

PART 1: Interpretive Report

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MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEM PROCESSES COMPONENT (EPC)

LEVEL ONE REPORT NO. 7

PART 1: INTERPRETIVE REPORT

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PREPARED FOR:

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PREFACE

This report is submitted in accordance with the Schedule of Deliverables set out in Contract 177-C-MDE-89 between the Maryland Department of the Environment (MDE), Chesapeake Bay and Special Projects and the University of Maryland, Center for Environmental and Estuarine Studies (CEES). This report contains a description of sampling procedures employed by the Ecosystems Processes Component (EPC) of the Maryland Chesapeake Bay Water Quality Monitoring Program, a complete hard-copy listing of all data collected by the EPC during the period of July 1984 through December 1989 and interpretation of data relative to water quality conditions in the Bay.

The SONE and VFX data tables in Appendices B and C respectively contain a complete compilation of the data collected for EPC and reflect the efforts begun in August 1989 to verify and standardize all EPC data files. Revised station code names used in all data tables can be found in Table 3-1.1. Detailed location and descriptive information for all stations is in Tables 3-1.2. and 3-1.3. Revised variable names together with a description of the units presently used in both SONE and VFX programs, together with the matching variable used in the public information data base of the Chesapeake Bay Program called CHESSEE are listed in Appendix A, Table A-1 and in the EPC Data Dictionary. 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. (301) 326-4281.

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| |

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 early May and mid October at two locations in the mainstem Bay, and at one to four locations in each of three tributary rivers.

Deposition rates are monitored at one mainstem Bay location. Deposition measurements are made almost continuously during the spring, summer and fall periods. This program was initiated in July 1984, and the basic data collection scheme has been followed through October 1989. This report considers data collected from April 1989 through November 1989 and contains a discussion of trends and relationships observed to date.

It appears that an important environmental event in 1989 was the delay of the spring freshet from the Susquehanna. In most years peak flows occur in either March or April, but in 1989 peak flows did not occur until May. This delay in the freshet (and nutrient loading) had a measurable influence on many of the variables monitored in the EPC program. At mainstem bay SONE stations (and the VFX station, R-64) surface salinities were abnormally low during late spring and early summer and oxygen concentrations in deep waters abnormally high. The onset of low dissolved oxygen (DO) conditions was delayed by five to six weeks when compared to 1988 data for station R-64. High concentrations of nitrite plus nitrate $(NO_2^- + NO_3^-)$ also persisted further into the late spring period than in previous years. Sediment Eh conditions remained positive through June which is also abnormal.

Chlorophyll-a concentrations at station R-64 were low, and sediment trap data indicated that there was only a weak spring bloom in late March. However, there appeared to be a very large fall deposition period in early October. The amount of material in the water column ("residual") available for sedimentation was well correlated with sediment trap collections corrected for resuspension, supporting the quantitative use of traps for measuring deposition in the mainstem bay. Sediment-water fluxes of oxygen in 1989 were lower than in previous years except in the Patuxent River; NH_4^+ fluxes generally increased; fluxes of $NO_2^- + NO_3^-$ from sediments to water continued to be the dominant pattern only in lower tributaries; inorganic phosphate (DIP) fluxes were higher than in previous years.

An examination of monitoring data for relations between nutrient loading to several areas of the bay and responses of key environmental variables was initiated. Strong relationships were found between river flow (as an index of nutrient loading) and annual primary production for a mesohaline bay site (R-64). Annual average chlorophyll-a stocks as well as benthic fluxes of PO_4^- and NH_4^+ were found to be well correlated with a function of Nloading. These results tend to confirm the utility of the conceptual model upon which the monitoring program was based and also indicate that sampling intensities are capable of detecting changes in processes and stocks at levels relevant for management.

2. INTRODUCTION

During the past decade much has been learned about the effects of nutrient inputs (e.g., nitrogen, phosphorus, silica), from both natural and anthropogenic sources, on such important estuarine processes as phytoplankton production and oxygen status (Nixon, 1981; D'Elia et al., 1983). While our understanding is not complete, important pathways regulating these processes have been identified and related to water quality conditions. For example, annual algal primary production and maximum algal biomass levels in many estuaries (including portions of Chesapeake Bay) are related to the magnitude of nutrient loading from all types of sources (Boynton et al., 1982a). Also, high, and at times excessive, algal production is sustained through the summer and fall periods by the benthic recycling of essential nutrients. Similarly, sediment oxygen consumption (SOC) is related to the amount of organic matter reaching the sediment surface, and the magnitude of this demand is sufficiently high in many regions to be a major oxygen sink (Hargrave, 1969; Kemp and Boynton, 1980).

2.1 Nutrient input and sediment deposition in Chesapeake Bay

The delay between nutrient additions and the response of algal communities suggests that there are mechanisms to retain nutrients in estuaries such as the Chesapeake. These nutrients can be mobilized for use at later dates. Research conducted in Chesapeake Bay and other estuaries indicates that estuarine sediments can act as both important storages and sources for nutrients as well as important sites of intense 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. In terms of storage, sediments in much of Chesapeake Bay, especially the upper Bay and tributary rivers, contain large amounts of carbon, nitrogen, phosphorus and other compounds. A large percentage of this material appears to reach the sediments during the warm periods of the year. Some portion of this same material is available to regenerative processes and therefore eventually becomes available for continued algal utilization. Nutrients and other materials deposited or buried in sediments represent the potential "water quality memory" of the 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 remineralized. Essential nutrients released during the decomposition of organic matter may then be utilized by algal communities. A portion of this newly produced organic matter sinks to the bottom, contributing to the development of anoxic conditions and loss of habitat for important infaunal, shellfish and demersal fish communities. The regenerative capacities and the potentially large nutrient storages in bottom sediments insures a large return flux of nutrients from sediments to the water column and thus sustain continued phytoplankton growth. Continued growth supports deposition of organics to deep waters, creating anoxic conditions typically associated with eutrophication of estuarine systems.

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Sediment-water processes and deposition of organic matter to the sediment surface are major features of estuarine nutrient cycles. These processes play an important role in determining water quality and habitat conditions. For example, during summer periods, when water quality conditions are typically poorest (*i.e.*, anoxic conditions in deep water, algal blooms), sediment releases of nutrients (*e.g.*, nitrogen, phosphorus) and consumption of oxygen are often highest as is the rate of organic matter deposition to the deep waters of the Bay. To a considerable extent, it is the magnitude of these processes which determines nutrient and oxygen water quality conditions in many zones of the Bay. Ultimately, these processes are driven by inputs of organic matter and nutrients from both natural and anthropogenic sources. If water quality management programs are instituted and loadings decrease, changes in the magnitude of the processes monitored in this program will serve as a guide in determining the effectiveness of strategies aimed at improving Bay water quality and habitat conditions.

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 important indications of the effectiveness of nutrient control actions.

2.2 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.

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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). 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 1989.

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 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.). Four of the ten stations sampled as part of the SONE study are 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 additional stations are located in each of three tributary rivers (Patuxent, Choptank and Potomac), one in the turbidity maximum or transition zone and one in the lower mesohaline region. 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, 1985 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

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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 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 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, yet it is still close to the MDE station.

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

| 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 | 77 |
| _ | 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 |

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

NOTES:

A = Stations sampled in SONE 1 - 20, August 1984 - June 1989. Numerical ranking indicates the order in which they appear in the data tables.

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

- * = 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.

1 = This is the only current VFX station.

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).

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| 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° 38.13' | 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' | 75° 58.30' | 3.8 | NONE | ET5 |
| Potomac River | | | | | |
| RGPT | 38° 09.86' | 76° 35.52' | 16.5 | XBE9541 | LE2 |
| MDPT_ | 38° 21.37' | 77 ⁰ 11.49' | 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 |

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. ($R \text{ km}^1 = 31.5$) | |
| Choptank River | | |
| HNPT | 4.0 nautical miles downstream of Route 50 Bridge at Cambridge, MD. ($R \text{ km}^1 = 18.6$) | |
| 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. ($R \text{ km}^1 = 29.8$) | |
| MDPT | 1250 yards SE of Buoy R-18. (R km ¹ = 71.0) | |
| Chesapeake | | |
| Mainstream | | |
| PNPT | 3.2 nautical miles East of Point No Point. (R km ¹ = 129.0) | |
| R-64 | 300 yards North East of channel Buoy R-64.* (R km ¹ = 177.4) | |
| DRBH | West of channel Buoy R-64.* ($R km^1 = 177.4$) | |
| 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 km ¹ = 225.8) | |
| SLPD | 700 yards West of channel marker 41.* ($R km^1 = 258.1$) | |

NOTE:

* 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.

| STATION CODE | SALINITY CODE |
|-----------------------|---------------|
| Patuxent River | |
| STLC | <u>M</u> |
| BRIS | M |
| MRPT | M |
| BUVA | 0 |
| Choptank River | |
| HNPT | M |
| WDHL | 0 |
| Potomac River | |
| RGPT | M |
| MDPT | 0 |
| Chesapeake Mainstream | |
| PNPT | M |
| R-64 | M |
| TMPT | M |
| R-78 | M |
| SLPD | 0 |

Table 3-2. Station Salinity

The Salinity Zone layer codes are as follows:

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| SALINITY CODE | DESCRIPTION | | |
|---------------|----------------------------|--|--|
| F | Freshwater | | |
| 0 | Oligohaline 0.5 - 5.0 ppt | | |
| М | 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 - May).

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 - August).

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

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 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 depositional 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 depositional 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 interannual 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 period. VFX measurements also coincide with other monitoring program sampling activities. The sampling schedule for 1984-1986 is shown in Figure 3-2.1. and 1987-1989 in Figure 3-2.2. for this component of the monitoring program (also EPC Data Dictionary Figures B-3 and B-4). 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.

Figure 3-2.1. SONE and VFX Sampling Schedule for 1984-1986

Figure 3-2.2. SONE and VFX Sampling Schedule for 1987 - 1989

| 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 | 13 NOV | Aquarius |
| SONE 11 | APR 1987 | 20 APR | 23 APR | Aquarius |
| SONE 12 | JUN 1987 | 10 JUN | 15 JUN | Aquarius |
| SONE 13 | AUG 1987 | 17 AUG | 20 AUG | Aquarius |
| SONE 14 | NOV 1987 | 09 NOV | 16 NOV | Aquarius |
| SONE 15 | APR 1988 | 17 APR | 22 APR | Aquarius |
| SONE 16 | JUN 1988 | 01 JUN | 07 JUN | Aquarius |
| SONE 17 | AUG 1988 | 15 AUG | 21 AUG | Aquarius |
| SONE 18 | NOV 1988 | 01 NOV | 09 NOV | Aquarius |
| SONE 19 | APR 1989 | 04 APR | 10 APR | Aquarius |
| SONE 20 | JUN 1989 | 12 JUN | 16 JUN | Aquarius |
| SONE 21 | JUL 1989 | 12 JUL | 14 JUL | Aquarius |
| SONE 22 | AUG 1989 | 14 AUG | 16 AUG | Aquarius |
| SONE 23 | OCT 1989 | 16 OCT | 18 OCT | Aquarius |

Table 3-3.1. SONE Cruise Identifier

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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 |
| 16 OCT 1984 | 790 | Aquarius |
| 30 NOV 1984 | 802 | Aquarius |
| 17 DEC 1984 | 1082 | Orion |
| 19 FEB 1985 | 809 | Aquarius |
| 05 MAR 1985 | 1090 | Orion |
| 01 APR 1985 | 815 | Aquarius |
| 15 APR 1985 | 1097 | Orion |
| 27 MAY 1985 | 1109 | Orion |
| 05 JUN 1985 | 829 | Aquarius |
| 18 JUN 1985 | 1113 | Orion |
| 27 JUN 1985 | 833 | Aquarius |

