Estuaries Vol. 19, No. 3, p. 562–580 September 1996

Sediment-Water Oxygen and Nutrient Exchanges Along the Longitudinal Axis of Chesapeake Bay: Seasonal Patterns, Controlling Factors and Ecological Significance

JEAN L. W. COWAN[1]
University of South Alabama
Dauphin Island Sea Lab
P.O. Box 369-370
Dauphin Island, Alabama 36528

WALTER R. BOYNTON
University of Maryland System
Center for Environmental and Estuarine Studies
Chesapeake Biological Laboratory
P.O. Box 38
Solomons, Maryland 20688

ABSTRACT: Sediment-water oxygen and nutrient (NH_4^+, $NO_3^- + NO_2^-$, DON, PO_4^{3-}, and DSi) fluxes were measured in three distinct regions of Chesapeake Bay at monthly intervals during 1 yr and for portions of several additional years. Examination of these data revealed strong spatial and temporal patterns. Most fluxes were greatest in the central bay (station MB), moderate in the high salinity lower bay (station SB) and reduced in the oligohaline upper bay (station NB). Sediment oxygen consumption (SOC) rates generally increased with increasing temperature until bottom water concentrations of dissolved oxygen (DO) fell below 2.5 mg l^{-1}, apparently limiting SOC rates. Fluxes of NH_4^+ were elevated at temperatures >15°C and, when coupled with low bottom water DO concentrations (<5 mg l^{-1}), very large releases (>500 μmol N m^{-2} h^{-1}) were observed. Nitrate + nitrite ($NO_3^- + NO_2^-$) exchanges were directed into sediments in areas where bottom water $NO_3^- + NO_2^-$ concentrations were high (>18 μM N); sediment efflux of $NO_3^- + NO_2^-$ occurred only in areas where bottom water $NO_3^- + NO_2^-$ concentrations were relatively low (<11 μM N) and bottom waters well oxygenated. Phosphate fluxes were small except in areas of hypoxic and anoxic bottom waters; in those cases releases were high (50–150 pmol P m^{-2} h^{-1}) but of short duration (2 mo). Dissolved silicate (DSi) fluxes were directed out of the sediments at all stations and appeared to be proportional to primary production in overlying waters. Dissolved organic nitrogen (DON) was released from the sediments at stations NB and SB and taken up by the sediments at station MB in summer months; DON fluxes were either small or noninterpretable during cooler months of the year. It appears that the amount and quality of organic matter reaching the sediments is of primary importance in determining the spatial variability and interannual differences in sediment nutrient fluxes along the axis of the bay. Surficial sediment chlorophyll-a, used as an indicator of labile sediment organic matter, was highly correlated with NH_4^+, PO_4^{3-}, and DSi fluxes but only after a temporal lag of about 1 mo was added between deposition events and sediment nutrient releases. Sediment O:N flux ratios indicated that substantial sediment nitrification-denitrification probably occurred at all sites during winter-spring but not summer-fall; N:P flux ratios were high in spring but much less than expected during summer, particularly at hypoxic and anoxic sites. Finally, a comparison of seasonal N and P demand by phytoplankton with sediment nutrient releases indicated that the sediments provide a substantial fraction of nutrients required by phytoplankton in summer, but not winter, especially in the mid bay region.

Introduction

The exchanges of nutrients, oxygen, and other materials across the sediment-water interface in shallow coastal and estuarine systems have been the focus of considerable study (Hargrave 1973; Nixon et al. 1976; Boynton et al. 1980; Callender and Hammond 1982; Cloern 1982; Hopkinson and Wetzel 1982; Koop et al. 1990). Results indicate that nutrient regeneration in the sediment supplies a significant portion of phytoplanktonic nutrient demand during some periods of the year (Fisher et al. 1982; Koop et al. 1990). In eutrophic

[1] Corresponding author; tele 334/861-7586; fax 334/861-7540; e-mail jwcowan@jaguarl.usouthal.edu.

estuaries, sediment nutrient releases have the destabilizing effect of further stimulating the cycle of algal growth, deposition of organic matter to sediments, and subsequent loss of oxygen in deeper waters (Kemp and Boynton 1992; Roden and Tuttle 1992). On the other hand. estuarine sediments not subjected to chronic hypoxic or anoxic conditions can be sites of intensive nitrification coupled to denitrification (Jenkins and Kemp 1984), which may remove 50% of nitrogen inputs, thereby providing a nutrient buffering or homeostatic effect on nutrient cycling (Seitzinger 1988). Nixon (1981) has argued that low sediment N:P nutrient release ratios may result from sediment denitrification and that this may in turn lead to low N:P ratios of dissolved nitrogen and phosphorus compounds in the water column and ultimately to nitrogen limitation of estuarine phytoplankton production.

The importance of sediments in estuarine nutrient cycling has stimulated efforts to understand factors controlling these processes. For example, strong correlations between temperature and sediment-water exchange rates have been reported (e.g., Hargrave 1969; Boynton et al. 1980). Macrofaunal communities have been found to enhance sediment processes via direct consumption of organic matter and excretion of nutrients, and via stimulation of microbial communities by sediment mixing (Henriksen et al. 1980; Kemp and Boynton 1981; Kanneworff and Christensen 1986; Banta 1992). Finally, water quality conditions in overlying waters exert an influence on sediment nutrient processes; phosphate is typically released from sediments under anoxic conditions (Gachter et al. 1988; Sundby et al. 1992), nitrate diffuses into sediments when water column concentrations are high and may subsequently be denitrified (Boynton and Kemp 1985), and mineralization of dissolved organic matter may be less effective under anoxic conditions (Hansen and Blackburn 1991). However, it appears that organic matter supply rates to sediments ultimately regulates the magnitude of sediment processes. Graf et al. (1982) found rapid responses in benthic activity in Kiel Bight to several different types of organic matter inputs, and Balzer (1984) found that only about 22% of deposited organic matter was buried in the sediment column at the same site. Jensen et al. (1990) documented marked increases in NH_4^+ and PO_4^{3-} fluxes from sediments in Aarhus Bight, Denmark, after sedimentation of the spring bloom; microcosm experiments using sediments from the same area and exposed to simulated bloom deposition yielded similar results. Sediment nutrient regeneration was found to be proportional to primary production in marine mesocosms (Kelly and Nixon 1984; Kelly et al. 1985) as were rates of anaerobic respiration (Sampou and Oviatt 1991) and Mn^{2+} fluxes (Hunt 1983).

Chesapeake Bay is a large estuarine complex with a variety of habitats ranging from tidal fresh in the northern portion to polyhaline near the ocean boundary. Because of this, it offers the opportunity to study in situ sediment processes exposed to different water quality, deposition, and nutrient loading conditions. The present study was conducted as part of a larger Land Margin Ecosystem Research (LMER) program in which the overall goal was to improve understanding of the sources, transport, transformations, and fate of organic matter and nutrients as they moved from land through the estuarine environment to the coastal ocean. While there have been a number of sediment process measurements made in Chesapeake Bay, most have been made in tributary rivers (e.g., Boynton et al. 1980; Callender 1982), and there has yet to be a series of sediment oxygen and nutrient flux measurements made through an annual period in the mainstem bay. The purpose of this study was to make such a series of measurements at three distinctive locations in the mainstem bay and to use contemporaneous measurements of water column and sediment characteristics to arrive at some conclusions regarding the factors influencing sediment processes in different sectors of this estuarine system. In recognition of the duality of benthic-pelagic coupling, we also estimated the influence of sediment processes on several water column characteristics.

Study Area and Station Locations

The Chesapeake Bay is a large coastal plain estuary approximately 270 km in length, 8–40 km in width, and about 9 m in depth. However, the upper and lower thirds of the bay are considerably shallower (5 m and 9 m, respectively) than the middle portion (12 m; Cronin and Pritchard 1975). Approximately 60 tributaries enter the bay, producing a mean freshwater discharge of 7×10^{10} $m^3\ yr^{-1}$, yielding a freshwater fill-time of about 1 yr (Fig. 1). The Susquehanna River at the head of the bay accounts for approximately 50% of the flow and the Potomac and James rivers supply much of the rest (United States Geological Survey 1990). The ratio of drainage basin area to estuarine surface area is 28:1 indicating a large potential terrestrial influence on the estuary (United States Environmental Protection Agency 1982).

Highest river flow normally occurs in the late winter-early spring. Average total nitrogen (TN) and total phosphorus (TP) loading rates for the entire Chesapeake Bay system are approximately 1.45×10^8 kg N yr^{-1} and 1.19×10^7 kg P yr^{-1},

