates (mid-depth deployment) for both spring (March through June) and summer (July through August) periods (Figure 6-8.2). Interestingly, the slope of the summer correlation is twice that for spring. These slopes indicate that algal deposition reflects turnover times of phytoplankton stocks in euphotic zone of 7 and 14 days for summer and spring, respectively. Although sediment-trap data presented for other coastal systems suggest possible correlations between chlorophyll stocks and deposition (e.g., Steele and Baird, 1972; Wassmann, 1984), previous studies have generally not reported quantitative relations. Based on a more limited data set, however, Kamp-Nielsen (1980) and Billen and Lancelot (1988) have presented correlations between chlorophyll standing stocks and deposition rates measured using traps, with slopes of these relations varying from 0.1-0.2 d⁻¹.

The possible implication of relations between chlorophyll stocks and deposition rates (Figure 6-8.2) for the monitoring program is that we could obtain estimates of seasonal sedimentation of particulate organic matter from water column chlorophyll data, which is routinely measured by MDE, rather than that with the relatively expensive VFX program. We investigated the generality of the relations by developing individual correlations between chlorophyll-a stocks and deposition rates for surface and mid-depth deployments during spring, summer and fall of 1985 through 1990 (Table 6-8.1). By separating 1985 and 1986, the relations are generally weaker than they had been for the two years combined; in fact, the relation for surface traps in summer was non-significant. Overall, the spring relations for mid depth traps were highly significant ($r^2 > 0.50$) for all years except 1987 and for 1985 through 1988 with the surface traps. In summer the relations were highly significant ($r^2 > 0.50$) and reasonable (positive slopes) only for surface traps in 1985 and 1987 and for mid depth traps only in 1986 and 1987; significant but weaker ($r^2 < 0.50$) relations were observed for surface traps in 1988 and 1990. While slopes for the summer relations were approximately twice those for spring in 1985 and 1986, this pattern did not persist for later years. Relations for autumn data were erratic and difficult to interpret (often with negative slopes). We must conclude from this initial analysis that water column stocks are not a consistent predictor of deposition rates; we will, however, continue to analyze these relations.



Figure 6-8.1 Seasonal trends of phytoplankton chlorophyll and carbon-fixation (Malone *et al.*, 1987) in relation to deposition of chlorophyll (bars) and carbon (points) for 1985 and 1986 at Station R-64 in mesohaline portion of Chesapeake Bay.



Figure 6-8.2 Relation between chlorophyll concentrations in water column (integrated over euphotic zone) and chlorophyll deposition rates for spring (open symbols) and summer (closed symbols) in 1985 (circles) and 1986 (squares) at Station R-64 in mesohaline portion of Chesapeake Bay.

Table 6-8.1 Regression analyses between total chlorophyll-a concentrations in surface waters (mg m^{-3}) and deposition rates for surface and mid-depth deployments (mg $m^{-2} d^{-1}$). Asterisks indicate that relationships were not significant at the 0.05 probability level.

<u>YEAR</u>	<u>SEASON</u>		SURFACE CUP	MID CUP
1985	SPRING	Slope	0.686	0.636
		r2	0.775	0.902
	SUMMER	Slope r2	1.200 0.688	-0.076* 0.002*
1986	SPRING	Slope	0.510	0.374
		r2	0.457	0.512
	SUMMER	Slope	-1.258*	0.712
		r2 Slana	0.197*	0.582
	FALL	Siope	0.409	-12.20/
		12	0.091*	0.787
1987	SPRING	Slope	0.433	0.167*
		r2	0.543	0.070°
	SUMMER	Slope	0.507	0.703
	FALL	r2 Slope	0.929 0.538*	0.571 0.729
		r2	0.160*	0.897
1988	SPRING	Slope	1.794	0.590
		r2	0.588	0.486
	SUMMER	Slope	0.599	-0.003*
		r2	0.302	0.000*
	FALL	Slope	-2.6/4*	4.518
		r2	0.286*	0.699
1989	SPRING	Slope	0.388*	0.480
		r2	0.145*	0.415
	SUMMER	Slope	0.031	-0.176
	5 411	r2 Slapa	0.126* 1 278	0.063* 1 579
	FALL	Siope	0.668	0.939
		12	0.000	0.000
1990	SPRING	Slope	0.206*	0.337
	0.00	r2	0.184* 0 259	0.885 -0 032*
	SUMMER	Siope	0.000	-0.002
			0.407	0.003

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6.9 Influence of Local Resuspension on Estimates of Deposition

For several decades sediment traps have been used effectively to estimate deposition of newly produced (autochthonous) organic matter in lakes (Bloesch and Burns, 1980). In many aquatic systems and especially for coastal marine environments, resuspension of bottom sediments complicates interpretation of sediment trap collection rates (Steele and Baird, 1972). A simple scheme, using organic fraction as an index to differentiate between bottom resuspension versus pelagic sources, has been employed for sediment trap deployments in lacustrine (Gasith, 1975) and marine (Taguchi, 1982) environments. In these systems resuspension accounted for between 60 and 70 percent of the total sediment trap collection rate. Apparently, traps deployed in deep waters remotely located from littoral areas are less influenced by resuspension (Bloesch and Burns, 1980).

Previously, preliminary corrections for sediment trap data from Station R-64 were made using this approach for representative dates over the course of the 1985 season (Table 6-9.1; details concerning resuspension calculation are provided in the notes to this table). These calculations suggested that resuspension accounts for 15 and 40 present of the total dry weight of material collected in upper and mid traps respectively. Greatest effects of resuspension occurred during the meteorologically active autumn periods. In computing this resuspension correction, bottom sediments at the trap deployment site were assumed to represent all resuspended material collected (2 - 3 percent organic). In fact, bottom sediments had similar organic content at both the R-64 (20m) and the adjacent Dares Beach (10m) stations. Bottom sediment characteristics are in general, similar along a cross-bay transect in this portion of the estuary at water column depths > 5m (Ward, 1985). In addition, the closest shoal areas (with < 5m depths), susceptible to frequent wind resuspension, are located more than 10km from the sediment trap deployment site.

The Gasith (1975) correction factor has systematically been applied to both surface and mid depth arrays (Figures 6-9.1 and 6-9.2) data. The results are somewhat different than those of the preliminary analysis; in this case, it appears that resuspension often accounted for 60-80% of the collection rates (similar to the reports of Gasith, 1975 and Taguchi, 1982). The calculated deposition rates no longer correspond well with other indices of the quantity or timing of POM sedimentation: the spring deposition event is not evident in most years and the amount of organic carbon reaching the sediment is only 20-30% of primary productivity (cf. Malone *et al.*, 1987) rather than the 40-60% value which would be consistent with the general literature (*e.g.*, Smetacek, 1984). There are a number of possible explanations for this discrepancy, but it is assumed that they are related to the assumptions of percentage organic carbon content for the resuspended material. There are serious doubts as to whether or not the Gasith (1975) approach should be applied to these data.