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Table 3-3.4. VFX Cruise Dates (23rd July 1984 to 30th November 1989) for Station R-64 and Dares Beach (11th July 1985 to 14th November 1986).¹

| 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 | 9 59 | Aquarius |
| 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 | <u>15 JUL 1987</u> | 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 30th November 1989) for StationR-64 and Dares Beach (11th July 1985 to 14th November 1986).1 - Continued

| DATE | CRUISE NO. | RESEARCH VESSEL | DATE | CRUISE NO. | RESEARCH VESSEL |
|--------------------|--------------|--------------------|-------------|------------|--------------------|
| 16 NOV 1987 | 1003 | Aquarius | 23 NOV 1988 | 1408 | Orion |
| 01 DEC 1987 | 1005 | Aquarius | 08 FEB 1989 | 1082 | Aquarius |
| 18 DEC 1987 | 1335 | Orion | 27 FEB 1989 | 1084 | Aquarius |
| 09 FEB 1988 | 1341 | Orion | 10 MAR 1989 | 1087 | Aquarius |
| 25 FEB 1988 | 1346 | Orion | 22 MAR 1989 | 1089 | Aquarius |
| 10 MAR 1988 | 1352 | Orion | 05 APR 1989 | 1091 | Aquarius |
| 23 MAR 1988 | 1355 | Orion | 20 APR 1989 | 1093 | Aquarius |
| 06 APR 1988 | 1015 | Aquarius | 02 MAY 1989 | 1426 | Orion |
| 22 APR 1988 | 1017 | Aquarius | 09 MAY 1989 | 1098 | Aquarius |
| 02 MAY 1988 | 1366 | Orion | 16 MAY 1989 | 1429 | Orion |
| 09 MAY 1988 | 1368 | Orion | 23 MAY 1989 | 1104 | Aquarius |
| 16 MAY 1988 | 1370 | Orion | 31 MAY 1989 | 1432 | Orion_ |
| 23 MAY 1988 | 1372 | Orion | 07 JUN 1989 | 1435 | Orion |
| 01 JUN 1988 | 1027* | Aquarius | 12 JUN 1989 | 1110 | Aquarius |
| <u>08 JUN 1988</u> | 1027* | Aquarius | 21 JUN 1989 | 1441 | Orion |
| 17 JUN 1988 | 1376 | Orion | 27 JUN 1989 | 1112 | Aquarius |
| <u>22 JUN 1988</u> | 1378 | Orion | 05 JUL 1989 | 1114 | Aquarius |
| <u>28 JUN 1988</u> | 1034 | Aquarius | 12 JJL 1989 | 1118 | Aquarius |
| 05 JUL 1988 | 1380 | Orion | 19 JUL 1989 | 1120 | Aquarius |
| <u>13 JUL 1988</u> | 1038 | Aquarius | 26 JUL 1989 | 1122 | Aquarius |
| 19 JUL 1988 | 1039 | Aquarius | 02 AUG 1989 | 1450 | Orion |
| 27 JUL 1988 | 1385 | Orion | 09 AUG 1989 | 1128 | Aquarius |
| 04 AUG 1988 | 1043 | Aquarius | 14 AUG 1989 | 1129 | Aquarius |
| 11 AUG 1988 | <u>13</u> 89 | Orion | 24 AUG 1989 | 1131 | <u>Aquarius</u> |
| 17 AUG 1988 | 1047 | Aquarius | 06 SEP 1989 | 1455 | Orion |
| 06 SEP 1988 | 1392 | Orion | 14 SEP 1989 | 1457 | Orion |
| 13 SEP 1988 | 1050 | Aquarius | 20 SEP 1989 | 1458 | Orion |
| 19 SEP 1988 | 1395 | Orion | 03 OCT 1989 | 1141 | Aquarius |
| 12 OCT 1988 | 1401 | Orion | 12 OCT 1989 | 1464 | Orion |
| 17 OCT 1988 | 1404 | Orion | 17 OCT 1989 | 1146 | Aquarius |
| 24 OCT 1988 | 1066 | Aquarius | 02 NOV 1989 | 1469 | Orion |
| 01 NOV 1988 | 1067* | Aquarius | 08 NOV 1989 | 1470 | Orion |
| 09 NOV 1988 | 1067* | Aquarius | 15 NOV 1989 | 1155 | Aquarius |
| 17 NOV 1988 | 1070 | Aquarius | 30 NOV 1989 | 1156 | Aquarius |

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

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 m 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 (DIP or PO₄⁻), 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 due to reduction in finances related to the grant supplied by the funding agency.

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 Plexiglas 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 O2 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 Plexiglas liner filled with bottom water, incubated and sampled as described above serves as a blank. Overlying water samples are filtered and immediately frozen for later analysis for ammonium (NH_4^+) , nitrite (NO_2^-) , nitrite plus nitrate $(NO_2^- + NO_3^-)$, dissolved inorganic phosphorous (DIP or PO_4^-) 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 using the volume: area ratio of each core.

Beginning in July 1989 fluxes of hydrogen sulphide (H₂S) were measured at SONE stations exhibiting bottom water DO $< 1 \text{mgl}^{-1}$ or when sulfide in bottom water was detected by smell.

It should be noted that at low oxygen concentrations ($< 2mgl^{-1}$) SOC rates become proportional to oxygen concentrations as we noted in our previous report(Boynton *et al.*, 1988). 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) which is independent of oxygen conditions.


Figure 4-1. Schematic Diagram of the Incubation Chamber

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4.1.2 VFX Study

At the VFX station, a water column profile of temperature, salinity and dissolved oxygen is obtained at 2m 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.

4.1.2.1 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.

4.1.2.2 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 m and 9 m 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

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

4.1.3 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 (DIP or PO₄⁻) 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 Paasche (1973); total suspended solids (seston) are determined by the gravimetric technique of EPA (1979).

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5. DATA MANAGEMENT

The level one data and progress report includes tabular listings of all variables measured during SONE and VFX monitoring programs. 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 VFX (EPC Data Dictionary).

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 only available 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.

5.2 VFX Study

VFX data, currently only collected 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.

5.3 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.

| ANALYSIS PROBLEM CODE | DESCRIPTION |
|--------------------------|---|
| A | Laboratory accident |
| B | Interference |
| С | Mechanical/materials failure |
| D | Insufficient sample |
| N | Sample lost |
| P | Lost results |
| | 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. |

Table 5-1. Analysis Problem Codes

6. CONSIDERATIONS OF HISTORICAL PATTERNS OF SOC AND NH_4^+ FLUX

In our previous Level I reports (e.g. Boynton et al., 1989) we identified several locations in the bay where sufficient sediment flux data were available to allow investigation of historical patterns. Data collected at these stations prior to August 1984 are compared to more recent data collected in the MDE monitoring program. Several patterns emerge and we continue to pursue these types of comparisons and to relate trends in sediment fluxes to patterns of river flow.

6.1 Patuxent River Patterns

At the Buena Vista station (BUVA, upper Patuxent River) patterns of sediment oxygen consumption (SOC) and ammonium (NH_4^+) regeneration were relatively distinct in the earlier period (1978-1980) with annual maxima occurring in mid-July and late August, respectively (Figure 6-1). In the more recent period (1983-1988), rates were generally lower with seasonal peaks of SOC and NH_4^+ flux occurring in spring and early summer, respectively. SOC fluxes in 1989 were close to the lowest yet observed at this station although the seasonal pattern characterized by a spring peak was still evident. Fluxes of NH_4^+ were also somewhat low but within the range of values observed since 1985.

Some additional insight into sediment processing of nitrogen can be gained by comparing oxygen to ammonium fluxes (O:N ratios on an atomic basis). The utility of this exercise is based on stoichiometric considerations of the type of organic matter being metabolized (decomposed) at the sediment surface. If nutrient replete phytoplanktonic detritus is being decomposed to the level of NH_4^+ , an O:N flux ratio of about 13 would be expected. If the O:N ratio exceeds 13 then it is probable that NH_4^+ is entering other pathways (*i.e.* nitrification) in sediments rather than being released to overlying waters and continuing to be available for phytoplanktonic uptake. During 1989 at Buena Vista O:N flux ratios ranged from 9 to 28 with only the April value (28) being appreciably above 13. Values for June through October averaged about 12 indicating that simple decomposition of organic matter predominated at the sediment surface.

At the St. Leonard Creek station (STLC, lower Patuxent River) the seasonal temperature pattern in 1989 was similar to that observed in previous years (Figure 6-2). In fact, there has been only one significant departure (May, 1981) from an otherwise repetitive pattern. However, it appears that a different pattern is developing in more recent SOC data in comparison with older SOC data. In the early 1980's SOC reached maximum levels (2-3 g $O_2 \text{ m}^{-2} \text{ d}^{-1}$) in the spring with slightly lower rates in the summer (Figure 6-2). Since 1987 SOC rates have been lower throughout the year except in the fall. Additionally, there is only a slight indication of a spring peak in SOC in recent years. Two explanations for this pattern are possible and involve oxygen concentration in deep waters and the availability of labile organic matter. Low SOC rates can be caused by low oxygen concentrations, generally < 2mg l⁻¹. At St Leonard Creek we have observed oxygen concentrations as low as 1.8mg l⁻¹, and this was associated with an SOC rate of 1g O_2 m⁻² d⁻¹. However, similarly low SOC rates have been observed at this station during the June-August period when bottom water DO concentrations were well in excess of 2mg 1⁻¹. It is doubtful that depressed SOC rates were the result of low DO conditions. A more likely explanation is that June through August SOC rates were low, because labile organic matter deposited from the spring bloom

had already been largely consumed. Ammonium fluxes were low in the spring and fall of 1989. Late spring (June) and summer (July and August) fluxes were comparable to those recorded in the late 1980's but lower than those observed in 1980 and 1981.

In previous reports we considered the possibility that changes in the magnitude and seasonality of sediment-water fluxes at two locations in the Patuxent estuary were in response to alterations in temperature or river flow (as an index of nutrient loading) between the 1978-1983 period and the more recent 1985-1989 period (Figure 6-3). Some temperature differences between the earlier and recent periods were found. Spring temperatures were somewhat higher in the recent period, while peak summer values were higher in the earlier period (an exception: data collected during August 1986). Temperatures in 1989 were also consistent with the pattern of recent years. However, the temperature differences observed between the two periods could at best explain about 30% of the observed flux differences (assuming a Q_{10} of 2.0).

Annual mean flow of the Patuxent (monitored at Bowie, MD) was substantially higher from 1978-1980 (ca. 520 cfs) than from 1983-1985 (ca. 380 cfs). Flows during 1986-1988 were even lower (ca. 280 cfs). These patterns of flow generally coincide with SOC and NH₄⁺ regeneration rates at Buena Vista where rates were higher in the early period and lower in more recent years. This observation is consistent with a simple conceptual model which postulates a direct chain of influence: (1) river flow delivers dissolved nutrients, (2) this supports plankton production, some of which is deposited to the sediment surface, (3) this fuels SOC and NH₄⁺ regeneration, and (4) the cycles of excessive oxygen consumption by sediments and algal blooming supported by recycled nutrients are perpetuated (*e.g.* Boynton *et al.*, 1982b).

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Figure 6-1. Annual patterns of mean water temperature and ranges in SOC and ammonium regeneration at Buena Vista for several time periods: 1978-1980; 1985-1988; and 1989 (shown as separate symbols). SOC rates are plotted as positive values by convention but represent flux of oxygen from water to sediments.



Figure 6-2. Annual patterns of water temperature, SOC and ammonium regeneration from sediments for St. Leonard Creek Station (STLC) in the Patuxent River estuary between 1980 and 1989. Given are the means and standard deviations for three replicate flux measurements. SOC rates are plotted as positive values by convention but represent flux of oxygen from water to sediments.





6.2 Sediment Flux Patterns in the Bay and Lower Tributaries

Summer (August) and Spring (May) rates $(x\pm SD)$ of SOC and NH₄⁺ regeneration for stations in the open Bay (R-64) and in the lower tributaries (HNPT and STLC) for 1980-1981 and 1985-1989 are shown in Figure 6-4.

SOC fluxes were higher in both summer and spring of the earlier period (1980-1981). Since 1985 there has been a general trend towards lower SOC values at these stations, with particularly large (\approx 3x) reductions at the station in the lower Choptank River (HNPT). Our conceptual model would suggest that the differences in SOC rates between the lower Patuxent and Choptank Rivers ultimately result from different nutrient loading rates. There were also very large reductions in SOC at station R-64 between the 1980-1981 period and more recent years (1985-1989), particularly in August. It appears that the high rates observed during the earlier period at this station were the result of deep waters being reoxygenated prior to the measurement. In later years (1986-1989) O₂ concentrations in deep waters at R-64 were extremely low (>0.4 mg l⁻¹; often less than 0.2 mg l⁻¹) at the time of measurement and hence SOC was small. In this case, the sharp reduction in SOC does not indicate improved conditions in sediments (and hence water quality) but rather a shift from aerobic (monitored as SOC) to anaerobic metabolic pathways.

Ammonium fluxes were low (generally <100 μ MN m⁻² hr⁻¹) in the spring (May) at all stations compared to summer fluxes. Summer fluxes at the mainstem station (R-64) exhibited considerable interannual variation (210-700 μ MN m⁻² hr⁻¹) and averaged about 500 μ MN m⁻² hr⁻¹ through the measurement period. In contrast, August fluxes at the lower Choptank (HNPT) and Patuxent (STLC) stations were much higher in 1980 than in more recent years and interannual variability is much reduced. For the period of record, August NH₄+ fluxes in the Choptank and Patuxent averaged about 270 μ MN m⁻² hr⁻¹ or about one half those observed in the mainstem bay.