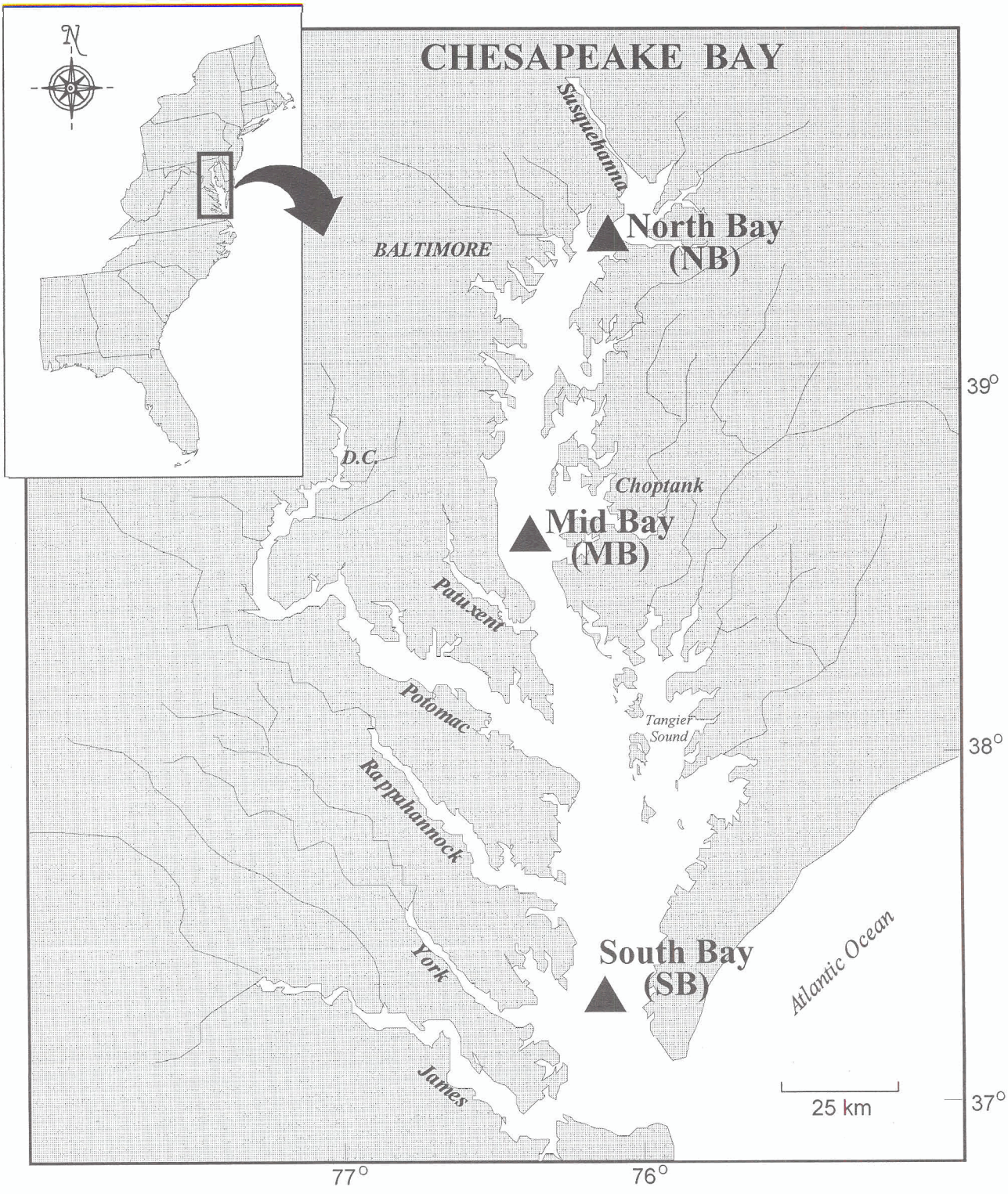


Fig. 1. A schematic diagram indicating major geographical features of Chesapeake Bay, the extent of the drainage basin in relation to the bay, and the location of sampling stations in the northern (station NB), middle (station MB) and southern (station SB) bay, respectively.

about 60% of which is from riverine sources (Boynton et al. 1995). On an areal basis average TN and TP loading rates amount to about 13 g N m^{-2} yr^{-1} and 1 g P m^{-2} yr^{-1}, respectively. These loading rates are moderate to high for TN and moderate to low for TP compared to other estuarine and coastal marine systems (Nixon et al. 1986).

The circulation of the bay is generally two-layered (Pritchard 1967), although more complex circulation patterns have been observed in various regions of the bay (Boicourt 1982). The mainstem bay is seasonally stratified, with the most intense stratification occurring during the late spring-summer periods. Decreased freshwater flow during summer and fall and cooling of surface waters during early fall lead to vertical mixing in the fall throughout the area. However, surface and bottom waters are not completely separated during the period of stratification. Strong wind events and cross-bay seiching have been shown to be capable of mixing surface and bottom waters, although stratified conditions are generally reestablished within a few days (Chuang and Boicourt 1989; Sanford and Boicourt 1990; Sanford et al. 1990).

There are also strong longitudinal gradients in chemical and biological variables which were considered in the selection of station locations in this study. The northern bay (station NB) is characterized by weak stratification; very high NO_3^- + NO_2^-, DSi, and suspended sediment concentrations; low rates of primary production; and well oxygenated bottom waters. In contrast, the mid bay (station MB) is characterized by strong stratification, lower water column turbidity, high rates of primary production, high chlorophyll-a concentrations, generally low nutrient concentrations (except in spring when NO, + NO, and DSi concentrations are high) and hypoxic and/or anoxic conditions in bottom waters during the warm portions of the year. The southern bay (station SB) has even lower turbidity conditions, moderate primary production rates, low nutrient concentrations, minimal hypoxia in bottom waters, and a well-developed benthic infaunal community (Malone et al. 1986; Magnien et al. 1990). One sampling station was located in each of these regions of the bay (Fig. 1). Stations NB, MB, and SB were at depths of 9 m, 16 m, and 11m, respectively. The sediment type at station NB was silty clay, station MB sediments were silt, and station SB sediments were silty sand.

Materials and Methods

Sediment Oxygen and Nutrient Fluxes

Shipboard measurements of oxygen and dissolved nutrient exchanges were made at three stations at least nine times from December 1988 through November 1989; additional measurements were made at stations NB and MB in 1989 and at all stations in 1987, 1988, 1990, and 1991. During each sampling, three cores of undisturbed sediment were obtained using a box corer. The box corer was equipped with a Plexiglas liner (inner dimensions: 8.8 × 15.8 × 34.0 cm) within which the sediment core was contained. Overlying the sediment was 1,800–2,000 ml of bottom water. Plexiglas bottom and top plates with Neoprene gaskets were attached to each core and were held in place with bungi cords to seal the incubation chamber. The top plate had two portals: one for an oxygen and temperature probe (Orbisphere model no. 2610), equipped with a stirring motor and rod; the other for sampling and replacement water tubing (Fig. 2). An additional incubation chamber was filled with ambient bottom water and used as a water column control. All chambers were placed in a water-filled holding tank immediately after coring. Just prior to beginning flux measurements, the overlying water in each core was completely replaced with ambient bottom water to insure that water quality conditions closely resembled in situ conditions. The oxygen-temperature probes and sampling tubes were inserted and the cores were placed in a darkened, water-filled incubator that was held at ambient temperature using a recirculating water temperature control bath.

Dissolved oxygen and temperature were monitored hourly during the incubation period. A total of five water samples were withdrawn from the chambers at 2.5-h 3.0-h intervals over the 10–12 h incubation period. As a water sample was extracted, an equal amount of ambient bottom water drained in through the replacement tube from a darkened, insulated cubitainer at a rate slow enough to ensure that no sediment resuspension occured. At hypoxic or anoxic stations, the replacement water was bubbled with N, gas to prevent reoxygenation. Water samples were filtered (Whatman GF/F 2.5 cm diameter, 0.7-pm porc size glass-fiber filters) and frozen for analysis of NH_4^+, NO_3^- + NO_2^-, PO_4^{3-}, DSi, and total dissolved nitrogen (TDN) for calculation of dissolved organic nitrogen (DON). Analytical methods followed those of Bran and Luebbe (1990) and United States Environmental Protection Agency (1979) as modified by D'Elia et al. (1977). Measured analytical variability for each nutrient is as follows: NH_4^+, 0.6 μM; NO_3^- + NO_2^-, 0.6 μM; NO_2^-, 0.2 μM; PO_4^{3-}, 0.04 μM; DSi, 3.0 μM; TDN, 3.0 μM. Primary amines were analyzed following the methods of Dawson and Liebezeitt (1983). Urea was analyzed following the methods found in Parsons et al. (1984).

Oxygen and nutrient fluxes were estimated for

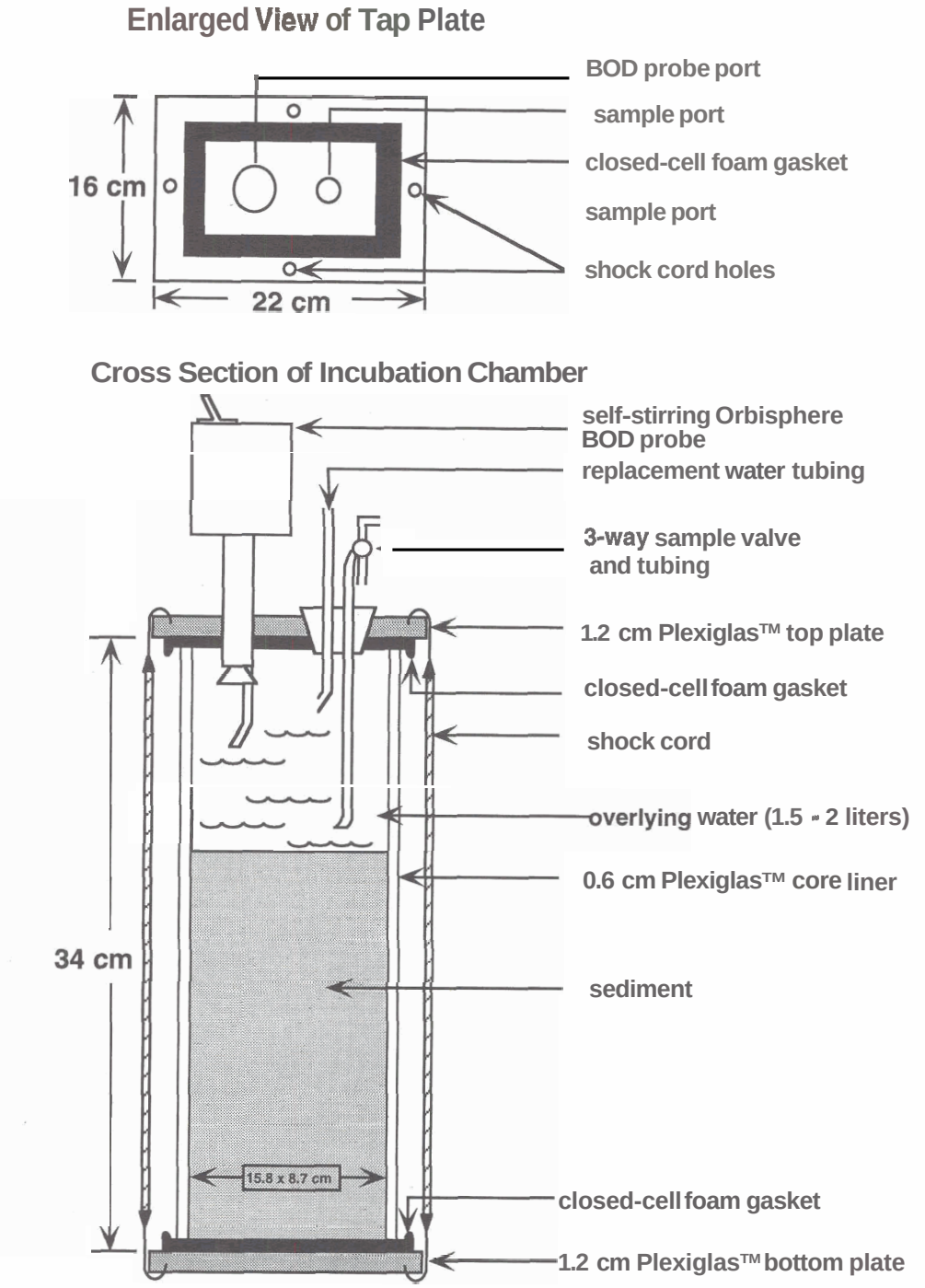


Fig. 2. Schematic diagram of the incubation chamber used in making measurements of net sediment-water oxygen and nutrient exchanges.

each core by calculating the mean rate of change in concentration during the incubation period using regression analysis. Nonsignificant regressions ($p > 5\%$) that involved changes in concentration during the incubation period greater than our analytical variability were not used to calculate flux; these were considered to be noninterpretable data. These should not be confused with net zero fluxes which were defined as nonsignificant regressions of time versus concentration wherein concentra-

tion changes during the incubation period were less than analytical variability. The blank core rate of change was then subtracted from the sediment core rate of change; this volumetric rate of change was then converted to a flux using the volume: surface area ratio of each core.