The resuspension corrections for organic carbon deposition rates are lower than those for total dry weight deposition since the ratio of organic carbon content in seston versus bottom sediments is about 5:1 (Table 6-9.1). Chlorophyll content (as a percent of dry weight) of seston is much higher than that in the upper one centimeter of bottom sediments, because the pigment decomposes rapidly once it reaches the bottom. The ratio of chlorophyll content in seston to bottom sediments ranged from 25:1 to 100:1 during 1985. Therefore, resuspension contributions to the chlorophyll weight collected in traps can be considered negligible. Consequently, chlorophyll deposition rates do not need to be corrected, and composition ratios (C:Chl, N:Chl, etc.) can be applied to chlorophyll rates to estimate deposition of other materials. For 1985 data, annual deposition of organic carbon estimates in relation to chlorophyll sedimentation, using a typical C:Chl ratio for seston (75), yields a value equal to about 55% of ¹⁴C production rates (Malone *et al.*, 1987).



Figure 6-9.1a/6-9.1b Bar graphs showing estimated deposition rates of particulate organic carbon for the period 1985 through 1990 based on the data collected at station R-64 in the mid Chesapeake Bay.

a. Data collected from surface water collecting cups (5 meter depth).

b. Data collected from deep water collecting cups (9 meter depth).

Values were corrected for resuspension influences using the method of Gasith (1975). The height of each bar indicates the estimated rate of deposition of particulate organic

carbon while bar widths represent the time interval the collecting cups were deployed.



Figure 6-9.2. Seasonal estimates of the carbon metabolism balance for the water column (a) and relationship between plankton net community metabolism (NCM) and particulate organic matter (POM) deposition rates (b) at a location in the mesohaline portion of the bay (R-64). Gross production estimates are made from Malone et al. (1989) and were based on ¹⁴C measurements. Lower and upper water column respiration rates were based on dark bottle 0₂ measurements and converted to carbon assuming a respiratory quotient of 1.0. POM deposition rates were corrected for deposition using the method of Gasith (1975).

Table 6-9.1 Estimation of fraction of material collected in sediment traps originating from bottom sediment resuspension for selected deployment periods in 1985.

Deployment Period		Correction for Resuspension ²					
	Sesto Mid	n (ft) Top	Trap Mid	(fs) Top	Bottom Seds(f _R)	Mid	Тор
Feb 19 - Mar 5	13.9	15.0	13.3	19.5	2.9	0.85	1.00
Apr 30 - May 8	10.4	7.9	6.5	17.2	2.7	0.49	1.00
Jun 5 - Jun 18	12.7	12.1	9.5	11.9	2.9	0.68	0.98
Jul 24 - Jul 30	9.2	14.3	6.9	· _ 9.3	2.5	0.66	0.58
Aug 13 - Aug 20	9.3	11.9	6.3	9.7	2.4	0.57	0.77
Oct 1 - Oct 16	11.3	8.9	5.7	6.8	2.4	0.37	0.68
Mean						0.62	0.84

NOTES:

1. "Top" refers to upper layer 0-5m depth; "mid" refers to 4-10m depth region.

New Carbon Deposited

-- = $(f_s - f_R) (f_t - f_R)^{-1}$ based on Gasith (1975). 2. Correction factor = Total Carbon Deposited

Estimates from mean of May 27 - June 18. .

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Table 6-9.2 Calculation of total annual deposition rates in traps for comparison with geochronological estimates of long-term sediment accumulation.

Time Period	Daily Carbon Deposition ¹ (gC m ⁻² d ⁻¹)	Ratio ² (gDW:gC)	Total Dry Wt. Deposotion ³ (gDW cm ⁻² y ⁻¹)	Bulk Density ⁴ (g cm ⁻³)	Sediment Accumulation (cm y ⁻¹)
Mar - Nov (275 days)	0.8	10	0.22	0.65	0.34
Dec - Feb (90 days)	0.3	20	0.05	0.65	0.08
Annual (365 days)	0.6		0.27*		0.42

NOTES:

1. Estimated from mean of values summarized for 4 time periods; also estimated from all 1986 sediment trap data as simple mean, corrected for resuspension by 0.85 (Gasith 1975).

Estimated by time-weighted averaging of percent carbon data, where (Apr, 1010 (10%) + Jun, 440 (10%) = Aug, 870 (13%) + Sep, 460 (5%) + 2760 = 10.0% C, and (Dec - Feb) = 5% C.

3. Note that $10^4 \text{ cm}^2 = 1 \text{ m}^2$.

4. Typical values based on measurements of sediments at "R64"; Pb = Ps $(1 - \Phi) = 2.6 (1 - 0.75) = 0.65 \text{ g cm}^{-3}$

* Compare to value of 0.1 - 0.3 g DW cm⁻² y⁻¹ given by Officer et al. (1984).

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Annual rates of sediment accumulation calculated from the sediment trap data can be compared with estimates of net sediment deposition derived from other geochemical tracer techniques (Table 6-9.2). In 1985, sediment accumulated below station R-64 at a rate of approximately 4mm yr⁻¹. Since organic carbon comprises between 10 and 15 percent (Table 6-9.2) of the dry weight of deposited material, total organic weight would be 20 to 30 percent. Assuming that most of this organic matter is remineralized, the long-term net deposition rate would be ca. 3mm yr⁻¹, which is within the range of values estimated by geochronologic techniques (²¹⁰Pb) for this region of Chesapeake Bay (Officer *et al.*, 1984). This agreement between methods suggests that sediment trap data are not distorted by systematic methodological errors, and that measured rates are reasonably representative of actual net deposition. Similar close comparisons between ²¹⁰Pb and sediment traps were reported for two Swiss lakes (Bloesch and Burns, 1982).