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Figure 6-4. Sediment oxygen consumption and ammonium regeneration from sediments at an open Bay station (R-64) and two stations near the mouths of tributaries, St. Leonard Creek [STLC] and Horn Point [HNPT], for 5-6 time periods. Means and standard deviations are shown for three replicate flux measurements. SOC rates are plotted as positive values by convention but represent flux of oxygen from water to sediments.

7. SEDIMENT OXYGEN DEMAND AND NUTRIENT FLUXES

Sediment fluxes considered in this section were collected during five years of the MDE monitoring program from May 1985 to December 1989 (SONE Cruises 3-23). This data base now comprises 20 sets of flux measurements and supporting environmental data for each SONE station. In this section we examine these data for general patterns of flux variability and spatial and temporal patterns in SOC and nutrient fluxes.

7.1 Variability in Benthic Flux Measurements

We have conducted a thorough review of the SONE data base, re-verifying data files and computer algorithms used to generate the sediment fluxes. As before, if the the results from a sediment core did not meet specific quality-control criteria these data were excluded from further analysis (see EPC Data Dictionary). About 4% of the flux data, which now consists of 2700 individual flux determinations, failed to meet the criteria for "interpretable" fluxes and had to be removed from the data base. In 1989 5% of the fluxes (33 of 660) were not interpretable. The success rate for flux measurements since the inception of the monitoring program has therefore been about 96%.

The coefficient of variation [CV = (std. dev./mean) x100] is a useful statistic for comparing the relative variability among sets of similar measurements (Snedecor and Cochran, 1967). Overall variability in the flux data can be estimated by comparing CV's for all flux measurements made at each station (*i.e.*, combining the data from several SONE cruises) with those determined for a typical set of three replicate measurements from an individual cruise (Tables 7-1 and 7-2). The variability within each set of flux measurements ranged between 49-368% for all fluxes except NO₂⁻ + NO₃⁻. The much higher variability associated with NO₂⁻ + NO₃⁻ fluxes resulted from large sporadic fluxes into or out of sediments driven by high NO₂⁻ + NO₃⁻ concentrations in the water column (*see* Boynton *et al.*, 1988 page 85) or nitrification in sediments, respectively. The variability, as indicated by coefficients of variation, includes not only the variability associated with a single triplicated flux measurement but also variability associated with seasons of the year. There are strong seasonal variations associated with most fluxes and variations among stations in the magnitude of fluxes. Coefficients of variation, averaged for all SONE stations, were: 67, 85, 752, 160 and 66 percent for SOC, NH₄⁺, NO₂⁻ + NO₃⁻, DIP (PO₄⁻) and Si, respectively.

We have also determined CV's for several typical flux measurements at a specific station (Table 7-2). In this case, where variability associated with seasonality is not included, CV's were much lower, ranging between 7-22%, except for $NO_2^- + NO_3^-$ fluxes which were again higher. For comparison, the CV's for some environmental variables such as bottom water temperature, salinity, oxygen and NH_4^+ concentrations, determined in conjunction with the benthic fluxes at the SONE stations, ranged from 10-100% (Table 7-3).

The CV calculations reflect the overall within-station variability in sediment fluxes. They also indicate that the within-station variability for oxygen and nutrient fluxes was remarkably uniform among the ten SONE stations. Oxygen and silicate fluxes exhibited the least overall variability (CV's of $\approx 66\%$); the flux of nitrate + nitrite (NO₂⁻ + NO₃⁻) was the most variable (CV's in excess of 750%) of the benthic nutrient fluxes. With the exception of NO₂⁻ + NO₃⁻ flux, seasonal and site-related variability encountered during SONE monitoring produced CV's that ranged between 66 - 160%. This degree of total variability in the measured fluxes

| Station | O ₂ | NH4 ⁺ | NO2"+NO3" | DIP | Si |
|----------------------|----------------|------------------|-----------|-----|-----|
| STLC | 67 | 81 | 152 | 126 | 70 |
| BUVA | 49 | 63 | 184_ | 100 | 64 |
| HNPT | 70 | 64 | 218 | 125 | 62 |
| WDHL | 50 | 96 | 2594 | 125 | 56 |
| RGPT | 88 | 79 | 22753 | 105 | 60 |
| MDPT | 60 | 96 | 163 | 368 | 73 |
| PNPT | 78 | 72 | 1417 | 197 | 62 |
| R-64 | 82 | | 439 | 126 | 60 |
| R-78 | 65 | 91 | 1282 | 190 | 67 |
| SLPD | 59 | 119 | 316 | 140 | 90 |
| Average | 67 | 85 | 752* | 160 | 66 |
| Total # of Fluxes | 459 | 454 | 459 | 445 | 455 |

Table 7-1. Comparison of coefficients of variation(%) of sediment fluxes from
SONE cruises 2-18

NOTES:

* Does not include data from Ragged Point.

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| <u>Station</u> | | 0- | NH . + | | קוח | e: |
|----------------|---------|-------|--------|----------|-------|-------|
| Station | <u></u> | | | 102 -103 | | |
| June 1988 | X | -1.46 | 291.2 | -1.41 | 15.23 | 335.5 |
| | SD | 0.17 | 21.5 | 1.99 | 3.33 | 56.4 |
| | CV | 11.64 | 7.4 | 141.42 | 21.88 | 16.8 |
| August 1988 | x | -0.80 | 214.3 | -2.22 | 50.26 | 523.1 |
| | SD | 0.10 | 43.3 | 4.63 | 5.51 | 86.0 |
| | CV | 13.15 | 20.2 | 208.55 | 10.97 | 16.4 |
| June 1989 | x | -1.67 | 219.6 | -129.24 | 14.67 | 332.0 |
| | SD | 0.39 | 40.5 | 16.89 | 4.84 | 102.9 |
| | CV | 23.04 | 18.5 | 13.07 | 33.02 | 31.0 |
| August 1989 | x | -1.02 | 252.3 | -26.89 | 51.21 | 430.3 |
| | SD | 0.18 | 61.8 | 12.54 | 27.59 | 165.8 |
| | CV | 17.82 | . 24.5 | 46.63 | 53.88 | 38.5 |

Table 7-2.Flux characterizations (mean, standard deviation, coefficient of
variation) developed from data collected in June and August, 1988 and 1989
at the Buena Vista [BUVA] station (upper Patuxent River)

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Table 7-3. Coefficients of variation of some typical water quality characteristics of near-bottom water at station R-64 determined with a sampling design identical to that of SONE flux measurements (n=30 to 36)

| Station | [O ₂] | [NH4 ⁺] | Temperature | Salinity |
|---------|-------------------|---------------------|-------------|----------|
| STLC | 50 | 54 | 23 | 12 |
| BUVA | 30 | 114 | 21 | 16 |
| HNPT | 27 | 87 | 24 | 19 |
| WDHL | 18 | 81 | 22 | 27 |
| RGPT | 78 | 70 | 24 | 10 |
| MDPT | 26 | 59 | 22 | 43 |
| PNPT | 69 | 61 | 24 | 12 |
| R-64 | 93 | 47 | 27 | 14 |
| R-78 | 88 | 36 | 28 | 15 |
| SLPD | 22 | 54 | 25 | 58 |

appears to be inherent in field measurements of ecological processes and is consistent with previous measurements of sediment-water fluxes in Chesapeake Bay (Boynton and Kemp 1985, Callendar and Hammond, 1982) and other temperate estuaries (Nixon *et al.*, 1976).

7.2 Spatial Patterns in Station-Averaged Fluxes of Oxygen and Nutrients

7.2.1 Sediment oxygen consumption (SOC)

Station averages of sediment oxygen consumption (SOC) at ten SONE stations ranged between -0.54 and -1.57 g O_2 m⁻² d⁻¹ during SONE cruises 3-23 (Table 7-4; Figure 7-1). During the calendar year 1989, SOC ranged from -0.02 to -2.00g O_2 m⁻² d⁻¹. These rates of benthic oxygen consumption are moderate to large when compared with SOC rates reported for other temperate estuaries (Table 7-5). It is important to note that SONE monitoring does not include measurements during the winter. Comparisons of our station averages with other seasonally or annually averaged flux data, which may include winter measurements, should therefore be done cautiously. Since completion of the BEST program (see Garber et al., 1989) it is now clear that SOC is low, as are nutrient fluxes in the mainstem Bay, when temperatures are below 10C.

Oxygen flux data collected prior to 1988 indicated that SOC tended to be highest at the shallow tributary stations and lower in the deeper mainstem bay. The inclusion of 1989 data further strengthened the finding of differences in SOC rates in tributaries and the mainstem bay. As shown in Figure 7-2, SONE stations could be separated into three groups based on average station SOC: high average SOC's were found in the Patuxent and Choptank Rivers; rates were intermediate at the upper bay station at Still Pond (SLPD) and considerably lower in the Potomac River and mid-mainstem bay.

Caution must be exercised in utilizing SOC rates as a general indicator of sediment metabolism. Difficulties arise in areas where dissolved oxygen concentrations are reduced (*i.e.*, $<2mg \ l^{-1}$). In those situations SOC appears to be reflecting ambient DO conditions rather than sediment metabolism. With this in mind we interpret the lower average SOC rates observed in the lower bay and in hypoxic areas as indicative of chronic low oxygen conditions in overlying waters rather than low rates of sediment metabolism limited by a low rate of organic matter supply. In short, SOC is not a good indicator of sediment metabolism in areas exposed to chronic hypoxia; we need to begin using another measure of sediment metabolism (probably dissolved inorganic carbon flux) as soon as possible.

At the remaining three areas (upper bay and upper and lower tributaries) low oxygen conditions are rare, and SOC is a reasonable measure of sediment metabolism. We speculate that the differences between tributary and upper bay sites is primarily regulated by the quality of organic matter reaching the sediment surface. The quality is higher in the tributaries where phytoplanktonic debris dominates and is lower in the upper bay where refractory terrestrial detritus is important.

In the future, we need to seperate SOC data into categories where oxygen concentrations are high enough to influence oxygen fluxes, and therefore reflect sediment metabolism, or where oxygen concentrations are low, affecting fluxes so that sediment metabolism cannot be determined. Those values reflecting sediment metabolism can be detrended for temperature effects and grouped by season to better determine among station differences and among year trends at particular stations.



Figure 7-1. Average station fluxes ($\bar{x}\pm$ SD) for net sediment-water exchanges at all SONE monitoring stations. Each mean is based on all observations at a particular station from April 1985 - October 1989.



Figure 7-2. Average net sediment-water fluxes ($\bar{x}\pm$ SD) for distinctive areas of the Maryland portion of the Bay.

Areas included the following station groupings: Upper Tributaries = BUVA, WDHL and MDPT; Lower Tributaries = STLC and HNPT; Upper Bay = SLPD; Lower Bay = PNPT; Hypoxic Areas = R-64, R-78 and RGPT. Means are based on all data collected between April 1985 and October 1989. Table 7-4. Average station fluxes ($\bar{x} \pm SD$) for SONE Monitoring Stations. Means in both (A) and (B) were determined using data from SONE cruises 3 - 23 (May, 1985 - October, 1989). In (B) area groupings included the following: Upper Tributaries = BUVA, WDHL, MDPT; Lower Tributaries = STLC, HNPT; Upper Bay = SLPD; Lower Bay = PNPT; Hypoxic Areas = R-78, R-64, RGPT. Units are: for SOC ($gO_2m^{-2}d^{-1}$); for all others (μ Mm⁻²hr⁻¹ as N, P or SI).