Sediment Profiles

At each station an intact sediment core collected with a modified Plexiglas liner (equipped with 2-mm diameter sampling ports along the side spaced at 1-cm intervals) was used to measure Eh in the sediment column to a depth of 10 cm. Eh was measured using a calomel reference electrode and a platinum sample electrode. Both electrodes were calibrated in Zobel's solution. The calomel electrode was placed in the overlying water and the platinum electrode was placed at the appropriate depth through sampling ports in the side of the Plexiglas liner. The platinum electrode was cleaned in Zobel's solution between measurements (Whitfield 1969).

Surficial sediment samples were also taken for analysis of particulate organic carbon, particulate organic nitrogen, particulate phosphorus (PC, PN, and PP, respectively), and total chlorophyll-a. Open-ended 50-ml syringes were used to take subcores. The top 1.0 cm of sediments were removed and frozen in a centrifuge tube for later analysis. Sediment PC and PN were analyzed as described in Control Equipment Corporation (1986). Sediment PP was analyzed as described in Aspila et al. (1976). Sediment chlorophyll-a was analyzed as described in Parsons et al. (1984).

Water Column Profiles

Water column profiles and bottom water Samples were obtained by two methods. Usually, profiles of oxygen, temperature, and salinity were measured using a Seabird conductivity, temperature, and depth sensor (CTD), and bottom water samples were retrieved using computer-triggered Niskin bottles. Occasionally, profiles were obtained using a Hydrolab 4000 temperature, oxygen, and salinity probe that was connected by hose to a Gould deep well submersible pump (flow rate: 40 1 min^{-1}). The pump was lowered at 2-m intervals from 0.5 m below the surface to approximately 0.5 m above the bottom. Bottom water samples were also taken from the pump hose after it had flushed for several minutes. Water samples were filtered and analyzed for NH_4^+, $NO_3^- + NO_2^-$, PO_4^{3-}, DSi, and chlorophyll-a, as previously described,

Results and Discussion

Water Column and Sediment Characteristics

For most variables there were clear differences in water column characteristics along the longitudinal axis of the estuary (Fig. 3). For example, salinity ranged from <0.1 psu (station NB) to 27.1 psu (station SB) and distinct salinity regimes could be identified among stations. Dissolved oxygen (DO) conditions at stations NB and SB were similar; however, DO at station MB ranged from 12.1 mg l^{-1} in February to hypoxic or anoxic conditions from early June through late August (Magnien et al. 1990). This was due to reduced vertical mixing and to high rates of organic matter loading to sediments in this region of the bay (Boicourt 1992). Both $NO_3^- + NO_2^-$ and DSi concentrations were typically highest at station NB, suggesting the importance of riverine sources of these compounds. In contrast, differences in bottom water concentrations of PO_4^{3-} and NH_4^+ among stations were not as pronounced. However, they exhibited strong seasonality with summer peaks in concentration, which were probably caused by sediment releases of these compounds. Only a limited number of DON measurements were made in bottom waters and hence it is difficult to discern temporal or spatial patterns. It does appear that concentrations were somewhat lower at station NB than at other stations, suggesting an internal, rather than riverine, source for this nitrogen fraction (Hansen and Blackburn 1991).

At stations NB and MB concentrations of surficial sediment PC ranged from 2.1% to 5.5% (sediment dry weight). There was little seasonality in concentration at station NB but a distinctive peak at station MB during June–July and later in November (Fig. 4). Sediment concentrations of PC at station SB were much lower (0.5–0.9%) but did double in late spring. Differences in sediment PN concentrations were very distinctive among stations (MB > NB ≫ SB) and again seasonal patterns were most obvious at station MB, attenuated at station SB, and not apparent at station NB. Sediment concentrations of PP were similar among stations and there were large increases in concentration at all stations between late winter and early summer. To further characterize surficial sediment organic matter, C:N, C:P, and N:P ratios (atomic) were calculated (Fig. 5). Each panel in Fig. 5 has a horizontal band indicating-the approximate composition ratio expected if organic matter was primarily composed of healthy phytoplankton (Redfield 1934). At all stations, sediment organic matter was poor in nitrogen relative to carbon; the difference was most extreme at station NB, where the influence of terrigineous organic matter of low nitrogen content from the Susquehanna River was apparent (Summers 1989). Ratios of C:P were generally higher than Redfield proportions at stations NB and MB, particularly in late winter, and were much lower than expected and decreased through-

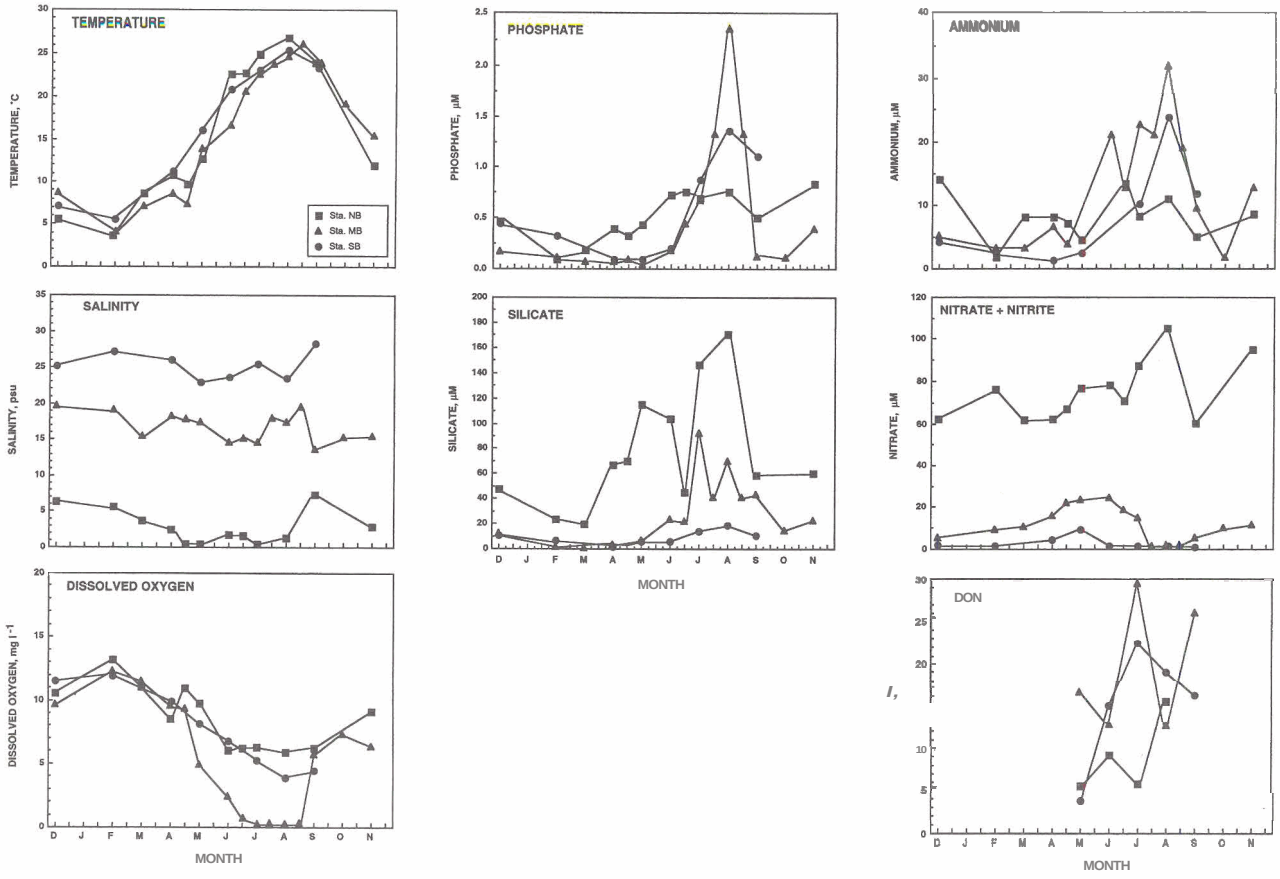


Fig. 3. Monthly bottom water temperature, salinity, dissolved oxygen conditions, and bottom water concentrations of phosphate (PO_4^{3-}), silicate (DSi), and dissolved nitrogen compounds (NH_4^+, NO, + NO_2^-, DON) at three stations (NB, MB, and SB) along the main axis of Chesapeake Bay. Data were collected between December 1988 and November 1989.

out the year at station SB, suggesting that phosphorus was being sequestered in these sediments in forms other than phytoplanktonic debris. Ratios of N:P were generally lower than expected from the Redfield model, particularly at station SB. This reflects the generally low PN and high PP content of sediments at station SB.

Primary production (Fig. 6) was low at station NB (145 g *C* m^{-2} yr^{-1}), higher at station SB (287 g C m^{-2} yr^{-1}), and highest at station MB (464 g *C* m^{-2} yr^{-1}; Malone personal communication). However, bottom water chlorophyll-a concentrations did not reflect production rates in overlying waters. In fact, highest values were observed at station NB, where production was lowest, and the reverse was observed at stations MB and SB. In addition, there were no clear seasonal patterns evident at any station, although temporal variability appeared to decrease in a down-bay direction. In contrast, sediment chlorophyll-a concentrations did exhibit spatial and seasonal patterns. At all stations there was a spring peak in concentration followed by a summer decline. A smaller fall increase was seen at stations MB and SB. The relative magnitude of sediment concentrations between stations generally followed a pattern more closely reflecting primary production rates in overlying waters (MB > SB > NB). While additional analyses are provided later, this observation suggests that sediment chlorophyll-a may be a good indicator of benthic-pelagic coupling at least in terms of the amount of labile organic matter available to sediment processes. Sediment Eh values were generally high at station NB (150–400 mV), intermediate at station SB (50–350 mV), and distinctly lower at station MB (275 mV to −125 mV). Although there was considerable temporal variability, lowest Eh values were observed during spring-early summer at stations NB and SB and during summer at station MB.

