

MARYLAND DEPARTMENT OF THE ENVIRONMENT

MARYLAND CHESAPEAKE BAY WATER QUALITY MONITORING PROGRAM

ECOSYSTEM PROCESSES COMPONENT (EPC) LEVEL I REPORT NO. 4

(July 1986 - June 1987)

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1. ABSIRACT

1.1 Program Objectives

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

- 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.
- determine the long-term trends that might develop in sediment-water exchanges and vertical 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. Measurements of sediment-water nutrient and oxygen exchanges are made on a quarterly basis at four locations in the mainstem Bay, and at two key locations in each of three major tributary rivers (Patuxent, Choptank, and Potomac). Vertical deposition rates are monitored at one mainstem Bay location, in the central anoxic region. Measurements are made almost continuously during the spring, summer and fall periods, with a lower frequency 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.

1.2 Justification

Sediment-water processes and deposition of organic matter to the sediment surface are major features of estuarine nutrient cycles and 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

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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.

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 demand (SOD) 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).

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.

2.1 Justification

Processes associated with estuarine sediments have a considerable influence on water quality and habitat conditions in the Bay and its tributaries. 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 these communities then 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 insure a large return flux of nutrients from sediments to the water column and sustain continued phytoplankton growth, deposition of organics to deep waters and anoxic conditions typically associated with eutrophication of estuarine systems.

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

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

- 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.
- determine the long-term trends in sediment water exchanges and vertical 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

3.1 Sampling Locations

3.1.1 <u>General</u>

Figure 3-1 shows the sampling locations for both the sediment oxygen and nutrient exchange study (SONE) and the vertical flux study (VFX). Brief descriptions and exact locations of SONE and VFX stations are given in Table 3-1 referenced to MDE station numbers. Four of the 10 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 monitoring study station is located in the mainstem of the Bay in the central anoxic region (Fig. 3-1).

3.1.2 Justification of Station Locations

Locations of SONE stations (Fig. 3-1 and Table 3-1) 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, 1984 and Boynton and Kemp, 1985) reported the following: 1) along the mainstem of the Bay, fluxes were moderate in the upper Bay, reached a maxima in the mid-Bay and were lower in the higher salinity regions and, 2) fluxes in the transition zone of tributaries were much larger than those observed in the higher salinity downstream 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 three tributaries (Potomac, Patuxent, and Choptank), one in the transition zone and one in the lower estuary. In all cases, station locations were selected to have depths and sediment characteristics representative of the estuarine zone being monitored.



Fig. 3-1. Locations of SONE and VFX monitoring stations in the Maryland portion of Chesapeake Bay.

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Table 3-1. Locations and descriptions of stations sampled as part of the Ecosystem Processes Component of the Monitoring Program.

Characteristics **Oligohaline** Oligohaline Oligohaline Oligohaline 01igo-Meso haline Mesohaline Salinity Mesohaline Mesohaline **Vesobaline** Mesohaline ε Depth, 9-10 5-16 13-14 13-14 9-10 15-16 Total 7-8 3-4 6-7 3-4 38°30.96¹ 76°39.85 Latitude Longitu<u>de</u> 38°22.74 76°30.08 38°41.43 75°58.42 38°21.36 77°11.52 38°57.28 76°23.58 38°07.98 76°15,10 38°37.07 76°07,80 38°09.77 76°35.58 38°33,60 76°25.64 39°20.91 76°10.87 7.5 naut. mi of upstream of Patuxent River mouth 4.0 naut. mi downstream Rt. 50 bridge at Cambridge, MD 200 yds. NNW of channel buoy "78" 10.0 naut. mi upstream of Rt. 50 bridge at 300 yds. NE of channel buoy R-64 700 yds. W of channel marker "41" 1250 yds. SE of buoy R-18 1.5 naut. mi WNW of BW "51B" 0.75 naut. mi N of Rt. 231 Bridge at Benedict, MD of പ Cambridge, MD 3.2 naut. mi Pt. No Pt. General Location (Nearest MDE Station) Pt. No. Pt. (MCB5.2) Bu. Vista (XDE 9401) Md. Pt. (XDA 1177) Rag. Pt. (XBE 9541) Code Name St. Leo (XDE 2792) Horn. Pt. (MET5.2) Stil. Pd. (MCB2.2) R-78 (MCB3.3C) R-64 (MCB4.3C) Wind. HL (NONE) St. Leonard Creek Point No Point Station Name Maryland Point Ragged Point Buena Visța Windy Hill Horn Point Buoy² Still Pond Buoy R-78 R-64 Ches apeake Mainstem Choptank River Patuxent Sediment Potomac River River Bay

¹Seconds of latitude and longitude are expressed as hundreths of a minute. ²Also serves as the VFX Station.

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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, sediments type, and depth; therefore, this program retains a high degree of comparability with other program components (Boynton et al., 1982b).

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 (Fig. 3-1) to monitor the vertical flux of particulate organics reaching deeper waters. This location is close to, but does not exactly coincide with, MDE station 4.3.C in this area. Since sediment traps are moored pieces of gear and exposed to damage or loss by commercial boat traffic, the location was selected to be out of main traffic lanes, but still remain close to the MDE station.

3.2 Sampling Frequency

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 influenced by the presence of a large macrofaunal community (springearly summer), 2) a period during which macrofaunal biomass is low but water

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temperature and water column metabolic activity high with anoxia prevalent in deeper waters (August), 3) a period in the fall when anoxia is not present and macrofaunal community abundance is low but re-establishing and 4) an early spring period (April-May) when the spring phytoplankton bloom occurs, and water column nutrient concentrations are high (particularly nitrate). 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, as described above, distributed in zones characteristic of mainstem Chesapeake Bay and tributary rivers.

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 considerably lower during winter periods (November-March). Resuspension of near-bottom 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 (weekmonth) and other, less well described, features of the Bay. Given the importance of obtaining inter-annual estimates of organic matter deposition rates to deep waters of the Bay, sampling is almost continuous during springfall (March-November) and only occasionally during the winter (December-February). Direct measurements of organic deposition to Bay sediments were monitored 19 to 27 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 the period July 1986 - June 1987 is shown in Table 3-2 for this component of the Monitoring Program.





sediment trap deployment

sediment trap retrieval and deployment of new traps

sediment trap retrieval

duration of sediment-water flux monitoring

Fig. 3-2. Sampling schedule for VFX and SONE programs from July 1986 - June 1987.

3.3 Field Methods

Details concerning methodologies are described in the Ecosystem Processes Component Study Plan (Garber et. al, 1987). The following section provides an overview of field activities.

3.3.1 SONE Study

3.3.1.1 <u>Water Column Profiles.</u> At each of the 10 SONE stations, vertical water column profiles of temperature, salinity and oxygen are obtained at 2 m intervals from the surface to the bottom immediately prior to obtaining intact sediment cores for incubation. Near-surface (\pm lm) and near-bottom (\pm lm) water samples were also collected using a high volume submersible pump system. Samples are filtered, where appropriate, using 0.7 um GF/F filter pads and immediately frozen. Samples are analyzed for the following dissolved nutrients and particulate materials: anmonium (NH4⁺), nitrate (NO3⁻), nitrite (NO2⁻), total dissolved nitrogen (DON), dissolved inorganic phosphorous (PO4⁻ ³), dissolved organic phosphorus (DOP), silicious acid (Si(OH)4), particulate carbon (PC), particulate nitrogen (PN), particulate phosphorous (PP), chlorophyll-a and seston.

3.3.1.2 <u>Sediment Cores</u>. Intact sediment cores are obtained at each SONE station using a modified Bouma box corer. After deployment and retrieval of the box corer, the plexiglass liner containing the sediment sample is removed and 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 (Fig. 3-3). Prior to beginning incubation, the overlying water in a core is replaced by 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 water samples (35 ml) are extracted from each core every 30

FIG. 3-3. Schematic diagram of the incubation chamber used in SONE program.



or 60 minutes (depending on the rate of oxygen uptake) over the 2-5 hour incubation period. During the incubation period, 5 or 6 water samples are extracted from each core. As a nutrient sample is extracted from a core, an equal amount of ambient bottom water is added. An opaque plexiglass liner filled with bottom water, incubated, and sampled as described above serves as a blank. Water samples are filtered and immediately frozen for later analysis for NH4⁺, NO3⁻, NO2⁻, PO4³ and Si(OH)4 concentrations. Nutrient and oxygen 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.

3.3.1.3 <u>Sediment Profiles</u>: At each SONE station an intact sediment core is used to measure Eh at 1 cm intervals to about 10cm. Additionally, surficial sediments are sampled for particulate nitrogen, particulate carbon, particulate phosphorous, and chlorophyll concentrations.

3.3.3 VFX Study

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At the VFX station, a water column profile of temperature, salinity and oxygen is obtained at 2 m intervals from 0.5 meters to 1 meter off of the bottom to characterize the column's general physical features. Water samples are also collected at 3 depths using a submersible pump system. Routinely, a sample is taken from near-bottom and near-surface waters, and at the depth of the mouth of the middle sediment trap. Water samples are analyzed for particulate materials including PC, PN, PP, chlorophyll-<u>a</u> and seston. These data provide descriptions of the particulate matter in the field at that moment and are useful in evaluating results developed from sediment trap collections.

3.3.3.1 Sediment Sampling. During previous VFX monitoring cruises a surficial sediment sample (surface lcm) was obtained using either a Van Veen grab or the Bouma box corer. During this reporting period the Bouma corer was used almost exclusively because it obtains a better surficial sediment sample. Sediment samples are later analyzed to determine PC, PN and PP concentrations

and chlorophyll-<u>a</u> content. Subsamples are also examined to determine the composition of surficial sediment particulates (e.g. algal species, zooplankton fecal pellets, etc.)

3.3.3.2 VFX Sampling. The sampling device used to develop estimates of the vertical flux of particulate materials has a surface buoy connected to a lead or concrete anchor-weight (200 kg) by a series of stainless steel cables (0.8 cm diameter, Fig. 3-4). The array is maintained in a vertical position through the water column by 2 sub-surface buoys (45 cm diameter, 40 kg positive buoyancy and 33 cm diameter, 16kg positive buoyancy). Collecting frames with cups are attached at about 5, 9 and 14 m beneath the water surface To obtain estimates of vertical flux of particulates from the surface euphotic zone to the pycnocline, flux across the pycnocline to deep waters and flux of materials associated with the near-bottom which includes local resuspension of sediments as well as net deposition.

The sediment trap string is routinely deployed and retrieved using CEES research vessels with normal sampling periods lasting 1-2 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 PC, PN, PP, chlorophyll-<u>a</u> and seston concentrations. Additionally, a 10 ml sample is 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 vertical flux to the depth at which the collecting cup was suspended by consideration of the cross-sectional area of the collecting cup, deployment time and sample and subsample volumes. Further details concerning this monitoring program are provided in Boynton et al. (1985).



3.3.3 <u>Chemical Analyses</u>

In brief, methods for the determinations of dissolved and particulate nutrients are as follows: NO3, NO2, NH⁴ and PO4³ are measured using the automated method of EPA (1979); dissolved organic phosphorus (DOP) analysis uses the digestion and neutralization procedure of D'Elia et al. (1977) followed by DIP analysis (EPA 1979); silicious acid is determined using the Technicon Industrial System (1977) method; dissolved organic nitrogen (DON) analysis follows the method of D'Elia et al. (1977); PP concentrations are obtained by acid digestion of muffled-dry samples (Aspila et al. 1976); PC and PN samples are analyzed using a model 240B Perkin-Elmer Elemental Analyzer; biogenic silica is measured using the method of Paasche (1973); methods of Strickland and Parsons (1972) and Shoaf and Lium (1976) are followed for chlorophyll <u>a</u> analysis; total suspended solids are determined by the gravimetric technique of EPA (1979).