A preliminary calculation for the balance of organic carbon metabolism in the water column at the R-64 site of the sediment traps provides perspective on factors regulating POC deposition (Figure 6-9.2). In this analysis, all rates are based on oxygen measurements converted to carbon assuming photosynthetic and respiratory quotients of 1.2. Previous measurements (Kemp and Boynton, 1980; 1981) at a nearby site (6m depth) revealed significant correlations between plankton production and both the respiration of the plankton ($r^2 = 0.66$) and the benthic communities ($r^2 = 0.35$). This suggests that production and respiration are closely coupled, and the combined slopes of these relations indicate that 85-90% of the autochthonous production is consumed in place. On time scales of days to weeks, however, POC deposition is poorly correlated with primary production, and it is the variability of the respiration-production relation which may be more important than production per se, in determining deposition rates. Using 1986 measurements at the R-64 station for production and respiration, we subtract respiration rates for the upper layer (0-8m) and lower layers (8-20m) of the water column from gross production, leaving a "residual" term in the budget (Figure 6-9.2a). This residual corresponds to the POC available for deposition to the sediment surface. It is evident from this analysis that the April and August periods of peak POC deposition (Figure 6-8.1) result from relatively low rates of plankton respiration rather than high rates of production. In the spring, increases in respiration lag those for production because of low temperatures. In late summer, the precipitous decline in respiration probably results from changing trophic interactions in the planktonic community. On a time scale of weeks, we can compare the calculated "residual" portion of organic production, which is not consumed and respired by planktonic organisms, with the sediment trap collection rates for POC. If this residual calculated at 2-4 week intervals is compared to mean sediment trap collection rates (Chlorophyll-a deposition with a C:Chla ratio of 75) for the same time periods, a remarkably close correlation is obtained (slope=0.71, $r^2 = 0.88$), further supporting the quantitative robustness of the sediment traps as quantitative measures for deposition of particulate organic matter (Figure 6-9.2b).

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6.10 Chemical Characterization of Particulate Materials

6.10.1 Overview

In this section the chemical composition of particulate material in the water column and material collected in sediment trap cups is considered. Examination of composition ratios, such as carbon:chlorophyll-a, carbon:nitrogen and carbon:phosphorus, provide insight as to the chemical nature of material in the water column and material which is in the process of sinking out of euphotic waters. More specifically, composition ratios can provide some insight as to the quality of sinking material relative to it's food potential, the degree to which particulate material has been processed by water column grazers and an indirect assessment of the possibility that either nitrogen or phosphorus was limiting biomass production. Boynton *et al.* (1989) reported composition ratios of material collected in sediment trap cups and particularly emphasized seasonal changes in carbon:phosphorus ratios. A portion of this work is outlined here as are results of a more comprehensive examination (on seasonal and annual time-scales) of composition ratios of material collected in the water column as well as in sediment trap collecting cups.

6.10.2 Initial Observations

Strong seasonal trends have been observed in both C:P and N:P ratios of particulate material collected in sediment traps, an example of which is shown in Figures 6-10.1 and 6-10.2 for the years 1985 through 1988. Highest values for both ratios occurred from late winter through late spring while the lowest values were recorded in summer and through the autumn. Comparing ratios with expected proportions based on the Redfield model (e.g., Boynton *et al.*, 1982b), a relative deficiency in phosphorus from winter through summer is apparent. Only in the autumn do values approach Redfield ratios. This deficiency may be more severe than is apparent here, because a substantial percentage (40-60%) of PP is associated with inorganic particulate materials. Ratios of C:N for sediment trap collections were generally between 7 or 8, indicating a consistency with expected phytoplankton proportions.

We are not aware of any other reports of phosphorous ratios for marine sediment trap material. However, C:N ratios of sediment trap collections often exceed Redfield proportions, especially in late winter and spring (Webster *et al.*, 1975; Hargrave and Taguchi, 1978; Davies and Payne, 1984), suggesting possible nitrogen deficiencies in phytoplankton. In contrast, relatively high C:P ratios have been reported for particulate matter collected in sediment traps from lakes in summer, with peak values greatly in excess of Redfield ratios (White and Wetzel, 1975; Gachter and Bloesch, 1985). This pattern, evidently widespread for lakes, has been interpreted as indicative of phosphorus limitation for phytoplankton growth (Gachter and Bloesch, 1985).

For the 1989 data set we have included measurements of "% organic content" and "C:CHL ratio" in addition to N:P and C:P as indices of the qualitative nature of the sedimenting particles (Figure 6-10.3). Percent organic content of particles was calculated assuming that carbon constitutes half of the mass of particulate organic material. Values in 1989 ranged from about 10-40% of the total dry weight, with a seasonal pattern generally following the temperature cycle and an annual mean value of about 20% The low values in winter and late autumn probably indicate a relatively increased proportion of resuspended material collected in the traps. Unlike previous years, particulate material in spring was characterized by a relatively high C:Chl ratio, indicating that organic matter in traps was dominated by zooplankton feces (or resuspended material). Low C:Chl ratios in the 1989



Figure 6-10.1 Particulate carbon to phosphorus (C:P) ratios (atomic) based on material collected in surface traps for the period March 1985-December 1988. The horizontal line on each panel represents a Redfield C:P ratio of about 100.



Figure 6-10.2 Particulate nitrogen to phosphorus (N:P) ratios (atomic) based on material collected in surface traps for the period March 1985-December 1988. The horizontal line on each panel represents a Redfield N:P ratio of about 16.



Figure 6-10.3 Percent organic matter, carbon:chlorophyll-a ratio, N:P ratio (atoms), and C:P ratio (atoms*100) based on material collected in surface traps for the period February - November 1989. The horizontal lines on the bottom three panels represent Redfield ratios (atomic bases) for healthy phytoplankton.

Table 6-10.1 Summary of annual average composition ratios (PC:PN, PC:PP, PN:PP) of particulate materials from surface and mid-depths of the water column and in surface and mid-depth sediment trap collecting cups for the years 1985-1990. Asterisks indicate that r^2 values were not significant at the 0.05 probability level. Boxed values were re-analyzed by season and the results provided in Table 6-10.2.

YEAR	COLLECTION	C:N RATIO			C:P RATIO		N : P RATIO	
	DEPTH		Water Column (C:Nw)	Sediment Traps (C:Nt)	Water Column <u>(C:Pw)</u>	Sediment Traps (C:Pt)	Water Column <u>(N:Pw)</u>	Sediment Traps (<u>N:Pt)</u>
1985	Surface	Slope	6.1	6.6	144	87	19.4	10.3
		r2	0.88	0.75	0.84	0.73	0.71	0.60
	Mid	Slope	7.0	6.7	109	80	15.7	8.6
		r2	0.88	0.83	0.66	0.63	0.72	0.40
1986	Surface	Slope	5.5	4.9	111	42	24.2	9.2
		r2	0.77	0.89	0.39	0.52	0.74	0.68
	Mid	Slope	7.1	5.6	230	29	35.5	4.4
		r2	0.91	0.95	0.50	0.32	0.77	0.23
1987	Surface	Slope	10.0	6.7	16*	99	6*	15.5
		r2	0.83	0.92	0.00*	0.54	0.05*	0.65
	Mid	Slope	6.9	7.2	98	108	17.0	14.1
		r2	0.87	0.96	0.26	0.56	0.42	0.51
1988	Surface	Slope	5.1	6.7	81] 116	17.9	17.0
		r2	0.83	0.92	0.51	0.70	077	0.72
	Mid	Slope	7.0	6.6	120	128	20.4	17.1
		r2	0.92	0.90	0.37	0.52	0.57	0.46
1989	Surface	Slope	6.4	5.4	145	84	23.8	14.9
		r2	0.95	0.91	0.73	0.82	0.86	0.81
	Mid	Slope	5.9	5.5	77	98	12.2	17.1
		r2	0.91	0.96	0.62	0.94	0.61	0.90
1990	Surface	Slope	5.6	6.7	95	81	19.3	13.2
		r2	0.85	0.87	0.48	0.49	0.73	0.68
	Mid	Slope	7.2	6.9	84	111	12.5	16.5
		r2	0.96	0.88	0.28	0.68	0.33	0.81