Seasonal Patterns of Sediment-Water Oxygen and Nutrient Exchanges

Average SOC rates ranged from about 0.05–0.86 g O_2 $m^{-2}d^{-1}$ among all stations (Fig. 7). Overall,

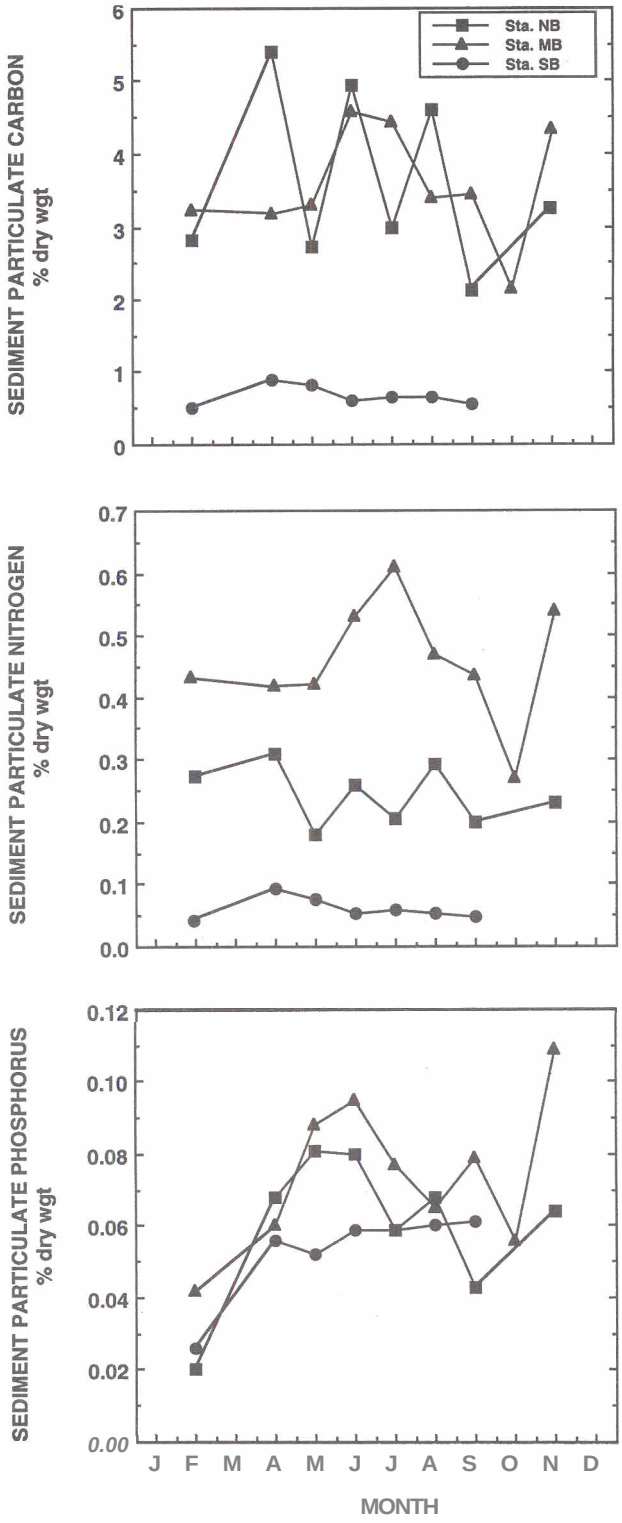


Fig. 4. Monthly surficial sediment concentrations (1.0 cm depth) of particulate carbon, nitrogen, and phosphorus at three stations (NB, MB, and SB) along the main axis of Chesapeake Bay. Data were collected between February and November 1989.

rates were low compared to those observed in tributary rivers of Chesapeake Bay (Boynton et al. 1980) and low compared to many other estuarine sites (Boynton et al. 1991). At stations NB and SB the SOC rates were correlated with temperature throughout the study period (Table 1). However, at station MB the SOC rates were limited by low DO concentrations in summer when temperatures were highest. Anaerobic respiration (SO_4^{2-} reduction) accounts for most organic matter utilization during summer months at this site (Tuttle et al. 1987) and rates correspond to potential oxygen demands of 1–2 g O_2 m^{-2} d^{-1}. Similarly high SO_4^{2-} reduction rates have been reported from station SB as well (Roden and Tuttle 1993), which indicate the importance of anaerobic sediment processes in this enriched system, even at sites where overlying waters remain oxygenated.

Average PO_4^{3-} fluxes ranged from about −16.5 pmol P m^{-2} d^{-1} to 148 pmol P m^{-2} d^{-1} among all stations (Fig. 7). Fluxes at stations NB and SB were low compared to those observed in tributary rivers of Chesapeake Bay (Boynton et al. 1980) and low compared to many other estuarine sites (Boynton et al. 1991). However, fluxes at station MB were among the highest observed in any portion of Chesapeake Bay and were high relative to other estuarine sites. Largest PO_4^{3-} fluxes (>20 pmol P m^{-2} h^{-1}) occurred when dissolved oxygen concentrations were <0.05 mg l^{-1}.

Average DSi fluxes ranged from about −30 ymol Si m^{-2} d^{-1} to 450 ymol Si m^{-2} d^{-1} among all stations (Fig. 7). These rates are comparable to rates observed in other regions of Chesapeake Bay and are high relative to those observed in other estuarine systems (Boynton et al. 1991). Fluxes of DSi at all stations were highest in summer. The range in magnitude of fluxes among the three stations was large, and was in agreement with primary production rates at these stations (MB > SB > NB), suggesting that supply rate of biogenic silica is a key factor regulating rates (Paasche 1980; Aller and Benninger 1981; D'Elia et al. 1983).

Average NH_4^+ fluxes ranged from about −35 ymol N m^{-2} d^{-1} to 506 pmol N m^{-2} d^{-1} among all stations (Fig. 8). These rates are high relative to rates observed in other regions of Chesapeake Bay and are high relative to those observed in other estuarine systems (Boynton et al. 1991). Ammonium release from sediments increased with increasing temperature and decreasing DO concentrations (e.g., station MB, Fig. 9). The relative magnitude of fluxes among stations (MB > SB > NB) is also in good agreement with primary production rates at these stations.

Average $NO_3^- + NO_2^-$ fluxes ranged from about −120 μmol N m^{-2} d^{-1} to 35 pmol N m^{-2} d^{-1}

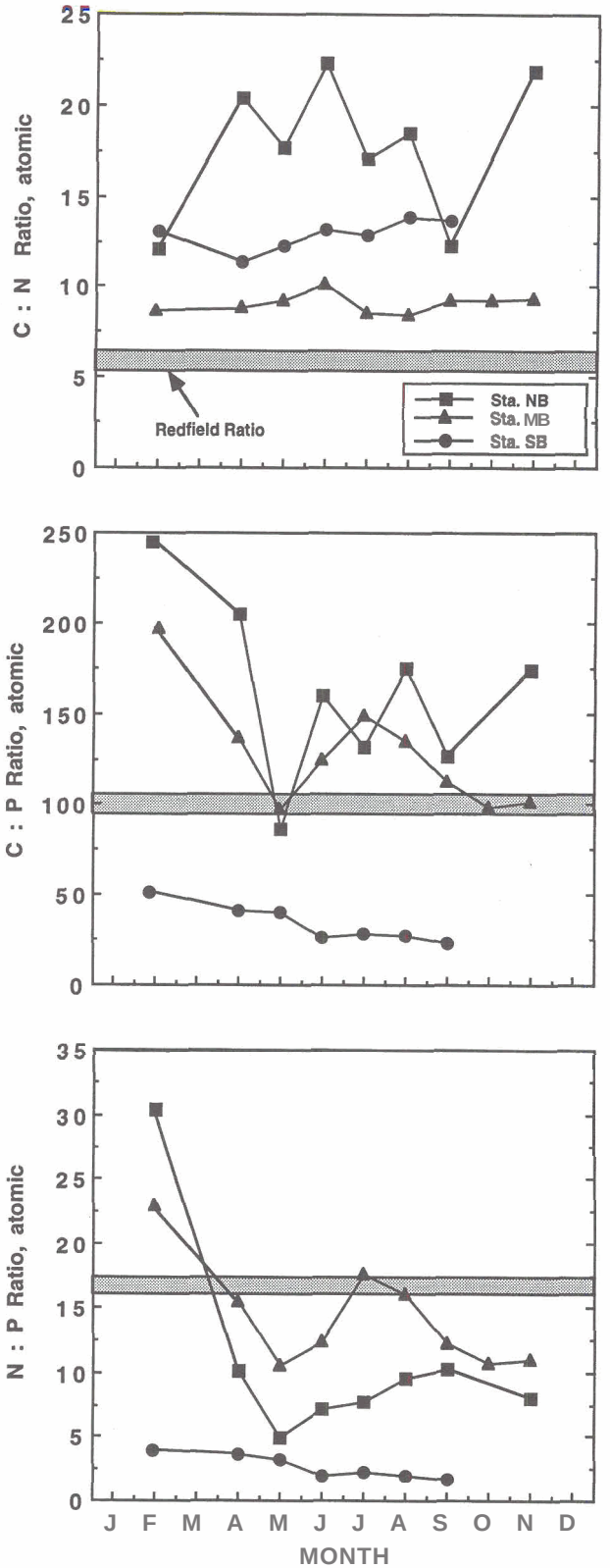
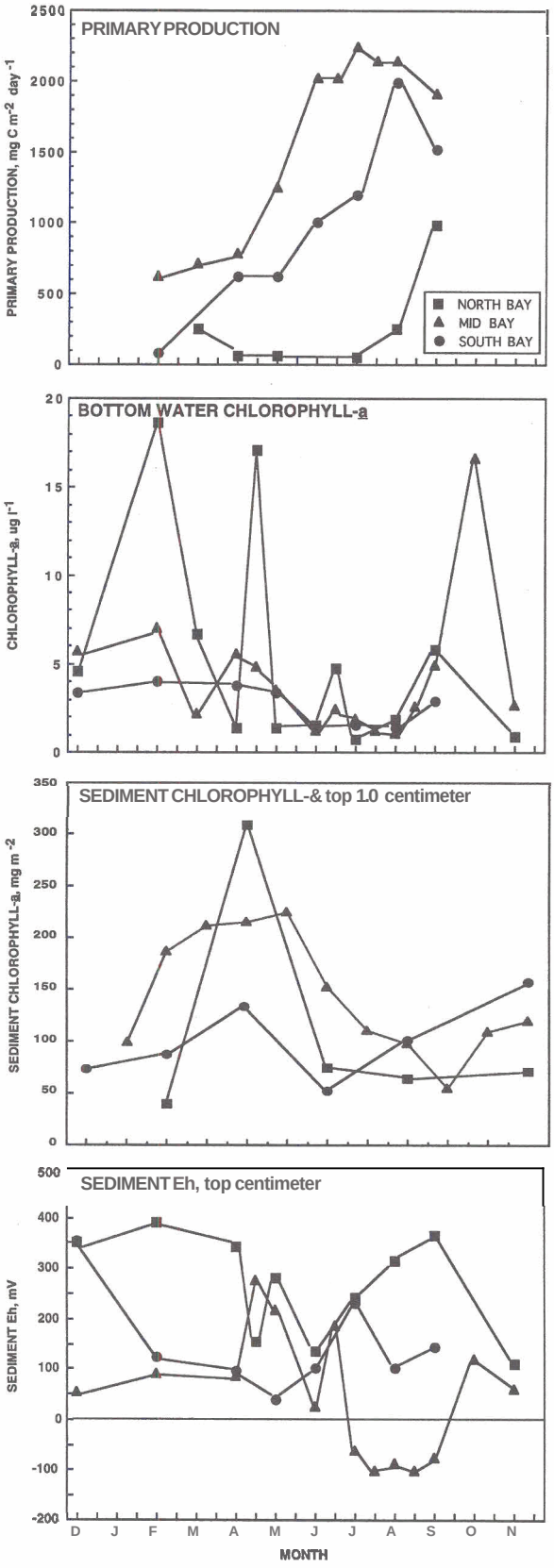