3.3.4 <u>Algal</u> <u>Identification</u>

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Identification of particulates is accomplished by microscopic examination. Phytoplankton samples settle for three or more days prior to concentration and subsequent analysis. Net plankton (<40 u on longest axis) and nannoplankton are counted using the random field technique (Lund et al., 1958; Venrick, 1978), which requires a minimum of 10 fields to be enumerated with 200 cells or more present. This random field technique is done at 200x magnification, with species identification confirmation at 400x as required. Following the identification of more than 200 cells via random field analysis, a 100X scan is made of the entire settling chamber to identify the large net forms and rare species present. Algae are identified to species whenever possible. Additionally, non-algal particles are also examined and identified (i.e. zooplankton fecal pellets, cysts, skeletal fragments) to further characterize the composition of depositing materials.

3.4 Level I Analysis

3.4.1 SONE Study

Level I interim reports include tabular listings of all variables measured. At each SONE station, sediment Eh, net sediment-water nutrient and oxygen flux, surface and bottom water dissolved nutrient concentrations and vertical profiles (2M intervals) of dissolved oxygen, temperature and salinity are reported. Summary statistics including means and standard deviations are provided for nutrient and oxygen flux data. Additionally, preliminary interpretations of data are presented.

3.4.2 VFX Study

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Each level I report includes tabular listing of all variables measured. Specifically, at each VFX station deposition of particulate materials to collection cup depth, characterization of surficial sediments, particulate material concentration in the water column and vertical profiles (2m intervals) of dissolved oxygen, temperature and salinity are reported. Additionally, preliminary interpretations of the data set are presented.

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4. CONTINUED CONSIDERATIONS OF HISTORICAL PATTERNS OF SOC AND NH4⁺ FLUX

In our previous Level I report (Boynton et al. 1986) we identified several locations in the bay where sufficient sediment flux data were available to allow initiation of an investigation of historical patterns. Data collected at these stations prior to August 1984 were compared to more recent data collected in the MDE monitoring program. Several patterns emerged (see Boynton et al. 1986). Additionally, in the previous report we examined the two different methodologies used to measure sediment-water exchanges (insitu chambers prior to 1984; shipboard incubation of intact cores from 1984 through present time). Such an evaluation is essential prior to conducting a comparative analysis in order to avoid substantial biases. Direct comparisons of the two methodologies conducted in 1986 revealed no consistent differences and for the sake of the current historical evaluation the methods are considered to be comparable.

4.1 Patuxent River Patterns

At the Buena Vista station, patterns of Sediment Oxygen Consumption (SOC) and ammonium regeneration were relatively distinct in the earlier period (1978-1980) with annual maxima occurring in mid July and late August, respectively (Fig. 4-1). In the period for which annual data are available (1983-1986), rates appear to be lower with seasonal peaks occurring about two months earlier in late April and mid-June, respectively. In addition, the range of rates observed in a given month is much greater for the recent period. Ammonium and SOC data collected in early and late spring 1987 were near or slightly above the range of values observed during the 1984-1986 period. If data are grouped into four periods (Apr.- May; June - July; Aug. -Sept.; Oct. - Nov.), general comparisons can be made. Thus, we find that SOC values in the MDE data were lower from June through November, while ammonium fluxes were lower in the Aug. - Sept. period. The overall trend is highlighted in Fig. 4-2 where the ranges of rates in the two time periods are outlined and mean values of recently collected data are shown.



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Fig. 4-1. Annual patterns of water temperature, sediment oxygen demand (SOD) and ammonium regeneration from sediments for the Buena Vista station in the Patuxent River estuary between 1978 and 1987. Given are means and standard deviations for three replicate measurements.



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Fig. 4-2. Annual patterns for mean water temperature and ranges in SOD and annonium regeneration at Buena Vista for several time periods: 1978-1980; 1983-1986 (through June); and 1986-1987 (shown as separate symbols).

One finds no striking differences in SOC between the two time periods at the St. Leonards Creek station, except the June 1987 flux was unusually low, possibly because of low bottom water oxygen conditions (<2mg/l). Some indication of higher NH4⁺ fluxes was apparent during August in the earlier period (1978-1980); however, substantially fewer data are available for comparisons at this station (Fig. 4-3). A suggestion of the same trend was noted for Buena Vista, but it is less pronounced at St. Leonards Creek perhaps because of insufficient measurements and the absence of data before 1980.

4.2 Potential Factors Regulating Flux Patterns

In our previous Level I report 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 flows between the early 1978-1983 period and the more recent 1984-1986 period. Consistent temperature differences between the earlier and recent periods (including 1987) are 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). However, as concluded in the previous report, the temperature differences observed between the two periods could only explain about 30% of the observed flux differences (assuming a Q10 of 2.0). Other factors are clearly involved.

Annual mean flow of the Patuxent (as monitored at the Bowie, Md. gauge) was substantially higher from 1978-1980 (ca. 520 cfs) compared to the 1983-1985 period (ca. 380 cfs). Flow during most of 1986 was even lower (ca. 200 cfs). This flow data coincides with the greater annual mean values of SOC and ammonium regeneration at Buena Vista in the earlier period (Fig. 4-4). The above correlation is consistent with a simple conceptual model which postulates a direct chain of influence: river flow delivers dissolved nutrients which support plankton production, some of which is deposited to the sediment surface, thereby fueling SOC and NH4⁺ regeneration (e.g. Boynton et al. 1982b). However, the observed seasonal shifts would not necessarily be predicted from this model. In fact, data presented by Cory (1974) for primary production in the Patuxent near Buena Vista indicate the opposite response to



Fig. 4-3. Annual patterns of water temperature, SOD and ammonium regeneration from sediments for St. Leonards Creek Station in the Patuxent River estuary between 1980 and 1987. Given are the means and standard deviations for three replicate flux measurements (means for Aug. 1986 - June, 1987 data).

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Fig. 4-4. Patuxent River flow (from gauging station near Bowie, Md.): (a) annual means for 1978-86; (b) monthly means (and ranges in some cases) for 3 time periods (USGS Water Resources Reports 1978-1986).

increased nutrient loading from sewage effluents, that is, the time of maximal rates shifted from spring to summer. River flow, however, also peaked 3 months earlier in the 1978-1980 period compared to 1983-1985 (Fig. 4-4), and in combination with the temperature differences, might account for the seasonal shift in fluxes. This explanation would require a 3-4 month lag between time of peak river flow and peak sediment-water fluxes, which is consistent with the previously described scheme relating nutrient inputs, productivity and sediment-water fluxes (Kemp and Boynton 1984).

In context with the model presented above, flux data collected at the Buena Vista site during 1986-87 (May-Nov. 1986 and April-June 1987) tended to be high, while river flow (and associated nutrient loading from diffuse sources) was the lowest during the time periods considered and temperatures were near record highs. For example, SOC in May, 1986 was in excess of 3g 02 $m^{-2}d^{-1}$ while NH4⁺ flux was about 400ug-at N $m^{-2}hr^{-1}$ in June and August. The SOC value is the highest on record for this time period at the Buena Vista site and the NH4⁺ fluxes were exceeded only by measurements made in August 1978 and 1979 (Fig. 4-1). River flow data for 1987 are not yet available; therefore, it is impossible to compare fluxes observed in the first part of 1987 with river flow. At this point, the linear cause-effect model described earlier is still apparently applicable. Specifically, temporal patterns of SOC follow the pattern for low-flow years with peak values in the early spring-followed by lower rates in the summer with ammonium flux values following a similar pattern. The important point to emerge from the analysis is that in low nutrient loading years (e.g. 1986) benthic fluxes tend to be lower; the highest fluxes tend to occur prior to the time when benthic fluxes could promote continuation of hypoxic-anoxic conditions characteristic of earlier periods (e.g. 1978-1980).

4.3 Sediment Flux Patterns in the Bay and Lower Tributaries

Summer (Aug.) and spring (May) rates of SOC and ammonium regeneration for stations in the open Bay and in the lower tributaries between 1980-1981, 1985, 1986 and the first half of 1987 are shown in Fig. 4-5. SOC fluxes were higher

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in both summer and spring of the earlier period. With the exception of Station R-64, SOC at all sites was similar between 1985, 1986 and 1987. The high and low values observed at R-64 in 1980 and 1986 were probably the result of high (>2.0 mgl⁻¹) and low (ca. $0.1mgl^{-1}$) oxygen concentrations in bottom waters existing at the time that measurements were made.

 $NH4^+$ fluxes appear more complex. For example, fluxes were generally low (>100ug-at $Nm^{-2}h^{-1}$) in the spring (May) for the three years of comparable data. However, there was considerable variability among years in summer $NH4^+$ flux, with fluxes generally larger than those observed in the spring. Focusing on the results from Sta. R-64 and Still Pond (in the mesohaline and oligohaline portions of the bay, respectively), one observes high summer $NH4^+$ fluxes associated with years of high spring freshwater input (and nutrient loading) and lower fluxes in the year of lower flow (Fig. 4-6). This signal is inconsistent at the lower tributary stations of the Patuxent and Choptank rivers although fluxes were higher in the high flow year of 1980.

Annual peak flows of the Susquehanna River (Fig. 4-6) were almost twice as high in 1980, 1981, and 1986 as in 1985. Again, this observation suggests a direct relation between river flow and sediment-water fluxes, as mediated by nutrient inputs and plankton production (Boynton et al. 1982b). Effects of river flow other than nutrient delivery (e.g. increased stratification associated with high river flow) may also enhance cross-bay circulation and benthic-pelagic coupling (Malone et al. 1986).

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Fig. 4-5. Sediment oxygen demand and anmonium regeneration from sediments at two open Bay stations (R-64; Still Pond, SP) and two stations near the mouths of tributaries (St. Leonard's Creek, SLC; Horn Point, HP) for three time periods: Aug. 1980, May 1981; Aug. 1985, May 1986; Aug. 1986, May 1987. Given are means and standard deviations for three replicate measurements.



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5. MONITORING PARTICLE DEPOSITION RATES (VFX) 5.1 Seasonal Patterns of Deposition Rates

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 for the 1985 and 1986 cycles. In this report we emphasize intra- (as opposed to inter-) annual patterns using these two data sets. Our purpose here is to establish a sound understanding of annual cycles before attempting to make detailed analyses of year-to-year trends.

Although some small differences are evident in the annual sequences of carbon and chlorophyll deposition rates, data for the two years are essentially similar (Fig. 5-1). Three periods of peak deposition are repeated in the two years, one in spring (Apr.), one in summer (Aug.) and one in autumn (Oct.-Nov.). Relatively low rates occur in winter (Jan.-Mar.) and in late spring (May-Jun.). Also, deposition rates are apparently low in late summer (Sept.) and later autumn (Dec.); 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⁻²d⁻¹); however, the spring and autumn events were relatively larger in 1985.

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 (Fig. 5-1). 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. No obvious relationship occurs between production and deposition on the indicated weekly to monthly time-scales. Malone et al. (1986), however, observed 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).



Fig. 5-1. 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.

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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 (Fig. 5-1). Temporal trends in chlorophyll deposition rates tended to correspond to trends in 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 (Mar.-Jun.) and summer (Jul.-Aug.) periods (Fig. 5-2). 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), no previous studies have reported quantitative relations. Based on a more limited data set, however, Kamp-Nielsen (1980) has presented similar correlations with seasonally varying slopes.