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Table 6-10.2 Summary of composition ratios (PC:PP, PN:PP) by season, of particulate materials from surface and mid-depths of the water column and in surface and mid-depth sediment trap collecting cups for the years 1985-1990. Only selected observations were examined for seasonal changes in composition ratios. Asterisks indicate values were not significant at the 0.05 probability level.

YEAR		<u>SEASON</u>		C:P Ratio Water Column Sediment Trans		N:P Ratio Water Column Sediment Trans	
				<u>(C:P)</u>	<u>(C:P)</u>	(N:P)	<u>(N:P)</u>
1985	Surface						
	Mid						
1986	Surface	Spring	Slope	171*	37		
		•	r2	0.44	0.37		
		Summer	Slope	120	54		
			12	0.63	0 /6		
	Mid	Spring	Slope	197	58		5.8
			r2	0.64	0 82		0.28
		Summer	Slope	199	50		8.6
			r2	0.50	0.91		0.91
1987	Surface	Spring	Slope	1 99*		14.6*	
		_	r2	0 19		0.10	
		Summer	Slope	-60*		2.2*	
			r2	0.03		0.01	
	Mid	Spring	Slope	240			
			r2	0.52			
		Summer	Slope	101			
			r2	0.52			
1988	Surface	Spring	Slope	204			
			r2	0.53			
		Summer	Slope	75*			
			r2	0.18			
	Mid	Spring	Slope	229			
			12	0.72			
		Summer	Slope	135			
			r2	0.61			
1989	Surface						
	Mid						
1990	Surface	Spring	Slope	200			
		_	r2	0.80			
		Summer	Slope	93			
			r2	0.38			
•	Mid	Spring	Slope	53*			
		-	r2	0.44			
		Summer	Slope	76			
			r2	0.62			

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July and October through November deposition events suggest that the majority of sedimenting material was intact diatoms (Figure 6-10.3). Again, the low summer C:Chl ratios in 1989 contrast sharply with those observed in 1985 and 1986, where most of the materials deposited in the summer during previous years were fecal pellets. Seasonal patterns of N:P and C:P in 1989 (Figure 6-10.3) were similar to those reported for previous years with consistent evidence of P-deficient particles compared to Redfield ratios.

6.10.3 Recent Analyses of Water Column and Sediment Trap Data

Composition ratios (C:N, C:P, N:P; atomic basis) were calculated based on surface and middepth particulate matter collections at the sediment trap site (station R-64) for the years 1985-1990. Comparable ratios were also calculated for material collected in sediment trap cups for the same time period. Results are summarized in Tables 6-10.1 and 6-10.2. In the first table ratios were determined by plotting the various elements against one another, as appropriate, and taking as the annual average composition ratio the slope of the best fit linear regression model. The r² value associated with each regression is also shown. In some cases (e.g., C:P and N:P ratios) the results of annual time scale analyses are enclosed in rectangles. These data were also analyzed on a seasonal basis (spring and summer seasons) and the results are given in Table 6-10.2.

The most consistent result of these analyses is that C:N ratios of material in surface and mid-depth waters and in surface and mid-depth sediment trap collections are remarkably constant. With the exception of surface water collections in 1987, annual average water column C:N ratios ranged from 5.1 to 7.2 and sediment trap collections ranged from 4.9 to 6.9. There were no significant differences between surface ($x = 6.5\pm1.6$) and mid-depth ($x = 6.9\pm0.4$) water column C:N ratios nor were there significant differences between surface ($x = 6.2\pm0.7$) and mid-depth ($x = 6.4\pm0.6$) sediment trap collections. In addition there were only very slight indications of seasonal shifts in C:N ratios of either water column or trap samples. In most cases r² values were greater than 0.85 and in half of the total number of tests exceeded 0.90. The Redfield model of phytoplankton composition indicates that healthy plankton have C:N composition ratios of about 6.6 (atomic basis). Our data suggest that both material in the water column as well as material collected in sediment traps has carbon and nitrogen in proportions remarkably like that of healthy phytoplankton.

6.11 Spring Bloom Deposition Rates and Relationships to Nutrient Loading Rates, Sediment-Water Nutrient Exchanges and Deep Water Oxygen Conditions

6.11.1 Overview and Approach

The conceptual model used as a general guide in these monitoring studies indicates that nutrients from all sources promote the growth of phytoplankton. A portion of the phytoplankton sinks from the surface mixed layer to deeper waters and some smaller portion of this material reaches the sediment surface where it continues to decompose. These processes are connected in a cause-effect chain. In sections 6.2, 6.4 and 6.6, we have characterized separate portions of this cause-effect chain including both deposition and sediment-water processes relative to magnitude, seasonal patterns and inter-annual trends.

The purpose of this section is to examine these data for inter-relationships or causal linkag suggested by the conceptual model. Specifically, inter-annual differences in spri phytoplankton bloom deposition rates are described and then related to several differe nutrient loading rates. Deposition rates throughout the year are then analyzed for influences on nutrient releases from sediments. Finally, spring deposition rate data an examined for possible biological influences on oxygen depletion rates in deep waters, as ar temperature and salinity data for indications of physical influences.

Inspecting monitoring data for signs of causal relationships is essential for managemen applications. However, it is also time-consuming and conceptually difficult, yielding inconsistent results far more often than clear signals. We are at an early stage in this process and the results presented here should be considered preliminary and subject to refinement and re-evaluation as our concepts develop and as further monitoring data become available. At this stage we are optimistic concerning the eventual success and utility of these efforts because of the positive results already achieved.