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| Α | | | | | | | | | | | |
|---------|-------|----------|-------|-----------------------|--------|----------------|-------|----------|-------|---------|--|
| STATION | SOC | SOC FLUX | | NH4 ⁺ FLUX | | NO2 + NO3 FLUX | | DIP FLUX | | Si FLUX | |
| | AVG. | SD | AVG. | SD | AVG. | SD | AVG. | SD | AVG. | SD | |
| STLC | -1.44 | 0.93 | 108.1 | 81.1 | 20.29 | 31.76 | 6.05 | 6.81 | 322.8 | 200.6 | |
| BUVA | -1.47 | 0.69 | 187.2 | 121.6 | 1.65 | 39.53 | 17.34 | 14.94 | 276.0 | 177.6 | |
| HNPT | -1.24 | 0.90 | 152.2 | 92.2 | 18.52 | 37.04 | 7.74 | 8.90 | 326.1 | 199.5 | |
| WDHL | -1.57 | 0.83 | 164.2 | 168.9 | -15.63 | 69.67 | 17.30 | 20.69 | 383.7 | 226.5 | |
| RGPT | -0.74 | 0.70 | 241.3 | 193.0 | -3.25 | 38.32 | 17.80 | 19.48 | 223.7 | 118.5 | |
| MDPT | -0.99 | 0.60 | 151.7 | 134.7 | -4.71 | 68.40 | 2.22 | 12.77 | 229.8 | 173.3 | |
| PNPT | -0.78 | 0.57 | 117.5 | 80.0 | -4.85 | 15.87 | 4.92 | 9.07 | 316.0 | 196.8 | |
| R-64 | -0.67 | 0.49 | 258.3 | 182.8 | -11.94 | 27.46 | 25.55 | 31.07 | 377.7 | 214.9 | |
| RP78 | -0.54 | 0.36 | 89.6 | 87.9 | -4.02 | 35.77 | 9.89 | 15.15 | 174.6 | 112.2 | |
| SLPD | -1.02 | 0.59 | 89.2 | 94.5 | -28.60 | 38.24 | 3.78 | 4.09 | 168.7 | 152.5 | |

В

| STATION | SOC FLUX | | SOC FLUX NH4 ⁺ FLUX | | NO2" + NO3" FLUX | | DIP FLUX | | Si FLUX | |
|----------------------|----------|------|--------------------------------|-------|------------------|-------|----------|-------|---------|-------|
| | AVG. | SD | AVG. | SD | AVG. | SD | AVG. | SD | AVG. | SD |
| Upper Tributaries | -1.34 | 0.75 | 168.7 | 141.0 | -19.82 | 63.41 | 12.29 | 17.73 | 289.0 | 200.1 |
| Lower Tributaries | -1.34 | 0.92 | 130.2 | 89.6 | 19.40 | 34.51 | 6.89 | 7.97 | 324.5 | 210.3 |
| Upper Bay | -1.02 | 0.59 | 89.2 | 94.5 | -28.60 | 38.24 | 3.78 | 4.09 | 168.7 | 152.5 |
| Lower Bay | -0.78 | 0.57 | 117.5 | 80.0 | -4.85 | 15.87 | 4.92 | 9.07 | 316.0 | 196.8 |
| Hypoxic Areas | -0.65 | 0.54 | 200.1 | 179.7 | -6.49 | 34.53 | 18.02 | 23.98 | 261.6 | 179.3 |

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| Table 7-5. | Comparis | son of ox | ygen, DIN | and DIP flu | xes at SON | E monitor | ing stations |
|------------|------------|-----------|-----------|-------------|-------------|-----------|--------------|
| with | summer | rates of | oxygen a | nd nutrient | fluxes from | n various | near-shore |
| mar | ine syster | ns. | | | | | |

| | Measurement Period | SOC gm ⁻² d ⁻¹ | NH4 ⁺ Flux μMNm ⁻² d ⁻¹ | DIP Flux µMPm ⁻² d ⁻¹ | Ref. |
|----------------------------|-----------------------|---|---|--|------|
| Lock Ewe, Scotland | June - July | 0.6 - 1.05 | 20 - 80 | - | 1 |
| Buzzard's Bay, MA | June | 1.42 | 125 | -15 | 1 |
| Eel Pond, MA | July | 1.08 | 85 | 16 | 1 |
| Narragansett Bay, RI | June - August | 1.80 | 200 | 30 - 50 | 1 |
| Long Island Sound, NY | July | - | 50 - 200 | 5 - 20 | 1 |
| New York Bight, NY | August | 0.84 | 25 | 2 | 1 |
| Patuxent River Estuary, MD | June - August | 3.03 | 710 | 48 | 1 |
| Pamlico River Estuary, NC | Unknown | - | 45 | - | 1 |
| South River Estuary, NC | May | 1.57 | 250 | 17 | 1 |
| Cape Blanc, West Africa | Unknown | - | 235 | 50 | 1 |
| Vostoc Bay, USSR | August | 1.08 | 150 | 20 | 1 |
| Maisuru Bay, Japan | July | - | 13 - 32 | - | 1 |
| Kaneohe Bay. HA | Annual Mean | 0.46 | 54 | 3 | 1 |
| La Jolla Bight, CA | July - August | - | 40 | 6 | 1 |
| Yaquina Bay mudflat, OR | Unknown | -6.0 - 6.8 | -91 - 204 | -5 - 19 | 2 |
| Chesapeake Bay, MD | | | | | |
| Upper tributaries | April - November | 1.5 | 163 | 11 | 3 |
| Lower tributaries | April - November | 1.4 | 210 | 11 | 3 |
| Mainstream bay | April - November | 0.9 | 125 | 12 | 3 |
| Upper bay (Still Pond) | April - November | 1.3 | 90 | 2 | 3 |

References: 1. Modified from Table 1 in Nixon 1981

2. Collins 1986

3. Location means from SONE Monitoring, this report

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7.2.2 Dissolved inorganic nitrogen fluxes

7.2.2.1 Ammonium flux

The results of SONE monitoring are consistent with earlier studies in Chesapeake Bay (Boynton *et al.*, 1980) and elsewhere (Nixon *et al.*, 1976, Hammond *et al.*, 1985, Zeitzschel, 1980) in showing that NH_4^+ generally dominates benthic fluxes of fixed inorganic nitrogen in productive temperate estuaries. The release of NH_4^+ from sediments at the SONE stations was generally many times greater than the net exchange of nitrate + nitrite. At most stations NH_4^+ flux accounted for 70-100% of the total DIN flux (the sum of NH_4^+ plus nitrate + nitrite) from the sediment. There were two exceptions: NH_4^+ fluxes at Maryland Point and Still Pond contributed a smaller fraction to the net exchange of DIN, probably because NO_3^- concentrations in the water column were generally very high.

Average station fluxes of NH₄⁺ ranged from 89 μ MN m⁻² hr⁻¹ at Still Pond to 258 μ MN m⁻² hr⁻¹ at R-64 (Table 7-4 and Figure 7-1). The average flux at most stations fell between 100-200 μ MN m⁻² hr⁻¹. Two of the stations exhibiting the highest rates of NH₄⁺ release from the sediments (Ragged Point and R-64) are subject to summer anoxia. Station R-78 is subject to summer anoxia as well, but NH₄⁺ fluxes at this station appear to be anomalously low. Relatively high fluxes were also found at Buena Vista, an upper tributary, and there it remains aerobic all year. The factors responsible for these between-station differences are probably related to several environmental variables including temperature, the concentration gradient of ammonium across the sediment-water interface, the redox state of the sediments and overlying water, activity of the benthic organisms and the rate of deposition of particulate nitrogen. Overall, for ammonium "area averaged" fluxes were as follows: Hypoxic areas > Upper Tributaries > Lower Tributaries > Lower Bay > Upper Bay (Figure 7-2).

Viewed in this way, high fluxes in hypoxic areas would be expected, because: (1) there is a large supply of organic matter to the sediment surface to fuel ammonification, and (2) hypoxic conditions would prevent the transformation of ammonium to NO_3^- and subsequent denitrification. Lower ammonium fluxes might be expected in the lower and upper bay because deposition rates would be lower in the former and of low quality in the latter, and nitrification of some fraction of the ammonium produced is operative at both sites at least in the Spring and Fall(Twilley and Kemp, 1987 and Kemp, pers. comm.).

7.2.2.2 Nitrate + nitrite $(NO_2^{-} + NO_3^{-})$ flux.

Unlike ammonium, $NO_2^- + NO_3^-$ fluxes followed more pronounced spatial patterns (Figure 7-1, Table 7-4) which included shifts in direction of the fluxes across the sediment-water interface. The calculation of average station fluxes revealed that the behavior of $NO_2^- + NO_3^-$ differed among three groups of stations. Tributary stations in the Patuxent and lower Choptank were characterized by the net release of $NO_2^- + NO_3^-$ from the sediment to the water at rates that averaged around 20 μ MN m⁻² hr⁻¹. In contrast, the overall flux of $NO_2^- + NO_3^-$ was into the sediment in the upper Potomac and the uppermost mainstem bay. $NO_2^- + NO_3^-$ flux was variable at the remainder of the stations, resulting in station-averaged fluxes that were small (<10 μ MN m⁻² hr⁻¹). In June 1989, $NO_2^- + NO_3^-$ fluxes for individual cores ranged from maximum sediment release of 103 μ MN m⁻² hr⁻¹ in the lower Patuxent (STLC) to the maximum sediment uptake of -129 μ MN m⁻² hr⁻¹ in the Upper Patuxent (BUVA). However, most $NO_2^- + NO_3^-$ fluxes fell within an envelope bounded by -45 to +20 μ MN m⁻² hr⁻¹ (Figure 7-1).

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The net $NO_2^- + NO_3^-$ flux reflects the combined effects of chemical and biological factors that regulate NH₄⁺ production, nitrification, denitrification and the fluxes of solutes across the sediment interface. Nitrate concentration in waters over the sediments can influence the measured rate of $NO_2^- + NO_3^-$ uptake by limiting the amount of nitrate available for nitrate metabolism (and denitrification) as well as influencing diffusion-driven flux of nitrate at the sediment surface. Highest rates of sediment uptake of $NO_2^- + NO_3^-$ (i.e., the most negative rates of $NO_2^- + NO_3^-$ flux) generally occur at two upper estuary stations (Maryland Point and Still Pond) that were characterized by the highest levels of dissolved nitrate in the water over the sediments. Other factors influence $NO_2^- + NO_3^-$ fluxes in other regions of the bay. For example, although nitrate concentrations in bottom water at the upper tributary station in the Choptank River (Windy Hill) were relatively high, the average NO₂ + NO₃ flux at that station were not strongly negative. Oxygen content of the overlying water and sediment redox regime undoubtedly influence $NO_2^2 + NO_3^2$ exchange dynamics by influencing the nitrogen-transforming activities of the benthic microbial community. Ammonium oxidation is the first step in the formation of nitrate. Sediments throughout the bay appear to produce an abundance of NH4+, so it seems unlikely that the first step of nitrification, NH_4^+ oxidation, would be limited by NH_4^+ availability. However, nitrification is an obligately aerobic process, while nitrate metabolism occurs under predominantly anaerobic conditions. The rate of $NO_2^- + NO_3^-$ uptake must ultimately be limited by $NO_2^- + NO_3^-$ availability. The rates of NH_4^+ oxidation (nitrification) and nitrate reduction (especially denitrification) are strongly coupled, especially when sources of "new" nitrate from river flow diminish after the spring freshet.

The net releases of $NO_2^- + NO_3^-$ observed in the Patuxent and lower Choptank tributaries reflect predominantly oxidized environments both in surficial sediments and overlying waters. Such conditions would favor sediment-associated nitrification over denitrification, hence the net release of nitrate from the sediments. At other locations in the bay, the redox environment appears to shift between oxic and anoxic conditions, the former favoring nitrification, the latter favoring nitrate metabolism and denitrification. Nitrate formation and consumption appear at times to be in balance. This results in no net flux of $NO_2^- +$ NO_3^- at the sediment surface. However, along the mainstem bay where hypoxic and anoxic conditions prevail during the summer, the balance apparently shifts away from nitrate metabolism and little net removal of $NO_2^- + NO_3^-$ from overlying waters occurs. At these stations NH_4^+ regeneration appears to be the only significant route of nitrogen remineralization occurring in the sediments other than burial in the accreting sediment column.

7.2.3 Dissolved inorganic phosphorus (DIP) flux

During the SONE monitoring program DIP fluxes ranged from sediment uptakes of -23 μ MP m⁻² hr⁻¹ at Maryland Point in August 1987 to sediment releases of DIP of 92 μ MP m⁻² hr⁻¹ at R-64 in June 1986. Although sediment uptake of DIP occurred occasionally, station-averaged fluxes of DIP were always positive, *i.e.*, the net flux was from the sediment to the overlying water (Table 7-4 and Figure 7-1). The station-averaged DIP fluxes during five years at the ten SONE stations ranged from about 2.2 μ MP m⁻² hr⁻¹ at Maryland Point to 25.6 μ MP m⁻² hr⁻¹ at R-64 (Table 7-4). SONE stations could also be separated into two groups by calculation of station-averaged DIP fluxes: one group consisting of the lower tributary stations in the Patuxent and Choptank and the lower and upper mainstem Bay where average DIP fluxes were less than 7 μ MP m⁻² hr⁻¹ and the other group consisting of the upper tributaries and hypoxic areas where average station fluxes were in excess of 10 μ MP m⁻² hr⁻¹ (Figure 7-2). These results suggest that relatively high DIP fluxes occur in the low salinity reaches of some tributaries (the upper Potomac may be an exception) as well as the regions of the bay that experience summer anoxia.

Finding the mechanisms that seem to "turn on" and "turn off" DIP fluxes is clearly crucial to understanding phosphorus dynamics at the sediment-water interface. We have shown that the redox conditions of sediments and overlying waters is one such important factor, particularly in the mainstem bay (Boynton *et al.* 1989). However, the DIP flux data collected to date suggest that the mechanisms regulating DIP fluxes probably differ at various locations within the bay. For example, DIP fluxes tended to be highest along the deeper reaches of the mainstem bay and the upper tributaries. The release of DIP from sediments along the deep mainstem bay is most likely associated with the drop in redox potential that accompanies the depletion of oxygen in the overlying water. Such release of DIP from sediments during anoxic conditions is a well known process in lakes and fjords and involves the redox-driven dissolution of iron phosphates and other compounds(Krom and Berner, 1980 and Klump and Martens, 1981). It seems unlikely that a similar mechanism controls the relatively large fluxes of DIP from sediments in the upper tributaries, because overlying waters in these regions are always well-oxygenated. It seems probable that substantial PO₄⁻ fluxes in upper tributaries result from infaunal irrigation of sediments by the substantial benthic communities present at these sites (Holland, 1989).