5.2 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 and 1986 (Fig. 5-3). Highest values for both ratios occurred in late spring; the lowest values in 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. Ratios of C:N for these sediment trap collections were generally between 7-8, indicating a consistency with expected phytoplankton proportions.

No other reports of phosphorous ratios for marine sediment trap material exists. However, C:N ratios of sediment trap collection 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, with peak values greatly in excess of Redfield ratios often occurring in summer (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 (Gacher and Bloesch 1985).

Mean N:P ratios for both suspended and trapped particles are summarized in Table 5-1 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 the August date. At this time particulate N:P ratios also approach Redfield proportions at the bottom of the euphotic zone. In the upper layer, N:P ratios of particulates still exceed Redfield values. It is possible that an extreme phosphorus (or possible silicon) deficiency in the spring contributes to rapid settling of algal cells (Smetacek 1985). Indeed,



Fig. 5-3. Seasonal trends in elemental C:P and N:P ratios (atomic) of particulate material collected in upper sediment trap (4-5 m depth) for 1985 (open circles) and 1986 (closed circles). Shaded area represents expected ratios for phytoplankton.

Table 5-1.	Selected indica in mesohaline (ıtor variables for Chesapeake Bay for	nitrogen ver representati	sus phospt ive seasons	norus limitation s in 1986.	s on phytopla	inkton growth
		Dissolved In	organic Nutri	ients .		Particulate	e Nutrient [†]
Date (1986)	Concentrati N		Uptake Ki N:Ksn	inetics# P:K _{sp}	N:P (atoms)	N:P in Pho 0-4 m	stic Zone 6-10
Apr 9	22.7	0.1	>>1.0	>1.0	2 06	38 (26)	35 (27)
Jun 4	7.0	0.2	>1.0	~ 1.0	29	34 (24)	40 (25)
Aug 20	2.8	1.2	>1.0	>1.0	5	27 (25)	18 (23)
0ct 22	6 •9	0.1	>1.0	<1.0	49	27 (20)	20 (14)
*Concentrat [N03 ⁻], an	ions in surface d P is [P04 ³⁻].	(0-1 m) waters at	"R64" from M	ADE (1987,	unpublished); N	is [NH4 ⁺] p1	sn
#Ratios of of N and P	inorganic nutrie by phytoplankto	ent concentrations on assemblages (Ta	to half-satu ft et al. 197	ration coe 5; McCarth	efficients, K _{5β} . Jy et al. 1975β.	and K _{sp} , for	uptake

^tN:P ratios (atoms) for seston and sediment trap collections (parentheses) at station "R64" for approximately the same dates in 1986.

in Spring of 1985 there was a strong significant correlation between C:P and chlorophyll deposition rate (CDR):Y = (0.15)(CDR)-20.3, $r^2 = 0.72$. A similar but weaker relation was also found for Spring 1986 data: Y = (0.08)(CDR)-7.7, $r^2 = 0.40$.

A comparison of vertical distributions of C:P and N:P ratios for suspended and trap-collected particulates in the water column reveals a remarkable consistency in trends for both ratios during both years (Fig. 5-4). Ratios for seston and trapped material tend to decrease with depth, exceeding Redfield Ratios in the euphotic zone (0-10m) while conforming with these ratios in the lower layer. In early spring (Apr.), 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 (Auq.). This may reflect the higher spring run-off and stronger vertical stratification in 1986. These vertical patterns of C:P and N:P in seston and trapped 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 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 assimilation, 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.



Fig. 5-4. Vertical distributions of elemental C:P and N:P ratios (atomic) of particulate material: suspended in water column (points); collected in sediment traps (cross-hatched bars); and deposited on bottom sediments (darkened bars). Data are for four representative dates in two years (1985 and 1986) from Sta. R-64 in mesohaline portion of Chesapeake Bay. Dashed line indicates expected ratios for phytoplankton.

Although we have shown that particle deposition at Station R-64 is strongly related with phytoplankton standing stocks (Fig. 5-2), 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 less than 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 phytoplankton dynamics (Honjo 1982). Others have suggested a mechanism of mutual flocculation of algae and inorganic clays (Avnimelech et al. 1982) which may account for this pattern (Smetacek 1985).

5.3 Sediment Trap Measurements of Net Deposition

For several decades sediment traps have been used effectively to estimate new deposition 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).

Sediment trap data from Station R-64 have been corrected using this approach for representative dates over the course of the 1985 season (Table 5.2). 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. 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

Deployment Period	Seston Mid	Percen (f _t) Top	t Organic Trap Mid	<u>Content</u> (f _s) Top	t Bottom Seds (f _R)	Correct <u>Resusp</u> Mid	ion for <u>ension*</u> Top
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 5-18	12.7	12.1#	9.5	11.9	2.9	0.68	0.98
Jul 24-30	9.2	14.3	6.9	9.3	2.5	0.66	0.58
Aug 13-20	9.3	11.9	6.3	9.7	2.4	0.57	0.77
Oct 1-16 Mean	11.3	8.9	5.7	6.8	2.4	$\frac{0.37}{0.62}$	<u>0.68</u> 0.84

Table 5-2. Estimation of fraction of material collected in sediment traps originating from bottom sediment resuspension for selected deployment periods in 1985.

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

#Estimated from mean of 27 May - Jun 18.

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

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Dares Beach (10m) stations. Bottom sediment characteristics are in general, similar along a cross-bay transect in this portion of the estuary at water column depths >5m (Ward 1985). The closest shoal areas (with <5m depths) are greater than 10km from the sediment trap deployment site.

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 5.2). Chlorophyll content (as a percent of dry weight) of seston is much higher than that in 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 5.2.).

Annual rates of sediment accumulation can be calculated using either of these estimates of net sediment deposition (Table 5.3). In 1985, sediment accumulated below Station R-64 at a rate of approximately 4mm y^{-1} . Since organic carbon comprises 10-15 percent (Table 5.2) 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. 3mm y^{-1} , which is within the range of values estimated by geochronologic techniques (Pb-210) 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 P6-210 and sediment trap rates were reported for two Swiss lakes (Bloesch and Burns 1982).

Time Period	Daily Carbon Deposition ^a (gC m ⁻² d ⁻¹)	Ratio ^b (gDW:gC)	Total Dry Wt. Deposition ^C (gDW cm ⁻² y ⁻¹)	Bulk Density ^d (g cm ⁻³)	Sediment Accumulation (cm y ⁻¹)
Mar-Nov (275 d)	0.8	10	0.22	0.65	0.34
Dec-Feb (90 d)	0.3	20	0.05	0.65	0.08
Annua1 (365 d)	0.6		0.27e	<u> </u>	0.42

Table 5^{-3} . Calculation of total annual deposition rates in traps for comparison with geochronological estimates of long-term sediment accumulation.

^aEstimated 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).

^bEstimated 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.

CNote that 10^4 cm² = 1 m².

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^dTypical value based on measurements of sediments at "R64"; $\rho_{\rm b} = \rho_{\rm S}$ (1- ϕ) = 2.6 (1-0.75) = 0.65 g cm⁻³.

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

6. SEDIMENT OXYGEN DEMAND AND NUTRIENT FLUXES

Sediment fluxes considered in this section were collected during the first three years of OEP (now MDE) Monitoring, from August 1984 to June 1987 (SONE Cruises 1-12). This data base now comprises 12 sets of flux measurements and supporting environmental data for each of the ten SONE stations. In this section we examine these data for (1) spatial and temporal patterns in SOC and nutrient fluxes, including evidence for inter-annual trends, (2) correlations with environmental factors that may regulate sediment-water exchange dynamics, and (3) stoichiometric relationships (element ratios) in the net fluxes of oxygen and inorganic nutrients.

In the following discussion several levels of data aggregation are employed to examine spatial and temporal patterns in the benthic flux data: "average station flux" refers to the average of all flux measurements made over the three year period at an individual station; "average monthly flux" is the baywide flux for a particular month averaged over all ten stations. The most aggregated level, "average location flux", refers to the average of all fluxes at one of four classes of stations: (1) Upper Tributaries (Buena Vista, Windy Hill, Maryland Pt.), (2) Lower Tributaries (St. Leonard, Horn Pt., Ragged Pt.), (3) Mid-Mainstem Bay (R-78, R-64, Pt. No Pt.), and (4) Upper Mainstem Bay (Still Pond). The upper bay region, as characterized by the Still Pond station, was separated from the other mainstem stations and treated alone because the characteristics of this region (depth, hydrodynamics, sediment characteristics, and redox regime) are distinct from those found at the other three mainstem bay stations.

6.1 Variability in Benthic Flux Measurements

Sediment-water exchanges of dissolved oxygen and inorganic nutrients (SONE Monitoring) were determined four times per year, during the spring through fall, at each of ten stations in the Maryland portion of Chesapeake Bay. Station locations and flux measurement procedures were described in Section 3. For this report we conducted a thorough review of the sediment flux 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. Only 4% of the flux data, which now consists of 1770 individual flux determinations, failed to meet the criteria for "interpretable" fluxes, and had to be removed from the data base. The success rate for flux measurements since the inception of the monitoring program has therefore been about 96%.

In our previous Level I Report (Boynton et al. 1986) the analysis of the sediment flux data was based on averages of the three flux determinations made during each visit to the SONE monitoring stations. For this report the flux data have not been averaged; the results from all cores were considered individually in various plotting routines and statistical analyses. These data are given in Appendices 4 and 5.

The coefficient of variation [CV = (mean/std. dev.)x100] is a useful statistic for comparing the relative variability among sets of similar measurements (Snedecor and Cochran 1967). An estimate of overall variability in the flux data can therefore obtained by comparing CV's for all flux measurements made at each station (i.e., combining the data from all 12 SONE cruises) with those determined for a typical set of three replicate measurements from an individual cruise (Table 6-1). This exercise revealed that the variability within each set of flux measurements generally ranged between 20-60% for all fluxes except N+N (Table 6-1, see also Core vs. Dome Comparisons in Section 3 of our Level 1 No. 3 Report). Variability associated with our measurement techniques therefore appears to be a consistent and predictable component of total variability in the measured fluxes. For comparison, the CV for some environmental variables such as bottom water temperature, salinity, oxygen and NH4⁺ concentrations, determined in conjuction with the benthic fluxes at the SONE stations, ranged from 10-100% (Table 6-2).

The CV calculations reflect the overall within-station variability in sediment fluxes. They also indicate that the within-station variability

Table 6-1. Comparison of coefficients of variation (%) of sediment fluxes from all cruises SONE 1-12, Aug. 84 - June 87, with a single set of flux measurements made in June 1986.

	()2	NH	4	1	N+N		DIP	S	i	
Station	*A11	**1 set	A11	l set	A11	l set	 All	l set	All	l set	n
ST LEO	70	6	65	31	158	10	129	141	73	32	33-36
BU VISTA	48	22	66	10	96	10	100	21	71	4	33-36
HORN PT	63	12	101	14	231	13	247	32	55	5	33-36
WIND HL	58 (324	116	22	4973	814	126	39	47	30	2 9- 30
RAG PT	61	14	109	10	178	3	508	76	87	6	33-36
MD PT	69	93	68	39	1913	71	116	31	53	17	34-36
PT NO PT	67	22	131	2	4336	509	381	23	5 9	7	35-36
R 64	71	46	134	23	310	16	161 [.]	27	53	23	36
R-78	67	21	335	4	3847	21	370	23	56	22	36
STIL PD	48	25	165	45	152	21	278	42	75	54	36
Average: Tot. # of	67	58	128	20	4665	149	215	45	68	20	
Fluxes:	340		341		340		338		341		

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*All cores. SONE 1-12 ** Data from SONE 8. June 1986. triplicate cores

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Table 6-2 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	[0 ₂]	[NH4 ⁺]	Temperature	Salinity
ST. LEONARD	50	54	23	12
BUENA VISTA	30	114	21	16
HORN PT.	27	87	24	19
WINDY HILL	18	81	22	27
RAGGED PT.	78	70	24	10
MARYLAND PT.	26	5 9	22	43
PT. NO PT.	69	61	24	12
R 64	93	47	27	14
R78	88	36	28	15
STILL PD.	22	54	25	58

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 67-68%); the flux of nitrate + nitrite (N+N) was the most variable (CV in excess of 4600%) of the benthic nutrient fluxes. With the exception of N+N flux, seasonal and site-related variability encountered during SONE monitoring produced CV's that ranged between 50-200%. This degree of total variability in the measured fluxes appears to be inherent in field measurements of ecological process 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).