Fig. 5. **Monthly composition ratios** (C:N, C:P, N:P, **atomic**) of surficial **sediment (1.0 cm depth) organic matter at three stations (NB, MB, and SB) along the main axis of Chesapeake Bay. Data were collected between February and November 1989.**

among all stations. The dominant direction of fluxes was from water to sediments during spring-early summer periods at stations NB and MB, and the reverse at station SB (Fig. 8). These uptake and release rates are comparable to rates observed in other regions of Chesapeake Bay. However, NO_3^- + NO_2^- release rates were low relative to those observed in other estuarine systems (Boynton et al. 1991).

While our DON flux data are relatively sparse, we include them because there are so few of these data in the literature despite concerns that DON may be not only a large fraction of the total dissolved nitrogen pool in marine waters but also may be more utilizable by bacteria and phytoplankton than previously thought (Palenik et al. 1989; Bronk et al. 1994). We also include them to show that there is not a clear source of this nitrogen species from sediments in Chesapeake Bay. Nixon (1981) showed this to be the case in Narragansett Bay. Approximately **30%** of all DON flux measurements were not interpretable, meaning that concentration changes in water overlying intact sediment cores were analytically significant but erratic during incubation periods. Virtually all other flux measurements of other nutrient species were interpretable. Interpretable DON fluxes ranged from about **−250** μmol N m^{-2} h^{-1} to **550** μmol N m^{-2} h^{-1} among all stations. There was usually a net efflux of DON from the sediments at stations NB and SB and a net influx of DON at station MB. This type of spatial pattern was also shown to occur in the Atchafalaya Basin, Louisiana, by Teague et al. (1988), but maximum fluxes occurred during the cold months.

Primary amine and urea fluxes were measured at the three stations in 1990 to determine the importance of these compounds to the total DON flux. Both were found to be quite small (<5% of total DON flux). Total combined amino acids (TCAA) were found to be an important portion of the water column DON pool in Delaware Bay (Keil and Kirchman 1991) and could be an important component to the sediment DON pool in Chesapeake Bay. The flux of DON did constitute a large portion of the total dissolved nitrogen flux at certain times of the year, particularly in April at station SB and May–July at station MB. For this reason, understanding sediment DON dynamics is important and merits more attention.



Factors Influencing Seasonal and Interannual Sediment-Water Exchanges

Factors such as temperature, DO concentration and redox status of sediments, macrofaunal abundance and activities, and the quantity and quality of organic matter supply rate to sediments have all been suggested to be regulators of sediment-water exchange rates (e.g., Boynton et al. 1980; Henriksen et al. 1980; Kemp and Boynton 1981; Graf et al. 1982; Kelly and Nixon 1984; Boynton and Kemp 1985; Kelly et al. 1985; Kanneworff and Christensen 1986; Jensen et al. 1990; Banta 1992; Sundby et al. 1992). To begin to discern the relative contribution by the above factors in regulating patterns of sediment-water exchanges in Chesapeake Bay sediments, we performed product-moment correlation analyses on fluxes and measured variables that potentially influence exchanges (Table 1). As expected, temperature and DO concentrations immediately above the sediment surface were significantly correlated with some, but not all, fluxes. The temperature relationship was expected simply because of the influence of temperature on molecular diffusion, metabolic rates, and DO concentrations.

Some fluxes (NH_4^+ and PO_4^{3-}) may have been enhanced while others may have been reduced ($NO_3^- + NO_2^-$) due to the influence of low DO conditions on certain processes. For example, there is a strong relationship between redox conditions and the formation of FeOOH-PO, complexes. Under oxic conditions PO_4^{3-} will sorb to Fe^{3+} but will desorb under anoxic conditions (Krom and Berner 1980; Sundby et al. 1992). Gachter et al. (1988) also found that PO_4^{3-} cycling in lake sediments may also be influenced by utilization and decomposition of sediment microbial communities. In this study substantial PO_4^{3-} fluxes were a warm season event and were restricted to those regions of the bay experiencing hypoxic or anoxic conditions.

A similar, but more complex, situation may exist for sediment nitrogen dynamics. NH_4^+ production increased throughout the spring, possibly due to increasing organic matter supply and decomposition rates in sediments. Some of this NH_4^+ may be converted to N O , via nitrification in the presence of sufficient DO (Nedwell et al. 1983; Kemp et al. 1990); however, in low DO situations (e.g., station

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Fig. 6. Monthly rates of primary production, bottom water chlorophyll-a, sediment chlorophyll-a (top 1 cm of sediments), and Eh (top 1 cm of sediments) at three stations (NB, MB, and SB) along the main axis of Chesapeake Bay. Data were collected between December 1988 and November 1989.

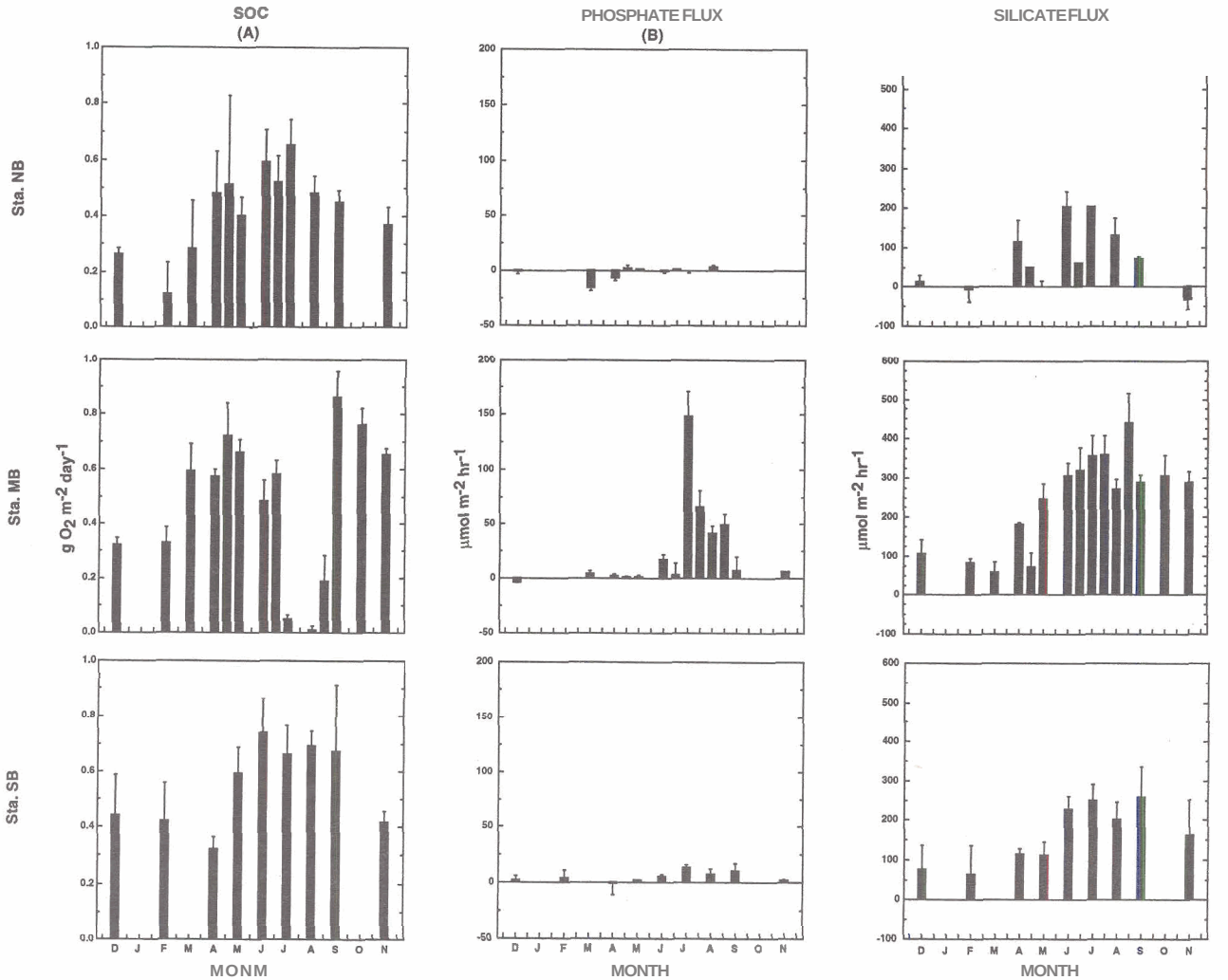

Fig. 7. Average values (arithmetic mean ± standard deviation) of (A) sediment oxygen consumption **(SOC)** rates, **(B)** phosphate flux, and *(C)* silicate flux at three stations **(NB,** MB, and **SB)** along the main axis of Chesapeake Bay. Data were collected between December 1988 and November 1989. All **SOC** measurements represent oxygen uptake by sediments; positive and negative nutrient fluxes represent fluxes out of and into sediments, respectively.