While we remain unable to define the processes that regulate DIP fluxes precisely, the magnitude of these fluxes are often sufficient to influence the concentration of DIP in the overlying water (cf. Nixon et al., 1980). Consequently, the benthic flux of DIP influences the amount of DIP available for phytoplankton production, as well as altering the the ratio of DIP to DIN in bay waters.

7.2.4 Dissolved silicate flux

The flux of silicate from individual cores during the monitoring period from 1985-1989 ranged from 0 to 1008 μ MSi m⁻² hr⁻¹. Station-averaged fluxes for all the stations were always positive (*i.e.*, from the sediment to the water) and of the order of 150-400 μ MSi m⁻² hr⁻¹ (Table 7-4, Figure 7-1). Highest fluxes occurred along the deep mainstem bay and in the tributaries. Lowest fluxes were observed in the upper mainstem bay areas (Figure 7-2). Silicate fluxes among major regions appear to increase in parallel with increasing salinity: Upper Bay < Upper Tributaries < Lower Tributaries < Hypoxic Areas. This pattern is consistent with a conceptual model which would predict increasing silicate cycling in higher salinity regimes (Yamada and D'Elia, 1984) in parallel with the increasingly important role of diatom production in the phytoplankton communities along the estuarine salinity gradient.

7.3 Temporal Patterns in Benthic Fluxes

7.3.1 Seasonal patterns in benthic fluxes at SONE stations

Our sampling schedule of four measurements per year (five beginning in 1989), skewed toward the summer, is not adequate to clearly define annual patterns of benthic fluxes. However, there is an important seasonal component of variability in the SONE measurements, and it needs to be considered in order to define year-to-year trends. In this analysis we have combined flux data for all years by month for each station. The purpose of this exercise is to identify patterns of seasonality in the flux data. The results of this analysis $(\bar{x} \pm SD)$ are presented as a series of plots (Figures 7-3a through 7-3j).

The results of this effort to identify seasonal signals in the flux data indicate that no single seasonal pattern adequately describes changes in fluxes that occur at the SONE stations throughout the year. The caveat is that our sampling program was not designed to produce

a high resolution, seasonal picture. For example, there was a clear indication of seasonality in all nutrient fluxes in the upper Choptank (WDHL) while essentially no seasonality could be discerned in nutrient fluxes in the upper mainstem bay (SLPD, Figure 7-3j).

Most SONE stations exhibited clear seasonality in SOC in which the highest rates of SOC occurred in May or June with a lesser peak in fall. This pattern clearly emerged at station STLC (Figure 7-3a). The intriguing feature of this pattern is that it is out of phase with the cycle of bottom water temperature (which reaches seasonal peaks at most stations in August) by 2-3 months. The upper Potomac appeared to be unique in that the seasonal maximum in SOC was shifted towards late summer (Figure 7-3f). At stations subject to periodic anoxia, seasonal patterns of SOC were strongly influenced by the timing and duration of low-oxygen conditions and the occurrence of re-aeration events. These factors contributed to the high variability and generally low rates in summer observed at R-64 and R-78 (Figures 7-3h and 7-3i). SOC fluxes observed in 1989 were lower than in previous years in the lower Potomac and Choptank Rivers and higher in the Patuxent and the lower mainstem bay.

Ammonium fluxes at SONE stations also followed fairly straightforward seasonal patterns with maximum rates of sediment release occurring in summer in most cases (Figures 7-3d and 7-3h). Exceptions to this pattern were observed at station R-78 where the seasonal peak in NH₄⁺ flux occurred earlier in the year and at Still Pond where no seasonal pattern could be discerned and fluxes were generally small (< 200 μ MN m⁻² hr⁻¹). It appears that the seasonal cycles of oxygen uptake and NH₄⁺ release from the sediment may be out of phase by 2-3 months in the lower tributaries and mid-mainstem bay. This pattern probably results because macrofaunal oxygen consumption and oxygen consumption by nitrifying bacteria are highest in the spring and decreases later in the summer. Additionally, NH₄⁺ flux is small in the spring in part because of sediment nitrification and because of incorporation of particulate nitrogen into macrofaunal biomass. In the early summer ammonium flux increases as nitrification decreases, macrofaunal stocks have declined and temperature exerts a strong influence on bacterial metabolism. Fluxes of NH₄⁺ in 1989 were either similar to those in 1987-1988 or higher. Particularly strong increases in NH₄⁺ fluxes were observed in both the lower Patuxent and lower mainstem bay.

Temporal variations in nitrate + nitrite $(NO_2^- + NO_3^-)$ fluxes were generally complex and differed among SONE monitoring stations (Figures 7-3a through 7-3j). The kinds of seasonal patterns in $NO_2^- + NO_3^-$ flux included: (1) pronounced unimodal change from sediment uptake in spring to maximum sediment release in fall (WDHL), (2) a bimodal pattern with periods of sediment release in spring and fall (BUVA), and (3) the most common pattern, best illustrated by the data from station RGPT (Figure 7-3e), included a rapid shift from positive or near-zero sediment $NO_2^{-} + NO_3^{-}$ flux to strong sediment uptake in spring. This was then followed by a shift toward sediment release in summer and fall. Some variation of this pattern occurred at stations STLC, HNPT and at all the mainstem bay stations with the exception of SLPD in the upper bay. The occurrence of a sediment $NO_2^{-} + NO_3^{-}$ sink in spring coincides with the high concentrations of $NO_2^{-} + NO_3^{-}$ in the water column introduced into the bay and tributaries during the spring freshet. Sediments appear to serve as a source of $NO_2^- + NO_3^-$ only in the lower tributaries and a small sink at all other SONE locations (Figure 7-2). However, $NO_2^- + NO_3^-$ fluxes are small in comparison to the flux of NH4+ at all places except, perhaps, the very low salinity reaches of Bay, *i.e.* SLPD. Since NH₄+ fluxes were almost always from the sediment to the overlying water, the magnitude of $NO_2^- + NO_3^-$ fluxes, either positive or negative, has a generally minor effect on the total flux of remineralized inorganic nitrogen from bay sediments. However, $NO_2^- + NO_3^-$ from sediments to overlying waters is a clear indication of sediment nitrification, and hence an indication of some degree of oxidized sediment conditions, which

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would generally indicate less eutrophic conditions. Positive $NO_2^- + NO_3^-$ fluxes could serve as a useful indicator of "healthy" sediments.

Seasonal variations in DIP fluxes were quite consistent at SONE stations (Figures 7-3a through 7-3j). All but two SONE sites followed a simple unimodal cycle with periods of maximum sediment release occurring during the warm periods of the year. Along the mainstem bay DIP fluxes were generally low in spring and fall, with highest fluxes from the sediment to the overlying water occurring in June-August (*e.g.*, Figure 7-3g). These patterns are consistent with the view that large sediment-water exchanges of DIP observed in the lower Potomac (RGPT) and along the mainstem bay (PNPT, R-64, R-78) are associated with low oxygen in the overlying water which occur during summer.

Spatial and temporal patterns in fluxes of dissolved silicate (Figures 7-3a through 7-3j) were the most striking and easiest to interpret of all the nutrients considered in the SONE monitoring program. Both the magnitude and seasonality of silicate fluxes increased with increasing salinity. Thus, with the notable exception of the upper Choptank little seasonality was apparent in the silicate fluxes from the low salinity regions of the Patuxent, Potomac and mainstem bay. In contrast, a very clear seasonal cycle emerged from the silicate data from the lower tributaries (e.g. STLC, Figure 7-3a) and mesohaline mainstem bay. The sequence of patterns in silicate fluxes as one proceeds down the mainstem bay is particularly striking. These seasonal and spatial patterns in silicate fluxes point to the coupling of diatom production in the plankton and silicate remineralization in the sediments. The patterns observed at mainstem stations R-64 and PNPT show that remineralization of silicate peaks in early summer as water temperatures are rising, then tapers off in summer even though water temperatures remain high. This indicates a strong interaction between silicate deposition following the spring diatom blooms and water temperature as factors that regulate benthic silicate fluxes.

7.3.2 Interannual trends in sediment fluxes

One of the primary objectives of the Ecosystem Processes Component of the Maryland Chesapeake Bay Water Quality Monitoring Program is to identify long-term trends in benthic fluxes in the Maryland portion of Chesapeake Bay. This report includes data collected from August 1984 through October 1989, a period of five calendar years and one partial year (1984). Although it is still early in the monitoring program, and dramatic changes in nutrient control strategies have not been implemented throughout the Northern Chesapeake basin, it is appropriate to examine these data for interannual trends. The technique employed for this examination of data was to compute the mean station flux for calendar years 1985 through 1989. We refer to these as "annual" values for the sake of brevity, but it must be noted that the SONE measurement period is from April to November rather than a full year. These statistics were then plotted (Figures 7-4a through 7-4f) and examined for trends.

Mean annual station SOC fluxes ranged from about 0.3 g $O_2 m^{-2} d^{-1}$ to 2.6 g $O_2 m^{-2} d^{-1}$ and were generally higher in the Patuxent and Choptank Rivers than at other sites throughout the five year period. With the exception of the stations in the Patuxent River, there was a clear interannual trend between 1985 and 1989 towards lower SOC in the lower Choptank and Potomac Rivers and along the lower mainstem bay (PNPT and R-64). In almost all cases the maximum differences in SOC rates among years were large (*e.g.* Figure 7-4c). Almost the opposite trend in SOC rates is evident in the lower Patuxent (Figure 7-3a station STLC; Figure 7-4a) where rates were high in 1985, dropped by a factor of 4 in 1986 and have progressively increased since then. Our conceptual model relates fluxes to organic matter loading rates and ultimately to nutrient inputs from all sources.



Figure 7-3a. Seasonal variation $(\bar{x}\pm SD)$ in net sediment-water oxygen and nutrient fluxes at St. Leonard Creek [STLC] in the lower Patuxent. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3b. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at Buena Vista [BUVA] in the upper Patuxent. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3c. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at Horn Point [HNPT] in the lower Choptank. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3d. Seasonal variation ($\bar{x}\pm$ SD) in net sediment-water oxygen and nutrient fluxes at Windy Hill [WDHL] in the upper Choptank. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3e. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at Ragged Point [RGPT] in the lower Potomac. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3f. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at Maryland Point [MDPT] in the upper Potomac. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3g. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at Point No Point [PNPT] in the lower Chesapeake Bay. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3h. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at station R-64 in the mid Chesapeake Bay. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.


Figure 7-3I. Seasonal variation (x±SD) in net sediment-water oxygen and nutrient fluxes at station R-78 in the mid Chesapeake Bay. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement.



Figure 7-3]. Seasonal variation ($\bar{x}\pm$ SD) in net sediment-water oxygen and nutrient fluxes at Still Pond [SLPD] in the upper Chesapeake Bay. Means and standard deviations are calculated using the means of all flux measurements made in a specific month between April 1985 and October 1989. Means without error bars are based on a triplicate flux measurement. Assuming that low oxygen conditions in bottom waters (less than $2mg l^{-1}$) are not confounding patterns, we would expect high SOC rates during periods of high nutrient loading and low SOC rates during periods of low loading. If we use river flow as a surrogate variable for nutrient loading, the increasing flows in the Patuxent (Figure 6-3) from 1986 through 1989 are consistent with increasing SOC rates. We speculate that the very high rates observed in 1985 were supported in part by the high flow years 1983 and 1984.

Strong interannual trends were also evident for fluxes of NH₄⁺. During the five year period mean annual fluxes ranged from about 450 μ MN m⁻² hr⁻¹ in the lower Potomac in 1986 to 70 μ MN m⁻² hr⁻¹ in the lower bay in 1987. Highest fluxes were observed in areas exposed to strong seasonal oxygen depletion (*e.g.*, R-64 and Ragged Point) while fluxes were lower in the lowest and highest salinity portions of the mainstem bay. There have been substantial interannual differences in annual mean fluxes of NH₄⁺ in the Potomac River along the main axis of the Bay with fluxes decreasing from 1985 to 1987 and then increasing in 1988 and 1989 (Figures 7-4d through 7-4f). However, NH₄⁺ fluxes at both stations in the Patuxent and at the higher salinity station, Horn Point in the Choptank, were quite constant throughout the period 1985 through 1989. However NH₄⁺ flux did increase substantially at St Leonard Creek in the lower Patuxent, possibly for the same reasons SOC flux increased.