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

6.2.1 Sediment oxygen consumption (SOC).

Station averages of sediment oxygen consumption (SOC) at the ten SONE stations ranged between -0.80 to -1.75 g O2 m⁻² d⁻¹ (Table 6-3). These rates of benthic oxygen comsumption are moderate to large when compared with SOC rates reported for other temperate estuaries (Table 6-4). 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.

As the SONE data base has grown our ability to identify differences among groups of stations has improved dramatically. Oxygen flux data considered in our previous Level 1 Report (Boynton et al. 1986) suggested that SOC tended to be highest at the shallow tributary stations and lower in the deeper mainstem bay, but statistically significant between-station differences were obscured by within-station variability. The inclusion of an additional year's data in this analysis further strengthened the finding of differences in SOC rates in some of the tributaries and the mainstem bay. As shown in Fig. 6-la, SONE stations could be separated into two groups based on average

Table 6-3. Average station fluxes (means and std. dev.) for SONE Monitor Stations. Means were determined using data from SONE cruises 1-12.

	02 FL	UX _	NH4+	FLUX	N+N F	LUX	DIP	FLUX	SI	FLUX
STATION	AVG.	SD	AVG.	SD	AVG.	SD	AVG.	SD	AVG.	SD
ST. LEONARD	-1.48	1.03	9 8	64	20.7	33	5.8	8	323	237
BUENA VISTA	-1.70	0.82	206	135	22.9	22	15.5	16	293	210
HORN PT.	-1.68	1.05	153	155	21.4	49	4.4	12	400	220
WINDY HILL	-1.75	1.01	141	165	1.2	61	14.0	18	387	181
RAGGED PT.	-1.12	0.77	365	251	-2.5	48	21.2	25	297	157
MARYLAND PT.	-1.13	0.69	13 9	152	-25.4	45	3.1	15	251	218
PT. NO PT.	-0.99	0.67	107	140	-0. 5	22	2.8	11	382	226
R-64	-0.96	0.68	209	282	-8.3	26	25.1	40	491	25 9
R-78	-0.80	0.53	65	218	1.2	46	6.6	24	228	129
STILL POND	-1.33	0.63	86	142	-32.3	4 9	3.5	10	184	13 9

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Table 6-4. Comparison of oxygen, DIN, and DIP fluxes at SONE monitoring stations with summer rates of oxygen and nutrient fluxes from various near-shore marine systems.

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	SOC	NH_4^+ Flux	DIP Flux	Ref.
	g/m2/đ	umol/m2/d	umol/m2/d	
Loch Ewe, Scotland	0.6-1.05	20-80		1
Buzzard's Bay, MA	1.42	125	-15	1
Eel Pond, MA	1.08	85	16	1
Narragansett Bay, RI	1.80	200	30-50	1
Long Island Sound, CN		50-200	5-20	1
New York Bight, NY	0.84	25	2	1
Patuxent River Estuary, MD	3.03	710	48	1
Pamlico River Estuary, NC		45		1
South River Estuary, NC	1.57	250	17	1
Cape Blanc, West Africa		235	50	1
Vostoc Bay, USSR	1.08	150	20	1
Maisuru Bay, Japan		13-32		1.
Kaneohe Bay, HA	0.46	54	3	1
La Jolla Bight, CA		40	6	1
Yaquina Bay mudflat, OR	-6.0-6.8	-91-204	-5-19	2
Chesapeake Bay, MD				
Upper tributaries	1.5	163	11	3
Lower tributaries	1.4	210	11	3
Mainstem bay	0.9	125	12	3
Upper bay (Still Pond)	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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Figure 6-1.

6-1. Average station fluxes of oxygen and inorganic nutrients at SONE monitoring stations. Panels show the mean (+ std. error) all determinations of each flux for each station.

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station SOC: high average SOC's were found in the Patuxent River, Choptank River, and the upper bay station at Still Pond. Significantly lower rates occured in the Potomac River and mid-mainstem bay. The division between the two groups occurred at SOC rates of $1.1-1.3 \text{ gO2m}^{-2}\text{d}^{-1}$. Lowest average SOC rates occurred at Station R-78. It is not clear why SOC and other nutrient fluxes at this station should be significantly lower than the other midmainstem stations. We have noticed that sediment at R-78 contains noticable amounts of slag-like material; it seems possible that aerobic benthic activity at this station may be suppressed by anthopogenic pollutants.

6.2.2 Dissolved inorganic nitrogen fluxes

6.2.2.1 <u>Annonium flux.</u> 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 NH4⁺ generally dominates benthic flux of fixed inorganic nitrogen in productive temperate estuaries. The release of NH4⁺ from sediments at the SONE stations was generally many times greater than the net exchange of nitrate + nitrite. At most stations NH4⁺ flux accounted for 70-100% of the total DIN flux (the sum of NH4⁺ + nitrate + nitrite) from the sediment. There were two exceptions: NH4⁺ fluxes at Maryland Pt. and Still Pond contributed a smaller fraction, averaging 59% and 36%, respectively, to the net exchange of DIN.

Average station fluxes of NH4⁺ ranged from 65 ug-at N $^{-2}h^{-1}$ at R-78 to 365 ug-at N $^{-2}h^{-1}$ at Ragged Pt (Table 6-3 and Fig. 6-1b). In our previous report we were unable to identify obvious spatial patterns in the averaged NH4⁺ fluxes except to note that the fluxes in the lower Potomac at Ragged Pt. were significantly greater than those found at the other SONE monitoring stations. As shown in Fig 6-1b, this spatial pattern in NH4⁺ fluxes at the SONE stations is becoming clearer. As before, with the exceptions of Ragged Pt. and R-78, the average flux at most stations fell between 100-200 ug-at N $^{-2}h^{-1}$. Two of the station exhibiting the highest rates of NH4⁺ release from the sediments (Ragged Pt. and R-64) are subject to summer anoxia. Station R-

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78 also is also subject to summer anoxia, but, as noted above with reference to low SOC rates, NH4⁺ fluxes at this station appear to be anomaloulsy low. Relatively high fluxes were also found at Buena Vista, which remains aerobic all year. The factors responsible for these between-station differences are not clear. Annonium fluxes appear to be controlled by multible interacting environmental variables including temperature, the concentration gradient of NH4⁺ across the sediment-water interface, redox state of the sediments and overlying water, activity of the benthic organisms, and the rate of deposition of particulate nitrogen.

6.2.2.2 Nitrate + nitrite (N+N) flux. Unlike NH4⁺, N+N fluxes followed more pronounced spatial patterns (Fig. 6-1c, Table 6-3) which included shifts in direction of the fluxes across the sediment-water interface. The calculation of average station fluxes revealed that the behavior of N+N differed among three groups stations. Tributary stations in the Patuxent and lower Choptank were characterized by the net release of N+N from the sediment to the water at rates that averaged around 20 ug-at N $^{-2}h^{-1}$. In contrast, the overall flux of N+N was into the sediment in the upper Potomac and the uppermost mainstem bay. N+N flux was highly variable at the remainder of the stations, resulting in station-averaged fluxes that were approximately zero. N+N fluxes for individual cores ranged from maximum sediment release of nearly 190 ug-at m⁻²h⁻¹ in the lower Choptank (Horn Pt.) in June 1985 to the maximum sediment uptakes of nearly -200 ug-at m⁻²h⁻¹ at Still Pond in August 1984. However, most N+N fluxes fell within an envelope bounded by -40 to +30 ug-at m⁻²h⁻¹ (Fig. 6-1c).

The net flux N+N reflects the combined effects of complex 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 N+N 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 N+N (i.e., the most negative rates of N+N flux) occur at two upper estuary

stations (Maryland Pt. and Still Pd.) that were also characterized by the highest levels of dissolved nitrate in the water over the sediments. Other factors obviously influence N+N 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 N+N flux at that station were not strongly negative. Oxygen content of the overlying water and sediment redox regime undoubtedly influence N+N 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 apppear to produce an abundance of NH4⁺, so it seem unlikely that the first step of nitrification, NH4⁺ oxidation, would be limited by NH4⁺ availability. However, nitrification is an obligately aerobic process, while nitrate metabolism occurs under predominantly anaerobic conditions. The rate of N+N uptake must ultimately be limited by N+N availability. The rates of NH4⁺ oxidation (nitrification) and nitrate reduction (especially denitrification) are strongly coupled, especially when sources of "new" nitrate from river flow diminish after the spring freshet. We can speculate that the net releases of N+N observed in the Patuxent and Choptank tributaries reflect predominantly oxidized environments both in the surficial sediments and the overlying water. 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 nitrate metabolism and denitrification. Nitrate formation and consumption appear at times to be in balance. This results in no net flux of N+N 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 N+N from the overlying water occurs. At these stations NH4⁺ regeneration appears to be the only significant route of nitrogen remineralization occurring in the sediments.

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6.2.3 Dissolved inorganic phosphorus (DIP) flux

During the first three years of SONE monitoring DIP fluxes ranged from sediment uptakes of -54 ug-at $m^{-2}h^{-1}$ at R-78 in August 1984, to sediment releases of DIP of 128 ug-at $m^{-2}h^{-1}$ at R-64 in June 1986. Although sediment uptake of DIP occurred at all but one station (Ragged Pt.) at some time during the monitoring period, station averaged fluxes of DIP were always positive, that is, the net flux of DIP at all stations is predominantly from the sediment to the overlying water (Table 6-3, Fig. 6-le). Three-year stationaveraged DIP fluxes at the ten SONE stations ranged from about 3 ug-at $m^{-2}h^{-1}$ at Still Pd. and Pt. No Pt. to 25 ug-at $m^{-2}h^{-1}$ at R-64 (Table 6-3). As shown in Fig. 6-le, SONE stations could be separated into two groups by the calculation of station-average DIP fluxes: in one group consisting of the higher salinity stations in the Patuxent, Choptank, and lower bay, the average DIP fluxes were less than 7 ug-at $P m^{-2}h^{-1}$. The remaining four stations (the lower salinity regions of the Patuxent and Choptank, the high salinity region of the Potomac, and the mid-bay at R-64) were characterized by station averaged fluxes in excess of 10 ug-at $P m^{-2}h^{-1}$. 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. Again, the results from R-78 do no fit this scheme. The mean DIP flux at R-78 appears to be low for a region that is hydrographically similar to R-64.

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 will show below that the redox environment of the sediment and overlying water is one such important factor, particularly in the mainstem bay. 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 <u>and</u> the upper tributaries. The release of DIP from sediments along the deep mainstem bay is most likely associated with the 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, 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 the overlying water in these regions is always well-oxygenated.

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 could influence the amount of DIP available for phytoplankton production, as well as altering the the ratio of DIP to DIN in bay waters.