6.11.2 Spring Bloom Characteristics, 1985-1990

Estimates of the magnitude of deposition resulting from the spring phytoplankton bloom for 1985 through 1990 are shown in Figure 6-11.1. These data were developed using both total chlorophyll-a and particulate organic carbon collections from surface and mid-water collecting cups. Within each year, individual observations of deposition rates were time weighted for the period of the spring bloom deposition event which typically lasts from mid-February through most of May. These data have not been corrected for resuspension effects. However, local resuspension effects on total chlorophyll-a deposition rates are believed to be small (Section 6.9).

Surface water collection rates of particulate carbon during the spring bloom deposition period ranged from about 450 mgC m⁻² d⁻¹ in 1989 to about 750 mgC m⁻² d⁻¹ in 1987. The lowest deposition rates occurred in 1989 when the spring freshet from the Susquehanna River was delayed until May and, as a result, there was a very weak spring bloom (Magnien *et al.*, 1990). Mid-depth collection rates of particulate carbon were considerably higher, ranging from about 875 mgC m⁻² d⁻¹ in 1985 to 1250 mgC m⁻² d⁻¹ in 1989. The inter-annual pattern of deposition at the depth of the mid-cups also differed from that of the surface collections.

The exact reasons for the differing patterns are not clear at this point, but several possible explanations exist. First, resuspension effects have not been considered. It seems reasonable to assume that such effects would be more pronounced closer to the sediment surface than in surface waters above the pycnocline. The correspondence of surface particulate carbon deposition rates with both surface and mid-water chlorophyll-a deposition rates is good, lending support to this interpretation (Figure 6-11.1). Alternatively, there may be some inherent differences in deposition rates between surface and deeper waters. For example, we know that the spring bloom starts in deeper waters, and through the early spring chlorophyll-a concentrations are considerably higher in deep rather than surface waters. However, later in the spring and throughout the summer the pattern is reversed with very low concentrations beneath the pycnocline. There appear to be some strong interactions between deposition rate and water column depth and temperature. Boynton et al. (1990) reported a very good relationship between deposition rates and the difference between phytoplankton production and water column respiration. Water column respiration has a strong temperature dependence and as a result a considerably smaller fraction of water column production is available for deposition during the summer.



Figure 6-11.1 Bar graphs showing estimates of the magnitude of spring bloom deposition rates for the years 1985-1990. Data have not been corrected for possible resuspension effects.

Deposition rates of total chlorophyll-a based on surface cup collections ranged between 4.5 mg m⁻² d⁻¹ in 1989 to about 11 mg m⁻² d⁻¹ in 1987. The inter-annual pattern of total chlorophyll-a deposition was similar to that observed for surface water particulate carbon collections. Mid-depth collection rates of total chlorophyll-a were higher than those of surface cups, ranging from about 6.5 mg m⁻² d⁻¹ in 1989 to 13 mg m⁻² d⁻¹ in 1990.

Three of the four estimates of spring bloom deposition rates reported here follow qualitative trends detected by EPC and other portions of the monitoring program (Magnien *et al.*, 1990). For example, 1989 deposition rates were low which is consistent with observations of the diatom bloom in that year. Deposition rates in 1987 and 1985 were large, again consistent with spring bloom characteristics for those years. Deposition rates of particulate carbon estimated from mid-depth collections had a different pattern but these values have not been corrected for resuspension effects. Natural variability has produced inter-annual spring deposition rates which differ by about a factor of two.

6.11.3 Spring Deposition Responses to Nutrient Loading Rates

One of the main goals of the Chesapeake Bay nutrient control program is to reduce nutrient loads to a point where oxygen depletion of deep waters does not occur or is substantially lessened in intensity. The loss of an adequate oxygen supply to deep waters is, in part, a result of density stratification of the water column through much of the year, which retards mixing and reaeration of these waters. Another feature which promotes chronic hypoxic/anoxic conditions is the decomposition of organic matter in deep water which is the ultimate source of deep-water oxygen demand. Thus, it is deposition of organic matter which links phytoplankton-nutrient processes in the surface layer with the oxygenconsuming decomposition process in deep waters. Given this conceptual relationship, it would be useful to be able to quantitatively link nutrient loading rates to deposition rates and to further establish a connection between deposition rates and oxygen conditions in deep waters. This section presents progress made to date on the former of these linkages.

Estimates of the magnitude of spring bloom deposition for the years 1985 through 1989 were developed from both surface and mid-depth collections. These included deposition rates of particulate organic carbon corrected for resuspension (PCcor, following method of Gasith, 1975), particulate organic carbon deposition (PC, not corrected for resuspension), total chlorophyll-a deposition (ChlT, not corrected for resuspension) and particulate organic carbon deposition rate data converted to carbon using carbon:chlorophyll-a ratios derived from water column samples taken at the beginning and end of trap deployment periods (PCc:chlT). The latter estimate of deposition represents an alternative approach to correcting deposition data for resuspension effects.

Several estimates of TN loads to the Maryland portion of the mainstem bay were also developed. All of these emphasized nutrient loading associated with the spring freshet but utilized loading data for various lengths of time during the freshet period. A number of time intervals were tested because we are not sure of which portion, if not all, of the spring freshet is involved in supporting the spring bloom. Specifically, average TN loads, expressed in units of kgN d⁻¹, were calculated for the following time intervals; December-April, December-March, December-February, January-May, January-April, January-March, February-May, February-April and February-March. In addition the maximum loading rate which occurred between December-April was used as another loading rate variable. These average loading rates were compiled for the years 1985 through 1989.

Simple linear regression analyses were conducted relating nutrient loading rates (independent variable) and deposition rates (dependent variable). A total of 80 regressions were performed, 40 using surface cup collections and 40 using mid-depth cup collections. For each collecting depth, the four deposition rate variables defined above were examined with each of the ten loading variables. Some regressions yielded significant results and many more suggest a positive relationship (*i.e.*, increased deposition with increased loading rates) but one data pair departed from the trend. A single strong departure from a general trend was sufficient to render these regressions non-significant which is not surprising given the small number of observations (n = 5).

There are several preliminary conclusions which can make based on these analyses. Nutrient loads averaged for the period December-April or December-March yielded the strongest load-deposition relationships. Loads which included May data or loads which excluded December or January were never associated with strong load-deposition relationships. These results indicate that nutrients entering the bay from early winter through early spring are most strongly reflected in spring bloom deposition rates. In 1989 the freshet was very late (May) and the spring bloom was very small in magnitude. Maximum monthly nutrient loading rates were generally not correlated with deposition rates suggesting that spring bloom deposition is not simply a response to extreme, relatively rare events.