MB) nitrification is suppressed or totally blocked (Henriksen and Kemp 1988) in which case all of the NH_4^+ produced can be released from sediments. Inhibition of nitrification may have served to enhance NH_4^+ fluxes in the seasonally hypoxic or anoxic mid bay region (Kemp et al. 1990). Conversely, sediment nitrification may have reduced NH_4^+ fluxes at the oxygenated upper and lower bay sites (NB and SB).

Finally, most substantial rates of NO_3^- + NO,- uptake occurred at bottom water NO_3^- + NO_2^- concentrations above 18 µM N. At station NB, it seems probable that this material diffused into sediments and was denitrified because there was not a contemporaneous return flux from sediments to water of either NH_4^+ or DON, nor did sediment porewater inventories of NH_4^+ increase (Cornwell personal communication). The case for denitrification of NO_3^- + NO_2^- at the MB site is less certain because there were large fluxes of NH_4^+ from sediments to overlying waters during the same time periods. However, Rosman and Kemp (personal communication) found that sediment denitrification rates at this site were higher than sediment nitrification rates, which suggests that at least a portion of the NO_3^- + NO_2^- diffusing into sediments was denitrified. Releases of NO_3^- + NO_2^- from sediments probably occurred when sediment nitrification rates exceeded sediment capacity for denitrification. This situation occurred primarily at station SB where highest efflux rates occurred at NO_3^- + NO_2^- concentrations below 2 µM N. The

TABLE 1. Summary of product moment correlation analyses of net sediment-water oxygen and nutrient exchanges with bottom water and surficial sediment characteristics. All data used in these analyses were tested for normality using Lillfor's test for normality. All entries axe significant at $p = 0.05$. Dashes indicate nonsignificant results. Designations NB, MB, and SB refer to station NB, station MB, and station SB, respectively. The abbreviations cc and n refer to coefficient and number of paired observations, respectively.

		Bottom Water Temperature (°C)		Bottom Water Dissolved Oxygen (mg l^{-1})		Primary Production (g C m^{-2} d^{-1})		Bottom Water Chlorophyll-*a* (µg l^{-1})		Sediment PC (%)		Sediment Chlorophyll-a (mg m^{-2})		Sediment Eh (mV)	
Flux	Station	cc	n	cc	n	cc	n	cc	n	cc	n	cc	n	cc	n
SOC	NB	0.746	11	−0.797	11										
	MB			0.536	14										
	SB	0.863	7	−0.813	7			−0.834	7						
NH_4^+	NB														
	MB	0.705	14	−0.805	14	0.795	10								
	SB	0.879	7	−0.917	7	0.843	7								
NO_3^-	NB														
	MB														
	SB							−0.775						0.753	7
PO_4^{3-}	NB														
	MB	0.524	14	−0.616	14										
	SB													0.818	7
Si(OH)	NB	0.705	11	−0.713	11										
	MB	0.903	14	−0.860	13	0.930	10					−0.872	6		
	SB	0.913	7	−0.895	7	0.795	7	−0.790	7						
DON	NB														
	MB														
	SB									0.762	6				

presence of worms at this station probably increased the potential for nitrification because nitrifying bacteria are known to be associated with worm burrows (Henriksen et al. 1983).

While the preceding observations reaffirm the obvious importance of temperature and DO concentrations in modifying sediment nutrient processes, there are severalindications that temperature per se is only one factor in the overall set of factors that shapes the seasonal pattern of sediment-water exchanges in Chesapeake Bay. For example, at station MB, maximum NH_4^+ fluxes occurred in July, and NH_4^+ fluxes from September-November were lower than fluxes measured during the spring, even though temperatures were usually higher in the fall (Fig. 10). Further, very appreciable spatial (Figs. 7 and 8) and interannual differences in fluxes have been observed (Boynton et al. 1991). However, spatial differences in temperature (Fig. 3), and interannual differences in both temperature and DO at any one station (Boynton et al. 1991) were not great enough to consider these to be primary factors driving observed variations in fluxes.

It appears that a better explanation for within-year spatial variations in fluxes along the axis of the estuary and for interannual differences in fluxes at specific locations involves differences in organic matter loading rates to the sediment surface. Enoksson (1987) and Boynton et al. (1990) have observed rapid sediment flux responses to the addition of labile organic matter to intact laboratory sediment cores, and Jensen et al. (1990) have measured similarly rapid responses to spring bloom deposition in a Danish estuary. As surrogates for direct deposition rate estimates, chlorophyll-a concentrations in bottom waters and PC, PN, PP, and total chlorophyll-a concentrations in surficial sediments (top 1.0 cm) were routinely collected at all sites in this study. However, as indicated in Table 1, these variables were rarely correlated with sediment fluxes at the time of measurement.

At one site in Chesapeake Bay (adjacent to station MB), sediment traps have been deployed for several years and sediment flux responses to phytoplankton deposition events have been observed through an annual period (Boynton et al. 1991). Large deposition rates were measured at this station during spring and occasionally during summer, but sediment fluxes remained relatively small until early summer when bottom water temperature increased to above 15°C. We therefore reasoned that if a temporal lag was introduced to account for this time period when resident microbial populations were apparently less intensively decomposing deposited plankton blooms because of relatively low temperatures, then stronger relationships might emerge between fluxes and the above measured sediment characteristics. This type of scheme has many similarities to the explanation of the delay between maximum allochthonous water-column nutrient loading rates and maximum phytoplankton production rates suggested by Kemp and Boynton (1984) based on observations made in the Patuxent River estuary.

After examining many combinations of sedi-

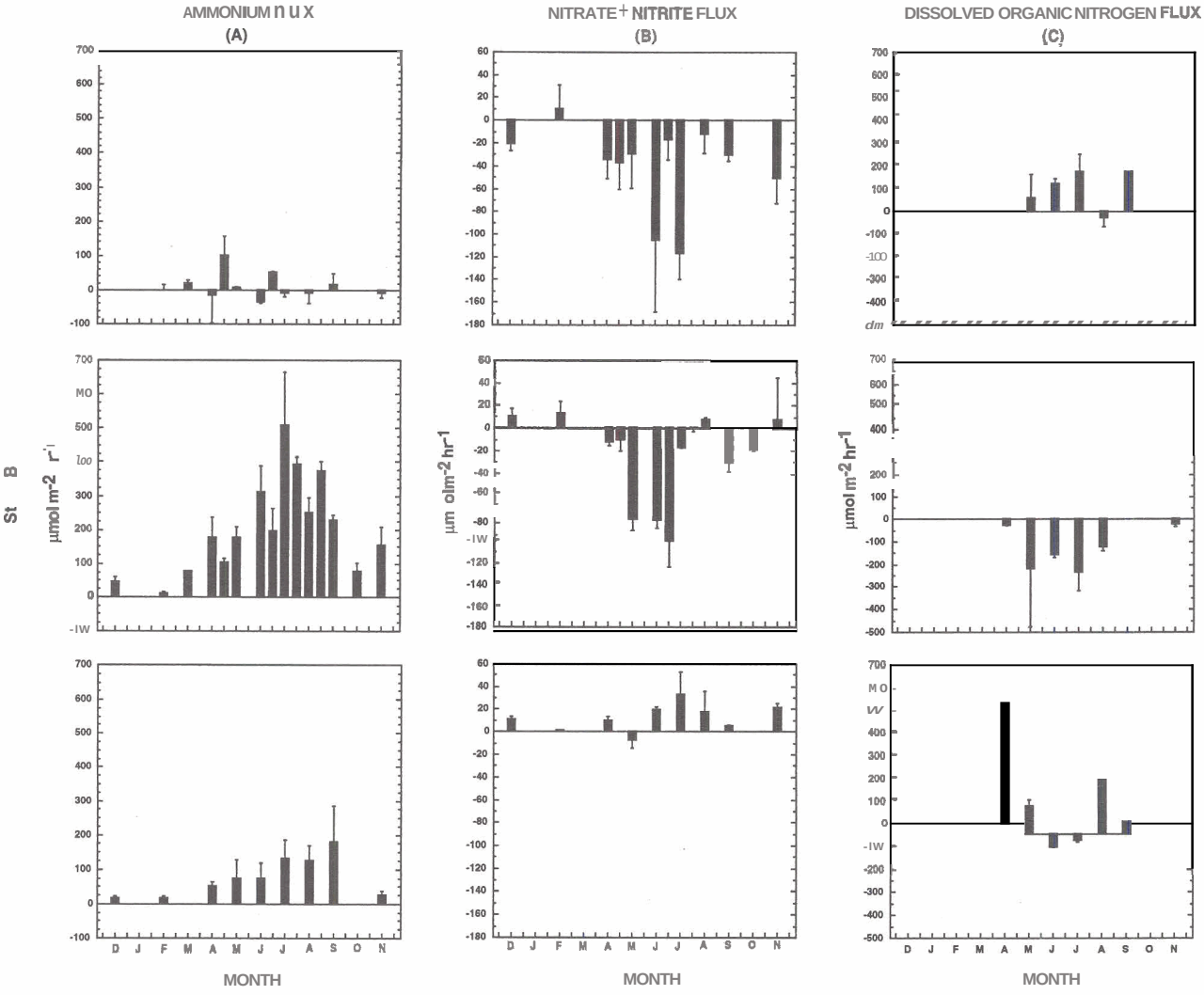

Fig. 8. Average values (arithmetic mean ± standard deviation) of (A) ammonium fluxes, (B) nitrate + nitrite fluxes, and (C) dissolved organic nitrogen fluxes at three stations (NB, MB, and SB) along the main axis of Chesapeake Bay. Data were collected between December 1988 and November 1989. Positive and negative nutrient fluxes represent fluxes out of and into sediments. respectively.

ment fluxes versus the above sediment characteristics at our three stations for several different years, we found total chlorophyll-a concentrations in the top 1.0 cm of sediments (averaged between days 80 and 220) to be the best predictor of spring-summer season fluxes (averaged between days 120 and 220) of NH_4^-, PO_4^-, and DSi (Fig. 11). Other predictors of flux (e.g., PC and PN but not PP) and different temporal averaging schemes yielded similar but statistically weaker results. These results suggest that the rate of labile organic matter deposition provides an upper bound to sediment-water exchanges, and is consistent with the magnitude of fluxes observed along the longitudinal axis of Chesapeake Bay.