6.2.4 Dissolved silicate flux

The flux of silicate from individual cores during the monitoring period ranged from 0 to over 1100 uq-at Si $m^{-2}h^{-1}$. The highest rates of silicate flux in individual sediment cores were observed at the lower bay stations (R-64 and Pt. No Pt.) in June 1985. Although no net flux of silicate was observed at all SONE stations except Horn Pt. at least once during the monitoring period, station averaged fluxes for all the stations were always positive (i.e., from the sediment to the water) and of the order of 200-500 uq-at Si $m^{-2}h^{-1}$ (Table 6-3, Fig. 6-1d). The addition of the FY87 data to the monitoring data base reinforced the spatial pattern in silicate fluxes described in our previous Level 1 Report (Boynton et al. 1986). Highest fluxes occurred along the deep mainstem bay and Choptank River. Lowest fluxes were observed at the uppermost mainstem bay station (Still Pond). Although the differences in average silicate fluxes at the upper and lower stations within a tributary were not statistically significant, average fluxes at the . lower tributary stations were consistently lower than those observed at the upper station. This pattern remains when went the data are aggregated into location averages (Table 6-5). Silicate fluxes at the four major regions appears to increase in parallel with increasing salinity: Still Pond < Upper Tribs. < Lower Tribs. < Mainstem Bay. This pattern is consistent with a

conceptual model which would predict increasing silicate cycling in higher salinity regimes in parallel with the increasingly important role of diatom production in the phytoplankton communities along and estuarine salinity gradient.

6.3 Temporal Patterns In Benthic Fluxes

6.3.1 Seasonal patterns in benthic fluxes at SONE stations

Our sampling schedule of four measurements per year, skewed toward the summer, is not adequate to clearly define annual patterns of benthic fluxes or lead to accurate estimates of annually integrated flux rates. Nevertheless, the seasonal component of variability in SONE measurements is potentially important and needs to be defined in order to define year-to-year trends in the data. In our previous Level 1 report (Boynton et al. 1986) some indication of bay-wide seasonality in SOC rates was indicated by examining data averaged by month for all stations and years. For this report we combined the flux data for all years by month for each station. The purpose of this exercise was to identify patterns of seasonality in the flux data. The results of this analysis are presented as a series of boxand-whisker plots in Figs. 6-2 through 6-6. In each plot vertical bars give the range of data; the median is given by the horizontal line in each box; the boxes themselves give the range of each quartile above and below the median. Thus 50% of the data for each flux is enclosed within the box. Data falling more than 1.5 times the quartile range from the median are shown with an asterisk as "outliers."

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 (Table 6-6). The caveat here is that our sampling program was not designed to produce a high resolution seasonal picture. Nonetheless, some intriguing differences emerge among the SONE stations for each of the flux measurements. For example, there was a clear indication of seasonality in all nutrient fluxes in the upper Choptank (Windy Hill) while essentially no seasonality could be discerned in nutrient fluxes in the upper mainstem bay (Still Pond).

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Table 6-5. Average location fluxes (means and std. dev.). Table reports the average of sediment fluxes at SONE monitoring grouped by location for SONE cruises 1-12.

	O2 FL	XU	NH4+	FLUX	N+N F	LUX	DIF	P FLUX	SI	FLUX
LOCATION	AVG.	SD	AVG.	SD	AVG.	SD	AVG.	SD	AVG.	SD
Upper Tributaries	-1.5	0.9	163	154	-1	50	11	17	307	212
Lower Tributaries	-1.4	1.0	210	212	13	45	11	18	338	212
Mesohaline Mainstem bay	-0.9	0.6	125	234	-4	32	12	30	367	239
Upper Mainstem bay	-1.3	0.6	90	142	-35	47	2	7	187	140

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Table 6-6. Summary of temporal patterns of sediment fluxes at SONE monitoring stations. This table summarizes data presented in Fig. 6-2 - 6-6 by indicating the month (5=May, 6=June, etc.) or months of seasonal maximum. Additional notations are explained in table footnotes.

	SOC	NH4 ⁺	N + N	DIP	Si
BUENA VISTA	6	6	6,10 (B)	6	5
ST. LEONARD	6	8!	NS	6!	6!
MD. PT.	8-10	8	4	NS	10
RAGGED PT.	5?	8	4(+),5(-)	8	NS
WINDY HILL	5?	81	10!	81	18
HORN PT.	61	?	NS	10	6
STILL PD.	6	NS	NS	NS	NS
R78	NS	6?	5(-),10(+)	6?	6
R64	NS	8	5(-),10(+)	6	6!
PT. NO PT.	NS	8	5(-),10(+)	6	61

? = questionable seasonal pattern

NS = no apparent seasonality

! = well-defined seasonal pattern

(-) = sediment uptake; (+) = sediment release

(B) = bimodal seasonal pattern

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in the Patuxent and Potomac Rivers. of data is given in text.

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Seasonal variations in sediment-water oxygen fluxes at SONE monitoring stations in the Maryland portion of the mainstem Chesapeake Bay. Figure 6-2c.

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Most stations except those in the lower mainstem bay exhibited some seasonality in SOC in which the highest rates of SOC occurred in May or June. This pattern emerged most clearly at Horn Pt. (Fig. 6-2b). 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 (Fig. 6-2a). At stations subject to periodic anoxia, seasonal patterns of SOC were strongly influenced by the timing and duration of low-oxygen conditions and the occurance of reaeration events. These factors contributed to the high variability in summer SOC rates observed at Ragged Pt., R-64 and R-78 (Figs. 6-2a,c,).

Armonium fluxes at most of the SONE stations followed fairly straightforward seasonal patterns with maximum rates of sediment release occuring in August. The best examples of this pattern were observed at the lower Patuxent, lower Potomac, and upper Choptank Rivers (Fig. 6-3a,b). Although somewhat obscured by significant rates of sediment uptake of NH4⁺ during the first SONE cruise (August 1984), essentially the same pattern of NH4⁺ fluxes were observed at mainstem stations R-64 and Pt. No Pt. (Fig. 6-3c). Exceptions to this pattern were observed in the upper Patuxent and mainstem station R-78 where the seasonal peak in NH4⁺ flux occurred earlier in summer. No seasonal pattern could be discerned at Still Pond. 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.

Temporal variations in nitrate + nitrite (N+N) fluxes were generally complex and differed widely among the SONE monitoring stations (Fig. 6-4, Table 6-6). The kinds of seasonal patterns in N+N flux included: (1) no apparent cycle (Still Pond), (2) pronounced uni-modal change from sediment uptake in spring to maximum sediment release in fall (Windy Hill), (3) a bimodal pattern with periods of sediment release in spring and fall (Buena Vista), and (4) the most common pattern, best illustrated by the data from Ragged Pt. (Fig. 6-4a), included a rapid shift from positive or near-zero

sediment N+N 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 "check-mark"-like seasonal cycle occurred at St. Leonard, Horn Pt., and all the mainstem bay stations except Still Pond. The salient feature of seasonality in N+N flux at many of the stations appears to be the shift from strong sediment uptake in spring to positive or near-zero net flux in summer and fall. The occurance of a sediment N+N sink in spring coincides with the high concentrations of N+N in the water column introduced into the bay and tributaries during the spring freshet. Whether the sediments serve as a net source or sink of N+N still needs to be resolved. However, net N+N fluxes are small in comparison to the flux of NH4⁺ at all places except, perhaps, the very low salinity reaches of bay. Since NH4⁺ fluxes were almost always from the sediment to the overlying water, the magnitude of N+N fluxes, either positive or negative, has a minor effect on the total flux of remineralized inorganic nitrogen from bay sediments.

Seasonal variations in DIP fluxes also followed a variety of patterns (Fig. 6-5, Table 6-6). In some regions the cycle followed a fairly simple cycle with periods of maximum sediment release occurring either in June (both Patuxent stations), August (Windy Hill), or November (Horn Pt.). 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. DIP fluxes in August along the mainstem bay are highly variable. These patterns are consistent with the view that the large sediment-water exchanges of DIP observed in the lower Potomac and along the mainstem bay are associated with low oxygen in the overlying water.

Spatial and temporal patterns in fluxes of dissolved silicate (Fig. 6-6, Table 6-6) were among the most striking and easily interpretable 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 (Fig. 6-6b) little seasonality was apparent in the silicate fluxes from the low salinity regions of the Patuxent, Potomac, and mainstem bay (Fig.6-6a,c). In contrast, very clear seasonal



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Seasonal variations in sediment-water nitrate + nitrite (N+N) fluxes at SONE monitoring stations in the Choptank River. Figure 6-4b.



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Figure 6-4c. Seasonal variations in sediment-water nitrate +nitrite (N+N) fluxes at SONE monitoring stations in the Maryland Portion of the Chesapeake Bay.










Figure 6-6a. in the Patuxant and Potomac Rivers. of data is given in text. Seasonal variations in sediment-water silicate fluxes at SONE monitoring stations Explanation of box-and-wisker presentation

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cycle emerged from the silicate data from the lower tributaries (e.g. St. Leonard, Fig. 6-6b) and mesohaline mainstem bay (Fig. 6-6c). The sequence of patterns in silicate fluxes as one proceeds down the mainstem bay (cf. Fig. 6-6c) is particularly striking. These seasonal and spatial patterns in silicate fluxes point to the coupling of diatoms production in the plankton and silicate remineralization in the sediments. The patterns observed at mainstem stations R-64 and Pt. No Pt. (Fig.6-6c) 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 clearly suggests a strong interaction between silicate deposition following the spring diatom blooms and water temperature as factors that regulate benthic silicate fluxes.

6.3.2 Inter-annual trends in sediment fluxes

As stated in the introduction, one of most important objectives of the Ecosystem Processes Component of the bay monitoring program is the identification of long-term trends in sediment deposition and benthic fluxes in the Maryland portion of Chesapeake Bay. This report covers data collected from August 1984 through June 1987 — a period of two full calendar years (1985 and 1986) and two partial years (1984 and 1987). Although it is still early in the monitoring program, it seemed appropriate to begin to examine these data for inter-annual trends.

The technique employed for this initial pass-through of the data was to compute the mean and standard deviation for all sediment fluxes observed at each station during calendar years 1984 throught 1987. These statistics were then plotted (Figs. 6-7a through 6-7e) and examined by eye for trends. This approach is unquestionably simplistic, qualitative, and perhaps misleading due to to the unequal sample sizes available for each year (4 SONE cruises in 1985 and 1986, but only 2 SONE cruises in 1984 and 1987). The results should therefore be considered only a starting point for examining the EPC data for longer term trends.

As shown in Fig. 6-7a-e, annual within-station variations in sediment-water fluxes generally overwhelms differences among annual mean fluxes at the SONE monitoring stations. Nevertheless, some qualitative patterns emerged that warrant closer study. For example, the annual average of SOC, NH4⁺, and DIP flux measurements at Buena Vista in the upper Patuxent appear to have increased steadily since 1984. At nearly all the other SONE stations, the estimate of mean annual oxygen flux peaked in 1985 and appears to have decreased in 1986 and 1987. There were several striking inter-annual trends in NH4⁺ fluxes, including the upward trend at Buena Vista mentioned above, and downward trends in the Potomac (Maryland Pt. and Ragged Pt.) and lower mainstem bay (R-78). Downward trends in N+N fluxes since 1985 were indicated at St. Leonard Cr. and Windy Hill. Upward trends in DIP fluxes and downward trends in silicate flux may be occurring along the mainstem bay, especially in the region of stations R-78 and R-64.