We initially did not expect to detect strong interannual trends in $NO_2^- + NO_3^-$, because fluxes tended to be small and could be directed either into or from sediments. Despite these characteristics, some interannual patterns did emerge. First, at stations which experience seasonal oxygen depletion (*i.e.*, Point No Point, R-64 and Ragged Point; Figures 7-4d through 7-4f) the interannual pattern of $NO_2^- + NO_3^-$ fluxes was characterized by: (1) mean fluxes less than 30 μ M m⁻² hr⁻¹ through all years (2) a predominance of fluxes from water to sediments (3) high intraannual variability emphasizing the extreme seasonal nature of $NO_2^- + NO_3^-$ fluxes.

Since $NO_2^- + NO_3^-$ fluxes are rarely if ever large enough to have a very significant impact on nitrogen concentrations in overlying waters, we have come to believe that the best use of nitrate flux data, especially on an interannual basis, is as an indicator of sediment conditions. Specifically positive nitrate $(NO_2^- + NO_3^-)$ fluxes (*i.e.*, from sediment to water) are indicative of sediment nitrification, a process which requires modestly oxidized sediment conditions. In situations where organic matter loading to sediments is excessive, oxygen is rapidly depleted, and nitrification ceases to be an active nitrogen transformation process. Thus we would interpret an interannual pattern of increasingly positive $NO_2^- + NO_3^-$ fluxes as indicative of improved sediment and water quality conditions.

Second, the patterns in both the lower Patuxent and Choptank Rivers were very similar, with $NO_2^- + NO_3^-$ fluxes from sediments to water decreasing over the years and in some cases (Buena Vista) actually changing direction (*i.e.* $NO_2^- + NO_3^-$ fluxes were directed into sediments). Finally, $NO_2^- + NO_3^-$ fluxes were always directed into sediments in the upper Potomac and upper bay. Clear interannual patterns were evident for both stations, however fluxes increased over the years in the upper Potomac and decreased at Still Pond.

Interannual trends in PO_4^- fluxes were also apparent (Figure 7-4). For example, there was an indication of increasing PO_4^- fluxes in the upper Patuxent River (Buena Vista) and strong decreases in the lower river (St. Leonard Creek). However, fluxes in the Choptank River, lower Potomac, and mainstem bay have increased for the past one to four years. For example, PO_4^- fluxes at station Point No Point have increased steadily since 1986 (Figure 7-4e).

As we found with SOC rates, there were consistent and strong interannual patterns in Si fluxes, and there were striking similarities at all stations between Si and SOC fluxes. With

the exception of the upper Patuxent station, Si fluxes were higher in 1989 than in several previous years.

The message we glean from examination of these annual rates is that it is quite possible to detect interannual differences in the magnitude of sediment-water fluxes. The patterns we have discussed in this report are qualitative rather than rigorously statistical, being based mainly on an examination of mean values. In many cases estimates of variance are very high (e.g., Figures 7-4a through 7-4f), which would be expected given the strong seasonal signals we have seen in these data. Our next step is to begin more rigorous statistical analyses aimed at detecting trends using seasonal groupings of data to avoid missing trends due to seasonal variations in flux rates.

The qualitative trend in SOC is towards reduced fluxes (except in the Patuxent) and NH_4^+ fluxes are increasing as are fluxes of PO_4^- (except in the lower Patuxent). Secondly, and perhaps more important in the long-run, there are some very substantial commonalties in trends among nutrient species being measured and among monitoring sites. This suggests that factors influencing the magnitude of sediment-water exchanges are operative at most or all of our sites. At the outset of the monitoring program we outlined a conceptual model which would generally apply throughout the Bay, wherein nutrient loading from all sources ultimately regulates phytoplankton production and biomass. This, in turn, influences deposition rates which impacts sediment-water fluxes and these fluxes contribute to establishing water quality conditions in the Bay. Now that we have begun interannual descriptions of sediment-water exchanges, we can synthesize data from our study and other portions of the monitoring program towards the goal of better understanding the set of linkages which serve to establish water quality conditions.

7.4 Initial Results from New SONE Stations

For the past several years there have been intense managements efforts focused on reducing nutrient loadings to the Patuxent River. It appears that reductions achieved to date have had a detectable effect on water quality conditions in the upper reaches of the estuary (Magnien, *pers. comm.*). In May 1989 the Maryland Department of Environment indicated the need for additional sediment-water flux monitoring of the lower, estuarine portion of the estuary for purposes of detecting responses in the system to management activities. Accordingly, two additional SONE stations were added to the EPC program and sampling was initiated in July 1989. Additional measurements were made in August and October 1989. The new stations are located at Marsh Point (MRPT adjacent to MDE station XDE5339) and at Broomes Island (BRIS adjacent to MDE station XDE2792). Both stations are identified in Figure 3-1 of this report and further described in Tables 3-1.1., 3-1.2., 3-1.3. and 3-2. and in the EPC Data Dictionary (Table B-52 and Figure B-6).

Net sediment-water fluxes at these sites are given in Figure 7-5 for the July, August and October 1989 cruises. Complete data files are given in Boynton *et al.* (1990).

At these sites SOC ranged from $0.2 \text{ gO}_2 \text{ m}^2 \text{ d}^{-1}$ at Broomes Island in July to $0.99 \text{ gO}_2 \text{ m}^{-2} \text{ d}^{-1}$ at Marsh Point in October. SOC rates at both stations increased as the fall approached. It appears that low summer SOC rates at both stations were, in part, related to low dissolved oxygen concentrations in deep waters, particularly in July, 1989. Deep water oxygen concentrations and SOC rates at these stations and dates were significantly correlated (r = 0.83, n = 6, p>0.05). The SOC rates we observed were low when compared to sites both upstream and downstream in the Patuxent River. However, these other sites did not exhibit such depressed dissolved oxygen levels. Finally, a series of six sedimentwater flux measurements were made in the vicinity of Marsh Point between July 1979 and

May 1980 (Boynton *et al.*, 1980). During this earlier period SOC rates ranged from 1.4 to $2.2 \text{ gO}_2 \text{ m}^{-2} \text{ d}^{-1}$, considerably in excess of the values observed in the latter half of 1989.

Fluxes of NH₄⁺ ranged from 36 to 313 μ MN m⁻² hr⁻¹ and were consistently higher at both sites during July and August than in the fall. Mean fluxes at Broomes Island exceeded those at Marsh Point on all three sampling locations, particularly in August. Ammonium fluxes at Broomes Island were comparable to those observed upriver at Buena Vista and exceeded those observed at Marsh Point and St. Leonard Creek by about a factor of two. Finally, earlier measurements of NH₄⁺ flux at the Marsh Point site averaged about 300 μ MN m⁻² hr⁻¹ during the summer period of 1979 or about double those recorded in summer of 1989.

Fluxes of $NO_2^- + NO_3^-$ were relatively small (compared to NH_4^+ fluxes) and were directed into sediments during the summer and from sediments to water in October at both stations. Nitrate fluxes into sediments have often been observed at other locations (Boynton *et al.*, 1989), and the magnitude of such fluxes is often directly proportional to $NO_3^$ concentrations in overlying waters. This proportionality was not observed at Broomes Island and Marsh Point during the summer of 1989, but that is not surprising because concentrations of NO_3^- were low during all measurement periods. During the October cruise NO_3^- was released by sediments at both stations, indicative of sediment-based nitrification. Again, this is a frequent observation at other locations in the fall when sediments and overlying waters are oxidated, and NO_3^- concentrations in overlying waters low.

Station averaged fluxes of PO₄⁻ ranged from 18 to 77 μ MP m⁻² hr⁻¹ and were higher at Marsh Point than at Broomes Island, particularly in July 1989. However, PO₄⁻ fluxes were of substantial magnitude at both sites in July and August and much lower in October. Summer PO₄⁻ fluxes observed at these station were similar in magnitude to those observed at Buena Vista and much higher than those recorded at St. Leonard Creek. In the case of PO₄⁻ fluxes, those observed in 1989 at Marsh Point were quite comparable or slightly larger than those recorded during the summer of 1979.

Station averaged fluxes of Si ranged from 22 to $431 \ \mu\text{MSi} \ \text{m}^{-2} \ \text{hr}^{-1}$. However, the range is smaller (136-431 $\mu\text{MSi} \ \text{m}^{-2} \ \text{hr}^{-1}$) if one low set of flux values recorded at Broomes Island in August is excluded. Values recorded at these stations were comparable to or somewhat lower than other Si fluxes observed during the of 1979.

The early results from these stations considerably extend spatial coverage in the Patuxent River and include two areas that were exposed to severe hypoxic conditions in 1989. The magnitude of fluxes appear to fit the pattern where highest fluxes are found in upper tributary areas and lower fluxes are characteristic of downriver locations in the Patuxent and other similar systems. The addition of May and June 1990 data will complete the first annual record of sediment-water fluxes for these locations, and a more complete evaluation will be possible at that time.



Figure 7-4a. Annual average (x±SD) net sediment-water fluxes at St. Leonard Creek [STLC] in the lower Patuxent River 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-4b. Annual average (x±SD) net sediment-water fluxes at Buena Vista [BUVA] in the upper Patuxent River 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-4c. Annual average (x±SD) net sediment-water fluxes at Horn Point [HNPT] in the lower Choptank River 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-4d. Annual average (x±SD) net sediment-water fluxes at Ragged Point [RGPT] in the lower Potomac River 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-4e. Annual average (x±SD) net sediment-water fluxes at Point No Point in the lower Chesapeake Mainstem River 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-4f. Annual average (x±SD) net sediment-water fluxes at station R-64 in the mid Chesapeake Mainstem Bay 1985-1989. Annual mean fluxes are calculated by averaging the mean flux values for the individual SONE cruises conducted each year from 1985-1988. The "annual" values only include the period April - November for each year.



Figure 7-5. A summary of net sediment-water oxygen and nutrient fluxes at two new stations Broomes Island [BRIS] and Marsh Point [MRPT] in the Patuxent River. Means and standard deviations (x±SD) of triplicate flux measurements are shown.

7.5 Relationships between Nutrient Loading and Primary Production, Algal Biomass and Sediment-Water Oxygen and Nutrient Exchanges

Monitoring data provides useful information in developing characterizations of the status of various ecological/water quality conditions in the bay and for detecting trends in key environmental variables in response to management actions and climatic variations. In addition, monitoring data can also be used to infer cause-effect linkages which are useful as guides in assessment and decision making. A recent review of marine monitoring programs by the National Research Council (1990) emphasized the need for this last item as a means for making the diverse array of collected data relevant to management.

To date, the EPC program has focused mainly on characterizing intra- and interannual patterns of sediment-water oxygen and nutrient exchanges and deposition rates of particulate organic matter. While such information has many uses in and of itself, (e.g., calibration and verification of water quality models and detection of system responses to management actions), additional and important insights into system function and probable responses can be developed by linking EPC data with data available from other parts of the monitoring program. We have initiated such efforts as part of the overall monitoring effort and report here preliminary results.

The synthesis work we have begun is ultimately based on the conceptual model shown in Figure 7-6. At this stage we have not investigated the potential for linkages among all of the components shown in the diagram but have rather emphasized possible relationships between nutrient sources (*i.e.* loading rates), primary production, algal biomass and benthic nutrient releases. We have chosen to start with these, because nutrient reduction is a primary management objective, and because nutrient loading is thought to be a prime regulator of algal production and biomass. These, in turn, are major factors in establishing and maintaining summer conditions characterized by hypoxic and anoxic deep waters. We have also chosen to examine data for relationships between loading and benthic nutrient fluxes because these fluxes appear to be largely responsible for stimulating summer algal blooms which exacerbate poor water quality conditions.

Initially, we choose to approach these analyses using annual data for most variables. In a few cases, summer season data were also examined. Annual time intervals were chosen, because there are such strong "seasonal forcings" in the bay related to many variables including insolation, temperature, salinity, stratification, nutrient loading and others. The assumption here is that meaningful signals can be detected on an annual basis. Secondly, we have emphasized four locations in the bay area including the lower portions of the Choptank, Patuxent and Potomac Rivers and including the mainstem mesohaline bay. Based on the data of Summers (1989) it is clear that annual nutrient loading rates (*i.e.* $gN m^{-2} yr^{-1}$) vary considerably among these sites, thus enhancing the possibility of detecting signals.

While these examinations are preliminary, the results are very promising, a few of which are summarized in Figure 7-7. Essentially, these plots suggest strong relationships between primary production, algal stocks and sediment nutrient releases. In the upper left panel annual primary production and river flow in the current and preceding year were examined. Here river flow is used as a surrogate for nutrient loading because loading data are not available for all of the years considered (1966-1967, 1971-1977, 1985-1988). The x-axis in this panel was developed by taking the river flow observed during a particular year for which primary production data were available and adding it to the river flow for the preceeding year. In effect this formulation suggests that primary production is a function of nutrient loading in both the current and preceeding years. A substantial upward trend is evident, and

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the fact that the two successive years of flow provide the best fit of the data suggests some degree of memory in the system, possibly related to sediment nutrient releases.