Ecological Significance of Sediment Oxygen and Nutrient Fluxes

We have thus far largely focused on the influences of water column and sediment properties and organic matter supply rate on the magnitude and characteristics of sediment-water exchanges of oxygen and dissolved nutrients. However, the concept of benthic-pelagic coupling implies that there are pathways of causation going both from water to sediments and from sediments to water. Some aspects of benthic-pelagic coupling have been summarized by Kemp and Boynton (1992) and Kemp et al. (1992) for Chesapeake Bay and other systems with particular emphasis on the role sediments play in causing low oxygen conditions. In the fol-

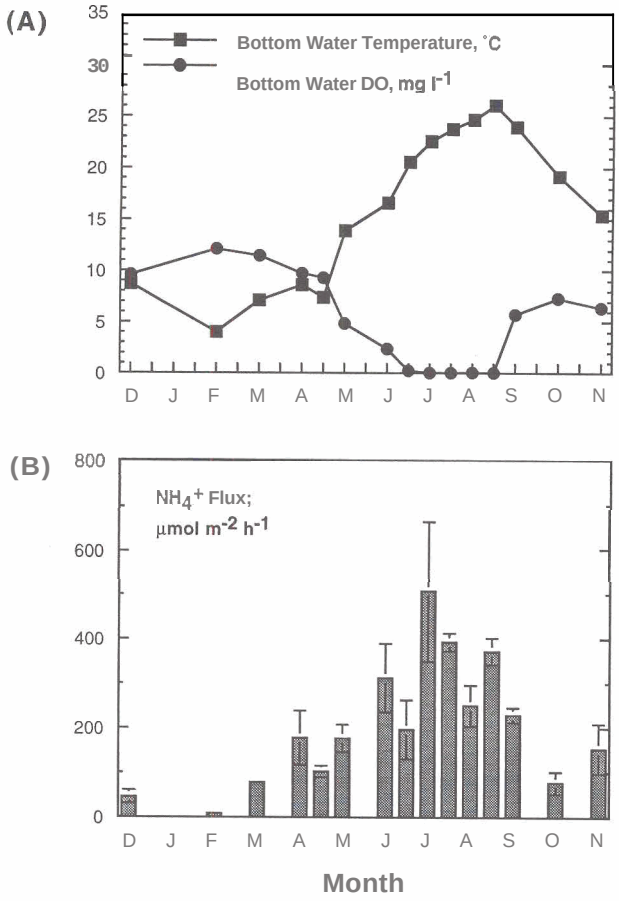

Fig. 9. Monthly bottom water temperature and dissolved oxygen (A) and monthly ammonium flux (B) at station MB. Data were collected between December 1988 and November 1989.

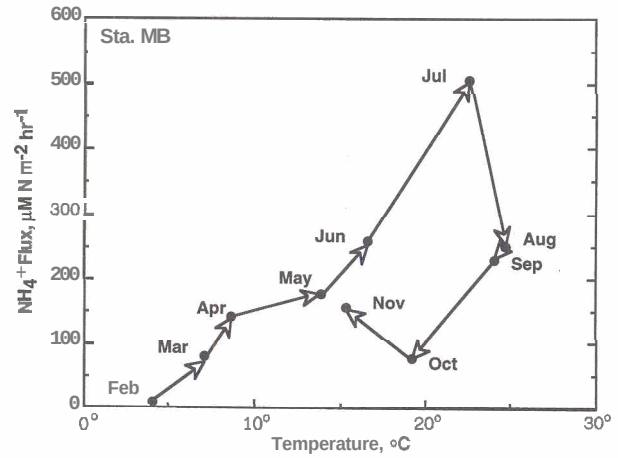

Fig. 10. Scatter plot of bottom water temperature versus ammonium flux at station MB in the mesohaline region of Chesapeake Bay during 1989.

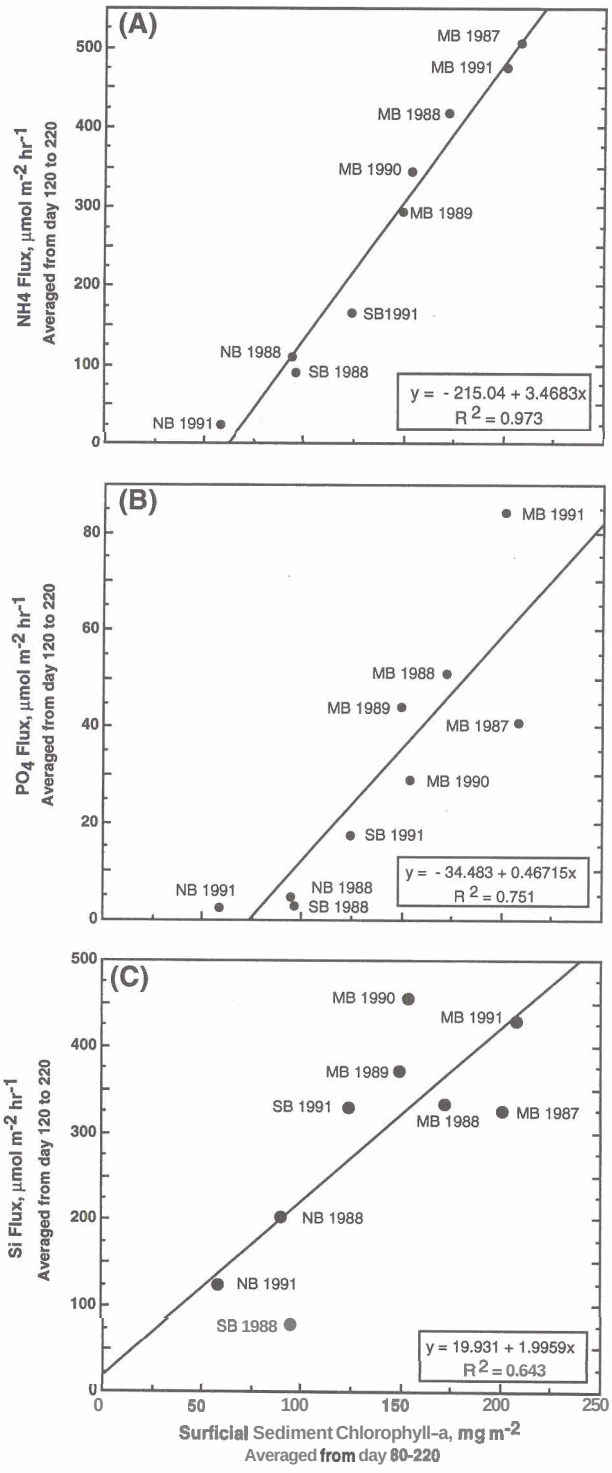

Fig. 11. Scatter plots of surficial sediment chlorophyll-aversus ammonium flux (A), phosphate flux (B), and silicate flux (C) at three stations along the main axis of Chesapeake Bay. Surficial sediment chlorophyll-*a* data (top 1 cm of sediments) were averaged within each year for the period between days 80 and 220; sediment nutrient flux data were averaged for the period between days 120 and 220 of each year.

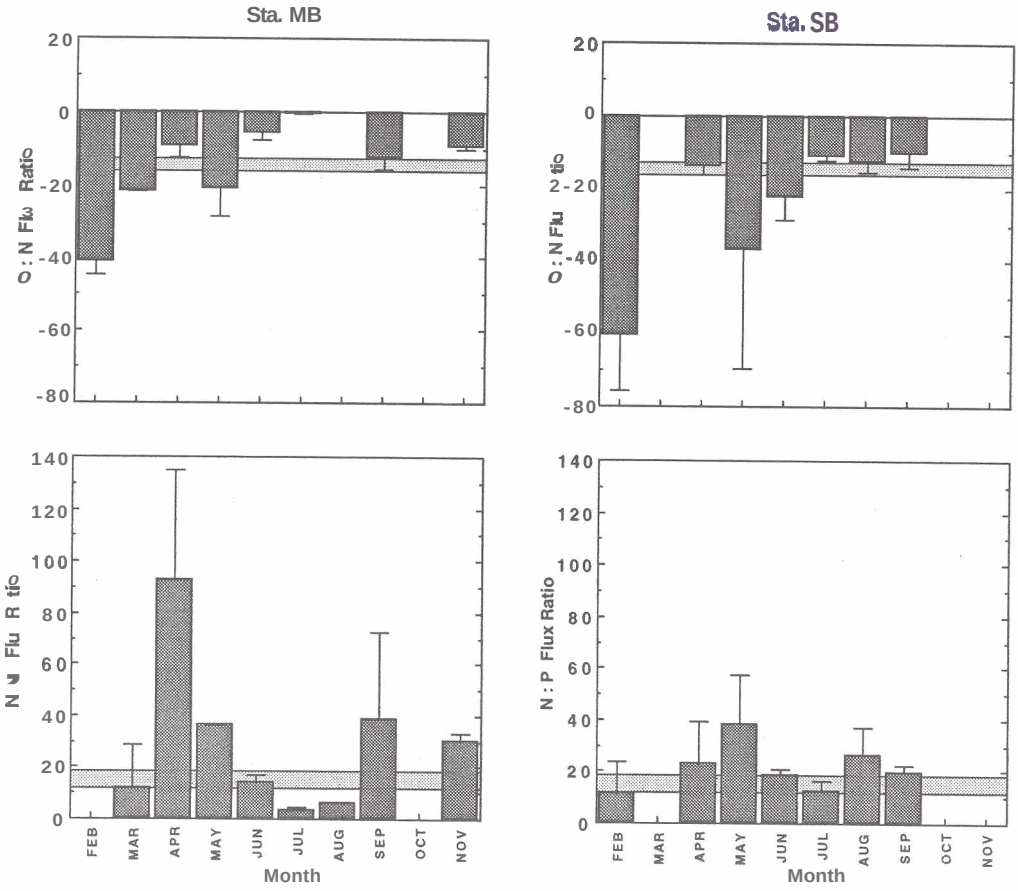

Fig. 12. Bar graphs of average (arithmetic mean ± standard deviation) sediment oxygen and nument flux ratios at two stations (MB and SB) along the main axis of Chesapeake Bay.

lowing section we focus on the feedback role of sediments in modifying the relative proportions of dissolved nitrogen and phosphorus in the water column, and in supplying dissolved nutrients needed for phytoplankton production.