There were also four different estimates of deposition rates in surface and mid-depth waters used in these analyses. All indices of deposition in surface waters, except total chlorophyll deposition, exhibited some significant relationships or trends to nutrient loading, especially with loadings for the seasonal periods indicated previously. The strongest correlations were found using corrected particulate carbon and total chlorophyll-a (PCc:chlT) deposition rates. There were fewer strong load-deposition relationships apparent for mid-depth collections and this is disappointing because the material collected at depth is far more likely to be deposited at the sediment-water interface than is material collected above the pycnocline. Mid-depth collections may be confounded by resuspended material.

It appears that there is considerable work yet to be done before strong and consistent empirical relationships between loading and deposition will emerge. However, these initial attempts are encouraging as some strong correlations emerged from this first level of analysis. It is hardly surprising that load-deposition relationships in some years do not neatly follow those in other years given the numerous other factors that operate to either produce or consume organic matter in the water column. There were numerous combinations of loading and deposition similar to that shown in Figure 6-11.2 where deposition in one year departed from the apparent trend for reasons that are not clear at this point. It seems that the challenge now is to continue to examine these data, looking for inter-annual differences in loads and other *in situ* environmental conditions which would provide new clues as to the nature of load-deposition relationships.

6.11.4 Deposition Rates and Sediment-Water Nutrient Exchanges

In past years, several factors influencing sediment-water fluxes, particularly sediment oxygen consumption (SOC), have been identified. These include temperature, dissolved oxygen conditions, redox potential (Eh), macrofaunal characteristics, and organic loading to the sediment surface. To date, all of these factors, except organic matter loading rates, have been studied extensively (Andersen and Kristensen, 1988; Doering *et al.*, 1987; Enoksson and Ruden-Berg, 1983; Hargrave, 1969; Hargrave, 1972; Henriksen *et al.*, 1980; Kristensen and Blackburn, 1987; and Murphy and Kremer, 1985). The importance of

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Spring Deposition Rate vs TN Loading Rate

Figure 6-11.2 Scatter diagram relating spring bloom deposition rates (mgC $m^{-2} d^{-1}$) to TN load (kgN d^{-1}) to the Maryland mainstem bay. TN loads were averaged for December - March periods for the years 1985-1989. Deposition rates were based on collections from mid-depth cups. Deposition rates (PCc:chiT) have been corrected for resuspension using the carbon:chlorophyll-a ratio approach (See section 6.11.3 for details). The data indicated by the open circle were not included in calculating regression coefficients.

organic deposition has been recognized since the late 1960's (Carey, 1967; and Hargrave, 1973), but relatively little research has been conducted to clarify this relationship.

Studies that have addressed the influence of organic loading on sediment processes include those by Hargrave (1973), Kelly and Nixon (1984), and Jensen *et al.* (1990). Hargrave calculated a direct relationship between primary production, mixed layer depth, and SOC. He showed that in shallow areas, where organic matter has a higher probability of reaching the sediment surface before being degraded in the water column, SOC is significantly correlated with primary production. He also noted that Pamatmat and Banse (1969) found that in Puget sound, temperature differences only explained 30 % of the variation seen in SOC. It appeared that a significant part of the remaining variance was due to differing rates of organic matter deposition.

Kelly and Nixon (1984) found experimentally that the magnitude of organic deposition has a substantial effect on the magnitude of SOC and NH_4^+ flux. They also found that nearly all deposited organic matter was remineralized in as short a time as 1 to 2 months. The speed with which material was decomposed was also influenced by temperature and the quality of organic matter reaching sediments.

Jensen *et al.* (1990) conducted a field study in Aarhus Bight, Denmark where they measured, NH_4^+ flux, $NO_2^- + NO_3^-$ flux, and bottom water dissolved oxygen concentrations for 18 months. They found that NH_4^+ flux was low, $NO_2^- + NO_3^-$ flux was directed out of the sediments, and DO concentration was relatively high at most times of the year except in April, following deposition of the spring bloom. Decomposition of the flocculent surface layer (1-2 mm thick) decreased bottom water DO concentrations (8.12 mg l⁻¹ in late March to 4.29 mg l⁻¹ in early April) and reduced the sediment oxic zone from 5 to 1.5 mm in the same time period. NH_4^+ flux also increased from 15.8 to 62.5 μ M m⁻² h⁻¹ and $NO_2^- + NO_3^-$ flux decreased from 14.6 to -33 μ M m⁻² h⁻¹ in the same period. Rapid $NO_2^- + NO_3^-$ uptake most likely occurred because of reduced nitrification due to the shallow oxic zone and presence of H₂S below this zone. By mid- May, NH₄+ flux had decreased to late March rates, which agrees with Kelly and Nixon's (1984) organic matter remineralization times of 1 to 2 months. Jensen *et al.* (1990) also concluded that the rapid decline in NH₄+ flux was be due to the exhaustion of the labile organic nitrogen pool.

Similar results were obtained experimentally in 1990 using middle Chesapeake bay cores. Intact sediment cores were brought back to the lab and sealed using methods employed in SONE studies. Cores were stabilized for 48 hours at 18 C and then half were dosed with enough recently killed diatoms (Thallassiosira fluviatilis) to represent about one week of deposition during a spring bloom deposition event. Flux measurements were made eight times over a 45 day period. Dissolved oxygen in the overlying water was maintained above 6 mg 1-1 at all times between flux measurements. During the 45 day time interval, SOC dropped from 1.75 to 0.6 gO₂ m⁻² d⁻¹. The substantial decline in SOC rates we observed were similar to those reported in other studies. High SOC rates in our studies were probably supported by newly deposited labile organic matter and declined rapidly as this material was consumed. While there is not a large amount of literature concerning deposition-sediment fluxes it is clear that this linkage exists, that responses of sediments appears rapid and that temperature and the quality of deposited organic matter modify the linkage. The purpose of this section is to examine SONE and VFX data relative to deposition-sediment flux relationships.

This discussion is begun by examining a data set collected by Kemp and Sampou (1986, *Unpub. manuscript*) at a site in the mainstem bay adjacent to R-64. The goal of this program, which was partially supported by Maryland Sea Grant, was to better understand the sequence of events in spring which produce hypoxic and anoxic conditions in late spring and summer.

Deposition rates and sediment-water exchange rates were intensively measured (nine sets of observations during a 55 day period) from the beginning of April through the middle of May. A summary of these data are shown in Figure 6-11.3. Particulate nitrogen deposition rates exhibited a broad peak reflecting deposition of the spring bloom followed by decreasing rates through early May. Ammonium fluxes were relatively low (<100 μ MN m⁻² hr¹) through April and then increased sharply for a brief period. To examine depositionflux relationships a scatter plot of these variables was developed by matching up peaks and valleys of deposition and flux. There were some fairly obvious time lags between deposition and flux which were considered in developing the scatter plot. The temperature at the time of deposition was also noted and in the final panel of Figure 6-11.3, the time interval between deposition and sediment response was plotted against temperature. A clear relationship between lag time and temperature emerged in which the time interval between deposition and sediment responses decreased sharply as temperature increased. It appears that very discernable sediment responses to deposition rates can be observed if the sampling intensity is sufficiently high. In addition, the time lag between deposition and sediment responses is short (days-week) even at the low to moderate temperature characteristics of spring periods.