6.4 Factors Influencing Benthic Fluxes of Oxygen and Inorganic Nutrients

Relationships between sediment nutrient fluxes and various environmental factors such as water temperature, water depth, sediment characteristics, mixed layer depth, and rates of organic matter deposition have been reported for nearshore ecosystems (e.g. Hargrave 1969, Nixon et al. 1976, Hammond et al. 1985). As an initial attempt to identify sources of variability in the SONE flux data, and to eventually develop a predictive model of sediment-water exchanges, we examined our benthic flux data for correlations with a suite of environmental factors that were monitored in conjunction with sediment-water fluxes at each SONE station. In this report we extended this analysis to include both correlations on a bay-wide and station-by-station basis. As before, this single-variable approach is overly simplistic and misses important features of the data such as inter-annual variations, multivariate interactions, and co-variance among the variables. Nonetheless, some intriguing features of the data have emerged from this approach.

Correlation coefficients (r) were computed to examine the simple linear relationships sediment-water fluxes and some environmental factors







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of ammonia (mean + std. dev.) at SONE monitoring stations.







Figure 6-7d. Inter-annual trends in annually averaged sediment-water flux s of DIP (mean + std. dev.) at SONE monitoring stations.



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Figure 6-7e. Inter-annual trends in annually averaged sediment-water fluxes of silicate (mean \pm std. dev.) at SONE monitoring stations.

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that we <u>a priori</u> thought might influence the magnitude of sediment-water exchanges. Matrices of r were generated for most SONE stations individually (Windy Hill, Pt. No Pt., and Still Pd. were not completed for this report) and by combining the data from all stations.

In contrast with our earlier report, many significant single-variable correlations were found among the sediment-water fluxes themselves as well as between the fluxes and various environmental variables (Tables 6-7a-e) including bottom water temperature, salinity, the concentrations of dissolved oxygen and nutrients in bottom waters, and characteristics of the surficial sediment. The number and strength of these correlations varied widely among the stations for each constituent flux. For example, all fluxes from Buena Vista and R-64 tended to be highly correlated with features of the water column and sediment; at Maryland Pt. and R-78 these relationships appeared to be much weaker.

6.4.1 Sediment characteristics and relationships with SONE fluxes.

As a first approximation the amounts of particulate carbon (PC), nitrogen (PN), and phosphorus (PP) found in estuarine sediments reflect the long-term net effects of the opposing processes of organic matter deposition and diagenesis (remineralization). We therefore suspected that some relationships might exist between the organic deposition rates, benthic nutrient fluxes, and the resulting organic composition of the sediment. Given the current interest in extending the SONE flux measurements to other regions of the bay using some kind of areal weighting based on sediment characteristics, we continued to examine relationships between sediment characteristics and SONE fluxes in more detail.

Surficial sediments at SONE tributary stations generally contained 2-5% total particulate carbon (Fig. 6-8a) with the higher values associated with regions of sediment accumulation. Windy Hill in the upper Choptank (about 5% PC) apparently receive considerable detrital organic material from bordering marshes; sediments in the lower Potomac at Ragged Pt. are also fairly carbon rich (about 4% PC) perhaps because the hydrography of

TABLE 6-7a

SUMMARY OF SIGNIFICANT CORRELATIONS BETWEEN SEDIMENT FLUXES OF DXYGEN AND ENVIRONMENTAL FACTORS AT SOME STATIONS

FACTOR	: ALL :STATIONS :	ST. : LEDNARD :	BUENA : VISTA :	HORN PT.	RAGGED : PT.	MD. PT.	PT. : NO PT. :	R54	R78 :	STILL POND
DD FLUX	:									
AMM FLUX	: *	ŧŧ	ŧŧ	ŧ			NR :	- t	** ;	NR
N+N FLUX	; ##		***	++		Ŧ	NR	- ##		NR
DIP FLUX	:		***			ŧŧ	NR	- ##		NR
SI FLUX	: ++	**	***	***		ŧŧ	NR	Ŧ	+++	NR
BOT. WAT. 02	: ##		- ##		: **	- t	NR	ŧŧ		NR
BOT. WAT. NH4+	: - ##	- +	- ###	- ##	: - ##	- +	: NR	- ##		NR
BOT. WAT. N+N	:		- ++	- +	: - ##	- #	: NR			NR
BOT. WAT. DIP	; - +	: - ##	- ++	: - +	:		: NR	- +++	: - ##	NR
BOT. WAT. SI	; ##	: ** ;	: ++	: ++	: - ##	:	: NR		:	NR
BOT. WAT. TEMP.	: ++	; ***	; + i	; f	: - *	: +	: NR	- t	:	NR
BOT. WAT. SAL.	: - ##	: - *	; - ##	: - *	: +	:	: NR	: +++	:	NR
SURF. SED. eH	: **	: +++	;	; ++	; +	:	:	; +	; - ++	NR
SURF. SED. PC	;	: - ++	; +**	; - #	: +	; ; t	: : NR	; - { **	;; : - **	NR
SURF. SED. PN	; *	: - ++	:	:	:	: ##	: NR	; ; - { * !	:	NR
SURF. SED. PP	: ++	: - ##	: **	: - ##	:	:	: : NR		: **	NR
SURF. SED. CHLa	3: - #	:	; ; ##	: : - *	;	;	NR NR	: - ***	:	NR
n	: 340	: 33	: 36	: 36	: 34	: 35	: 36	: 36	: 36	
					;		;			

NOTES:

- = negative correlation
= r sig. at 5% level
= r sig. at 1% level
= r > .80, sig. at > 0.5%
NR = correlations not computed

empty cells indicate correlation was not significant

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TABLE 6-7b

SUMMARY OF SIGNIFICANT CORRELATIONS BETWEEN SEDIMENT FLUXES OF AMMONIUM AND ENVIRONMENTAL FACTORS AT SONE STATIONS

•••••••	: ## :	:	:						
·		TT	## :			: NR :		: ŧ :	NR
•	1			:	;	1	:	;	
:	:	++ ;	++	:		NR :	:	- ## ;	NR
++ ;	ŧ;	++ :		++	+ ;	NR :	***	++ :	NR
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NOTES:

- = negative correlation
* = r sig. at 5% level
** = r sig. at 1% level
*** = r > .80, sig. at > 0.5%
NR = correlations not computed

empty cells indicate correlation was not significant

TABLE 6-7c

SUMMARY OF SIGNIFICANT CORRELATIONS BETWEEN SEDIMENT FLUXES OF NITRATE + NITRITE AND ENVIRONMENTAL FACTORS AT SONE STATIONS

FACTOR	: ALL :STATIONS	ST. : LEONARD :	: BUENA : : VISTA :	HDRN PT.	RAGGED : PT. :	MD. PT.	PT. : NO PT. :	R64	R78	STILL Pond
DO FLUX	;; ;		: ***							NR
AMM FLUX	;;				- ##	; 	NR I		- ++	NR
N+N FLUX	;									
DIP FLUX	;		***		; - ##	++	: NR	+ '	- ++	NR
SI FLUX	:	;;	***	: ##	: - ++	:	NR		- ++ ;	NR
BDT. WAT. 02	:	:	: - ***	- +	: #*	;	: NR	-+		NR
BOT. WAT. NH4+	; - +	;	; - t ##	: - ##	:	;	: NR	£ŧ		NR
BOT. WAT. N+N	: - ##	: +++	: - ***	; - ++	: ***		: NR	: - ##	•••••	NR
BOT. WAT. DIP	:	: * *	; - t i	: - I		;	: NR	: #*	: +	NR
BOT. WAT. SI	: ++	; ***	: ++	: ++	: - ++	;	: NR	; ++	:	NR
BOT. WAT. TEMP.	: **	;	; **	; ++	: - +++	•	: NR	; +	;;	NR
BOT. WAT. SAL.	: ++	: ++	: - ++	; - 	:	; - t	: : NR	; ; - {]	: ++	NR
SURF. SED. eH	:	;	;	; ;	;	;	: NR	; - +	:	NR NR
SURF. SED. PC	:	:	; ; ***	;	: - +++	; ++	: NR	; #ŧ	: **	NR
SURF. SED. PN	: +	: +	; +++	: - +	: - ***	;	 NR	: ##	; - **	 NR
SURF. SED. PP	;	; ++	; **	; ; - ***	;	: - ++	: NR	:	:	NR
SURF. SED. CHLa		; - +++	; ##	; - ##		:	: NR	; ##	; - ++	NR
n	: 340	: 36	: 32	: 34	: 35	: 34	: 35	; 36	: 36	
	•	•	•	•	•		•	•	•	•

NOTES:

- = negative correlation
= r sig. at 5% level
= r sig. at 1% level
= r > .80, sig. at > 0.5%
NR = correlations not computed

empty cells indicate correlation was not significant

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TABLE 6-7d

SUMMARY OF SIGNIFICANT CORRELATIONS BETWEEN SEDIMENT FLUXES OF DISSOLVED INORGANIC PHOSPHOROUS AND ENVIRONMENTAL FACTORS AT SONE STATIONS

FACTOR	: ALL : :STATIONS :	ST. : LEONARD :	BUENA : VISTA :	HORN : PT. :	RAGGED : PT. :	MD. : PT. :	PT. : ND PT. :	: R64 :	R78 :	STILL : POND :
DO FLUX	:		+++		;	++ :	NR :	:		NR :
ANM FLUX	: ++	ŧ	ŧŧ		***		NR	***	ŧŧ	NR
N+N FLUX	:		***		- ##	ŧŧ	NR	++ ;	- 1 1	NR
DIP FLUX										
SI FLUX	1	ŧŧ	+++			Ŧ	NR		ŧ	NR
BOT. WAT. 02	; ++	- ###	- ++	- I I	- +++	- ##	NR	- i i i		NR
BDT. WAT. NH4+	: - ++		: - ***	ŧŧ	***		NR	***		NR
BOT. WAT. N+N	: ##	:	: - ++	- ŧ	- ++		NR	- ###		NR
BOT. WAT. DIP	: - ##	: ++	; - ##	ŧ	: ***		NR	+++		: NR
BOT. WAT. SI	: ##	:	: ##	Ŧ	: ***		NR I	***	ŧ	NR
BOT. WAT. TEMP.	; ##	:	: #*	ŧŧ	: ***	÷÷	: NR	***		: NR
BOT. WAT. SAL.	: +	:	; - ##	; - ##	:	- #	NR :	- +++	: - +++	. NR
SURF. SED. eH	; - ++	; - ##			; - #	•	: NR	- +++	: ++	. NR
SURF. SED. PC	: *	; ***	; **		; +++	; ; ;	: NR	++	; - #	: NR
SURF. SED. PN	; ##	; +++			. **	; ++	NR	; ++	; ++ ; ++	NR
SURF. SED. PP	:	: +++	: ##	•	: - *	: - ## 	: NR	, ; - ## 	: - ++ 	: NR
SURF. SED. CHL	3: 11		; ##	, - 1	:	,	NR	, ; ti ,	:	: NR
n	: 338	: 35	: 34	: 23	: 35	. 33	. 36	: 36	. 36	: :
		•		•		•	,	•	•	•

NOTES:

- = negative correlation
= r sig. at 5% level

= r sig. at 1% level

= r > .80, sig. at > 0.5%
NR = correlations not computed

WK - CONVENENDING NOT COmputed

empty cells indicate correlation was not significant

TABLE 6-7e

SUMMARY OF SIGNIFICANT CORRELATIONS BETWEEN SEDIMENT FLUXES OF SILICATE AND ENVIRONMENTAL FACTORS AT SONE STATIONS

FACTOR	: ALL	ST.	BUENA :	HORN	RAGGED :	: MD. :	PT. :			STILL
	:51A110N5	: LEUNARD : ::	VI51A :	; PI.	: PI. : ::	P1. 	: NU P1. :	K64	: K/8 :	PUND
DO FLUX	; 	; ** ;	; +++ ;	***	:	;	NR :	**	***	NR
AMM FLUX	: **	; 	÷ŧ ;		; ** :		NR :	÷÷	** :	NR
N+N FLUX	:	:	***	**	; - ##		NR		- ++	NR
DIP FLUX	; **	; ##	***	+	:	Ŧ	NR		ŧ	NR
SI FLUX	; ;	· :			:					
BOT. WAT. 02	: - ##	; - +++	- 11	- +	: - i	- ###	NR	- ++	- ##	NR
BOT. WAT. NH4+	:	:	- ##	- ##	:		NR			NR
BDT. WAT. N+N	: - ##	:	- ##	- ##	; - ++	- ##	NR			NR
BOT. WAT. DIP	: - *	:	- ##		:		NR		- #	NR
BOT. WAT. SI	: *	: *			; **		NR		ŧ	NR
BOT. NAT. TEMP.	: #:	: **	. , ,	; ;	: ++		NR	++	**	NR
BOT. WAT. SAL.	:	; - +	: - ##	; - : ;	: - ##		: NR		: **	NR
SURF. SED. eH	:	:	;	; ;	: ++		: NR	- ++		NR
SURF. SED. PC	:	:	: ***	:	: **	;	: NR	- * *	: - ##	NR
SURF. SED. PN	: **	:	; ;	;	: **	;	: NR	; - **	; ##	NR
SURF. SED. PP	:	;	: ++	; - ##	: -+++	:	: NR	- +++	:	NR
SURF. SED. CHL:):		; ##	; - ##	: ##	:	: NR	; - ##	:	NR
n	: 341	: 36	: 32	: 33	: 36	: 33	: 36	36	: 36	
					;	;	;	,	*	

NOTES:

- = negative correlation
= r sig. at 5% level
= r sig. at 1% level
= r > .80, sig. at > 0.5%

NR = correlations not computed

empty cell indicates correlation was not significant





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that region favors either the sedimentation or preservation of relatively organic rich material. Sediment PC decreased in a regular north-to-south fashion along the mainstem bay from about 4.5% PC in the upper bay at Still Pond to about 2% PC at our southernmost station near Pt. No Point. Sediment PN and PP exhibited significantly different spatial patterns (Fig. 6-8b,c). Although the sediments at Windy Hill and Ragged Pt. were relatively nitrogen rich compared with that found at the other tributaries, sediment PN <u>increased</u> from Still Pond to the mainstem station at R-64. Sediment PP presented an altogether different pattern (Fig. 6-8c): upper tributary sediments were consistently enriched in PP relative to the sediments found downstream. In contrast, sediment PP appears to remain essentially uniform or perhaps decrease slightly with distance down the mainstem bay.

The abundances of C, N, and P in sediments at the SONE monitoring stations suggest that the sediments accumulating in the upper tributaries and perhaps the upper mainstem are enriched in carbon and phosphorus relative to nitrogen. These patterns can also be seen in the sediment property-property plots shown in Fig. 6-9. Sediments from the lower tributaries and lower mainstem bay (Locations 2 & 3) are the most rich in nitrogen relative to carbon. Sediments from the upper tributaries and Still Pond (Locations 1 & 4) form groups of points well above (i.e., depleted in nitrogen) the main group representing the mainstem and lower tributaries. Similarly, plots of PN vs. PP (Fig. 6-9b) and PC vs. PP (Fig. 6-9c) illustrate that the sediments from the upper tributaries are rich in PP relative to PN and PC compared with sediments from the mainstem bay. Deposition of carbon and phosphorus via sorption, flocculation, and perhaps precipitation reactions in the low-salinity reaches of the tribuataries and bay are probably responsible for the observed sedimentation patterns of these elements.

There are two explanations for the apparent discrimination against nitrogen in the sediments of these regions. The sediments may simply reflect the deposition of terrestrial or fluvial sediment. On the other hand, organic nitrogen may be preferentially remineralized in these sediments and returned to the water as some form of dissolved inorganic nitrogen.



Scatter plots showing relationships among particulate carbon (PC), nitrogen (PN), phosphorous(PP), and chlorophyll (CHLa) in surficial sediments at SONE monitoring stations. Data are coded by location: 1, upper tributaries; 2, lower tributaries; 3, mainstem bay; 4, Still Pond. Figure 6-9.

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The main point of this section, however, is to examine the relationships between sediment composition and benthic fluxes of oxygen, DIN, and DIP. Plots of these relationships for all SONE fluxes (SONE cruises 1-12), coded by station locations, are shown in Fig. 6-10. Although some locations tend to separate into groupings of points (for example, SOC along the mainstem bay and DIP in the upper tributaries) these scatterplots reveal no consistent relationships between the carbon content of the sediment and SOC, or the phosphorus content of the sediment and DIP flux. This finding agrees with earlier studies that reported little or no relationship between benthic community metabolism and most sediment characteristics (Pamatmat 1977).

On the other hand, the positive correlation between NH4⁺ flux and sediment PN content (Fig. 6-10b) was significant (r = 0.351, n = 340). To our knowledge this is the first time this type of relationship has been found. We suggest that the correlation between DIN flux and sediment PN can best attributed to the effects of oxygen concentration on the net products of microbial nitrogen transformations in the sediment. The layering of aerobic water and sediments over deeper anaerobic sediments favors the loss of fixed nitrogen from the sediment via the following reaction sequence: NH4⁺ formation ----> NH4⁺ oxidation and nitrification ----> nitrate reduction and denitrification. Nitrification ceases when both sediments and overlying water are anoxic. Denitrification also ceases when the supply of nitrate is cut Thus, under anoxic conditions the reaction sequence stops at NH4⁺ off. production. Nitrogen remineralization appears to be less complete under anaerobic conditions. Fixed nitrogen therefore tends to accumulate as sediment conditions become more reducing.

6.4.2 Correlations between benthic fluxes and other environmental parameters.

Correlation analyses (Table 6-7) revealed some intriguing patterns of relationships among benchic fluxes and a number of relevant environmental parameters. In the context of MDE's monitoring efforts the relationships between bottom water oxygen concentration and benchic fluxes demands particularly attention. Figure 6-11a shows the general form of the



Scatter plots showing relationships between sediment-water fluxes and oxygen concentration of bottom water at SONE stations. Data coded by location as in Fig. 6-9. Figure 6-11.



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relationship between SOC and bottom water oxygen concentration. Within a wide envelope associated mostly with the high SOC in tributaries sediments (Groups 1 and 2), SOC generally increased as bottom water oxygen increased. This relationship was strongest along the mainstem bay. Sufficient dissolved oxygen in bottom waters therefore appears necessary for high rates of SOC, but other factors clearly contributed to high rates of SOC periodically observed in the tributaries.

The relationship between bottom water oxygen and NH4⁺ flux was statistically significant and opposite that of SOC and dissolved oxygen (Fig. 6-11b). In spite of considerable scatter in the data from the tributaries, ammomnium flux was generally greastest when bottom water oxygen content was low. The inverse relationship between NH4⁺ flux and bottom water oxygen was strongest along the mainstem bay. This, we think, offers further evidence for the coupling of inorganic nitrogen remineralization and redox status of sediments discussed above: high NH4⁺ fluxes along the mainstem bay appear related to low oxygen conditions. Conversely, low NH4⁺ flux, due to a combination low NH4⁺ flux from the sediments and negative N+N fluxes (i.e., sediment uptake) occur when oxygen concentration of bottom waters is high.

Several factors appear to contribute to a complex relationship between DIP flux and bottom water oxygen (Fig. 6-11c). High DIP fluxes along the mainstem bay occur when hypoxic or anoxic conditions prevail in the overlying water, but low oxygen conditions are not always accompanied by high DIP fluxes. In fact, substantial rates of DIP uptake were measured under hypoxic--not totally anoxic--conditions. Benthic DIP fluxes in the lower tributaries and along the mainstem bay were generally less than 15 umol $m^{-2}h^{-1}$ when oxygen in the overlying exceeded 4 mg 1^{-1} . However, significantly higher fluxes occurred occassionally in the upper tributaries. The origin of these spikes in DIP release is not known.

6.5 Nutrient Stoichiometries At SONE Stations

Over fifty years ago, Redfield and others discovered that nutrient elements were extracted from and returned to sea water in constant proportions

that reflected the average elemental composition of planktonic organisms (Redfield et al. 1963). The method of examining stoichiometric relationships between oxygen, carbon, nitrogen, and phosphorus (0:C:N:P ratios) continues to be a useful means of examining the coupling of energy flow and nutrient cycles in various compartments of an aquatic system. Such analysis has been largely responsible for current focus on estuarine sediments as sites of important nutrient transformations (Nixon and Pilson 1984).

In our last report (Boynton et al. 1986) we used SONE and VFX data from station R-64 to assemble a stoichiometric model for the formation, deposition, and remineralization of organic matter in the central meso-haline region of the bay. For this report we began to explore how general these patterns may be by examining how the ratios of nutrients in sediment fluxes vary spatially.

Element ratios (02:NH4⁺, NH4⁺:DIP, DIN:DIP, etc.) were calculated for individual sediment cores; these ratios were then averaged by station (Fig. 6-12). This exercise revealed important spatial patterns in the stiochiometries of oxygen and nutrient fluxes. For example, the ratios of oxygen uptake to DIN release (O/N ratio) in sediments from the stations that are subject to periodic anoxia (Ragged Pt., R-64, and R-78) were significantly lower than those from stations that remain oxic year round. Particuarly high O/N ratios occurred in the Patuxent River, Choptank Rivers, and most southern mainstem bay station (Pt. No Pt.). The amount of NH4⁺ released from the sediment relative to the flux of DIP also varied among the stations, some regions (e.g., the Potomac) producing ratios that were somewhat higher than the Redfield ratio of 16:1, while others (e.g., Patuxent and mainstem stations at Pt. No Pt. and R-78) averaged significantly below the Redfield ratio. These patterns suggest that sediment nutrient fluxes may not be low in nitrogen relative to the amounts of oxygen consumed in the sediment or the amounts of DIP released from the sediment probably in regions that undergo periodic anoxia.





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7. SEASONAL EVALUATIONS OF SEDIMENT AND DEPOSITIONAL PROCESSES ON WATER QUALITY CONDITIONS

In this section we continue to evaluate oxygen and nutrient budgets to put into perspective the relative influence of sediment deposition and benthic fluxes on water quality conditions in portions of Chesapeake Bay. The first budget compares the magnitude of deep-water oxygen stocks with sediment oxygen consumption (SOC) for several different periods of the year at Station R-64 which often experiences hypoxic or anoxic conditions. The second budget is similar but focuses on the impact of sediment-water fluxes of NH4⁺ and NO3⁻ relative to N stocks in the water column and estimated phytoplankton demand. The final budget considers the degree of water column-benthic coupling at Station R-64 in the mainstem of the Bay.

Estimates of the influence of SOC on deep-water oxygen stocks at Station R-64 are given in Table 7-1. Considerable variability in the total height of the deep layer (i.e., distance from the sediment surface to the pycnocline) exists among seasons. The combination of changing deep layer depth and ambient oxygen concentrations in this layer produced large seasonal excursions in the magnitude of deep-water oxygen stocks. For example, the oxygen stock at R-64 ranged from about 113 g m⁻² in April 1987 to 0.0 g m⁻² in August 1986 (Fig. 7-1). At all deep stations, oxygen stocks were high in fall and early spring and low in summer, paralleling the pattern observed for oxygen concentration.