An even stronger relationship, using data from five sites around the bay, was observed between annual average integrated chlorophyll-a stocks (mg m⁻²) and nutrient loading normalized for estuarine size, depth and flushing characteristics. Details concerning the formulation of the x-axis in this plot are given in Vollenweider, 1976. There are clear and quantitative indications here that algal biomass will respond to changes in nutrient loading rates.

The same pattern, though not quite so clean, emerged for sediment-water fluxes of NH_4^+ and PO_4^- . In both cases there were increases in sediment-water nutrient releases under conditions of higher nutrient loads. However, there were several outlying points in both cases, and these will need to be further investigated in the context of environmental conditions at the time the measurements were taken. Finally, there was an inverse relationship observed between SOC and nutrient loading which at first glance appears counterintuitive. The low SOC rates observed at high nutrient loading rates resulted largely, because these sites were either hypoxic or anoxic for significant portions of the annual measurement period. High rates of SOC in this context are an indication of good water quality conditions at the sediment surface. Further, since we are interested in using integrative measures of system function, we should consider adoption of total CO_2 flux as an additional monitoring variable, because this measurement is useful under both aerobic and anaerobic conditions.

We have examined a number of nutrient loading terms (but by no means all) for relations to production, biomass and sediment fluxes. Total nitrogen (TN) and total phosphorus (TP) loading, annual river flow as recorded at gauging stations and estimated total basin flow have been used. In addition, the "Vollenweider term", which further adjusts areal loading according to system depth and flushing time, has been examined. We have found that stronger relationships have emerged using TN loading rather than TP loading, suggesting the overall importance of N relative to P. Gauge flow and basin flow yield results similar to those for TN loading in most cases. However, none of these yield very satisfactory relationships with Si flux from sediments, and this needs additional examination.

While preliminary, these emerging relationships indicate that the basic eutrophication model we are using is valid. Given the early success we have had, it seems appropriate to continue these synthesis efforts, considering alternative time and space scales, other methods of scaling estuarine sites to improve comparability and different loading functions. Results such as those reported here provide an additional and alternative approach to water quality models in assessing the likely outcomes of management actions.

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Figure 7-6. A simple conceptual model of the main ecosystem components and processes involved in influencing water quality conditions in Chesapeake Bay. Potentially important interactions are indicated with solid arrow heads and coded open circles.

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Figure 7-7. Summary of relationships between nutrient loading and annual primary production (Station R-64), and summer SOC, PO_4^* and NH_4^+ fluxes. The lower three panels are based on data (1985-1988) from the lower Choptank, Potomac and Patuxent Rivers and the mesohaline mainstem Bay. These sites, plus the Patapsco estuary, were included in the upper right panel. The x-axis of that panel is the standard Vollenweider term (Vollenweider, 1976).

8. MONITORING PARTICLE DEPOSITION RATES (VFX)

Particle deposition rates have been measured at Station R-64 in the mesohaline reach of Chesapeake Bay since the summer of 1984. All data are currently available from July 1984 through December 1989. In this report we emphasize intraannual and interannual patterns using this data set. Our purpose here is to establish a sound understanding of annual cycles and begin exploration of year-to-year trends.

8.1 Seasonal Patterns of Deposition Rates

Although some small differences are evident in the seasonal pattern of carbon and chlorophyll deposition rates, data for the years 1985 and 1986 are essentially similar (Figure 8-1). Three periods of peak deposition are repeated in the two years, one in spring (April - May), one in summer (July - August) and one in autumn (October - November). Relatively low rates occur in winter (January - February) and in late spring (June). Also, deposition rates are apparently low in late summer (September) and later autumn (December); however, data are limited for these periods. In general, the magnitude of each of these seasonal peak deposition rates is similar (10-15 mg Chl m⁻² d⁻¹). As discussed in the following section, deposition data collected in 1987 exhibit the exact same pattern (*i.e.* 3 deposition pulses) while 1988 data were similar but there was no evidence of a fall pulse (Figure 8-4).

The consistency in seasonal patterns of deposition for 1985 and 1986 is remarkable in view of the differences in primary production cycles for the two years (Figure 8-1). Hydrologically, Susquehanna River flow in both years was low relative to the 30-year mean (Malone *et al.*, 1987). The maximum monthly flow in the spring freshet was, however, about twice as large in 1986 compared to 1985. Phytoplankton production in 1986 exhibited a smooth seasonal cycle directly correlated to temperature, while in 1985 production was generally higher, with elevated rates also occurring in early fall, coincident with the peak deposition event in 1985. No obvious relationship occurs between production and deposition on the indicated weekly to monthly time-scales. Malone *et al.* (1986), however, did observe a significant correlation between sediment deposition rates at Station R-64 and phytoplankton production at two sites flanking the sediment trap array to the east and to the west (10 m depth).

Annual deposition cycles reported for many coastal waters in northern Europe are dominated by a single large event associated with the spring phytoplankton bloom (Smetacek 1984; Wassmann 1984). In other coastal systems, two major deposition events have been observed, one in spring and the other in summer (Steele and Baird, 1972; Hargrave and Taguchi, 1978; Forsskahl *et al.*, 1982) or autumn (Webster *et al.*, 1975). For several of these descriptions of annual cycles, periods of peak deposition generally correspond to periods of maximum phytoplankton production (Steele and Baird, 1972; Hargrave and Taguchi, 1978; Forsskahl *et al.*, 1982). For other systems peak summer production rates are not accompanied by high deposition values (Smetacek, 1984). In many lakes a strong temporal correspondence between plankton production and carbon deposition has been observed (Bloesch *et al.*, 1977).

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 8-1). Temporal trends in chlorophyll deposition rates tended to correspond to trends in chlorophyll stocks in the euphotic zone during



Figure 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.

chlorophyll stocks in the euphotic zone during spring. Although chlorophyll stocks were lower in the summer of 1985 and 1986, an indication of increasing concentrations during the deposition events of both summers exists. In fact, by combining data from the two years, significant correlations between chlorophyll stocks and deposition rates were observed for both spring (March-June) and summer (July-August) periods (Figure 8-2). Interestingly, the slope of the summer correlation is twice that for the spring relationship. 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.

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 8-3). 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=0.81) and of the benthic communities (r=0.59). 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) for the water column from gross production, leaving a "residual" term in the budget (Figure 8-3). 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 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.

8.2 Interannual Patterns of Deposition Rates

Annual patterns of particulate carbon (PC) flux to the mid-depth trap (located near the base of the pycnocline) for the period 1984-1988 are shown in Figure 8-4. During this period, values ranged from 0.3 to 1.6 gC m⁻² d⁻¹, the majority of these values ranging between 0.5 and 1.0 gC m⁻² d⁻¹. In general, deposition values in all years tended to be highest in the spring.

We now have sufficient data to begin to link the sources of organic matter (primarily phytoplanktonic production in overlying waters) with deposition events among years. A reasonably strong signal has emerged which indicates that a large percentage of the spring bloom (March-April) is deposited to deeper waters whereas a considerably smaller fraction of new organic matter is deposited during the summer period (June-August). Specifically, during spring periods from 1985-1988, 42 to 140% of plankton production was captured in the traps, whereas during the summer seasons 18 to 47% was captured. Thus, the picture which has emerged for these two time periods is one wherein most material appears to sink to deep waters in the spring ($\approx 90\%$), but in summer a smaller percentage ($\approx 30\%$) ends up

reaching the deep waters. As indicated in Figure 8-4 fluxes are substantial (0.8-1.3 gC $m^{-2} d^{-1}$) during both time periods.

While there is always some degree of variability between years in most variables associated with primary production and algal stocks, there is a remarkably stable interannual pattern of deposition, as indicated in Figure 8-4. At this point interannual differences appear to be related to the magnitude rather than patterns of deposition. In each year monitored to date there is a clear indication of a spring deposition period, the peak of which occurs from late April through early May, despite the significant temporal shift in the timing of high nutrient loads from the Susquehanna River. Following the spring depositional period, there is 3-4 month period (June - September) characterized by moderately high and low deposition rates ranging from 0.4-1.3 gC m⁻² d⁻¹. Finally, there is a consistent fall (October -November) deposition period although the magnitude and duration of this event is smaller and shorter than the spring event. We have insufficient information to characterize depositional patterns in winter months.

During the period for which we have complete spring through fall deposition data (1985-1988) there have been, as indicated previously, some among-year variations in river flow (and nutrient loading). Specifically, the spring peak in 1985 was very attenuated; in 1986 and 1987 there were also clear spring pulses which occurred in early March and April, respectively; in 1988 the pulse was again attenuated but with small peaks in February and May. Qualitatively the pattern of spring river flow is reflected in spring deposition rates. For example, in the springs of 1985-87 there was a single spring peak in river flow (early March-April) followed by single peaks in deposition (early May). Additionally, peak deposition rates were lower in 1985, a year characterized by lower than normal spring river flow. Finally, in 1988 there was a bimodal freshet (February and May) and a bi or tri-modal spring deposition pattern.

The annual cycles for deposition of PC, PN, PP and total chlorophyll-a are provided in Figure 8-5 for comparison with previous years of measurement (1985-1988). While the timing and magnitude of the spring PC deposition peak were similar for 1989 as in the earlier years (compare Figures 8-4 and 8-5a), rates of chlorophyll deposition were reduced by 30-60% in 1989 (compare Figures 8-1 and 8-5d). Relatively high rates of PC collections in February and March of 1989 strongly suggest that resuspension may be responsible for much of the spring 1989 PC rates. Evidently, the late freshet (May) and the relatively cold and cloudy spring of 1989 markedly inhibited the development of the spring phytoplankton bloom. The magnitude of the summer peak chlorophyll deposition rate was similar in 1989 to previous years; however, the normally sharp August maximum was poorly defined in 1989. In contrast, the fall bloom (as evidenced by PC and chlorophyll deposition rates) was the strongest on record since our study began in 1984, with rates in excess of 25 mg chlorophyll and 1.6 gC m⁻² d⁻¹. Patterns of PN and PP deposition in 1989 closely resembled those for PC.

8.3 Qualitative Character of Sedimenting Particles

Strong seasonal trends were observed in both C:P and N:P ratios of particulate material collected in sediment traps for 1985-1988 (Figures 8-6 and 8-7). Highest values for both ratios occurred from late winter through late spring; the lowest values in summer through 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 (see Section 9 of this report). Ratios of C:N



Figure 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.

associated with inorganic particulate materials (see Section 9 of this report). Ratios of C:N for these sediment trap collections were generally between 7-8, 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 8-8). 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 (Figure 8-1), 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 July and October - November deposition events suggest that the majority of sedimenting material was intact diatoms (Figure 8-8b). Again, the low summer C:Chl ratios in 1989 contrast sharply with those observed in 1985 and 1986 (Figure 8-1), 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 8-8) were similar to those reported for previous years (Figures 8-6 and 8-7), with consistent evidence of P-deficient particles compared to Redfield ratios.

Mean N:P ratios for suspended particles are summarized in Table 8-1 for representative dates and depths. These particulate ratios are compared to ratios of dissolved inorganic N and P in surrounding waters. In addition, concentrations of DIN and DIP are compared to typical values of half-saturation kinetic coefficients for phytoplankton nutrient assimilation. Based on these criteria, phosphorus deficiency and growth limitation is suggested for all but a few dates. At these times particulate N:P ratios also approach Redfield proportions. It is possible that an extreme phosphorus (or possible silicon) deficiency in the spring contributes to rapid settling of algal cells (Smetacek, 1985).

A comparison of vertical distributions of C:P and N:P ratios for suspended and trapcollected particulates in the water column reveals a remarkable consistency in trends for both ratios during 1985 and 1986 (Figure 8-9). Ratios for seston and trapped material tend to decrease with depth, exceeding Redfield Ratios in the euphotic zone (0-10m) while in the lower layer conforming with these ratios. In April, water column seston ratios are generally higher than trapped seston ratios. Vertical trends in June of 1986 resemble those of the previous April, while in June of 1985 the trends were similar to those observed later in the summer (August). This may reflect the higher spring run-off and stronger vertical stratification in 1986. These vertical patterns of C:P and N:P in suspended seston and trapped seston particulates reflect nutrient dynamics in the mesohaline region of Chesapeake Bay. Explanations are, however, not straightforward, and we are limited to speculations. Gachter and Bloesch (1985) have considered several explanations for similar vertical decreases in C:P ratio of suspended and trapped particles in lakes. One conclusion

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Figure 8-3. Results of seasonal measurements of primary production, and respiration in the upper (above pycnocline) and lower water column. The residual (difference between production and respiration terms) represents an estimate of the material available for deposition.