Sediment-Water Flux Ratios

In the central and southern portions of Chesapeake Bay the primary source of organic material to sediments is of phytoplanktonic origin, and the stoichiometric characteristics (i.e., C:N:P ratios) of this material have been well characterized (Boynton et al. 1991). Redfield (1934) found that the simple decomposition of such organic matter yields one atom of nitrogen (as NH_4^+) for every 13.25 atoms of oxygen (O, not O_2) consumed and about 16 atoms of N for every 1 atom of P remineralized. However, the simple decomposition of organic matter does not always occur. It is therefore of interest to examine the fluxes that were measured to see if there were departures from this model and to infer which microbial or chemical transformations may have been responsible. Strong departures in sediment-water nutrient releases from the nutrient stoichiometry generally required for phytoplanktonic growth could influence nutrient limitation characteristics of overlying waters, especially in relatively shallow systems where sediments are an important nutrient source (Nixon 1981).

Oxygen and nutrient flux ratios (arithmetic mean and standard deviation; atomic basis) were calculated for each cruise at stations MB and SB (Fig. 12). Ratios were not calculated for station NB because fluxes of one or more elements were often from water to sediments (making ratio calculations meaningless) and because the origin of depositing organic matter was a complex mixture of terrestrial and autochthonous material of widely differing stoichiometries. Mean O:N flux ratios at the remaining stations ranged from almost 60 to zero during the study period. At both stations there was a reasonably consistent decline in the ratio from winter through early summer followed by a period

when flux ratios were fairly constant and close to Redfield proportions. This suggests that NH_4^+ remineralized from organic material during the summer and early fall remained in this form, and was not further speciated via nitrification and denitrification. The lower values observed at station MB during the summer period were influenced by low water-column dissolved oxygen concentrations limiting SOC rates; flux ratios returned to Redfield proportions in September when bottom waters were again oxygenated. The elevated O:N ratios observed during winter and spring suggest that other processes were active and the most obvious possibility is that some of the ammonium being produced in sediments was nitrified and subsequently denitrified.

At both stations, $NO_3^- + NO_2^-$ was released from sediments during winter and early spring, indicating that nitrification processes were active and some of the $NO_3^- + NO_2^-$ produced was diffusing through the sediment-water interface. At station SB, this continued through summer probably because surficial sediments remained oxidized. At station MB, $NO_3^- + NO_2^-$ diffused into sediments from overlying waters during late spring and summer when water column concentrations were high. and this nitrogen may also have been denitrified, although we have no direct evidence for this. During the December–April period SO_4^{2-} reduction was not a major pathway for organic matter degradation (Roden and Tuttle 1993), so sediment NH_4^+ production may be crudely predicted based on SOC measurements alone (assuming Redfield proportions of C:N:P). Using this approach, NH_4^+ flux was estimated to be 100 μmol N m^{-2} h^{-1}, which was well above observed values. If we subtract observed sediment efflux of NH_4^+ from this calculated rate, we would estimate sediment denitrification rates on the order of 50–80 μmol N m^{-2} h^{-1}, not far from rates measured for portions of the mainstem bay (Twilley and Kemp 1987).

Flux ratios of N:P ($N\text{-}NH_4^+$:$P\text{-}PO_4^{3-}$) exhibited some extreme seasonal fluctuations at station MB but not at station SB. At the former, ratios ranged from about 5 in July to over 90 in April. The very low ratios occurred during the hypoxic and/or anoxic months of June–August and were probably the result of the release of P from recently deposited organic matter to the sediment surface as well as the dissolution of P from $FeOOH\text{-}PO_4$ complexes under anoxic conditions (Klump and Martins 1981). At station SB, ratios ranged only from 13 to 38. The seasonal pattern here was very similar but much attenuated in magnitude compared to station MB, probably because sediments remained more oxidized at station SB. The station to station differences and the strong seasonal patterns in both O:N and N:P ratios indicates the importance of dissolved oxygen and redox conditions of surficial sediments on the characteristics of sediment-water exchanges.

There were appreciable differences in sediment flux ratios between stations and these appear to be related to differences in water quality conditions. At both locations there were indications of nitrification activity, but the indications were stronger and more persistent at station SB where the water column and sediments were more oxidized (Figs. 3 and 6). This suggests that at sites where sediment nitrification is possible there is a tendency for selective N removal from the system and at least a tendency for the sediments to promote N-limitation of phytoplankton. Second, the N:P flux ratios at station MB suggest a strong seasonal shift from being N-rich in spring to being P-rich in summer. The high ratios during spring resulted because P fluxes were extremely small. The very low flux ratios of summer resulted mainly because P fluxes were extremely high and both N and P fluxes were a significant nutrient source of nutrients for phytoplankton. These flux ratios are consistent with results of nutrient limitation assays which indicate P-limitation in spring and N-limitation during summer in this portion of the bay (Fisher et al. 1992).

Sediment Nutrient Fluxes and Phytoplankton Production

Recent nutrient budget calculations indicate that despite appreciable nutrient loading rates from terrestrial and atmospheric sources, nutrient recycling in the water column and sediments must be occurring at substantial rates to support the observed levels of phytoplankton production in most areas of the bay (Boynton et al. 1995). To estimate the extent of this support by sediments as a nutrient source for phytoplankton production, nitrogen (NH_4^+ and $NO_3^- + NO_2^-$) and phosphate (PO_4^{3-}) sediment releases were compared to calculated phytoplanktonic nitrogen and phosphorus demand based on Redfield composition ratios (C:N:P of 106:16:1; Table 2).

At station NB, sediment nutrient releases were not a major feature of phytoplankton production at any time of the year; the high spring N value resulted because calculated phytoplanktonic N demand was very small. The close proximity of this station to the Susquehanna River provides a huge lucustrine nutrient supply; low phytoplanktonic production apparently results from light limitation in this turbid zone of the bay. However, at stations MB and SB, sediment releases were sufficient to supply from 14% to 39% of N demand and from 6% to 74% of P demand (the high winter P value at station SB resulted because demand was very

TABLE 2. Calculated daily phytoplanktonic nitrogen and phosphorus demand and the fraction of that demand that could potentially be supplied by sediment nutrient releases. Phytoplanktonic demand was estimated by converting carbon fixation rates to N and P assuming a stochiometric C:N:P ratio of 106: 16:1 (Redfield 1934). Sediment nutrient supply rates are as in Figs. 7 and 8, converted to mmol m^{-2} d^{-1}. Sediment nutrient supply was divided by phytoplankton nutrient demand in order to ascertain the percent phytoplankton demand that was met by the sediments.

		Phytoplanktonic Nutrient Demand		Sediment *Nutrient* Supply	
Station	Season	N Demand (mmol N m^{-2} d^{-1})	P Demand (mmol P m^{-2} d^{-1})	% N from Sediments	% P from Sediments
NB	Winter	2.49	0.16	13	0
	Spring	0.55	0.03	93	15
	Summer	5.41	0.54	1	0
	Fall	0.86	0.05	0	0
MB	Winter	8.39	0.52	14	8
	Spring	16.97	1.06	28	8
	Summer	96.37	1.65	30	74
	Fall	12.49	0.78	20	6
SB	Winter	1.01	0.06	39	16%
	Spring	9.43	0.59	22	8
	Summer	19.67	1.23	21	22
	Fall	6.09	0.38	16	17

low). It appears that sediments at these stations supply N at a fairly constant rate relative to demand, but P is supplied more as a pulse during summer and amplified in regions experiencing hypoxic and/or anoxic conditions,

These calculations indicate a smaller role for sediments in supplying nutrients for phytoplankton than some previous evaluations (e.g., Boynton et al. 1980; Fisher et al. 1982). However, most of these were in systems considerably shallower than those in this study. Kemp et al. (1992) reported a relationship based on data from a variety of coastal systems, which indicated that planktonic respiration generally exceeded sediment respiration for systems deeper than 5 m. Nutrient recycling may have a similar pattern. Thus, both planktonic as well as sediment recycling play substantial roles at deeper sites in the mainstem Chesapeake Bay.

The ecosystem level effects of water column versus sediment recycling may be different, however. Water column recycling, especially in the upper mixed layer, may largely serve to maintain existing phytoplankton stocks against losses due to sinking and grazing. In contrast, nutrients from remineralization processes beneath the pycnocline and in sediments appears to enter the upper mixed layer during the warmer months via aperiodic mixing events (Malone et al. 1986; Boicourt 1992), and as such represent a "new" source of nutrients to the euphotic zone which can be used to enhance phytoplankton stocks. Ultimately the "new" nutrients from sediments are based on the deposition of nutrients which came from riverine sources; the latter operates on an annual time scale centered on the spring freshet while the former operates mainly during the warm season mixing events on weekly to biweekly time scales. In this view the relative support of phytoplankton production by water column versus sediment nutrient recycling takes on a different meaning. Sediment sources probably dominate immediately following mixing events and have more of an influence on algal bloom development than on the maintenance of existing algal stocks,

ACKNOWLEDGMENTS

We acknowledge the following colleagues for their assistance in completing this work Tom Malone for the use of water column nutrient, chlorophyll-a, and primary production data; Pat Glibert for water column dissolved organic nitrogen data; Janet Barnes for tireless training on the use of equipment and assistance in the field; Sharon Stammerjohn and David Jasinski for cheerful assistance in field and laboratory work; and Lisa Matteson and Frances Rohland for assistance in data management, Discussions with Michael Kemp and Jeff Cornwell were particularly helpful and we appreciate their insights and assistance. This work was supported by the National Science Foundation's Land Margin Ecosystem Research Program (grant no. BSR 8814272) and the Maryland Department of the Environment, Chesapeake Bay Water Quality Monitoring Program (grant number 177-GMDE-89). This is Dauphin Island Sea Lab contribution number 273 and Center for Environmental and Estuarine Studies of the University of Maryland contributionnumber 2682.

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Received for consideration, January 5, 1994
Accepted for publication, August 24, 1995