The relative influence of SOC on oxygen stocks is expressed as the portion of the deep water oxygen stock consumed in SOC per day. As shown in Table 7-1, values range from 1% to 6% per day at Station R-64. At other deep stations values ranged from 2% to 6% per day with a clear seasonal trend in the relative influence of SOC. When SOC rates were high, SOC influence on dissolved oxygen stocks was low if the deep waters were well oxygenated. However, SOC influence was relatively high at Station R-64 in the spring at the onset of anoxia. SOC is therefore an important O2 sink at these stations throughout the year, but it is particularly important during the spring when deep waters are becoming hypoxic and during the summer when hypoxic.

Table 7-1.	Potential influence of SOD on deep-water oxygen stocks at SONE
	Station R-64 which experiences seasonal hypoxia-anoxia and
	significant water column stratification. Deep-water oxygen
	stocks calculated by multiplying the height of the water column
	beneath the pycnocline by the mean 0_2 concentration in this
	water mass. Sediment oxygen demand is from appropriate
	Appendix Tables.

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Station	Date	Height of Deep Layer (m)	Deep-water Oxygen Stock (g02m ⁻²)	Sediment Oxygen Demand (g02m ⁻² d ⁻¹)	SOD: Deep-Water Oxygen Stocks (d ⁻¹)
R-64	Aug. '85	4.3	15.5	-0,63	0.05
	Oct.	4.1	23.8	-1.40	0.06
	May ' 86	5.4	47.5	-0.81	0.02
	June	3.4	9.8	-0.10	0.01
	Aug.	4.8	10.0	-0.04	0.01
	Nov.	7.2	51.1	-0.64	0.01
	Apr. '87	8.5	64.6	-0.59	0.01
	June	4.0	2.4	-0.15	0.06

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at Sta. R-64.



conditions prevail.

Our ability to assess the importance of sediments in carbon metabolism is limited during periods of severe hypoxia or anoxia since SOC becomes a minor pathway, replaced by sulfur-based metabolism which is not measured in the monitoring program. Data developed in other programs suggest that SO4⁻ reduction and the subsequent oxidation of reduced sulphur compounds contributes substantially to both carbon and oxygen budgets in the deep mesohaline portions of the bay.

The second budget (Table 7-2) involves a comparison of N stocks to selected rate processes in the surface mixed layer and deep waters at station R-64. N stocks ($NH4^+$ and $NO3^-$) in the deep and surface layers are compared to the phytoplanktonic demand for inorganic nutrients and contrasted to the rate of loss of PN to deep waters. This analysis shows that the total supply of dissolved inorganic nitrogen is sufficient to supply phytoplanktonic nutrient demand for only short periods of time (hours to days) for all seasons of the year except the early spring when fluvial inputs of nutrients (primarily NO3) dominate. However, the nitrogen stocks in deep waters are much more substantial and satisfy phytoplanktonic demand 2-20 times longer than the stocks in surface waters. One interesting observation to fall out of this analysis was that during times of the year when plankton production is highest (i.e., June-August), nutrient stocks in the upper mixed layer are smallest. However, nutrient stocks in the deep layer are very large at these times, representing a substantial nutrient source the magnitude of which is capable of supporting demand for 1 to 2 week periods. This raises a major question: How do the nutrient-rich deep waters reach the euphotic zone? Recent work by Malone et al. (1986) suggests that cross-bay tilting of the pycnocline may be an important mechanism in the transportation of deep water nutrients to euphotic waters. Additionally, they found that the frequency of these events were on the order of days to a week in the summer. This agrees well with estimated demand for nutrients for phytoplankton production.

These calculations suggest a possible explanation for the seasonal pattern of phytoplankton production generally seen in the mainstem regions of

	Sur	face Mixe	d Layer		Deep-Water Layer						
	Height Nutrient of Stocks Layer NH_4^+ NO_3^-		Phytoplankton N-demand ^a	Height of Layer	Nutri Stoc NH4 ⁺	ent ks NO3	Deposition of Particulate N ^b				
Date	(m)	(m	m^{-2})	$(mg-at N m^{-2}d^{-1})$	(m)	 (mmo]	. m ⁻²)	$(mg-at N m^{-2}d^{-1})$			
Aug. 85	5.5	12	16	26	11	234	25	8			
Oct. 85	6.8	11	37	29	10	138	31	9			
May 86	10.5	19	444	15	6	91	122	14			
June 86	8.0	5	4	20	9	246	26	9			
Aug. 86	4.8	15	4	22	11	221	6	12			
Nov. 86	7.2	58	43	10	9	110	32	8			
Apr. 87	12.5	151	569	12	5	62	70	16			
June 87	8.0			14	9			8			

Table 7-2. A comparison of nitrogen (N) stocks and selected rates in the surface mixed layer and deeper waters at Sta. R-64 in the mainstem of Chesapeake Bay.

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^a Mean values for month indicated (n=2-3).

^b Mean of 2 measurements prior to the SONE cruise in the month indicated. Data are from the mid-depth collection cups.

the Bay. In the spring (April-May) a bloom occurs which is largely supported by nutrients (especially NO3⁻) from terrestrial sources. Nutrient concentrations are typically high in the surface layer, as are standing stocks of phytoplankton. Additionally, the pattern is of sustained high production rates and stocks — there are few indications of rapid bloom and crash cycles. In contrast, during the summer period production is often high but the pattern of production is erratic. Patterns of very high and low rates occur, often separated by only a week or so, and continue for several months (see Sellner et al. 1987). This erratic summer signal suggests strong couplings exist between the upper mixed layer and deeper waters relative to nutrient supplies for primary productivity. Our conceptual model suggests that during the spring period euphotic waters are nutrient sufficient, hence, a sustained bloom. During the summer only temporary periods of nutrient sufficiency in euphotic waters occur. These periods are directly related to events which deliver nutrient-rich bottom waters to the euphotic zone; thus, the erratic nature of summer production.

Several pathways are missing from this conceptual model which may have important implications for water quality management and food-web dynamics. For instance, the impact of zooplankton grazing has not been considered. Is the spring bloom sustained because the grazing rates are low? Are the erratic summer patterns the result of differential grazing rates? As we continue to integrate various portions of the monitoring program answers to these questions will probably become available.

The final point related to Table 7-2 concerns the relative amounts of inorganic dissolved nitrogen used by primary producers vs. the amount of particulate nitrogen lost from the euphotic zone. This comparison represents the net exchange of dissolved nutrients available to support production and the net loss of nutrients in the particulate form to deeper waters. The seasonal data suggest a substantial loss of PN to deeper waters during all seasons, with losses being larger in fall and early spring. During the summer losses are smaller. Again, these observations are consistent with the conceptual model. In the fall and early spring, when metabolic rates are

slowed by low temperatures and the lack of a strong pycnocline, substantial vertical transport of particulates from the surface layer to deeper waters occurs. During summer periods, with higher temperatures and a typically stronger water column density structure, less transport of PN to deeper waters is observed. These patterns suggest a very substantial recycling of organics at or near the stratification depth during the warm portion of the year.

In the third and final budget we have evaluated several aspects of benthic-pelagic coupling at R-64, a central Bay location (Table 7-3). During the seasons considered, a considerable percentage of primary production was deposited to deeper waters. For example, the percentage of PC deposited ranged from 37%-118% of local water column primary production. Again, there were some notable seasonal trends. Deposition was apparently high during the spring and fall and lower during the summer. A probable explanation for these observations involves both biological and physical aspects of the system. During well-mixed (and cooler) periods organic matter produced in the euphotic zone is probably either grazed and transformed into rapidly sinking particles or simply settles quickly because of the generally larger sizes of particles. As a result, a large percentage of production reaches the bottom. However, during the summer the water column is well stratified and bacterial metabolism is high. Much of the sedimenting material appears to be utilized in the vicinity of the pychocline resulting in a smaller percentage of the overall production reaching the bottom. Of the material reaching deep waters or the bottom, a rather small percentage (1%-51%) appears to be consumed in aerobic metabolism. What is the fate of the remaining deposited material? Earlier studies (Boynton and Kemp, 1985) show that little of this material is buried in the accreting sediment column; therefore, much of the organic matter reaching deep waters must be involved in other metabolic reactions. The most probable answer involves the use of this material in SO4⁻ reduction under anaerobic conditions in the water column or sediments where SO4 serves as a terminal electron acceptor in the oxidation of organic material by anaerobic bacterial communities. The recent work of Tuttle et al. (1986) in the R-64 area of the Bay strongly supports this point of view. Hence, deposited organics can apparently be utilized through several distinct pathways in the

Year.	Month	Phyto and N C	plk. Prod utrient I N	I. (C) Demand P.	<u>,</u>	Organic Depositic N	n P.	Percent C Deposited C	Deposited <u>C Consumed</u> <u>C</u>	Deposi Remine N	ted N & P ralized P.	Benthic Remi Phytoplank N	neralization ton Demand P
			(mgm ⁻² d ⁻¹	·)		(mgm ⁻² d ⁻¹) (%)			(%)	(%)		(%)	
 1985	Aug.	2040	364		751	113	14	37	31	114	143	35	40
	Oct.	2280	407	56	989	124	23	43	51	94	22	29	9
1986	May	1150	205	28	1229	191	20	107	24	35	0	32	0
	June	1600	286	39	704	119	10	44	5	145	680	60	174
	Aug.	1700	304	41	1005	172	17	59	1	136	312	77	129
	Nov.	800	143	20	849	119	25	106	28	25	8	21	10
1987	Apr.	963	172	23	1077	162	14	118	20	8	7	8	4
	June	1060	189	26	712	111	11	67	10	54	200	32	108
Means								73	21	76	172	37	59

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deeper waters of the Bay. Only the former pathways tend to lead to larger organisms of commercial interest; however, all pathways act to use almost all of the organic matter produced and have an important influence on the transformation of particulate nutrients (N and P) in sediments and their interaction with overlying waters.

In addition, there was a seasonal pattern in the releases of nutrients from sediments to the water column. For NH4⁺, there was essentially a total return relative to deposited materials in the late spring and summer -- while in the early spring and fall a decrease (at times a dramatic decrease) occurred in the flux of NH4⁺ from sediments to water relative to the amount of organic material deposited. Phosphorus was generally not released from sediments during the spring and fall when the water column and sediments were oxic. In contrast, P release from the sediment during the summer and late spring equaled or greatly exceeded the amount estimated as being deposited. A possible explanation for these observations involves the oxygen condition of overlying waters and sediments. During periods when O2 concentrations are high and benthic macrofaunal communities are growing rapidly, there are multiple transformation routes for deposited N. For example, N compounds can be incorporated into benthic macrofaunal biomass, a portion can be buried in the accreting sediment column, and a portion can be nitrified and then denitrified. All of these pathways are very probably operative in the early spring and fall periods resulting in a smaller portion of deposited N being returned from sediments to the water column as NH4⁺.

Phosphorus recycling appears to be strongly influenced at this deep-water site by redox conditions. During the portions of the year when O2 levels are high, little of the deposited P is returned to the water column. However, when O2 levels become depressed (and sediments become anoxic) very large fluxes of P from sediments to the water column were observed probably as a result of the much higher solubility of reduced Fe-P compounds. Whatever the mechanism, large amounts of P are released from these sediments during the low O2 periods of the late spring and summer.

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Finally, a strong seasonal pattern in the proportion of nutrients supplied from the sediments for use in phytoplanktonic production is apparent. When nutrient supplies in the water column are generally high (i.e. following the spring freshet) the proportion supplied via sediment recycling is low. During other times of the year the calculated percentage is substantial at this deep station, ranging up to 77% for N and 174% for P. Similar percentages have been recorded for other Chesapeake Bay sites (Boynton and Kemp, 1985) indicating the importance and seasonal nature of sediment processes on water quality conditions of overlying waters.
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