Figure 8-5. Particulate carbon, particulate nitrogen, particulate phosphorus and total chlorophyll-a deposition rates based on mid-trap collections at station R-64 for the period February - November 1989.

is that settling organic particles (phytoplankton and phytodetritus) take-up dissolved inorganic phosphorus (DIP) from the water column (Gachter and Mares, 1985). Uptake of DIP may occur through a combination of physical-chemical sorption, algal or bacterial assimilation associated with decomposing algal cells. Another possible explanation would be resuspension of bottom sediments. However, C:P ratios of bottom water seston were often lower than bottom sediment ratios. Also, resuspension does not explain how ratios in bottom sediments were so consistently low (below Redfield Ratios). Concentrations of DIP tend to be directly related to water depth in a given site in the mesohaline Bay (Magnien *et al., unpubl.*), thus, supporting the proposed pattern of increased uptake (kinetic or equilibrium) with depth.

Although we have shown that particle deposition at Station R-64 is strongly related with phytoplankton standing stocks (Figure 8-2), broader sedimentological effects occur resulting from algal sedimentation. In general, sedimenting particles at this site contain about 10 percent organic carbon by weight. Phytoplankton biomass, in contrast, tends to be approximately 50 percent organic carbon, indicating that phytoplankton probably constitute an average of 20 percent of the mass of deposited material. Thus, while most of the deposited material is probably lithogenic in origin, the annual cycle is driven by processes of plankton production and consumption (Honjo, 1982). Others have suggested a mechanism of mutual flocculation of algae and inorganic clays (Avnimelech *et al.*, 1982) which may partially account for this pattern (Smetacek, 1985).

8.4 Sediment Trap Collections as a Measure of Net 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 60-70 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).

We have made preliminary corrections for sediment trap data from Station R-64 using this approach for representative dates over the course of the 1985 season (Table 8.2). This calculation suggests that resuspension accounts for 15 and 40 percent of the total dry weight of material collected in upper and middle 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 (20 m) and the adjacent Dares Beach (10 m) stations. Bottom sediment characteristics are in general similar along a crossbay transect in this portion of the estuary at water column depths greater than 5m (Ward, 1985). In addition, the closest shoal areas (with <5 m depths) susceptible to frequent wind resuspension are located more than 10 km from the sediment trap deployment site.



Figure 8-6. 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 8-7. Particulate nitrogen to phosphorus (C:P) ratios (atomic) based c material collected in surface traps for the period March 1985-December 1988. The horizontal line on each panel represents a Redfield N:P ratio about 16.



Figure 8-8. 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.



Figure 8-9. Vertical distributions of elemental C:P and N:P ratios (atomic) of particulate material: suspended in water columns (points); collected in sediment traps (cross-hatched bars); and deposited on bottom sediments (darkened bars). Data are four representative dates in two years (1985 and 1986) from station R-64 in mesohaline portion of Chesapeake Bay. Dashed line indicates expected ratios for phytoplankton.

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| Table 8-1. Selected indicator | r values for nitrog | en versus pho | osphorus | limitations on |
|-------------------------------|---------------------|---------------|----------|----------------|
| phytoplankton growth | in mesohaline (| Chesapeake | Bay for | representative |
| seasons in 1986-1989 | | • | • | • |

| Date | | Dis | solved inorga | nic Nutrien | | Particulate Nutrients ³ | | |
|------|-----|--|---------------|---|-------|------------------------------------|-------------------------------|--|
| | | Concentration (µM) ¹ N P | | Uptake Kinetics ² N:K _{sn} P:K _{sp} | | N:P (Atoms) | N:P in Photic Zone 0 - 4 m | |
| 1986 | Apr | 22.7 | 0.1 | >>1.0 | < 1.0 | 206 | 38 | |
| | Jun | 7.0 | 0.2 | > 1.0 | ~ 1.0 | 29 | 34 | |
| | Aug | 2.8 | 1.2 | > 1.0 | >1.0 | 2 | 27 | |
| | Oct | 6.9 | 0.1 | > 1.0 | < 1.0 | 49 | 27 | |
| | | | | | | | | |
| 1987 | Apr | 28.9 | 0.10 | > > 1.0 | < 1.0 | 289 | 59 | |
| | Jun | 0.7 | 0.19 | ~ 1.0 | ~ 1.0 | 3.5 | 18 | |
| | Aug | 1.55 | 0.13 | ~ 1.0 | < 1.0 | 11.2 | 18 | |
| | Oct | 14.1 | 0.31 | > > 1.0 | ~ 1.0 | 45.5 | 28 | |
| | | | | | | | | |
| 1988 | Apr | 68.3 | 0.13 | > > 1.0 | < 1.0 | 525 | 16 | |
| | Jun | 0.67 | 0.22 | ~ 1.0 | ~ 1.0 | 2.6 | 21 | |
| | Aug | 1.1 | 0.11 | ~ 1.0 | < 1.0 | 10.4 | 26 | |
| | Oct | 6.7 | 0.11 | >>1.0 | < 1.0 | 61.0 | 29 | |
| | | | | | | | | |
| 1989 | Apr | 40.21 | 0.10 | > > 1.0 | <1.0 | 416 | 28 | |
| | May | 47.50 | 0.06 | >>1.0 | < 1.0 | 736 | 32 | |
| | Jun | 36.86 | 0.19 | > > 1.0 | 1.0 | 190 | 31 | |
| | Jul | 16.50 | 0.16 | > > 1.0 | 1.0 | 102 | 28 | |
| | Aug | 16.50 | 0.19 | >>1.0 | 1.0 | 85 | 16 | |
| | Oct | 16.43 | 0.16 | >>1.0 | 1.0 | 102 | 28 | |

NOTES:

Concentrations in surface (0-1m) waters at "R-64" from MDE (1988, unpublished); N is [NH4⁺] plus [NO2] plus [NO3] and P is [PO4⁺].

2. Ratios of inorganic nutrient concentrations to half-saturation coefficients, Kan and Kap, for uptake of N and P by phytoplankton assemblages (Taft et al. 1975; McCarthy et al. 1977). Kap taken as 0.2µM and Kan as 0.5µM.

3. N:P ratios (atoms) for seston at station "R-64" for approxiamtely the same dates in 1986 - 1989.

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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 8-2). Chlorophyll content (as a percent of dry weight) of seston is much higher than that in upper 1 cm 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 estimated in relation to chlorophyll sedimentation was similar to that based on resuspension corrections (Table 8-2.).

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 8-3). In 1985, sediment accumulated below Station R-64 at a rate of approximately 4 mm y⁻¹. Since organic carbon comprises 10-15 percent (Table 8.2) of the dry weight of deposited material, total organic weight would be 20-30 percent. Assuming that most of this organic matter is remineralized, the long-term net deposition rate would be ca. 3 mm y⁻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 trap rates were reported for two Swiss lakes (Bloesch and Burns, 1982).

On shorter time scales of weeks, we can make an additional comparison of sediment trap collection rates with an alternative method of calculating deposition of particulate organic matter by referring back to Figure 8-3. Here, 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 PC. If this residual calculated at 2 - 4 wk intervals is compared to mean sediment trap collection rates (corrected for resuspension) for the same time periods, a remarkably close correlation is obtained (slope=0.94, $r^2=0.96$). This further supports the quantitative robustness of the sediment traps as quantitative measures for deposition of particulate organic matter (Figure 8-10).



Figure 8-10. Scatter plot of sediment trap collection rates versus water column residual production rates. Sediment trap rates have been corrected using the method of Gasith (1975).

Table 8-2. 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 | | | | | |
|----------------------|---------------|--|-------------|-------------|---------------------------------|------|------|
| | Sestor 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

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2. Correction factor = $(f_{s}-f_{R})(f_{t}-f_{R})^{-1}$ based on Gasith (1975). Total Carbon Deposited

* Estimates from mean of May 27 - June 18.

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Table 8-3. 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).

9. PRELIMINARY INVESTIGATIONS OF THE PARTITIONING OF SUSPENDED PARTICULATE MATERIAL BETWEEN ORGANIC AND INORGANIC FRACTIONS

9.1 Background

The chemical composition (*i.e.* bulk chemical properties such as particulate carbon, nitrogen, phosphorous and chlorophyll-a concentrations) of suspended particulate material in estuarine waters has often been used to characterize a variety of possible ecological conditions as well as to estimate the sizes of these stocks. For example, areal stocks of PC are often estimated by taking a series of samples through the water column and integrating the results to obtain a mass per unit area.

An additional use of such data involves developing ratios of one element to another with the goal being to characterize the source of organic matter or the physiological state of a dominant component of the water column particulate field. This approach relies on foreknowledge of the general stoichiometric ratios of probable water column components. For example, estuarine phytoplankton, which are nutrient sufficient exhibit C:N:P ratios (atomic basis) of about 100:16:1. If in a system where phytoplankton are known to be the dominant source of particulate material and this ratio departs strongly from the above ratio, then it is often concluded that one element may be in short supply and will limit production rates of biomass accumulation. It should be noted that such applications represent crude approximations and in some instances can be misleading.

One of the basic assumptions involved in all of these uses is that the particulate material is organic rather than inorganic. In previous EPC reports we (as have others) made this assumption in characterizing particulate matter fields. However, we are not aware of any previous work where this assumption has been verified in Chesapeake Bay. We report here the initial results of our attempt to better characterize the partitioning of water column particulate matter into organic and inorganic fractions.

9.2 Sampling Schedule and Analytical Methods

Surface and bottom water samples were collected from 9 locations in the Maryland portion of Chesapeake Bay in January, 1990. Appropriate amounts of water from each sample were filtered through Whatman GF/F filters ($0.7 \mu m$; precombusted) and immediately frozen.

Particulate carbon and nitrogen samples were analyzed for organic and inorganic components using the method of Hirota and Szyper (1975). Two replicates were pretreated by combustion in a muffle furnace at 500C for four hours to drive off organic components. Then, these two replicates, as well as two that were not combusted, were analyzed for total particulate carbon and nitrogen in a Control Equipment Corporation Elemental Analyzer Model 240XA. The difference between the two treatments was calculates as percent organic PC and PN.

Total phosphorus was extracted from replicate samples concentrated on filters with 1 N hydrochloric acid after a 2 hour ignition at 550C. Organic phosphorus was determined by the difference in the phosphorus content of the 1 N hydrochloric acid replicate extracts after ignition and the phosphorus content of the extract when the replicate samples were not
ignited (Aspila, et al., 1976). Aspila chose these methods after an extensive review of methodologies and comparative experimentation.

9.3 Preliminary Results

Results from the first survey are summarized in Table 9.1. It appears that during winter virtually all particulate carbon and particulate nitrogen in water column samples is organic. For both PC and PN the maximum amount of inorganic material in a sample was 3%. Thus, these data indicate that PC and PN values from water column samples can be considered to be organic. However, the situation for particulate phosphorus is quite different. The fraction of PP that appears to be organic ranged from 64-77% surface samples and from 43-77% in bottom waters. It appears, at least under winter conditions, that as much as half of the particulate phosphorus in the water column is bound in some form to inorganic materials. These results are from the first phase of a three part sampling effort. Additional samples will be collected during the spring and summer of 1990 to determine seasonal patterns of partitioning of particulate materials between organic and inorganic fractions. These preliminary data indicate that a substantial fraction of PP is inorganic and this should be considered when characterizing water column conditions.

| MDE Station | Depth | % Organic C | % Organic N | % Organic P |
|----------------|-------|----------------|----------------|----------------|
| MCB5.3 | S | 98 | 97 | 64 |
| MCB5.3 | B | 99 | 98 | 53 |
| MLE2.3 | S | 98 | 97 | 71 |
| MLE2.3 | В | 99 | 97 | 53 |
| MCB5.2 | S | 98 | 98 | 72 |
| MCB5.2 | В | 97 | 97 | 51 |
| MCB5.1 | S | 99 | 98 | 69 |
| MCB5.1 | В | 98 | 100 | 52 |
| MCB4.4 | S | 99 | 99 | 67 |
| MCB4.3C | S | 99 | 100 | 68 |
| MCB4.3C | В | 99 | 99 | 53 |
| MCB4.2C | S | 99 | 99 | 74 |
| MCB4.2C | В | 100 | 98 | 51 |
| MCB4.1C | S | 99 | 100 | 77 |
| MCB4.1C | B | 99 | 98 | 54 |
| MCB3.3C | S | 99 | 95 | 76 |
| MCB3.3C | В | 99 | 97 | 43 |
| MCB3.2C | S | 99 | 99 | 77 |
| MCB3.2C | B | 99 | 99 | 70 |

Table 9-1. Organic Contents of Particulate Samples collected by MDE in midChesapeake Bay January 8th and 9th, 1990.

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