For the most part, SONE data at station R-64 (location of the sediment trap array) are not collected frequently enough to conduct the type of analysis described above. In most years However. 4-5 sets of sediment-water exchange measurements are made at this site. sampling frequencies were higher in 1987, 1989 and, to a lesser extent, in 1990. In these years as many as 15 sets of flux measurements were made during the year. These measurements tended to be more frequent during summer than spring and overall were still not as intense as those developed by Kemp and Sampou. We attempted to overcome this problem by combining data from 1987, 1989 and 1990. This analysis, which followed the approach of Kemp and Sampou (matching peaks and valleys of deposition with subsequent peaks and valleys of sediment fluxes), emphasized late spring-summer periods because flux measurement intensity was highest during these periods of the year (Figure 6-11.4). While these plots provide some support for the deposition-flux concept they are not unequivocal for several reasons. First there is considerable variability in flux which is not accounted for by deposition, especially in the case of NH₄⁺ fluxes. Perhaps more importantly, the strong relationship between lag time (*i.e.*, time interval between deposition and sediment response) and temperature reported by Kemp and Sampou was not nearly as strong in this analysis. There were several divergent point and overall the relationship was not significant. We emphasized late spring and summer deposition and flux data. It may be that responses to deposition are sufficiently fast at these temperatures that even a modestly intensive flux measurement program was not sufficient to detect enough temporal variations of fluxes to properly resolve time lag-temperature relationships. Nevertheless, it is still accurate to say that we found either increases or decreases in fluxes shortly after corresponding variations in deposition rates.

As an alternative approach to establishing three types of relationships, deposition and flux data from station R-64 were averaged for periods which encompassed the spring bloom and a three month period following the bloom period, respectively. Again, data from 1987, 1989 and 1990 were used because sampling intensities were particularly high in those years. This yields an extremely limited data set (n = 3) but may be useful for suggesting approaches to be tested in the future. Results of this analysis are shown in Figure 6-11.5a and indicate a strong flux response to changes in deposition rates.

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Figure 6-11.3 A summary of spring deposition rate and NH4⁺ flux data collected at a location adjacent to station R-64 in the mainstem bay during 1986. Panels from top to bottom include: (a) Particulate organic nitrogen (PON) deposition rates from April-May, 1986; (b) sediment NH4⁺ fluxes for the same time period and location; (c) scatter plot relating PON deposition to lagged NH4⁺ fluxes; (d) line-plot relating time lag (days) between PON deposition and NH4⁺ fluxes and bottom water temperature conditions.

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- a. NH4⁺ fluxes.
- b. PO₄⁻ fluxes.

This type of analysis can be extended to include data from areas of the bay where direct measurements of deposition rates are not available. In this case, the assumption was made that the PC, PN, PP or total chlorophyll-a content of surficial sediments were an adequate index of deposition. In other words, it was assumed that sediment nutrient concentrations were a direct result of deposition activity. Two different types of scatter plots were developed. Average sediment NH₄⁺ fluxes were plotted against sediment total chlorophyll-a concentrations measured at station R-64 (Figure 6-11.5b). Again, the number of observations is too limited to make much of the results but there is a striking relationship between the variables. The data indicate that NH₄⁺ fluxes are quite sensitive to changes in sediment PN content.

To further increase the number of observations, this approach was extended to include all SONE stations located in the mainstem bay and the lower reaches of tributaries. The analysis could also be extended to include all SONE stations in the future. In this analysis several different flux variables were developed including "annual" values (average of flux rates measured between April and November of each year) and "summer" values (average of June-August measurements made each year). Sediment nutrient and total chlorophyll-a content was also calculated for spring, spring-summer, summer and "annual" temporal periods. An example of the type of result obtained from these analyses is provided in Figure 6-11.6. With a few exceptions, there appeared to be a strong correlation between sediment PN content and NH_4^+ and PO_4^- fluxes. Substituting summer flux values for "annual" average flux values did not seem to change results in any substantial fashion. However, surficial sediment PN content was a better predictor of flux than were either surficial sediment PC or total chlorophyll-a content. Sediment PP content was a very poor predictor of any flux, including PO₄ flux. Additionally, PN content averaged over the spring-summer period produced stronger relationships than did summer PN concentrations alone and was much better than spring PN concentrations alone. This suggests that summer as well as spring deposition play a role in maintaining sediment-water nutrient fluxes. It is also consistent with the idea that the labile fraction of organic matter in sediments is utilized rapidly (Boynton et al., 1991a) and that sediment nutrient fluxes would respond to future nutrient load reductions. Finally, there were a few measurements that diverged from the general pattern. We have no ready explanation for the unusually high NH₄+ fluxes observed at R-64 and Ragged Point (RGPT) in 1986. There were especially large nutrient loads entering these systems during the late fall-early winter period of 1985. However, it is not clear how these loads may have influenced fluxes. There was no indication of high nutrient content of sediments at these sites in 1986. Finally, NH4+ fluxes measured in the lower Choptank River were almost always high relative to those measured in areas of generally similar sediment characteristics. Again, we have no ready explanation but it may be that benthic infaunal communities play a role in enhancing fluxes in this region of the bay. An effort should be made to examine benthic infaunal community abundance and sedimentwater nutrient exchanges using the data collected by Holland et al. (1989).

6.11.5 Spring Deposition and Hypoxia in the Mainstem Bay

One of the main water quality problems in the bay is the yearly development of zones of hypoxic or anoxic water in deep areas during summer periods. The conceptual model used to guide the EPC program indicates that as nutrient loads to the bay decrease, algal biomass accumulation in the euphotic zone, deposition rates of organic matter to deep waters and deep water and sediment oxygen consumption rates should also decrease. The end result would be a diminution of low oxygen conditions. One of the main goals of the 1991 re-evaluation effort is to determine just how much nutrient loads need to be reduced to alleviate low oxygen conditions.



Figure 6-11.5 Scatter plots of average NH4⁺ flux versus total chlorophyll-a deposition rates and sediment total chlorophylla concentrations. Deposition rate and sediment total chlorophyll-a data were averaged from day 80-230 in 1987, 1989 and 1990. Sediment NH4⁺ flux data were averaged from day 130-230 for the same years. All data were collected at station R-64 in the mainstern bay.

- a. Total chlorophyll-a deposition rates.
- b. Sediment total chlorophyll-a concentrations.



Figure 6-11.6 Scatter plots of "annual" average sediment fluxes versus sediment PN concentrations. Sediment PN concentrations (% dry weight) were averaged over the period April-August for each year. Sediment flux data (μ MN or P m⁻² hr⁻¹) were averaged over the period April through November for each year. Data were collected at stations St. Leonard Creek (STLC), Horn Point (HNPT), Ragged Point (RGPT) and R-64 for the years 1985 through 1990. Data from Broomes Island (BRIS) for 1989 are also included in the plot.

- a. NH4+ fluxes.
- b. PO4⁻ fluxes.

Developing relationships between nutrient loading rates and oxygen conditions is not a simple task for many reasons. A state-of-the-art mathematical simulation model has been developed to address this and other questions. One of the more difficult aspects of this problem is separating the influence of stratification, which inhibits oxygen supplies to waters beneath the pycnocline, from other sources of oxygen demand which are ultimately based on organic matter availability. EPC data are certainly not adequate to entirely resolve this problem but it did appear possible to develop relationships between deep water oxygen characteristics and organic matter deposition rates for any region of the mainstem bay where seasonal oxygen problems are chronic.

Data collected by the EPC, and other components of the monitoring program (Magnien *et al.*, 1990), exhibited deep water oxygen characteristics in the mainstem bay which suggested that deposition-oxygen status relationships might exist. First, severe hypoxic or anoxic conditions have developed in deep waters for some period of time during each year since the monitoring program began in 1984. Even the lowest nutrient loading conditions during this period produced enough phytoplankton biomass to "organic matter saturate" the system and produce low oxygen concentrations. Second, in 1989 the spring freshet (and associated nutrient load) did not enter the bay until mid-May. The spring phytoplankton bloom did not develop to any significant extent and deep water oxygen depletion was delayed for about a month.

These results suggested that deep water oxygen conditions were regulated, at least in part, by the amount of organic material deposited during spring. Vertical mixing of oxygen from surface to deep waters, which is influenced by the degree of water column stratification, is also involved. Separating the effects of biological and physical processes is one of the most difficult aspects of this problem to resolve. Finally, since it appears that the system usually receives enough organic matter to produce hypoxic/anoxic conditions, the inter-annual pattern of oxygen decline may largely be determined by the magnitude of early spring deposition. Deposition later in spring and early summer may have little to do with creating poor oxygen conditions but more to do with maintaining such conditions.

Bottom water oxygen concentrations are routinely measured, on a bi-weekly or weekly basis, at the VFX site located adjacent to station R-64 (Figure 3.1) in the mainstem bay. Water depth at this site is about 17m and vertical stratification characteristics are typical of this region of the bay. The rate of change in oxygen concentration (dO2/dt) and percent saturation $(dO_2 \text{ sat/dt})$ were calculated using these data for spring periods for the years 1985-1990. The time period over which rates of change were calculated varied slightly among years but always included the period from the beginning of March through the middle of May. The criteria used to determine the starting point was that the first observation used was not followed by any oxygen measurements of higher concentration. Typically, during late winter and early spring deep water oxygen concentrations exhibit both small increases and decreases over time but are generally close to saturation. The final oxygen measurement used was the last value greater than 1 mg l-1. The rates of oxygen decline for the years 1985 through 1990 calculated from these data were linear (r² values associated with linear regressions > 0.92); and differed appreciably among years (0.092 mg) 1-1 d-1 to 0.169 mg 1-1 d-1). X-variable equals time (day of year), y-variable equals either bottom water dissolved oxygen (DO) concentration or bottom water percent saturation. The number of observations (n) per year ranged from 6 to 10, while p values were all in excess of one percent (p > 0.01).

The "organic matter saturation" concept described above suggested that dissolved oxygen declines were caused by early deposition events rather than by events occurring later in spring or summer. Accordingly, average spring deposition rates of total chlorophyll-a (mid-depth collecting cups) were calculated for each year using deposition data collected between

early February and the beginning of May. In addition, maximum deposition rates were also organized for this period as were surface and deep water total chlorophyll-a concentrations. Significant relationships were found between the rate of oxygen decline $(dO_2/dt \text{ and } dO_2 \text{ sat/dt})$ and average total chlorophyll-a deposition rates during early spring periods (Figure 6-11.7). Less significant relationships were also found between both measures of dissolved oxygen decline and maximum deposition rates during the same time period. Average deposition rates which included May or May and June data were not well correlated with dissolved oxygen rates of decline. Neither surface nor bottom water total chlorophyll-a concentrations were consistently related to measures of dissolved oxygen decline although trends were similar to those observed for deposition rates.

These results are interesting because they indicate the general magnitude of biological processes on oxygen declines which can be related to nutrient-related processes which in turn are susceptible to management action. However, at least two alternative explanations exist and these, if true, do not readily lend themselves to management actions. First, it can be hypothesized that different spring rates of oxygen decline are caused by inter-annual differences in temperature regimes. Oxygen declines would be more rapid in warm years than in cool years simply because of the influence of temperature on respiration rates. In this scenario, organic matter needed to support respiration has never been limiting, even during the early spring period. This explanation seems unlikely to be the prime cause because inter-annual temperature differences have been small over the period of record and warm and cool springs were not correlated with high and low rates of oxygen decline (Figure 6-11.7).

Second, it could be hypothesized that the cause is related to inter-annual differences in the degree of water column stratification. In years when the water column is highly stratified, less mixing of oxygen from surface to deep water would occur and oxygen rates of decline would be greater. Stratification certainly plays a major role in determining deep water oxygen characteristics but there appears to be less of a case made for stratification being a dominant factor in causing inter-annual differences in oxygen rates of decline. As shown in Figure 6-11.7 there are inter-annual differences in average spring salinity gradients (bottom minus surface salinity). However, the years of high and low stratification do not correspond to years of high and low rates of oxygen decline as they should if stratification was a prime factor in causing these differences. It appears that the strongest case can be made for a biological cause of inter-annual differences based on organic matter supply rates to deep waters.

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Figure 6-11.7 Bar graphs of average bottom water temperature and salinity gradient (bottom minus surface salinities) during spring periods of 1985-1990 at station R-64 in the mainstem bay. Also shown are scatter plots of rates of change of dissolved oxygen (dO_2/dt) and dissolved oxygen saturation (dO_2 sat/dt) versus total chlorophyll-a deposition at mid-depth of the water column (Mid ChIT Depo, mg m⁻² d⁻¹). Deposition and dissolved oxygen data were also collected at station R-64 during spring periods of 1985-1990.

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